100th Anniversary of the Carpathian-Balkan Geological Association

XXII International Congress of the Carpathian-Balkan Geological Association (CBGA)

ABSTRACTS

Geologica Balcanica

Irena Peytcheva, Anna Lazarova, Georgi Granchovski, Rositsa Ivanova, Iskra Lakova, Lubomir Metodiev
(Editors)

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XXII International Congress
Carpathian-**B**alkan **G**eological **A**ssociation
CBGA2022 – Plovdiv, Bulgaria, 7–11 September 2022

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Preface

Welcome to the 22nd Congress of the Carpathian-Balkan Geological Association (CBGA2022), which is held on 7–11 September 2022 at the Agricultural University in Plovdiv, Bulgaria. *We celebrate the 100th anniversary of the Association!* Following the organization and traditions of previous congresses (Salzburg 2018, Tirana 2014), CBGA2022 aims to bring together geoscientists from Southeastern Europe with geoscientists from all over the world, for a meeting covering all disciplines of Earth sciences.

CBGA is an international scientific, non-governmental, non-political and non-profit-making union of geoscientists working in the Carpathian-Balkan Mountain region and the surrounding areas. The association consists of sixteen Country Members and is affiliated with the International Union of Geological Sciences (IUGS). Initially founded for discussions on the regional geology of the Carpathian area, the focus of CBGA has significantly widened and the congresses (one every four years, held by one or more Country Members) become forums where scientists can present and discuss their latest results not only from the Carpathian and Balkan regions, but also beyond them. In its hundred-year history, the unchanging aim of CBGA is to promote and encourage collaborative cross-border fundamental and applied geological studies, as well as training and specialization in the Carpathian-Balkan realm.

This abstract volume of CBGA2022 contains all presentations of the congress program. Initially, it was planned to include the contributions of a number of sessions proposed by conveners of General Themes and Special Sessions, covering virtually all fields of geosciences (including geophysics), their environmental implications and other related disciplines. Finally, a few sessions have been merged, but regardless, the abstract volume represents the sessions that comprise varied results of both regional studies and the studies by active interregional collaborations between researchers of various countries, as well as novel applications and advances in analytical and exploration methods worldwide. CBGA2022 also offered authors a choice of a dual submition mode, either with full papers (published after peer review) or short communications, to the official journals of CBGA: *Geologica Carpathica* and *Geologica Balcanica*. This initiative allowed authors flexibility, according to their presentation and publication needs, but in addition, it will raise awareness of the geology of the Carpathian-Balkan region.

The editors of the abstract volume gratefully acknowledge the efforts of conveners for their help in organizing sessions, but also in reading and reviewing abstracts. Warm thanks are also extended for the support of companies and institutions in helping organize CBGA2022. Among these, special mention should be made of Dundee Precious Metals Inc., Geotechmin OOD, Aurubis AG, Assarel Medet JSC, TotalEnergies EP Bulgaria B.V., Agricultural University (Plovdiv), University of Food Technology (Plovdiv) and the Geological Institute of the Bulgarian Academy of Sciences. The organizers of CBGA2022 believe that the 22nd Congress of the Carpathian-Balkan Geological Association will result in many fruitful discussions and will trigger many new collaborations. Thanks are given to all those who will join CBGA2022 to enjoy and share science together.

Sofia, August 2022 *Editors of the Abstract Volume of CBGA2020*

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The Carpathian-Balkan Geological Association – A successful geoscientific project during one hundred years of changing geopolitical environment

Ivan Zagorchev

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The Carpathian-Balkan Geological Association marks a century since its foundation as *Association Géologique Carpathique* during the 13th International Geological Congress in Brussels. The Founders who signed the first agreement chart on behalf of their countries were the prominent geoscientists R. Kettner (Czechoslovakia), J. Nowak (Poland), G. Murgoci (Romania), and V. Petković (Yugoslavia). The new Carpathian Geological Association (CGA) followed the established pattern of the International Geological Congress (IGC) and the International Union of Geosciences, found support from the national governments, geological surveys, and national universities, and stimulated the formation and establishment of national geological societies as professional unions of geoscientists and related professionals on NGO basis.

The importance of the geosciences for the industrial development of the independent states has been recognized since the 1830ies by the great powers. With the defeat and dissolve of four large European empires during WW1, the newly-formed national states of Central and Eastern Europe established and gradually developed their national institutions. The establishment of a regional organization for geological collaboration was needed both in view of the development of mining and related industries, and in the optics of national prestige. The CGA came in time to fulfill the tasks. Three consecutive congresses (1923, Poland; 1927, Romania; 1931, Czechoslovakia) gathered about 60 to 70 geoscientists each, and demonstrated the achievements of Carpathian geology in well-organized excursions in the three countries.

Established in a favorable geopolitical situation after the WW1, CGA became endangered together with the geological sciences and scientists in the atmosphere of uprising fascism, nazism, antisemitism, and communism. Geopolitical tumults embraced the whole region beginning with the early 1930ies, culminated in the years of WW2, and continued through the establishment of the communist regimes after the war. Thus, the whole history of CBGA is subdivided into 3 stages: the initial CGA stage (1922–1931), the post-war establishment and development of CBGA (1956–1989), and the post-socialist years after the wars in former Yugoslavia (after 1989/1990). The post-WW2 geopolitical situation was again favorable for the establishment of a Carpathian-Balkan regional organization of the geoscientists as far as all countries have been involved in the USSR orbit, and the ruling communist governments were interested to control such an organization as a counterpart to the West-dominated International Union of Geosciences. The CBGA congresses (Ukrainian SSR, 1958, 1977; Romania, 1961, 1981; Poland, 1963, 1985; Bulgaria, 1965, 1989; Yugoslavia, 1967; Hungary, 1969; Czechoslovakia, 1973) have been regularly organized with generous government help. The participants' number fast arose from about 250 in the Fourth Congress to over 400–500, and field trips have been skillfully arranged to cover the principal geological features of the organizing country. The thematic work of the commissions and subcommissions resulted in the compilation of important books and maps. After the 1989/90 transition to democracy and market economy, the CBGA congresses have been revitalized with active involvement and participation of new countries. Eight new congresses have been successfully organized by Greece (1995, 2010), Austria (1998, 2018), Slovakia (2002), Serbia (2006), Albania (2014), up to the present 22nd congress in Plovdiv (Bulgaria), and looking forward to the next 23rd Congress in Romania. Our predecessors had the right vision to the future, and the elapsed 100 years confirmed the vitality of their geoscientific project which has passed successfully all geopolitical changes and challenges in such an unstable region as the Carpathian and Balkan sectors of the Alpo-Himalayan Orogenic System. Farewell!

Structure and evolution of the Rhodopes

Nikolaus Froitzheim

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The tectonic structure of the Rhodopes is difficult to unravel due to a subduction polarity change during the Cretaceous, the European continent representing the lower plate in a Jurassic arc-continent collision but the upper plate during Late Cretaceous and Tertiary subduction and continent collision. This led to the interference of thrust systems of different transport direction, towards Europe and away from Europe. An additional difficulty comes from the intense overprint by Late Eocene-Oligocene extensional detachment faults and shear zones. Nevertheless, it has become more and more clear that the Rhodopes do not represent the hinterland of the Hellenides but are part of the Hellenides, and that lateral equivalents of the thrust complexes of the internal and external Hellenides are found in the Rhodopes.

The Lower Allochthon of the Rhodopes occurs in the metamorphic core complexes of Pangaeon-Pirin, Arda, Kesebir-Kardamos, and Byala Reka-Kechros and represents continental basement and shelf carbonates. I interpret at least the Pangaeon-Pirin and Arda domes as correlatives of the External Hellenides Platform (Adria). For the Kesebir-Kardamos and Byala Reka-Kechros domes, a derivation from the Pelagonian microcontinent is also possible.

The overlying Middle Allochthon is a mixture of Jurassic arc granitoids and ophiolites plus shelf carbonates and continental basement slivers. The ophiolites are very similar in age and composition to ophiolites from the Eastern Vardar Zone (Neotethys) and represent the Neotethys suture in the Rhodopes. The Upper Allochthon, following above the Middle Allochthon, is represented by the Vertiskos-Ograzhden Unit in the West and by the Krumovitsa-Kimi Unit in the Eastern Rhodopes. Both represent the continental margin of Europe and are tectonically overlain by low-grade metamorphic series including ophiolites: The Circum-Rhodope Belt in the West and the Mandrica and Maglenica Series in the Eastern Rhodopes. Just like the Middle Allochthon, these low-grade rocks were derived from Neotethys. They were obducted roughly northeastward onto the Upper Allochthon during Jurassic arc-continent collision. After the Cretaceous subduction polarity reversal, the Upper Allochthon carrying the Uppermost Allochthon was thrust towards southwest over the remaining Neotethys Ocean, now to be found in the Rhodope Middle Allochthon and in the Vardar Zone.

The boundary zone between the Lower and Middle Allochthons in the Arda dome is enigmatic in that it contains both Eocene, c. 40 to 45 Ma old eclogites and diamond-bearing gneisses (at Sidironero and Chepelare) whose metamorphism is much older, probably c. 160 Ma. I suggest that this is also due to the subduction-polarity reversal. The diamond-bearing gneisses are part of the Upper Allochthon enveloped from above in the post-Cretaceous, southwest-directed thrust of the Middle over the Lower Allochthon.

Porphyry copper systems: The role of magmatic sulfides in the process chain of metal enrichment

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Economic porphyry Cu (± Au – Mo – Ag – Pd – Pt) deposits are extremely rare occurrences requiring a perfect alignment of several processes leading to major enrichment of trace metals in small areas of the Earth's crust. This chain of processes links diverse scales, from plate configuration to the scale of small veins and mineral grains, and processes at each spatial scale occur at characteristic time scales within the same period. Thus, plate-scale processes during or after subduction generate the physical conditions favoring generation of specific magmas at the time scale of many millions of years, including in some cases even billions of years of lithosphere preparation. Magma evolution in the lower crust leads to H_2O enrichment in differentiated magmas, typically over several million years generating metallogenic provinces and epochs. These trans-crustal magma systems create hydrous magma volumes of hundreds of cubic kilometers, which on cooling and crystallization generate a magmatic hydrothermal fluid flux over a typical lifetime of X00'000 years. Cooling a focused fluid flux over X0'000 years leads to pulses of metal precipitation at the scale of mineable orebodies. These typically measure a cubic kilometer, in which metals are concentrated by 2-3 orders of magnitude compared to average crustal abundance. Thereby, ore metals are repeatedly precipitated in veins during even shorter times, approaching those of explosive volcanic eruptions.

Each of these members of the ore-forming process chain involves a step of element enrichment. Thus, single veins are more Cu-rich than orebodies; the fluids are more metal-rich than the magma from which they exsolve; and primitive mantle basalts are more Cu-rich than the mantle from which they are extracted by partial melting. The only exception is the step of magma evolution from mantle basalt to a so-called fertile evolved magma. This step includes enrichment of H_2O in the magma, but is posited to involve a step of partial depletion of ore metals due to saturation of magmatic sulfides and their removal to lower-crustal cumulates. Recycling of these cumulates back to the mantle is thought to explain the globally observed Cu-deficit of most volcanics above thin continental arcs and the overall deficit of Cu relative to less chalcophile elements like Ag in the bulk continental crust.

Given the rarity of giant porphyry deposits I doubt whether ore formation indeed allows a step of major metal loss in this overall chain of metal enrichment processes. Specifically I question whether lower-crustal saturation of magmatic sulfides necessarily means sulfide loss from the evolving magma. Physical modeling of the settling velocity of sulfide particles in evolving arc magmas suggests to me that small sulfide droplets or particles (< 0.X mm) are likely to be entrained when lower-crustal magmas ascend rapidly to the upper crust. Thermodynamic modelling indicates that any entrained sulfides that reach the upper crust are quantitatively resorbed as soon as the hydrous magma reaches fluid saturation. The two model processes, sulfide entrainment and its decomposition to sulfur- and metal rich fluid, effectively make chalcophile metals behave like incompatible elements, thus avoiding any intervening process of metal depletion despite early sulfide saturation and giving magmatic sulfide an active role in ore formation. This hypothesis calls for specific research to investigate accessory sulfides in arc magmas at all levels of the continental crust. Volcanics, porphyries, plutons and mantle xenoliths of the Srednogorie – Rhodope transect could be an excellent natural laboratory to test the role of sulfide saturation in porphyry Cu ± Au ± PGE mineralization.

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Chemical mohometry: assessing crustal thickness of ancient orogens using geochemical and isotopic data

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Convergent plate boundaries are key sites for continental crustal formation and recycling. Quantifying the evolution of crustal thickness and paleo-elevation along ancient convergent margins represents a major goal in orogenic system analysis. Chemical and in some cases isotopic compositions of igneous rocks formed in modern supra-subduction arcs and collisional belts are sensitive to Moho depths at the location of magmatism, implying that igneous suites from fossil orogens carry information about crustal thickness from the time they formed. Several whole-rock chemical parameters correlate with crustal thickness, some of which were calibrated to serve as "mohometers", *i.e.*, quantitative proxies of paleo-Moho depths. Based on mineral-melt partition coefficients, this concept has been extended to detrital zircons, such that combined chemical and geochronological information extracted from these minerals allows us to reconstruct crustal thickness evolution using the detrital archive. We discuss here the mohometric potential of a variety of chemical and isotopic parameters and show that their combined usage improves paleocrustal thickness estimates. Using a Matlab® app developed for the underlying computations, we present examples from the modern and the deeper time geologic record to illustrate the promises and pitfalls of the technique. Since arcs are in isostatic equilibrium, mohometers are useful in reconstructing orogenic paleoelevation as well. Our analysis suggests that many global-scale correlations between magma composition and crustal thickness used in mohometry originate in the sub-arc mantle; additional effects resulting from intracrustal igneous differentiation depend on the compatible or incompatible behavior of the involved parameters.

Rhenium-osmium (Re-Os) geochronology of sedimentary rocks and oils: Novel insights into the paleoenvironment and the formation of petroleum systems

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The Re-Os isotope system offers a unique view into the geologic history of our planet in general, and the inherently complex petroleum systems in particular. My talk will provide an overview on the established and emerging practical applications of this method for paleoenvironmental reconstructions and improving petroleum exploration efforts.

By itself, the Re-Os isotope system applied to sedimentary rocks provides information about the depositional conditions during accumulation of organic-rich source rocks and the degree of chemical preservation of the rock. The organophillic nature of both elements, combined with the radioactive decay of ^{187}Re to ^{187}Os with time enables direct radiometric dating of source rocks and constrains their Os isotope composition at the time of deposition. In turn, the initial Os composition tracks the changing balance between global weathering rates and global volcanic activity. Thus, Os isotope chemostratigraphic studies reveal the presence and duration of significant disturbances in the oceanic Os mass balance from large volcanic eruptions and major meteorite events.

Liquid, solid, or gaseous hydrocarbons form by thermally dependent modifications of the organic matter originally present in sediments. During hydrocarbon generation, a portion of the Re and Os budget of organic-rich sedimentary rocks is transferred into produced hydrocarbons. Although analytically more challenging than source rock measurements, Re-Os isotopic studies on different hydrocarbons (*e.g*., oil, oil fractions, bitumen, tar mats) similarly constrain the age of individual petroleum products and their unique Os-isotope composition at the time of hydrocarbon generation.

Combining the above, and integrating with geological and geochemical data, we can address three important aspects of petroleum systems. First, we provide the timing of formation of source rocks, petroleum, and subsequent hydrocarbon modification events like water-oil interaction. Second, we refine and improve source rock-source rock, oil-source rock, and oil-oil correlations. Third, we can recognize geochemical components and processes in oils systems that are generally inaccessible with common organic geochemistry techniques.

Most importantly, the combined Re-Os age and isotopic constraints allow modeling of the isotopic composition of individual components through time, thereby providing novel tools for testing genetic relations between components to improve our understanding of petroleum systems. I will illustrate these applications with recently published examples from the Norwegian North Sea, Barents Sea, Italy, Australia, East Greenland, Canada, and elsewhere.

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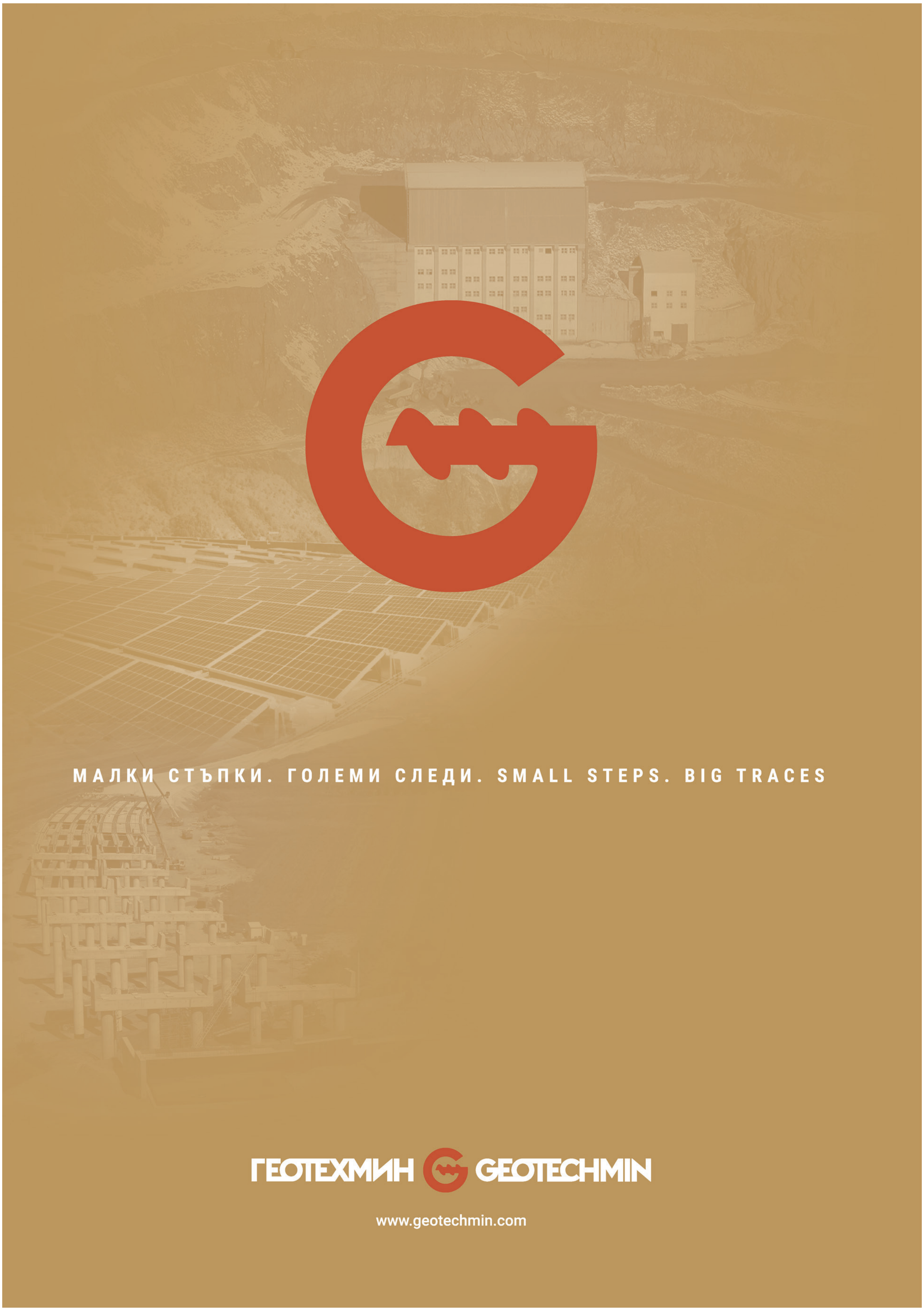
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Session GT1

Earth System Sciences

Conveners:

Kristalina Stoykova, Nataliya Kilifarska, Urs Schaltegger

Wavelet studies of geomagnetic field recordings in observatories

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In this study we analyse the time series of geomagnetic field, observed at six geomagnetic observatories (participating in the INTERMAGNET network) located at different latitudes and longitudes. We have selected major geomagnetic storms occurred in the first half of 2022. The geomagnetic storms are temporary disturbances of the Earth's magnetosphere caused by solar coronal mass ejections, coronal holes, or solar flares. The shock wave of the solar wind usually strikes the Earth's magnetosphere 24 to 36 hours after the solar event, and its enhanced pressure modify the ionospheric electric currents. Different techniques have been used to detect the spectrum of geomagnetic variation (induced by the ionospheric storm currents), *i.e.*, filtering, spectral analysis and wavelet algorithms with different mother functions at different levels (Asimopolos and Asimopolos, 2018; Daubechies, 1990), (Torrence and Compo, 1998). Wavelets allow local analysis of magnetic field components through variable frequency windows, allowing us to analyse low, middle and high frequency fluctuations in geomagnetic field (Chatfield, 1989; Gebbins and Herrero-Bervera, 2007). The data have been collected generally from the INTERMAGNET website, but we also used the data from the Surlari Observatory. The additional information about the analysed geomagnetic storms has been obtained from the website http://www.noaa.gov. The numerical analyses performed on the basis of these data, allowed us to compare the geomagnetic storm variability recorded at different geomagnetic observatories, with the corresponding changes in the physical parameters of interplanetary medium. Geomagnetic disturbances occur throughout the planet, but with different intensities depending on the latitude at which the observer is located. Geomagnetic storms may accompany sudden, short-period geomagnetic field variations. Sudden geomagnetic changes induce currents in power lines and pipelines. These induced currents may destroy power transmission systems and corrode pipelines. The threats posed by geomagnetic induced currents are well recognised – particularly in polar regions and at high latitudes, where strong ionospheric currents have been observed. However, recent observations have confirmed cases of strong currents induced in power lines during geomagnetic storms, even in middle to low latitude regions.

Acknowledgements. We gratefully acknowledge the contributions provided by our colleagues from geomagnetic observatories. This work was supported by project PN19450301 of the Romanian Ministry of Research, Innovation and Digitalization.

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Ozone response to short-lasting changes in galactic cosmic rays

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The intensity of galactic cosmic rays (GCR), arriving at the Earth's magnetopause, is modulated by the irregular structure of interplanetary magnetic field (IMF). The heterogeneity of IMF originates in the variations of solar activity at various time scales. This study is focused on the effect of the short lasting inhomogeneities in IMF – created by the active processes on the Sun (*i.e*., solar flares, coronal mass ejections, coronal holes, *etc*.) – and their effect on the GCR intensity approaching our planet.

The geomagnetic storm of June 2015 is a sequence of a several coronal mass ejections from the Sun. The interactions between solar plasma inhomogeneities in the interplanetary space lead to the peculiar variations of GCR intensity propagating through interplanetary medium. The worldwide network of neutron monitors recorder step-like decreases of GCR intensity (known as Forbush decrease) with two or more consecutive minima within the period 22–25 June 2015.

Due to the fact that energetic particles penetrating the Earth's atmosphere affect its chemical composition, this study is aimed to investigate their effect on the ozone density. Unlike the well-known ozone reduction in mesosphere and upper stratosphere, we are focused on the effect of GCR near the tropopause. At this level they create an ionization layer (known as the Regener-Pfotzer maximum), which favour the ozone creation at these levels (Kilifarska, 2013). Consequently, one should expect that the Forbush decrease of GCR will be accompanied by a depletion of the lower stratospheric ozone.

The ion density in the Regener-Pfotzer maximum is, however, unevenly distributed in Earth's atmosphere, due to the heterogeneous structure of geomagnetic field. This is a hint that the ozone response to the Forbush decrease of GCR should be irregularly distributed over the globe. We have found that at climatic time scales this is the true. At shorter time scales, however, the situation is not that clear, although there is some evidence for covariance between GCR and the lower stratospheric ozone at mid-latitudes (Kilifarska and Pegini, 2022).

This study is focused on: (i) establishing the time scale at which the ozone is able to follow the fluctuations in the GCR intensity, (ii) investigation of the peculiarities of ozone response to the Forbush decreases at different latitudes and longitudes.

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North Atlantic Oscillation (NAO) and factors affecting its variability

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The North Atlantic Oscillation (NAO) describes the pressure variations between subtropical Azores islands and subpolar Icelandic region. The higher than usual pressure over Azores or abnormally low pressure over Iceland (positive NAO) favours the intense meridional circulation, which is gradually turned east, due to the action of the Coriolis force. The intensification of mid-latitude westerlies brings the wetter air masses from Atlantic over the northern Europe, making the winters milder and snowy. On the other side the weakening of Azores high and Icelandic low pressure corresponds to the negative phase of NAO.

The pressure fluctuations over Azores and Icelandic regions are fairly well synchronised. This synchronisation motivates some authors to suggest that NAO mode fluctuates between its positive and negative phases. The fluctuations are irregular and cold be observes on annual basis, as well as at longer time scales – decades, centuries, etc.

The reasons for NAO variability are sought in the (i) amount of ice deposited in the Barentz and Kara seas, (ii) quasi-periodic 11-year solar magnetic cycle, (iii) explosive volcanic eruptions – tossing a great amount of sulphur dioxide (SO_2) in the atmosphere, etc. The mechanism of influence of all these factors on the NAO phase relies on the assumption of changes in atmospheric zonal circulations initiated by the mentioned factors (Velichkova, 2021).

Our previous analysis reveals, however, that the lower stratospheric ozone covariates with NAO index (in phase over the Iceland and in antiphase over the Azores, see Velichkova and Kilifarska, 2019). Moreover, the ozone in the lower stratosphere is strongly influenced by galactic cosmic rays, and the secondary ionisation layer created by them in the lower stratosphere, known as Regener-Pfotzer maximum (Kilifarska, 2013). The spatial distribution of the latter is controlled by the heterogeneous structure of geomagnetic field intensity, which focuses or defocuses energetic particles in certain regions over the globe (Kilifarska *et al*., 2022). This motivates us to explore the possibility for existence of relations between geomagnetic secular variations, NAO index, and sea-level pressure in a spatial grid with resolution 10° in latitude and longitude. The correlation maps created illustrate the strength and spatial distribution of the statistical relation between geomagnetic field and sea-level pressure.

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Geohazards and climate adaptation: Geosphere coupling-driven interaction

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We are studying satellite observations of the atmosphere, its thermal and electric properties, as well as the association between major geodynamic events and their potential impact on the atmosphere and climate. The focus is on the interaction between geohazards and Earth's environment.

There are numerous indications that the great amount of energy, accumulated in the periods of earthquakes preparation, is emitted before its sudden release as an earthquake. By using the space-borne NASA and NOAA data of atmospheric conditions, we have shown the consistent occurrence of radiative emission anomalies in the atmosphere over the region of earthquakes, volcanoes, and other sources of geothermal fluxes (Ouzounov *et al*., 2018). Moreover, we show that the latent heat released before the major earthquakes is larger than the seismic energy released during the quake (Ouzounov *et al*., 2018). We found that pre-earthquake phenomena in the atmosphere may create an additional contribution to the thermodynamic balance of the climate system – due to the degassing of the lithosphere and ionization of the near surface atmospheric composition by radon and other radioactive gases. This motivates our interest to investigate the interaction between geohazards and climate.

Besides the geohazard's influence on climate, McGuire (2010) suggests that climate change could produce additional geohazards. For example, it is likely that the removal of the ice, from the polar regions, could change the stress on the previously locked faults, triggering in such a way earthquakes. Furthermore, the change in the existing earthquake patterns could affect processes of climate adaptation.

We explore the coupling between geohazards and climate changes within the frame of the lithosphere–atmosphere–ionosphere–coupling (Pulinets and Ouzounov, 2011), putting the focus on the changes in the physical and thermodynamical processes over relatively small-time scales. (Ouzounov *et al*., 2021).

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External forcing as a possible influence on the North Atlantic climate variability

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The regional character of climate variability is still a problem that has not found its explanation. At the heart of this unresolved issue lies the fact that none of the examined external forcing factors – like solar variability, astronomical factors and increased concentration of carbon dioxide (CO_2) – can explain the regional nature of climate fluctuations. For this reason, the regional changes most often are associated with the emergence of stable spatial structures, called atmospheric modes (IPCC, 2013). The mechanisms behind their formation, however, are still under debate.

The focus of this study is put on the North Atlantic Oscillation (NAO), because Bulgaria is among the regions influenced by the changes of this climatic mode (Georgieva *et al*., 2021). Being the dominant mode of climate variability during the Northern Hemisphere winter (Thompson *et al*., 2003), it controls the strength and direction of westerly winds and location of storm tracks across the North Atlantic, determining in such a way the severity of winter in different regions of Europe (including Mediterranean and Balkans). Despite the wide investigation of NAO mode, the physical processes responsible for the different spectrum of its variability (*e.g.* seasonal/interannual, decadal and multidecadal-centennial) are still unknown.

There are a lot of difficulties in attempts to explain NAO variability in term of internal atmospheric variations. Various efforts to relate the NAO variability to changes in solar activity also meet a lot of obstacles (Kirov and Georgieva, 2002; Georgieva *et al*., 2007). For this reason the main goal of our research is to study the possible relations between NAO and various external forcings (*i.e.*, galactic cosmic rays, geomagnetic field, solar cycle, anthropogenic forcing, *etc*.).

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Hydrological and sedimentary regime changes of the Danube River at the Danube Delta apex

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This research aims to analyze the hydrological regime of the Danube River at the Ceatal Izmail bifurcation, localized at Nm 43 (km 80) at the Danube Delta apex.

The analysis of the hydrological regime parameters, such as, water level, water discharge, and sediment discharge were performed using data series from Ceatal Izmail gauging station. Over time, the distribution of water discharge into the analyzed bifurcation has undergone changes generated by natural and anthropogenic factors. River morphology is influenced by various factors such as water discharge, grain size, sediment input, riverbed slope, and human pressure (Dai *et al*., 2021). During the last centuries, most of the rivers have strongly been affected by anthropogenic pressures in different ways (Surian, 1999). The damming of the Danube River from the Iron Gates and its main tributaries led to a decrease in sediment discharge in the entire Romanian sector (Constantinescu, *et al*., 2015), studies show that sediment discharge has decreased by about 60% (Giosan *et al*., 2014).

The results of this paper highlight significant changes in the hydrological regime of the Danube. The percentage of the water discharges distributed among the bifurcation branches is determined by the size of the cross-section areas on the riverbed. To have a recent image of the water discharge distribution on the branches of the analyzed bifurcation, we performed measurements to determine the water discharge. We used a 600 kHz River Ray ADCP system (Acoustic Doppler Current Profiler) for measuring river speeds and water discharge using the Doppler Effect.

We found the percentage changes in water discharge on all three arms of the analyzed bifurcation over the last 100 years. The distribution of water discharge in the Ceatal Izmail bifurcation has changed significantly over time. The Kilia branch recorded a significant and continuous decrease in the water discharge from about 68% in 1921 to about 47% in 2019. For the Tulcea branch, the percentages of water discharge increased from 32% in 1921 to about 53% in 2019. Therefore, the average values of sediment discharge decreased drastically from about 1500 kg/s in 1920 to about 600 kg/s, in the last years at the Ceatal Izmail gauging station.

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Session GT2

Stratigraphy, paleontology and paleogeography

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A whisper from within the fossil bone: Dinosaurs, mammals, and the birth of paleohistological research in Bulgaria

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The paleohistology, or the study of fossilized bone and other mineralized tissues under a microscope, has about two hundred years of history. In recent decades, the dedicated efforts of myriad paleohistologists have brought this field of research to prominence within the wider science of paleontology – nowadays, paleohistology is a very powerful tool for inferring the paleobiology, thermophysiology, growth rates, life-history traits, and paleoecology of extinct vertebrates.

The Bulgarian vertebrate paleontology has a strong tradition, which in the last decades has been based mostly upon the study of Miocene and Plio-Pleistocene terrestrial vertebrate faunas. With several particularly productive fossil localities within this stratigraphic interval, which together have produced tens of thousands of specimens, the opportunities for implementation of paleohistological data in their research have been present before the Bulgarian paleontologists, but not utilized. Perhaps surprisingly, the discovery of Bulgaria's first non-avian dinosaur prompted the first paleohistological analysis carried on a local fossil material: an evaluation of the ontogenetic stage of a fragmentary ornithomimosaurian humerus (Mateus *et al*., 2010). The examination of the bone histology of possible hadrosauroid remains from the Labirinta Cave (Northwestern Bulgaria) and a diaphyseal fragment from the Upper Cretaceous sediments in the area of Vrabchov Dol (Western Bulgaria) for the purposes of the author's diploma thesis is the first attempt by a local researcher to study the osteohistology of fossil vertebrates. This attempt proved fruitful. Bone histology data revealed the specimen from Vrabchov Dol as the third record of a non-avian dinosaur in Bulgaria, a result which led to the discovery of important upper Santonian–lower Campanian vertebrate locality few years later.

Thanks to the wide scope of application of paleohistological data, recently, local research in this domain has seen development in two parallel directions. One deals with the osteohistology of non-avian dinosaurs and other Mesozoic tetrapods for the purpose of: *1*) a taxonomic identification of otherwise unidentifiable, extremely fragmentary remains; *2*) establishing the ontogenetic stage of collected material (especially small-sized dinosaur bones); and *3*) a histologically informed paleoecological inferences. The other involves descriptive and comparative osteohistological studies on the (1) taxonomy, (2) ontogeny, (3) life-history, and potentially (4) paleoecology of late Miocene hipparionins and artiodactyls.

The preliminary osteohistological data collected in the course of the aforementioned research promise intriguing results and paints paleohistology as an emergent paleontological field in Bulgaria.

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Integrated biostratigraphy, organic geochemistry and thermal maturity assessment of Upper Cretaceous deposits in the northern part of the Romanian Eastern Carpathians

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Eight geological sections, discussed in the current research, are located in the Pluton–Pipirig area (Neamţ County, Romania). All studied outcrops consist of Upper Cretaceous sediments of the Hangu Formation (Outer Moldavides of the Eastern Carpathians). Most of the analyzed samples contain palynological, foraminiferal and nannoplankton assemblages. The palynological assemblages are moderately rich in dinoflagellate cysts, spores and pollen grains. The dinoflagellate cyst bioevents allowed determination of upper Campanian deposits based on the first occurrences (FOs) of *Alterbidinium montanaense* and *Diconodinium wilsonii* and the last occurrence (LO) of *Odontochitina operculata*, characterizing the uppermost Campanian *Hystrichokolpoma gamospina–Samlandia mayi* zones in the Boreal Realm. Many of the studied outcrops contain lower Maastrichtian deposits indicated by the FOs of *Alterbidinium varium*, *Palaeocystodinium golzowense*, and the LO of *Alterbidinium acutulum*. The youngest deposits in the studied area are assigned to the lower part of the upper Maastrichtian, based on the FO of *Deflandrea galeata* and the LO of *Isabelidinium cooksoniae*.

The calcareous nannoplankton assemblage is dominated by *Micula staurophora* (up to 87%), accompanied by *Watznaueria barnesiae*, *Arkhangelskiella cymbiformis* and *Lucianorhabdus maleformis*. The constant occurrences of taxa whose LOs mark the uppermost Campanian (*i.e.*, *Eiffelithus eximius* in Zone UC15e and *Broinsonia parca constricta* in Zone UC16) suggest a late Campanian age for the studied deposits. However, the Maastrichtian age, revealed by dinoflagellate cysts, is not confirmed by calcareous nannoplankton marker taxa. The presence of upper Campanian marker taxa within the Maastrichtian deposits can be attributed to the reworking processes, recognized previously in some other sites.

The identified foraminiferal assemblages include both agglutinated forms (*Bathysiphon*, *Nothia*, *Saccammina*, *Reophax*) and calcareous benthic and planktonic forms (extremely poorly preserved). The occurrence of tubular, coiled or flattened-streptospiral forms, together with coarsely agglutinated taxa, suggest that the identified assemblages are typical for the "flysch-type" agglutinated foraminiferal biofacies.

Microfossil assemblages and palynofacies constituents, combined with organic geochemical data (gas chromatography–mass spectrometry, total organic carbon and total sulfur contents) were used to reconstruct the depositional environments during the Late Cretaceous. According to these data, during the late Campanian–early Maastrichtian, the deposition took place in outer neritic–open marine settings with contribution of redeposition from inner neritic zone. During the late Maastrichtian, the sedimentation gained deep-sea character shown by the upper part of the Hangu Formation.

The thermal maturity assessment of organic matter was obtained based on vitrinite reflectance measurements. These results show that the Upper Cretaceous succession in the studied area lies within the oil window (VR values ranges from 0.54% to 0.89% R_r).

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In search of the Ordovician–Silurian boundary in Bulgaria

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Several sections have been investigated in the Svoge Unit (W Srednogorie Zone) aiming at discovering of a continuous sediment sequence containing the Ordovician–Silurian boundary (Sachanski *et al.*, 2019). In most cases, this boundary interval is covered by deluvium; the contact is often tectonically disturbed and/or is dominated by bedded cherts (lydites). Thus, the extraction of identifiable graptolite fauna from these siliceous sediments is difficult or impossible. Until now, the only one appropriate section crops out in the Saltarski Dol near Batuliya Village. There, the first occurrence of *Akidograptus ascensus* has been recorded 80 cm above the boundary between the Sirman and Saltar formations.

During the fieldwork, a Paleozoic phyllocarid crustacean was found in a section near Balsha Village and was identified for the first time in Southeastern Europe (Sachanski, 2020). The phyllocarid remains occur in Wenlockian shales and consist of telsonal part and furcal rami. The latter are poorly preserved and has been assigned to *Ceratiocaris* sp. The presence of these fossil remains suggests that most probably phyllocarid crustaceans were common part of the Silurian shale-facies assemblages of the peri-Gondwanan Europe.

Additionally, two sandstone samples from the upper and lower parts of the Ordovician succession of the Svoge Unit were analyzed in order to determine their detrital zircon U-Pb age spectra using laser ablation inductively coupled plasma mass spectrometry (Georgiev *et al.*, 2021, 2022). One sample was collected from the Hirnantian siliciclastic glaciomarine deposits of the Sirman Formation. The other sample is a middle Darriwilian sandstone from the lower half of the Grohoten Formation. Multi-dimensional scaling statistical technique allowed a reliable objective identification of the potential source areas in North Africa and paleogeographic reconstructions were made. Both samples indicate a close proximity to the Trans-Saharan Belt provenance, which is the most probable source of the detrital component.

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Stratigraphy of the Devonian–Carboniferous flysch of the Carpatho-Balkanides of Serbia

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The Devonian–Carboniferous flysch of the Carpatho-Balkanides belongs to the Variscan Flysch Zone of the Circum Pannonian Region (Ebner *et al.*, 2008). Although previous research on this dominantly siliciclastic succession (Krstić *et al.*, 2008, and references therein) provided excellent framework for regional interpretation, new data obtained during fieldwork refined the stratigraphic record of this unit. The studied sections (of total thickness of ~650 m) of the flysch succession were interpreted based on lithofacies and their associations, which were used for the definition of the turbiditic depositional units and establishment of a sequence-stratigraphic model relatable to the global events.

The age constrains provided by scarce biostratigraphic markers were additionally refined by the analysis of paleoflora which indicated Tournaisian (Visean?) age. This is the first record of an assemblage belonging to the Mississippian phytochoria of the Euramerica Palaeokingdom (Opluštil *et al.*, 2021) in the Carpatho-Balkanides. Furthermore, the frequent occurrence of ichnofossil *Dictyodora liebeana* confirms the Mississippian age for larger part of the succession. Other trace fossils described here for the first time in the Carpatho-Balkanides show close resemblance to typical post-turbidite association of the Culm facies of Europe (Mikuláš *et al.*, 2004).

The structural analysis has revealed fairly simple folding fabric (open cylindrical folds with NW–SE axes) within the turbidites of the Kučaj zone (Getic Unit), while the overall deformational pattern appears much highly pronounced in the more western Lužnica Zone (Kraishte Unit) or in proximity to the major Alpine structures (*i.e.*, Timok fault). Likewise, the underlying Pre-Flysch unit, composed of fine-grained siliclastics and black cherts, had also been intensely deformed indicating an unconformity between these two units.

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Middle Miocene (Badenian) calcareous nannofossils and geochemical fluctuations in the Romanian Carpathian Bend Zone

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During the Middle Miocene (Badenian stage of the Paratethys), carbonates and evaporites were sedimented on large areas, from the Vienna Basin up to North Bulgaria. This type of deposits occurs also in the Eastern Carpathians, especially in their external thin-skinned nappes, namely Moldavides.

We have studied a succession positioned in the Outer Moldavides (Tarcău Nappe), cropping out in the axial part of the Slănic syncline, N of the Slănic-Prahova locality. The Badenian consists of several units (from the base up section): (i) Slănic Formation, with interbedded volcanic tuffs and marlstones, enclosing levels rich in *Globigerina* foraminifer taxa, (ii) Evaporites, with salt and gypsum, (iii) 'Radiolarian Shale', composed of rich-radiolarian shales, and (iv) '*Spirialis* Marls'. This work is focused on the 'Radiolarian Shale' Formation, which contains volcanic ash layers, their age being determined at 13.32 ± 0.07 Ma, based on $^{40}Ar/^{39}Ar$ analysis (de Leeuw *et al*., 2018).

The qualitative and quantitative calcareous nannofossil analysis made on samples collected from the Radiolarian Shale Formation indicated the zone NN6, based on the presence of significant biostratigraphic taxa, such as *Discoaster exilis*, *Discoaster musicus*, *Coronocyclus nitescens*, and *Cyclicargolithus floridanus*. The most common taxa are *Helicosphaera* spp. (mainly *H. carteri*) that, together with *Sphenolithus* spp., *Cyclicargolithus floridanus* and *Braarudosphaera bigelowii*, made up to 50% of total assemblages.

An interval showing a consistent increase of *Braarudosphaera bigelowii* was observed towards the lower part of studied successions, along with the dominance of a 'rounded' morphotype of the aforementioned species, while the typical one, with sharp corners and trapezoidal segments, is almost absent. This nannofossil event was previously reported from Miocene successions of the Central Paratethys (Bartol *et al*., 2008; Melinte-Dobrinescu and Stoica, 2013; Peryt *et al*., 2021). The carbon and oxygen isotopic values show wide ranges, with a negative shift of isotope $\delta^{13}C$ towards the upper part of the studied successions, in the upper Badenian sediments.

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Calpionellid revision and microfacies of the Torre de' Busi section (Lombardy Basin, J/K boundary)

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Calpionellid revision has provided new biostratratigraphic evidence of the upper Tithonian–lower Berriasian sequences of Torre de' Busi section (Lombardy Basin, northern Italy). It allowed identifying 4 standard zones and 6 subzones: Chitinoidella Zone (Boneti Subzone), Praetintinnopsella Zone and Crassicollaria Zone (Remanei, Intermedia and Colomi subzones) in the upper Tithonian, and Calpionella Zone (Alpina and Ferasini subzones) in the lower Berriasian. Generally, calpionellids are not very abundant, poorly preserved, and their redeposition was localy documented. Correlation with previously published magnetostratigraphy, calcareous nannofossil biostratigraphy and chemostratigraphy was performed (see Channell *et al*., 2010; Casellato and Erba, 2021).

The base of the Berriasian has been traced at the explosion of uniformly-shaped globular variety of *Calpionella alpina* Lorenz (Wimbledon, 2017). This event almost coincides with the first occurrence of the calcareous nannofossil species *Nannoconus wintereri* Bralower and Thierstein. The calpionellid index-species of the Chitinoidella and Praetintinnopsella zones first occur in the Rosso ad Aptici Formation and correspond to the calcareous nannofossil zone NJT 16 and the lower half of CM21n magnetozone up to uppermost CM20n2n magnetosubzone. Calpionellids start to be more frequent in the Crassicollaria Zone, just below the CM20n1r magnetosubzone. Calpionellid index markers of the Intermedia and Colomi subzones correlate with magnetic intervals CM19r and lower half of CM19n2n. The zone fits with upper part of the NJT 16, NJT 17 and base of NC0 zones. The Alpina and Ferasini subzones (Majolica Formation) correlate with the NC0 Zone and the upper part of CM19n, CM18r and CM18n magnetozones.

In most of the studied microfacies the dominant microfossil components are calcified radiolarians and spicules. Radiolarian wackestone/packstone, spiculite-radiolarian wackestone/packstone, also *Saccocoma*-spiculite-radiolarian wackestone, *Saccocoma*-radiolarian wackestone occur in the Kimmeridgian and lower Tithonian (Transitional Interval Radiolariti–Rosso ad Aptici and Rosso ad Aptici Formation). Calpionellid-spiculite wackestone/mudstone and calpionellid-spiculite-radiolarian wackestone microfacies dominate in deposits of the Transition Interval between Rosso ad Aptici and Maiolica Formation. In the Maiolica limestones, spiculite-calpionellid wackestone, calpionellid wackestone, calpionellid-radiolarian wackestone, and radiolarian-calpionellid wackestone prevail in the upper Tithonian Intermedia and Colomi subzones and in the lower Berriasian Alpina and Ferasini subzones. On the basis of standard microfacies (Flügel, 2004), a basinal environment of deposition is supposed. This is consistent with a reconstructed paleo-depth of some 1500 m.

The revised calpionellid data in the Torre de' Busi section coincide with coeval calpionellid zones, magnetozones and nannofossil biostratigraphy from the Tethyan Realm.

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Palaeoenvironmental changes and macroevolutionary trends during the early Toarcian mass extinction in Bulgaria

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The early Toarcian mass extinction (ETME) was one of the most important biotic crises of the Mesozoic Era, with Earth-scale disruptions in the marine realm resulting in the loss of ~20% of marine families and genera. This event is closely linked to the Karoo-Ferrar Large Igneous Province (LIP), the postulated driving mechanism for severe contemporary geochemical perturbations leading to anoxia and extinction. Despite the purported global nature of the extinction event, the majority of records are based on NW European epicontinental sedimentary successions and remains particularly focused on settings, in which the ETME was evidenced.

Herein, we focus on the Toarcian sections of the Moesian Basin in the Balkan Mts (Bulgaria) that were deposited on open-ocean facing carbonate shelf. Quantitative palaeoecological and facies data, alongside state-of-the-art geochemical records, has documented major sea-level fluctuations and track macroevolutionary trends of marine shelf ecosystems from an area closer to the open Tethys Ocean. Analysis of the C-isotope record has revealed a broad positive isotope excursion of 3‰ in $\delta^{13}C_{bel}$ through the early Toarcian, interrupted by a negative isotope excursion of 3.5‰ recorded in organic carbon (Tenuicostatum–Falciferum zones). Progressive warming of seawater and increased influx of freshwater into the Moesian Basin through the early Toarcian is recorded in the $\delta^{18}O_{bel}$ isotopes. Such changes are attributed to the eruption of the Karoo-Ferrar LIP, reflected in the Moesian Basin by an enrichment in Mercury (Hg) recorded as a shift in sedimentary Hg/TOC values synchronous with the negative C-isotope excursion. The lack of black shales in the Bulgarian sections, which are well recognised during the Toarcian in the NW European Boreal Realm, suggests that there was much weaker manifestation of anoxia in this near open Tethys Ocean region. A biotic crisis is recorded amongst bivalves and brachiopods during the ETME in Bulgaria, but it does not coincide with the spread of anoxia as seen from the local geochemical records and framboid analysis. Hence, oxygen deficiency cannot be considered a key driving mechanism for the ETME and other factors such as rapid warming may have been more important in the Moesian Basin.

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Interfluve waterlogged paleosols preserved within offshore shales? Preliminary data from the Aalenian of West Bulgaria

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The Aalenian–Bajocian siliciclastic rocks of the Etropole Formation have a key regional significance among the Middle Jurassic strata in Bulgaria. These sediments are generally considered to be deposited in offshore calm water shelf environments at medium water depths. Nevertheless, the mudrocks of the Etropole Formation are often interbedded with coarser sediments that denote a deposition at shallower setting and increased influence from a nearly located coast. We focus herein on unusual case of siderite formation from a single locality of the West Balkan Mts. A few-decimeters thick strata of mottled shales, containing wedge-shaped siderite nodules, have been observed at the very base of the Etropole Formation. The lowest beds of these shales enclose abundant ammonites, belemnites and small-sized bivalves, and less common crinoid stem fragments and echinoid spines, while the overlying beds do not contain any fossils. The ammonites mainly correspond to microconchs of *Leioceras subcostosum* Buckman, but larger specimens of *Leioceras* ex gr. *partitum–lineatum* Buckman are also present, both indicating mid-levels of the Aalenian Opalinum ammonite Zone. Belemnites compose a monospecific assemblage of *Holcobelus*, with a predominance of adults and a lack of orientation. The bivalves comprise a heterogeneous assemblage, which is dominated by *Palaeonucula*, but also displays a subordinate occurrence of *Chlamys*, *Camptonectes* and *Nicaniella*. The siderite nodules occur immediately above the fossiliferous beds. They range in diameter from 15 cm to 30 cm and are made up of massive interiors and thin oxidized external cores. Concretions consist of siderite and Mg-calcite, but may also contain kaolinite, hematite and dolomite. Quartz silts, muscovite, unclear recrystallized bioclasts, as well as unevenly dispersed pyrite and organic are also present in small amounts. Concretions include numerous root petrifactions (*sensu* Klappa, 1980). The latter are up to 2 cm in diameter and a few-centimeters long, conical in shape, and mainly in vertical position. Root petrifactions correspond to void-fillings with concentric structure, in which very thin iron hydroxide and calcite layers alternate. Scattered few-micron scale phloem cells, replaced by hematite, have been observed. The fossil abundance at the base of the Etropole Formation indicates an open-marine setting with normal salinity and water circulation. The structural features of the siderite nodules are typical, however, for the interfluve waterlogged paleosols that associate with coastal environments (*e.g*., Kraus, 1999). Such siderite formations are thought to be formed under poorly drained conditions, with water table fluctuation, and after an episode of erosion (*ibid*.). Hence, both the lithological and palaeontological data suggest a local disruption of the shelf depositional setting at the early Aalenian, a conspicuous feature that has not been recorded in Bulgaria before.

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Bukovo delta sediments as witness of climate and tectonic changes (SE Serbia, Dacian Basin)

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A small portion of the Eastern Paratethys and its successor, the Dacian Basin, could be found east of the Southern Carpathians, near the Serbia-Bulgaria-Romania national borders. Previously, these sediments were only sporadically studied (Stevanović, 1980, Krstić *et al*., 1992, among others), since most of the attention has been given to the prolific hydrocarbon Pannonian Basin to the west. Nevertheless, Bukovo delta sediments are important for the basin interconnectivity and as climate indicator and for regional event correlation. It is well-known that the Dacian endorheic basin water budget was under the strong influence of the regional climate and that the basin underwent significant water-level fluctuations (Lazarev *et al*., 2020).

The Bukovo delta sediments are settled on the west Dacian Basin rim, which was affected by tectonic impact and constant uplift of the southern part of the Carpathians during the middle and late Miocene. Delta sediments crop out at two localities: Bukovo Stream and above the Bukovo Monastery. The Bukovo Stream coarse grained delta sediments of Khersonian age end up with a caliche horizon which points to a change in depositional environment and dry climate conditions dated at 8.6–8.4 Ma in Romania (Palcu *et al*., 2019). The macrofauna is represented by *Mactra caspia, M. bulgarica, M. balcica, Congeria panticapea, Hydrobia turicaspia, Gibbula podolica, Pirenella disjuncta, Melania escheri*, etc. The given macrofauna association could allow recognition of *Mactra bulgarica* and *M. caspia* zones in the Lower Khersonian deposits.

A 500-m-thick section of the Meotian delta system above the Bukovo Monastery, dated by magneto-biostratigraphy at 7.65–7.5 Ma in the Romanian part of the Dacian Basin (Palcu *et al*., 2019), represents a change in climate conditions towards a more humid one. The following mollusc fauna was found: *Psilounio subrecurvus subrecurvus, P. subrecurvus porrectus*, *Congeria beregovi*, *C. panticapaea bulgarica*, *Teisseyrinia serbica*, *Turicaspia korobkovi*, *Theodoxus stefanescui*, etc.

The Bukovo coarse-grained sediments rich in shallow-water fauna points to a littoral environment close to the material source, while foresets and topsets are indicators of delta environments. The presence of two different age deltaic systems (within a 1 km radius) separated by the Great Khersonian drying event indicates a highly dynamic area in terms of both tectonic activity and climate change.

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The geological and paleontological heritage of the Southern Dobrogea (Romania)

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The SE Romania (Southern Dobrogea), located along the Black Sea coast, belongs from a tectonic point of view to the eastern part of the Moesian Platform. In the Southern Dobrogea, a carbonate platform developed during the Mesozoic (Upper Jurassic and Cretaceous), and continued through Paleogene up to the Miocene. The Cretaceous displays a complete sedimentary record of all its stages (Avram *et al*., 1993; Dragastan *et al*., 1998; Ion *et al*., 2004; Melinte, 2004): The Berriasian and Valanginian are represented by marine shallow water carbonates in the eastern part of the Southern Dobrogea and mainly by fluvial and continental deposits in the western part. The Hauterivian-early Aptian interval is characterized by the presence of marine shallow water carbonates. A fluvial-lacustrine sedimentation took place within the middle to late Aptian, followed by Upper Cretaceous glauconitic sandstones and chalk deposits. The Paleogene deposits are mainly constituted of Lower to Middle Eocene siliciclastic successions, which contain significant assemblages of large foraminifers (especially nummulites). The Neogene and Quaternary deposits cropping out in Southern Dobrogea, to the south of the Ovidiu-Capidava Fault, belong to the Middle-Late Miocene and Pleistocene intervals.

This study presents several protected geological and paleontological sites from the Southern Dobrogea. Some of them, *e.g*., 'The Cernavodă Fossil Site' contains Early Cretaceous macro- and microfaunas, along with 'The Limestone walls from Petroşani', exposing Upper Cretaceous and Middle Miocene rocks, and 'Credinţa Quarry', enclosing rich faunas of Miocene mammals and mollusks, are protected areas of national interest. Other sites, significant for their geological outcrops and paleontological context, are not yet protected, although their geoheritage is of an outstanding importance.

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New data on the stratigraphy of the Oxfordian–lower Tithonian strata from the Central Balkan Mts (Bulgaria)

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The Oxfordian–lower Tithonian rocks of the Etropole–Troyan region (Central Balkan Mts, Bulgaria) crop out into a long and narrow strip, in which they comprise three superpositioned lithostratigraphic units: Gintsi and Neshkovtsi formations, and the very base of the Cherni Osam Formation. The lower boundary of these sediments corresponds to a regional stratigraphic gap. Thinly-developed micritic limestones (filamentous packstones to wackestones) of the Yavorets Formation (Callovian, *pars.*) and lithobioclastic limestones (packstones to grainstones) of the Polaten Formation (upper Bathonian) are the underlying strata. A recent investigation of these rocks (Gintsi, Neshkovtsi and Cherni Osam formations), in a section along the Zavodna River (near Ribaritsa Village), resulted in the herein presented reinterpretation of the lithofacies and the new record of biostratigraphic data based on calcareous dinocysts that have not been previously studied.

The lower parts of the succession include a 6.5-m thick Gintsi Formation that is composed of nodular limestones, and less common micritic limestones (*Protoglobigerina* wackestones). These rocks yielded calcareous dinocysts that have defined the upper Oxfordian Fibrata Zone and the upper Kimmeridgian Moluccana Zone. It is noteworthy that the lower Kimmeridgian Parvula Zone is missing. Upwards, the succession continues with three vertically stacked lithofacies, with a total thickness of 29.5-m, referred to the Neshkovtsi Formation: hemipelagic marlstone-limestone facies, gutter cast facies, and thin-bedded mudstone-dominated overbank facies. The contacts between these lithofacies are short lithological gradations, and collectively, they span the upper Kimmeridgian (Moluccana and Borzai zones) and the lowermost lower Tithonian (Pulla Zone). The lowermost facies is dominated by poorly-laminated marlstones, which are interbedded with sheet-like to lenticular micritic and argillaceous limestones. The mid-lying lithofacies comprises silt-laminated marlstones, often surrounding carbonate gutter casts. The uppermost facies includes a rhythmic alternation, in which dozens of laterally extensive very thin beds and laminae of calcareous siltstones and shales are present. Up-section, this alternation rapidly grades in the fine-grained turbidites of the Cherni Osam Formation. It consists of thin-bedded turbidites (fine-grained sandstones to coarse siltstones with ripple laminations that are often deformed into convolutions), which alternate with calcareous shales and thin interbedded limestones. The lowermost 15 meters of the Cherni Osam Formation yielded calcareous dinocysts, which belong to the lower Tithonian Pulla Zone. In terms of their microfossil contents, it is worthy to note that in both the Neshkovtsi and Cherni Osam formations calcified radiolarians and *Saccocoma* are the dominant elements, while the calcareous dinocysts have been recorded in low to moderate abundances. Additionally, planktonic and rare benthic foraminifera, brachiopod, belemnite and bivalve fragments, rhyncholites and crinoids, as well as filaments, juvenile ammonites, aptychi, gastropods, ostracods, sponge spicules, spores of *Globochaete alpina* Lombard and echinoid spines also occur. These occurrences have allowed *Saccocoma–Bositra* wackestones, *Saccocoma* and *Bositra* wackestones, *Saccocoma*-radiolarian, radiolarian and spiculite wackestones to be recognized. As inferred from the general lithology, the Oxfordian–lower Tithonian strata seem to reflect a transition from pelagic/hemipelagic to channel-levee slope deposition, at a moderate distance from the continental edge.

Ostracods (Crustacea) as indicators of the middle Miocene Badenian marine transgression (Central Paratethys, Bosnia and Serbia)

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Middle Miocene Badenian (=Langhian) marine transgression was a significant regional event that affected the Central Paratethys (herein, Bosnia and Serbia represent its marginal part). The flood waters covered various rock units, both older, mostly Mesozoic formations, and the early Miocene continental-lacustrine deposits. Therefore, there is a transgressive and unconformable relationship between older rocks and the Badenian sediments that cover them (*e.g*., Ugljevik, Jadar Basin, Kolubara Basin, Belgrade area, central Serbia). The major indicators of such event are molluscs, foraminifers, calcareous nannoplankton, ostracods, algae, etc. Based on them, the timing of seawater movement was determined (*e.g*., Pezelj *et al*., 2013; Mandic *et al*., 2019; Jovanović *et al*., 2019). Ostracods are not key microfauna for the dating of that event, but they give important response regarding the water quality, temperature, salinity, aeration, depth of water column, and other paleoecological features (*e.g*., Mandic *et al*., 2019). In general, the following species dominate: *Acanthocythereis hystrix* (Reuss), *Aurila haueri* (Reuss), *Callistocythere canaliculata* (Reuss), *Cletocythereis haidingeri* (Reuss), *Cnestocythere truncata* (Reuss), *Costa edwardsii* (Roemer), *Heliocythere vejhonensis* (Procházka), *Henryhowella asperrima* (Reuss), *Krithe* sp., *Loxoconcha hastata* (Reuss), *Paracypris polita* Sars, *Parakrithe dactilomorpha* Ruggieri, *Pokornyiella deformis* (Reuss), *Pterygocythereis calcarata* (Bosquet), *Tenedocythere sulcatopunctata* (Reuss). Taxa such as *Krithe* and *Parakrithe* live in the infraneritic (circalittoral) to bathyal zone (Ayress *et al*., 1999). These genera and other deeper water ostracods (*e.g*., *Paracypris*) support an open sea influence. *Callistocythere*, *Henryhowella*, *Xestoleberis*, *Costa*, *Acantocythereis* and *Pterygocythereis* occupy the infraneritic zone. Some genera are truly cosmopolitan (*e.g*., *Aurila*, *Costa*, *Loxoconcha*, *Cnestocythere*) and inhabit other provinces of that time (Mediterranean, Indo-Pacific). The shell size, its ornamentation and pronounced ultrastructure (*e.g*., *Pokornyiella*, *Cletocythereis*, *Semicytherura*, *Tenedocythere*) indicate conditions of a warm, shallow subtropical sea (Mandic *et al*. 2019).

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The fossil assemblage from Măru: a new window into the late Pliocene continental faunas of the Dacian Basin (southern Romania)

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Covering extensively southern Romania, the Dacian Basin was the most important area of sedimentation during the Pliocene and Pleistocene. Isolated Pliocene–Pleistocene vertebrate remains are fairly common, but multitaxic assemblages are relatively rare. Fossil sites, such as Bereşti, Măluşteni, and Podari, (*e.g.*, Simionescu, 1930, 1932; Trif *et al.*, 2016), are of particular interest, since they also provide information on non-mammalian vertebrates.

Recent field work in the western Dacian Basin, in an area comprising Pliocene lignite beds, with interbedded mudstones that yielded diverse mollusk faunas, led to the discovery of a new vertebrate fossil site at Măru (Gorj County). In this locality, thin lignite beds are covered by mollusk-bearing dark mudstone layer, which were tested for the presence of small vertebrates and invertebrates. Screen-washing produced numerous fish remains (mostly fin rays, but also vertebrae, and isolated teeth) assigned to the families Cyprinidae (*e.g.*, *Leuciscus* sp., *Rutilus* sp., *Scardinius* sp., *Chondrostoma* sp., *Abramis* sp., *Barbus* sp., *Carassius* sp., *Tinca* sp.), Percidae (an indeterminate percid), Esocidae (*Esox* sp.), and Siluridae (*Silurus* sp.). A few isolated rodent teeth were also found and tentatively assigned to the arvicolid *Mimomys hajnackensis*, an important find that helps determining the age of the fossil bed to early late Pliocene. The invertebrates found in the same fossil layer include a large indetermined unionid bivalve, the gastropod *Viviparus* sp. and a small number of poorly preserved ostracods, *e.g.*, *Candona* sp., *Cypria* sp., and *Cyprideis* sp.

The new fossil site at Măru contains the most diverse Pliocene freshwater fish fauna of the Dacian Basin known to date. Besides, it provides valuable information on the evolution of ichthyofaunas in the region, as well as new data on the depositional environments.

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Biostratigraphy, paleoenvironmental and magnetic signatures across the Maastrichtian–Paleocene slumps and slides of the Subsilesian Unit (Outer Flysch Carpathians, Czech Republic)

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Bystřice section, previously interpreted as a continuous Cretaceous–Paleogene transition, was newly studied using biostratigraphy (planktonic foraminifera and calcareous nannofossils), magnetic properties and geochemistry. Biostratigraphy confirmed the presence of the upper Maastrichtian (nannozone UC20; *Abathomphalus mayaroensis* foraminifer zone) and the Selandian (nannozones NP5–NP7; foraminifer zones P3b–P4b). The Danian is completely missing. Very rare occurrence of Danian foraminifers *Eoglobigerina edita* indicates existence of Danian sediments in the basin.

Strong remagnetization of rocks does not allow establishing a magnetostratigraphy of the section. Magnetite concentration and lithological changes drive the variations in magnetic susceptibilities. The magnetic fabric (anisotropy of magnetic susceptibility) points to tectonic disturbance of the section.

Studied strata consist mainly of up to 20-m-thick paraconglomerates interpreted as slumps. The slumps contain pebbles and blocks of diverse exotic rocks, intraclasts and reworked carbonate concretions enclosed in grey marly matrix. Slump folds are frequent feature indicating the synsedimentary deformation. Polished pebbles of quartz evidence a large thickness of mass flows. The paraconglomerate bodies are separated by bedded grey silty marls, sequences of medium-rhythmic sandstone flysch or conglomerate. The sandstone sequences are classical turbidites with $T_{a–d}$ intervals and abundant bioturbation (*Thalassinoides, Scolicia, Chondrites, Palaeodictyon, Atrhrophycus, Rhizocorallium, Ophiomorpha*). Submarine landslides are manifested by folded and thrust sandstone beds, breccia of partly-lithified, partly-unlithified sandstones, and characteristic failure planes. Selandian upper part of the section contains, besides slumps, frequent lens-like bodies of calcareous sandstones with calcareous algal detritus.

Maastrichtian lower part of the section contains two levels of the biostratigraphically proved Selandian marls. Most likely, the whole studied sequence was deposited during the Selandian, while the Maastrichtian marls and paraconglomerates represent submarine mass flows. The deposition took part on basin slope in bathyal zone.

The geochemical proxy parameters from the Maastrichtian sediments indicate more reducing setting, higher input of terrestrial phytodetrite and higher surface-water temperatures. Warming episodes are confirmed also by the occurrences of low-latitude nannoplankton *Micula prinsii*, *M. murus* and *Ceratolithoides kamptneri* in otherwise cold-water assemblage. The Selandian sediments contain higher share of aquatic organic matter. Water column was oxygenated and lower surface-water temperatures are indicated by carbonate $\delta^{13}C$ and $\delta^{18}O$ isotopes. Foraminifer plankton/benthos ratio decreases in the Selandian, which may indicate lower surface-productivity.

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Biostratigraphy, stable isotopes and paleomagnetism across the Jurassic–Cretaceous boundary at the Ropice Section (Western Carpathians, Silesian Unit)

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The Ropice section is situated near Český Těšín, Czech Republic. It is studied in the framework of a worldwide effort for selecting the boundary criteria and potential GSSP candidates for the Berriasian Stage. A multi-proxy approach, combining the methods of biostratigraphy, magnetostratigraphy and geochemistry, is herein applied to obtain stratigraphic framework for interregional correlations with other studied sections (*e.g*., Štramberk, Kurovice, Snežnica, Golubac, Rettenbacher, Tré Maroua). The strata at Ropice belong to the Silesian Nappe Unit of the Carpathian flysch. The J/K boundary interval is situated in the turbiditic limestones of the Těšín Formation (grainstones, packstones and wackestones) interbedded with marlstones (mudstones). The limestones contain calpionellids, calcareous foraminifers, and calcareous dinoflagellate cysts. The mudstones yielded calcareous nannofossils, flysch-type agglutinated foraminifera, and organic-walled dinocysts. The lowermost Berriasian is determined based on the co-occurrence of *Nannoconus wintereri* and acme of *Calpionella alpina*.

Nannofossils are mostly etched by dissolution across the section. Dominant genera are *Watznaueria* (±76%) and *Cyclagelosphaera* (±19%). Stratigraphically important nannoconids, such as *Polycostella beckmannii*, *Helenea chiastia*, and *Cruciellipsis cuvillieri* were found rarely. The lowest occurrence of *Nannoconus wintereri* confirms the Subzone NC0a (Casellato and Erba 2021). Calpionellids are relatively well preserved. Calpionellid zones and subzones were documented as follows: uppermost lower Tithonian Chitinoidella Zone (Boneti Subzone), upper Tithonian Crassicollaria Zone (Remanei, Intermedia and Colomi subzones), and lower Berriasian Calpionella Zone (Alpina Subzone). Small calcareous foraminifera (*Spirillina*, *Trocholina*, *Lenticulina*, *Tristix*, *Marginulinopsis* and miliolids) and flysch-type agglutinated foraminifera (*Pseudoreophax cisovnicensis*, *Pseudonodosinella troyeri*, *Ammogloborotalia quinqueloba*, *Caudammina silesica*) are longer-ranging taxa of low stratigraphic value. Species *Hoeglundina caracolla* and *Patellina turriculata*, considered until recently as Cretaceous markers, were found in the Tithonian part of the section. Organic-walled dinocyst asmblage, with *Mendicodinium groenlandicum*, *Systematophora areolate* and *Systematophora orbifera* of late Tithonian age, occurs in the lower part of the section. Presence of *Amphorula delicata*, *Muderongia longicorna* and *M. tabulata* correlate well with the lowermost Berriasian Alpina Subzone.

The stable isotopic record ($\delta^{18}O$, $\delta^{13}C$) shows mostly lower positive values of the $\delta^{13}C$ (~0.5‰, PDB) with also several negative expressions reaching ~ –1.7‰, PDB, and typical negative values of the $\delta^{18}O$ (~–4.2‰, PDB). The weak $\delta^{13}C$ signal is consistent with the majority of the Outer Flysch Carpathian sections around the J/K boundary interval. Magnetic data indicate an extensive remagnetization, with the presence of weathering product goethite, across the whole section. Average magnetic susceptibility and natural remanent magnetization show low values, 48 E-6 SI and 0.17 mA/m, respectively. The highest susceptibility (143 E-6 SI) was found in bed 15.

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The fossil vertebrate site of Stăuceni (Moldavian Platform, northeastern Romania) – new data on age and depositional setting

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Sarmatian marine deposits are extensively present in the Moldavian Platform. A new fossil site has recently been described from the Stăuceni open pit (Botoşani County) that, since 2017, yielded numerous marine vertebrate fossils. The fossiliferous deposits were considered to be of Volhynian (late middle Miocene) age, based on the marine mammal fossil content, *i.e*., Phocinae indet., *Kentriodon fuchsii*, Kentriodontidae indet., Cetotheriidae indet. (Gol'din *et al*., 2020). However, subsequent excavations led to the discovery, in the same gravelly bed from the top of the analyzed succession, of terrestrial vertebrate remains belonging to Plio-Pleistocene ungulates (indeterminate equids and bovids). The two sets of fossil remains (*i.e*., marine Miocene and terrestrial Plio-Pleistocene vertebrates) recovered from the same bed found at the top of the succession, show different taphonomy and support the scenario of Miocene fossils being redeposited in the younger Plio-Pleistocene deposits in a fluvial or lacustrine depositional setting.

Additional investigations have been carried out, for better understanding the depositional setting and the age of the fossiliferous deposits. Screen-washing of silty sandstones, overlain by the fossil beds that yielded the large vertebrates, also produced a few small mammal remains, tentatively assigned to the arvicolid *Borsodia* sp. and to the sciurid *Spermophilus nogaici*, supporting a late Pliocene–early Pleistocene age for the containing deposits. Silty layers, underlying the small-mammal-bearing deposits, yielded a microfossil assemblage consisting of *Elphidium*, *Nonion*, and *Porosononion* foraminifer genera, suggesting that upper middle Miocene–lower upper Miocene deposits are also present at the bottom of the succession.

Preliminary palynological investigations allowed us to identify a poor assemblage of freshwater algae (*Sigmopollis laevigatoides*) and some angiosperm taxa. According to Casas-Gallego *et al*. (2020), *S. laevigatoides* is very abundant in the Pliocene deposits from the central part of the Dacian Basin, and this finding also supports the age indicated by the terrestrial mammal remains.

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A Turolian (MN 11-12) ochotonid from the Moldavian and Scythian platforms (Romania): biostratigraphy and palaeobiogeography

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Moldova region is situated in the eastern territory of Romania located between the Eastern Carpathians and the Prut River. Structurally, its basement consists of Moldavian and Scythian platforms. They share three "mega-cycles" (Ionesi, 1994) or, better said, sedimentary mega-sequences. The last mega-sequence lasted from late Badenian until Quaternary, and was developed in a tectonically stable regime. Two fossil localities from both platforms attracted attention in the past few years. Creţeşti-Dobrina 1 (=CR1, MN9 age, Moldavian Platform) and Fălciu-Prut 1 (=FP1, MN11-12 age, Scythian Platform). The two fossil sites have yielded different faunas of amphibians and reptiles (Codrea *et al*., 2017a, b, 2022), with just two common taxa (*Pelobates* sp. and Colubridae indet.). Until now, no common mammals have been published from these two localities. Recent excavations, however, have revealed the ochotonid *Ochotona* (*Proochotona*) cf. *eximia* Khomenko, 1914 in both locations. While CR1 locality yielded a moderate number of specimens [5 fragmentary dentaries and 12 teeth (p_3)], FP1 locality yielded just a single fragmentary dentary with all teeth *in situ*. Similar ochotonid findings are known from the region in Republic of Moldova: Taraclia, MN12 (Khomenko, 1914); Cioburciu, MN11 (Lungu and Rzebik-Kowalska, 2011); Leordoaia, MN13 (*ibid*.); and Grădişte, MN11-12 (Delinschi, 2014). These findings raise a question about the biostratigraphic assignment of the CR1 locality. It could be younger than presumed. New finds provide important data on the paleobiogeographical distribution of *Ochotona* (*Proochotona*) cf. *eximia* in the Upper Miocene of the Moldavian and Scythian platforms.

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Upper Jurassic–lowermost Cretaceous microfossils from Hăghimaş Mountains (Eastern Carpathians, Romania)

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The limestones of the Upper Jurassic–lowermost Cretaceous from the Hăghimaş Mountains were studied in the section from the upper part of the Fagu Oltului Valley, a tributary of the Olt River. A detailed study of the limestones from the Fagul Oltului section was published by Lazăr *et al*. (2011). The lower part of the succession is remarkable for the rich brachiopod fauna contained in a red limestone buildup, documented by the authors as a stromatactis mud-mound. The mound consists of bioclastic wackestones and packstones with numerous brachiopods, crinoids and sponges. The mud-mound is covered by intraclastic grainstones and fine-grained limestones with planktonic bivalves. The up-section lithological units pass in shallow water limestone with nerineid gastropods, calcareous algae and foraminifera, in a regressive sequence.

The micropaleontological association identified in the Upper Jurassic–lowermost Cretaceous limestones from Fagul Oltului includes calcareous algae, foraminifera, saccocomid crinoid fragments, annelid worm tubes, sponge fragments, rare calpionellids and microfossils with uncertain systematic position.

The lower part of the succession is rich in fragments of *Saccocoma* sp. These are represented almost exclusively by sections of secondary brachial parts (secundibrachials). Agglutinated annelid tubes of *Terebella lapilloides* are also present. *Crescentiella morronensis* is frequently associated with *Saccocoma* and *Terebella* in this part of the succession.

The calcareous algae are mainly represented by dasycladalean remains. Fragments attributable to *Actinoporella* sp. or *Clypeina* sp. and *Salpingoporella pygmaea* are relatively common. *Terquemella* sp. and rare fragments of *Rajkaella bartheli* are also present. It is worth noting the presence towards the upper part of the succession of some charophyte remains in a limestone containing terrigenous material. Rare cyanobacteria of the *Rivularia*/*Cayeuxia* type have also been identified.

The association of benthic foraminifera consists of *Bramkampella arabica*, *Textularia* sp., *Mayncina* sp., *Protopeneroplis* cf. *ultragranulata*, *Nautiloculina* sp, *Reophax* spp., *Ammobaculites* sp., *Trocholina conica*, ?*Seracenaria* sp., *Mohlerina basiliensis*, *Coscinoconus alpinus*, Epistominidae indet., Nodosariidae indet., *Spirillina* sp., *Lenticulina* sp. and encrusting foraminifera.

The incertae sedis *Muranella parvissima* was rarely identified. These are small spherical or ovoid corpuscles, often grouped in clusters, made up of calcite prisms developed around a micritic center with irregular outline. Their nature remains uncertain.

In one thin section we identified rare calpionellids, some of which certainly belong to the species *Calpionella alpina* Lorenz, representing small globular forms characteristic of the Upper Tithonian.

The microfossil species identified in the Fagul Oltului section have a wide stratigraphic distribution. The most important stratigraphic indicators are *Trocholina conica* (which does not exceed the Kimmeridgian) and *Calpionella alpina* (which does not appear before the late Tithonian). Based on the whole micropaleontological assemblage, the lower part of the succession can be ascribed to the Kimmeridgian–lower-middle Tithonian, and the upper part – to the upper Tithonian–Berriasian.

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Paleogene terrestrial vertebrates of Transylvania – key for better understanding the 'Grande Coupure' Event

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In Romania, mainly in Transylvania, but also in the Carpathian Foredeep and on limited areas in Southern Dobrogea, Paleogene shallow sea and terrestrial outcrops are available for study. Apart from the ones exposed on the southern border of the Transylvanian Basin at Turnu Roșu (=Porcești) and some other localities of same area (*e.g.*, Dobârca), the majority are located mainly on the NW side of the Transylvanian Basin (in Gilău, Meseș and Preluca sedimentary areas). In these areas, alternation of terrestrial and shallow marine facies was noticed. The fossils, mainly the vertebrates, evidence for the bio-events occurring around the Eocene/Oligocene boundary, documenting the 'Grande Coupure' turnover in Eastern Europe.

Of special interest are the vertebrate localities mentioned below. For the late Eocene, these are sites related to the Viștea Limestone Formation and Valea Nadășului Formation (both late Priabonian). For the former, Leghia Site holds attention; although it refers to marine limestones deposited in a shallow marine platform, fossils considered as (?) terrestrial representatives (the crocodilian *Diplocynodon*) were recently found. The latter formation is dominated by red beds of fluvial origin. The most illustrative is the classical locality Rădaia, where the hyracodontid *Prohyracodon orientale*, the brontotheriid *Brachydiastematherium transilvanicum*, as well as the crocodile *Diplocynodon* were reported already in the second half of the 19th century. A nearly coeval locality, Morlaca–Valea Răoasă, yielded turtle remains (Chelonia indet.), amynodontid *Amynodontopsis* aff. *bodei*, an anthracothere (?*Prominatherium*), as well as embrithopods (both large- and small-sized), documenting the appearance of the mammals of Asian origin in Europe prior to the Eocene/Oligocene boundary. Small-sized mammals of same Priabonian age are also known from Treznea and Bociu, both localities with fair potential for new faunal records. Valea Nadășului Formation is covered by the Cluj Limestone Formation, a marine succession, where the "foolish" bird *Eostega lebedinskyi* and the recently described crocodile species *Diplocynodon kochi* evidence terrestrial, near-shore influences.

In the Oligocene, the most relevant discoveries concern the Mera and Dâncu formations. In the former one, the rhinocerotid *Ronzotherium filholi* (="*R.*" *kochi*) and the oldest known giant rhinoceros of Transylvania (*Urtinotherium* sp.) were found at Cluj-Napoca and Fildu de Sus. For the latter one, in the localities Cluj-Napoca, Suceag and Mera, a rich fauna is recorded: fishes (various sharks, *Dapalis* sp., *Hemitrichas* sp., etc.), salamanders (*Mioproteus gardneri*), turtles, birds (*Rallicrex kolozsvarensis*), micro-mammals (mainly cricetids), and the anthracothere *Elomeryx* are known. This fauna shows the turnover occurring after the 'Grande Coupure' event in Transylvania.

In southern Transylvania, one can mention only Lutetian and Priabonian crocodile isolated teeth from Turnu Roșu of very probable terrestrial origin, and the amynodont *Sellamynodon zimborensis* from Dobârca locality (late Eocene or early Oligocene).

As a conclusion, the Paleogene terrestrial vertebrate localities show an important potential to enlarge the list of taxa by new discoveries, adding evidence about 'Grande Coupure' turnover in Eastern Europe.

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Eocene–Oligocene *Perissodactyls* of Romania: a short overview

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The main areas where Paleogene terrestrial deposits crop out in Romania are situated on the Northwestern margin of the sag? mega-sequence of the sedimentary basin of Transylvania (Danian–Chattian, in Krézsek and Bally, 2006, and references therein). It is an area with an alternation of shelf and slope marine deposits, and continental ones, of fluvial origin.

The continental deposits are rather scarce in vertebrate fossils, but in some localities, they can yet be found. The vertebrates of interest for this study are unearthed from the formations documenting the 'Grande Coupure' faunal turnover. The localities of origin of these fossil vertebrates are located in Gilău and Meseș sedimentary areas.

Among the terrestrial macro-vertebrates, the odd-toed are worth noting for study (Codrea, 2000). The oldest representatives in Transylvania were found over a century ago at Rădaia, in Valea Nadășului Formation (Priabonian). The hyracodontid *Prohyracodon orientale* is a species described by A. Koch. Its Asian origin is doubtless, as representatives of this genus were found in upper Eocene deposits of China, but none in Western Europe. From the same locality, the brontothere *Brachydiastematherium transilvanicum* was originally described in 1876. Its origin is also in Asia, as long as no other brontothere is known from Western Europe [the westernmost ever mentioned, *Titanotherium bohemicum* was found in the "diluvium near Prague" in the Czech Republic, is in fact a *nomen dubium* (Lucas and Schoch, 1989)]. New brontothere remains were found recently in Morlaca, also in Gilău area, where at least two forms are present: a large sized one (*Embolotherium* size) and a smaller one (*Dolicorhinus* or *Telmatherium* size). The research on this locality is still in progress.

In the lower Oligocene of Transylvania the rhinocerotid *Ronzotherium filholi* (="*R.*" *kochi*) and the oldest known giant rhinoceros of Transylvania (*Urtinotherium* sp.) were recorded at Cluj-Napoca and Fildu de Sus (Mera Formation). Higher, in Chattian (Cuzăplac Formation), the giant rhinoceros *Paraceratherium prohorovi* was recorded. The amynodont *Sellamynodon zimborensis* from Dobârca locality has a rather unclear geological age (late Eocene or early Oligocene).

The stratigraphic distribution of these odd-toed taxa is relevant for the faunal turnover which occurred around the 'Grande Coupure' in the Eastern Europe as a consequence of the Paleogene changing paleogeography.

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Charophyte flora (aquatic plants) from the Suceag Oligocene fossil site (western Transylvanian Basin, Romania): biostratigraphy, paleoecology and paleobiogeography

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The Gilău sedimentary area, located in North-Western Transylvania (Romania), has a rich history as it concerns the Paleogene terrestrial biota (Codrea and Fărcaș, 2002; Fărcaș, 2011, and references therein; Tissier *et al*., 2018). Amongst this terrestrial biota, charophytes (aquatic plants) constitute a part of the fossil record that is not fully understood. Recent investigations in the Oligocene deposits of the Dâncu Formation, near Suceag Village, have yielded a charophyte assemblage composed of six taxa, including *Harrisichara* sp., *Sphaerochara* cf. *hirmerii*, *Lychnothamnus pinguis* forma *pinguis*, *L. pinguis* forma *major*, *L. praelangeri*, and *Nitellopsis (Tectochara) merianii*. Suceag represents a key post-'Grande Coupure' fossil site and it is constituted by representatives of early Oligocene faunas. In agreement with these faunas, the herein studied charophyte assemblage confirms that the Dâncu Formation is Rupelian in age (ca. 29–30 Ma). Moreover, the presence of this flora completes the knowledge about the geological evolution of this area, bringing new insights about the paleoecology of Suceag and the distribution of these charophyte species in Eurasia during the Rupelian. The gyrogonites show evident signs of transport and charophyte thalli (stems) are missing. In addition, the associated fossils, *e.g.*, micro- and macro-mammals, turtles, crocodilians (*Diplocynodon* sp.), fishes (such as stingrays, *Dapalis* sp., *Hemitrichas* sp.), and invertebrate shells suggest that charophytes were deposited in an estuarine environment, near the mouth of a large river. This study also represents a revision of previous works about fossil charophytes performed in the same and nearby localities related tothe Dâncu Formation (Baciu and Feist, 1999; Baciu, 2003).

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The silicic igneous clasts in the Cretaceous successions of the Eastern Carpathian Moldavide tectonic units: paleogeographic insights

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Cretaceous turbidites occur in the Eastern Carpathians in two distinct tectonic units: in an inner (western) area, namely the Outer Dacides, containing rocks associated with the Protosilesian–Severin rift, and in an outer (eastern) one, within the Moldavides, consisting of unrooted nappes thrust on foreland units of poorly known origin. The presence of several ridges within the flysch basin has been inferred to explain the differences between the contemporaneous sedimentary successions in different nappes (*e.g.*, Săndulescu, 1984; Golonka *et al.*, 2021, and references therein).

The Cretaceous successions (starting from the Valanginian Stage) of the Moldavide nappes (Teleajen, Macla, Audia and Tarcău) locally contain fragments of acid igneous rocks (granodiorite, granite, rhyolite) forming arenitic to ruditic intercalations. Such fragments, assigned to an inferred Cuman Cordillera (Murgeanu, 1937), also occur in the Variegated Clay Nappe (located in between the Macla and Tarcău nappes) from the southern part of the Eastern Carpathians. Interestingly, in the Audia Nappe (*i.e.*, north of Chiojdu Village), the igneous clasts are locally associated with green phyllite fragments similar to the Ediacaran meta-turbidites of Central Dobrogea, which would argue for the position of the Cuman Ridge between the accumulation areas of the sedimentary successions in the Macla and Audia nappes. The mineralogical and petrographic selectivity of the igneous rock fragments (forming intercalations made up almost exclusively of these rocks) in the sediments of the Variegated Clay Nappe suggests a source close to the depositional area of the variegated clays (of early Campanian age, based on calcareous nannofossil biostratigraphy).

U-Pb zircon dating of the igneous clasts enclosed in Lower Cretaceous deposits (Audia and Macla nappes, Roban *et al.*, 2020) and Upper Cretaceous sediments (Variegated Clay Nappe) indicate an age of ca. 600 Ma. The clasts of igneous rocks show volcanic arc geochemistry, suggesting their formation during the Cadomian/Panafrican orogeny.

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The Middle–Upper Jurassic deposits in the Rahoveci (Kosovo) and Mirdita (Albania) areas

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The present study represents the investigations on the Middle–Upper Jurassic deposits in the Rahoveci area (Kosovo) and their comparison to coeval deposits in the Mirdita area (Albania). These areas are situated in the central part of Kosovo, north-west of the city of Rahovec and in the Puke–Mirdita region of Albania, respectively. The Rahoveci ophiolite unit, the Mirdita ophiolites and their associated sedimentary sequences are part of the Alpine Dinaric-Hellenic chain.

The Middle–Upper Jurassic deposits of the Rahoveci area are represented by the following units: *1*) Guri i Zi Mélange (block-in-matrix type mélange, similar to Simoni Mélange in Mirdita, Albania); and *2*) Çupeva radiolarian cherts, conformably overlain by the Volljaku Flysch.

The Guri i Zi Mélange includes blocks of diverse rocks, such as sandstones, cherts, limestones, basalts, etc., derived from both continental and oceanic crusts. This mélange, all along the Dinaric-Hellenic chain, starts its formation during the Middle Jurassic (Kodra and Hoxha, 2019). Preliminary data of radiolarian assemblages in Çupeva chert succession determined an Oxfordian–Kimmeridgian age (Suka, 2015), marking a noticeable contrast to the age of the chert successions recorded across the Mirdita area. The Volljaku Flysch is characterized by turbidites, consisting of arenaceous and pelitic lithofacies, interlayered with micritic limestones in its upper part.

The gradual transition between the Çupeva cherts and the Volljaku Flysch is of particular importance to understanding the Middle Jurassic–Early Cretaceous paleogeographic evolution of this area, as well as to the Dinaric-Hellenic chain.

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Paleozoic eurypterids and phyllocarid crustaceans in the Balkans

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Paleozoic phyllocarid crustaceans and pterygotid eurypterids have been documented for the first time in the Balkans (Western Bulgaria) in this century (Sachanski *et al*., 2008; Sachanski, 2017, 2020). Such fossils were found by one of us (MR) in Eastern Serbia in 2021. In peri-Gondwanan Europe, Silurian phyllocarid crustaceans and Devonian pterygotid eurypterids have only been established in the Czech Republic, Germany, France, Italy and Spain.

The Silurian phyllocarid crustaceans from the Balkans were found in the Wenlockian shale of the Svoge Unit, West Bulgaria (Sachanski, 2020), and in the upper Silurian? greish to yellow siltstones of the Gethicum Zone (=Kučaj Zone), Eastern Serbia. Both specimens represent a telson and furcal rami in connection. These phyllocarid remains are too poorly preserved to allow identification to species level, and have thus been assigned to *Ceratiocaris* sp. These finds, nevertheless, suggest that phyllocarids may have been a common component of assemblages present in shale facies from the Silurian in the peri-Gondwanan Europe.

The first reported eurypterids in Western Bulgaria are from the Lower Devonian (Lochkovian, *Uncinatograptus uniformis* graptolite zone) dark shales in the Lyubash–Golo Bardo Unit (Sachanski *et al*., 2008). One fragment shows a typical scale-like ornament found mainly on the tergites of pterygotid eurypterid genera, and two fragments of a chelicera belong to *Acutiramis bohemicus* and/or *Pterygotus barrandei* (Sachanski, 2017). A fragment of chelicera was also found in the Lochkovian black shales of the Ogradishte Formation in the Svoge Unit (Angelov *et al*., 2010). Prolongation of the Lyubash–Golo Bardo Unit in Eastern Serbia is the Gethicum Zone. Eurypterids here are represented by a fragment with the distinct scale-like ornamentation of the pterygotids, and a segment from a walking leg. The pterygotid remains were found together with a few graptolite taxa, which are characteristic for the lower part of the *U. hercynicus* graptolite zone (Lochkovian, Lower Devonian). There are at least two species in the world from this stratigraphic interval that correspond to the pterygotid eurypterid remains from Serbia, namely *Acutiramis perneri* Chlupáč and *Pterygotus barrandei* Semper. Without the chelicerae, however, it is impossible to make a precise identification.

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The Variscan basement of the North Dobrogea Orogen. Review of existing paleontological and geochronological data

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The Cimmerian Orogen of North Dobrogea was formed upon a Variscan basement, which is exposed in the area of North Dobrogea, and concealed north-west of the Danube River, between the Peceneaga-Camena and Sfântu Gheorghe Faults. Detrital zircon analyses obtained in the last decade from various basement lithologies has enabled a better understanding of their depositional ages, while U-Pb monazite and Ar-Ar ages are used to understand the Variscan metamorphic history. This paper presents a critical review of the existing paleontological data, monazite and Ar-Ar ages on metamorphic and magmatic rocks, as well as detrital zircon data and their interpretations.

In the Măcin Zone, the Variscan basement consists of two distinct metamorphic successions derived from an accretionary wedge and an island arc, showing a late Carboniferous–early Permian amphibolite facies metamorphism (based on monazite dating) of Cambrian protoliths (based on interpretations of detrital zircon data). Two lower-greenschist-facies metaterrigenous series are also exposed here, derived from Late Neoproterozoic and middle Ordovician protoliths, according to interpretation of detrital zircon data. Other Paleozoic deposits, ascribed to the Silurian, lower Devonian and upper Carboniferous–lower Permian, show a subgreenschist-facies metamorphism, with a penetrative development of slaty cleavages. Deformation of these successions predated the emplacement of Late Paleozoic intrusions.

In the Tulcea Zone, the basement of the Triassic successions consists of radiolarites and siliceous shales associated with distal turbidites, discontinuously exposed in the cores of two Cimmerian anticlines. A detailed biostratigraphy of these Paleozoic deposits is not possible, due to patchy outcrop area, complex folding and scarcity of fossils. In the Mahmudia anticline, Devonian deposits of the Beştepe Formation dominated by a thick sequence of red, green or black radiolarites were dated based on conodont assemblages from pelagic limestone interbeds. Recent detrital zircon data indicate that some parts of the turbidite succession were accumulated in the Silurian.

In the core of the southern, Somova anticline, boreholes intercepted an association of bedded cherts and greenish siliceous slates which yielded middle-upper Ordovician palynomorphs. The siliceous complex is overlain by black slates containing lower Silurian chitinozoans and acritarchs. Associated black radiolarites (lydites) were ascribed to the Silurian based on conodont-dominated microfauna identified in limestone blocks assumed to be interbedded in the siliceous deposits.

In sandstone-dominated turbidites exposed in Dealul Horia, upper Ordovician–Silurian acritarch-dominated palynological assemblages were identified, with subordinate chitinozoans. However, detrital zircon data yielded a late Devonian depositional age, and later an even younger, early Carboniferous depositional age. A possible explanation for the age discrepancies is that the Ordovician–Silurian palynomorphs have been reworked. Such depositional ages enable a correlation with the Culm facies from the Central European Variscides, as well as with coeval turbidites from the Istanbul zone in the Pontides. The depositional facies and deformational style might suggest that radiolarites and turbidites from the Tulcea Zone accumulated in a part of the Rhenohercynian back-arc basin, being subsequently displaced to SE along wrench faults of the Trans-European Suture Zone.

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Integrated paleontological and sedimentological study of the middle Miocene deposits (Galata and Evxinograd formations) from northeastern Bulgaria in connection with climate evaluation

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Deposits referred to the Galata and Evxinograd formations of middle Miocene age crop out on the Black Sea beach in the area of Sveti Nikola, near Varna. The Galata Formation is composed of fine-grained sands, fine-grained sands with mollusks, fine-grained clayey sands with carbonate nodules, and grey-green clays with mollusks at the base of the section, followed by alternation of fine- and medium-grained sands, grey and yellowish in color. Mollusk fauna of this formation is represented by *Ervilia pusilla* (Phil.), *Lutetia (Spaniodontella*) *gentilis* (Eichw.), *L.* (*S.*) *umbonata* Andrus., *Savanella andrussovi* (Toula), *Mohrenstern-nia subglobosa* Iljina, *M. barboti* Andrus., *Archashenia merklini* Zhgenti. The Evxinograd Formation is represented by grey limy clays, compacted clayey and limy sands with mollusk shells, above which laminated diatomaceous limy and sandy clays are described. Two layers enriched in small serpulid buildups are registered in the base of the formation, and two limestone beds – in the top of the section. The presence of kaolinite and illite in clay deposits reflects chemical weathering in the watershed with warm and high rainfall climate conditions. Mollusk fauna in this part of the Evxinograd Formation is presented by *Musculus* (*Musculus*) *sarmaticus naviculoides* (Koles.), *Plicatiforma praeplicata* (Hilb.), *Abra* (*Syndosmya*) *alba scythica* Sok., *Gibbula* (*Gibbula*) *angulatosarmates* (Sinzov), *G.* (*Colliculus*) *picta* (Eichw.), *Acteocina lajonkaireana lajonkaireana* (Bast.), *Retusa* (*Cylichnina*) *convolute* (Brocc.), *Obsoletiforma lithopodolica lithopodolic*a (du Bois), *Dorsanum* (*Duplicata*) *neutrum* (Koles.). Fossil diatoms of excellent preservation have been determined. The greatest species diversity has been identified of the genera *Grammatophora* Ehr., *Rhopalodia* O.Müller, *Licmophora* C.A.Ag., *Amphora* Ehr. & Kütz., *Cocconeis* Ehr., and *Diploneis* (Ehr.) Cleve. The diatom flora includes species suitable for age dating. Species characteristic for the association of the *Achnathes baldjikii var. podolica* Subzone are indicated. Its stratigraphic range corresponds to the Sarmatian Stage (Bessarabian Substage).

Sands from the Galata Formation had been transported by fluvial/deltaic processes and deposited in a high-energy environment on the beach. Alternation of fluvial and shallow marine environments was observed which may be explained by sea-level fluctuations in the littoral zone during the middle Miocene time. Mollusk fauna is characteristic of low and moderate water dynamics and shallow littoral zone with low salinity. Sediments of the Evxinograd Formation show typical features of deposition in the shallow marine environment, too. This is proved by the type of diatom flora. The common presence of epiphytic diatoms is a clear indication of the presence of standing macrophyte vegetation along the littoral zone of the shallow Varna–Balchik Bay. Mollusk fauna here evidences for low to moderate dynamics and depths of about 20–50 m and low to normal salinity.

Results from the integrated paleontological and sedimentological studies indicate relatively warm humid climate during the deposition of these sediments.

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Mapping the Paleogene sirenians in Transylvania

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Paleogene is an important period in Earth's history, not only marking the aftermath of the Cretaceous/Paleogene (K/Pg) mass extinction, but also showcasing numerous significant paleoclimate changes, tectonic movements and radiations of the flora and fauna, particularly that of the mammals.

The Transylvanian Basin is an intermountain depression, which is filled with Cenozoic deposits, and from the perspective of the Paleogene, the region primarily consists of shallow-marine and continental sediments. In the marine deposits, many sirenian fossil remains have been discovered through time. Sirenian mammals, commonly referred to as 'sea cows', are an order of mammals that nowadays are fully adapted to an aquatic lifestyle, with a number of unique adaptations. They are the among rare marine mammals that are strictly herbivorous, lack hind limbs, and their skeleton displays a feature (pachyosteosclerosis) that makes all the bones become thicker and denser, and lack internal marrow.

The first sirenian fossil remains from Romania were uncovered from the Eocene limestone in the Turnu Roşu site (former Porceşti) by Johann Michael Ackner, and were determined by Hermann von Meyer. Next came a number of fossils that were mentioned in various articles, beginning with Koch (1894, and references therein), who pointed out such finds in the upper Lutetian layers from Iara and Chioarului valleys, the lower Priabonian Leghia Limestone, the upper Priabonian Cluj Limestone (*e.g.*, in outcrops from Mănăştur, Hoia, Cheile Baciului), as well as other areas (*e.g.*, Jebuc, Baba, Buciumi, Prodăneşti, Stana). In the lower Oligocene, the frequency of sirenian fossils is lower, probably due to the decrease of the number of individuals after the 'Grande Coupure' turnover. For this age, one can mention the sirenian localities from the Mera Formation [*e.g.*, Cluj-Napoca (Hoia Hill), Mera, Stoiceni, Bizuşa]. In the upper Oligocene, seemingly the sirenians were not present at all in Transylvania, or if present, they had just exceptional occurrence.

Outside Transylvania, the Paleogene sirenian remains are only exceptional. Only a single fragment of a fossil sirenia rib was described by Grigorescu (1967) from the Albeşti Limestone (Carpathian Foredeep).

In conclusion, even if some findings were incorrectly attributed to the genus *Halitherium*, which today is recognized to have existed only during the early Oligocene–early Miocene time interval, these descriptions are important pertaining to the geographic distribution of the sirenians, in Romania, as well as Eurasia.

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Ichnofossils from turbiditic deposits of the Emine Formation (Campanian–Paleocene) in the Eastern Stara Planina Mountains, Bulgaria

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The Emine Formation (upper Campanian–upper Paleocene; 1670 m thick, Cretaceous – 820 m thick) in the Eastern Stara Planina Mountains (Bulgaria) is represented by typical flysch facies composed of sandstones, siltstones, and argillaceous limestones (Juranov and Pimpirev, 1989; Sinnyovsky, 2004), which were deposited in the "Emine trough" considered as a back-arc basin (Nachev, 1981; Sinnyovsky, 2004). These deposits contain abundant but poorly recognized trace fossils. Boshev *et al.* (1967) mentioned and illustrated *Scolicia strozzii* (their *Subphyllochorda*), *Scolicia prisca* (their *Palaeobullia*), *Helminthorhaphe* (their *Helminthoida* and *Cosmorhaphe*), *Paleodictyon* spp. (probably *P. minimum*, their *P. carpathicum*), *Multina* (their *Paleodictyon* in fig. 30), *Chondrites*, *Zoophycos*, *Spirophycus* (their spiral bioglif in fig. 36). For the present study, the best outcrops are cliffs along a transect running from Sveti Vlas Village, crossing the neighborhood of the Emona Village and the Cape Emine, which is the most eastern part of the Stara Planina Mts (the Upper Cretaceous part of the formation – see Sinnyovsky, 2004), and to north up to the Vaya River, where crops out the transition to Palaeogene.

The trace fossils include *Capodistria* sp., *Chondrites intricatus*, *Ch. targionii*, *Ch. affinis*, *Ch. stellaris*, *Cladichnus fischeri*, ?*Cosmorhaphe* isp., cf. *Dictyodora* isp., *Glockerichnus* isp., *Gyrolithes* isp., *Halimedides* isp., *Halopoa* isp., *Helminthopsis* isp., *Megagrapton* isp., *Multina minima*, *Nereites irregularis*, *Ophiomorpha annulata*, *O.* cf. *annulata*, *O. rudis*, *Palaeophycus* isp., *Paleodictyon* ispp., ?*Parataenidium* isp., *Phycosiphon incertum*, *Phymatoderma* isp., *Pilichnus* isp., *Planolites* isp., *Rosharichnus* isp., *Saerichnites* isp., *Scolicia prisca*, *S. plana*, *S. strozzii*, *Taenidium* isp., *Thalassinoides* isp., *Trichichnus* isp., *Tubulichnium rectum*, and *Zoophycos* isp.

The trace fossil assemblage represents the Paleodictyon ichnofacies and locally the Ophiomorpha rudis ichnosubfacies of the Nereites ichnofacies. Along with facies features, they suggest the middle-lower parts of the deep-sea fan depositional system, mostly depositional lobes and lobe fringes.

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Biostratigraphy of the Albian/Cenomanian boundary of the Dzirula Massif (Georgia)

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The Dzirula Massif is an exposed part of the pre-Alpine crystalline basement of the Black Sea-central Transcaucasian terranes. The first information about the Cretaceous deposits of the periphery of the massif came from the work of the French traveler DuBois de Montperreux from the 1830-s. Latter, Abich (1858) noted the presence of Upper Cretaceous layered limestones with multi-coloured cherts in the Kvirila River valley. The tectonics of the central zone of uplift of the massif was recently studied by Gamkrelidze (2000).

In the Dzirula Massif, the Upper Cretaceous deposits are mainly represented by carbonate rocks. In the southeast periphery of the massif, the Cenomanian strata cover transgressively, in places with angular unconformity, leans on the Albian. In the northern periphery, the Upper Cretaceous overlies transgressively the crystalline basement rocks.

The Albian deposits of the Southern periphery are represented by thin-layered, greenish-grey, fine-grained tuffaceous sandstones and tuffaceous breccias with clayey cement. They contain the bivalves "*Inoceramus*" *crippsi*, "*I.*" *pictus*, "*I.*" *tenuis* and the foraminifera *Parathalmanninella appenninica, Thalmaninella globotruncanoides, Th. brotzeni, Planomalina buxtorfi, Hedbergella infracretacea, Gavelinella suturalis*, and *G. agalarovae*. The upper part of the Albian is represented by grey sandy marls and marly clays, which contain foraminifera: *Lenticulina muensteri, Ammodiscus incertus, Gavelinella suturalis, Hedbergella infracretacea, Parathalmanninella appenninica, Thalmaninella globotruncanoides, Anomalina* sp. An ammonite, *Pervinquieria* cf. *inflata*, was also found.

The Cenomanian Khandevi series deposits conformably overlie the Albian complexes. The Cenomanian is represented by coarse-grained, greyish-brown carbonate clays and blue-green calcareous sandstones. This series contains bivalves, "*Inoceramus*" *pictus* and "*I.*" *neocaledonicu*, and foraminifera: *Praeglobotruncana gibba*, *Thalmanninella globotruncanoides*, *Rotalipora cushmani* and *Dicarinella imbricata*. Accordingly, the upper Albian deposits correspond to the *Parathalmanninella appenninica* foraminiferal zone, whereas the lower Cenomanian strata correspond to the *Thalmanninella globotruncanoides* and *Th. greenhornensis* foraminiferal zones. The terminal Albian was a time of manifestation of the anoxic event OAE 1d. The paleogeographic setting, which started during the Barremian, lasted till the end of the Albian. In the Caucasus region, the OAE event is expressed by the presence of interlayers of black clays. Volcanogenic and volcanosedimentary rocks were formed at the same time in the study area. According to some authors (*e.g*., Gavrilov *et al*., 2013), the increase in volcanic activity in the end of Albian and the beginning of Cenomanian was of sub-global character.

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Early Miocene insects and plant fossils from Valjevo-Mionica Basin (Western Serbia)

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The Valjevo-Mionica Basin, located in the western part of the Valjevo-Mionica-Belanovica Trough, formed during the Early Miocene (Ottnangian–Karpatian). The thickness of the deposits in this basin exceeds one thousand meters. Plant and insect fossils were extracted from Mionica Formation (pyro-bitominous), formally known as the „Bela Stena sediments“.

The paleoflora was collected from three different but not distant sites, whereas the fossil insects were collected in one of them (Šušeoka locality). Fossil remains of plants and insects come from one and same rock formation, the pyro-bituminous Mionica Formation; hence, a unified paleoecological consideration is possible.

The predominance (24.5%) of *Daphnogene* is clearly visible in the plant material. Other Laureaceae are also abundant (40%). The incidence and taxonomic diversity of Laureaceae indicate the optimum climate for this family. Many specimens of *Daphnogene polymorpha* forma *bilinica* (shape of sun-grown leaf), winged seeds, and bird feathers indicate that the fossil material was transported predominantly by wind.

Palaeotropical elements prevail in the paleoflora of the Valjevo-Mionica Basin (39 %), and arctotertiary elements are represented with 21% of all specimens.

Insect fossils are rare, compared to the floral fossils. Fossil insects are representatives of taxa that live in aquatic environment. Identified taxa are as follows: Heteroptera ? Notonectidae – abdomen, also known as “back-swimers”; Corixidae – larva, known as “rower bug”; Ephemeroptera – imaga, aquatic insect with wings in stage of imaga; Trichoptera – larva, aquatic and may be abundant in some cool, fresh water habitats; *Libellula doris* (Odonata fam.) – larva, fast-moving volant carnivore-insectivore.

It has been inferred that climate was warm and humid (subtropical) during the existence of these plants and insects. The lack of other limnic organisms (except fishes) suggests a lake setting with the described vegetation occurring along the banks. In the lake, the environment was anaerobic due to weak vertical circulation without freshwater supply and no oxygen deep in the lake. Fishes of the lake swam under the surface using oxygen from the air that dissolved only in the upper layer of the water column.

Thin-layered marlstones or “paper shale” indicates equal rates of deepening and sedimentation of the basin.

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Paleoecological characteristics of palynomorphs from Tertiary sediments of the Drmno Depression, Serbia

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The palynological material analyzed in this report from the morphological, taxonomic and paleoecological points of view comes from the Tertiary sediments of the Drmno Depression (90 km east of Belgrade) from the exploration wells Bradarac–Maljurevac and Bubušinac.

The palynomorphs were extracted by laboratory processing of samples (maceration procedure) in the Laboratory for Paleontology and Historical Geology of the Faculty of Mining and Geology.

Palynospectra include 32 genera and 53 species determined by morphological analysis: *Baculatisporites* cf. *nanus, Corrugatisporites microvallatus, Leiotriletes minor, Leiotriletes triangulus, Monoleiotriletes minimus, Intrapunctisporis balinkaënsis*, aff. *Neogenisporis* fsp. „2“, *Polypodiaceoisporites marxheimensis, Laevigatosporites*? *bisulcatoides, Laevigatosporites haardti, Equisetisporis equisetiformis, Abiespollenites maximus, Abiespollenites dubius, Abiespollenites cedroides, Abiespollenites latisaccatus, Abiespollenites* sp. 1, *Cathayapollenites uenoi, Cathayapollenites van campoe, Cathayapollenites echinatus, Cathayapollenites krutzschi, Cedripites deodaraeformis, Keteleeriapollenites pseudolaricis, Pinuspolenites macroinsignis, Pinuspollenites pristinipollinius, Pinuspollenites latisaccatus, Pinuspollenites argutus, Pinuspollenites pseudocristatus, Piceapollis tobolicus, Podocarpidites nageiaformis, Cunninghamiaepollenites janinae, Sequoiapollenites sculpturius, Taiwaniapollis miocaenicus, Sequoiapollenites rotunds, Inaperturopollenites verrupapillatus, Betulaepollenites betuloides, Ulmipollenites undulosus, Intratriporopollenites* cf. *microreticulatus, Intratriporopollenites cordateaformis, Intratriporopollenites insculptus, Myricipites rurensis, Myricipites bituitus, Platycaryapollenites miocaenicus, Quercopollenites petrea, Tricolpopollenites liblarensis, Tricolporopollenites* sp. Type "Centaurea“, *Tricoloporopollenites cingulum, Zelkovaepollenites thiergati, Magnoliaepollenites meogenicus neogenicus, Ostryapollenites rhenamus, Nyssapollenites pseudocruciatus, Nyssapollenites* sp. "A“, *Rhooipites psudocingulum, Juglandipollis juglandoides*. Based on the analysis of the floristic composition, the dominance of gymnosperms, significant presence of angiosperms and a small percentage of spores were observed.

The analysis of palynological material shows that in the palynospectra from exploration wells, floodplains and mesophilic forests, transitional complexes, as well as mountain vegetation complexes are the most abundant. Wetland and laurophilic complexes are present in a much smaller percentage. Aquatic plant complexes and coastal vegetation complex are missing. Climatic affinity of vegetations from the area of the Drmno Depression indicates a striking higher percentage of complexes of arctotertiary plants in relation to complexes of subtropical and moderately warm plants.

Paleoecological analysis indicates that around the sedimentary basin, at a great distance, there was a mountainous and forested region from where palynomorphs carried by wind reached the exploration area, while swamps that were located in the area of Bradarac-Maljurevac indicate a possible proximity to the coast of the sedimentation basin. The results of paleoecological analysis indicate that during the deposition of palynomorph-bearing strata in the Drmno Depression, there was a hilly-mountainous region, as well as wetlands, around the exploration area. In that time, there was a cold climate with elements of moderately warm and subtropical climate.

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Biostratigraphy on ammonoids of the Jurassic sediments of the Ukrainian Carpathians

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The Ukrainian Carpathians occupy an intermediate position between the South-Eastern (Romanian) and Western (Polish and Slovak) Carpathians and, together with them, constitute an important element of the northern branch of the Alpine folded region.

In the Ukrainian Carpathians, root outcrops of the Jurassic deposits have not been found. Jurassic rocks are most widespread in the Internal Carpathians, namely in the Pieniny Klippen Belt which is a well-known structural–tectonic formation among the Alps and Carpathians researchers. Repeating the configuration of the Carpathian arch, this belt in the form of a narrow strip is traced through all the Ukrainian Carpathians. The distinguishing feature of this tectonic structure is the presence of numerous different-sized olistoliths of Jurassic limestones surrounded by Upper Cretaceous marly formations. In the Ukrainian Carpathians, the Pieniny Klippen Belt is presented not so well, as in the Western Carpathians and Eastern Alps, and occurs just in fragments. Separate outcrops of olistoliths are distributed in the basins of the Uzh, Latoritsya, Borzhava, Luzhanka rivers.

During the investigation of the Pieniny Klippen Belt in the Ukrainian Carpathians conducted during the last decade, we collected numerous new fossils, including ammonites. Among them, 50 species were distinguished, of which 37 taxa are characterized by wide geographical distribution and are typical for many regions of the Mediterranean paleozoogeographical province. These are: *Schlotheimia charmassei, Echioceras declivis, Vermiceras* cf. *spiratisium, V. nodotianum, Coroniceras* cf. *kridion, Arietites* cf. *romanicus, Arnioceras* cf. *ceras, Bisiphites striatum, Grammoceras saemanni, Dactylioceras commune, Ludwigia literata, L. carinata, Leioceras acutum, Lytoceras ophioneum, Leioceras costosum, Oppelia* cf. *subradiata, O. (Oxycerites)* cf. *limosa, Leptosphinctes vermiformis, L. leptus, Phylloceras asisbekovi, Eurystomiceras polyhelictum, Pseudophylloceras kudernatschi, Calliphylloceras heterophylloides, Stephanoceras (Cadomites) deslongchampsi, Thysanolytoceras* cf. *cinctum, T. eudesianum, Valentolytoceras* cf. *elegans, Calliphylloceras* cf. *subdisputabile, Dinolytoceras crimea, Holcophylloceras zignodianum, Calliphylloceras disputabile, Perisphinctes defrancei, Paracenoceras* cf. *okensis, Paracenoceras* cf. *calloviensis, Sowerbyceras tortisulcatum, Phylloceras serum.*

Thirteen index-species were identified: *Alsatites liasicus, Arietites bucklandi, Asteroceras obtusum, Echioceras raricostatum, Uptonia jamesoni, Dactylioceras tenuicostatum, Harpoceras falciferum, Grammoceras thouarsense, Leioceras opalinum, Ludwigia murchisonae, Stephanoceras humphriesianum, Parkinsonia parkinsoni, Peltoceras athleta.*

Macropaleontological investigations of the Jurassic of the Ukrainian Carpathians produced new biostratigraphic data. The presence of all Jurassic stages and 13 biostratigraphic zones is confirmed based on Ammonoidea. The presence in olistoliths remains of numerous ammonites which are characteristic of the area of Tethyan phylloceratids, lytoceratids and haploceratids, indicates that there was a close connection between the Tithonian basin of the Carpathians and the Mediterranean paleozoogeographical province.

Coal "exotics" in the flysch of the Ukrainian Carpathians

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In the Cretaceous–Paleogene flysch of the Carpathians, beside fragments of Precambrian, Paleozoic and Mesozoic rocks, numerous fragments of coal occur. On the territory of the Polish Carpathians, they were studied by T. Wiśniowski, J. Nowak, M. Ksiazkiewicz, S. Bukovy, Ya. Tserndt, E. Turnau and others. The age of coal fragments is determined according to palynological data. In Polish Carpathians Ya.Tserndt for the first time revealed their Carboniferous age; afterward, E. Turnau made more exact age determination of the coal exotics as Westphalian. In the Ukrainian Carpathians, fragments of coal in the flysch were described by F. Kreits, R. Zuber, T. Wiśniowski, B. Kropachek, P.I. Kalushn, A.M. Ishchenko, I.I. Partyka, T.O. Boldyreva, V.V. Hlushko, and H.D. Dosyn. During the palynological study of coal fragments, their age was determined as Bashkirian (middle Carboniferous; now Pennsylvanian). The researchers proved that coal exotics are spread practically in all Ukrainian Carpathians, in the flysch deposits of Upper Cretaceous and Paleogene age, and also in the inner part of the Precarpathian Foredeep (Polyanytsia deposits).

For the first time, we have studied coal fragments that are spread in the flysch of the Stryi Formation (Upper Cretaceous) in the Dnister River valley between Rozluch and Strilky villages of the Lviv Region. They are represented by a great number of angular coal fragments of different sizes – from small (diameter of cross-section equals a few millimeters) to large blocks (60×30×30 cm) that in the appearance of considerable accumulations are in the sandstones of the Stryi Formation. All components of unsoluble dispersed organic matter have been studied. Among them, large scraps of elongated form of integumentary and conducting tissues of higher spore plants dominate, large angular elongated and isometric fragments of vitrinite are also very abundant, inertinite, spores, rare spiny acritarchs (*Hyrtellosphaeridium* sp.) occur. There following spore species have been determined: *Leiotriletes subintortus* (Waltz), *L. inermis*, *L. ornatus*, *Calamospora*, *Granulatisporites*, *Cyclogranisporites*, *Densosporites irregularis*, *Cingulizonates*, *Lycospora pusilla*, *Bellisporites*, *Murospora primitiva*, *Callisporites*, *Proprisporites laevigatus*, *Vertispora*, *Strumulispora crassa*, *Schulzospora*, *Laevigatosporites vulgaris*, *Ahrensisporites*.

Important for age determination are *Proprisporites laevigatus* – index-species of the same name zone of Serpukhovian (Mississippian) of the Lviv–Volyn and Donets basins of Ukraine and *Vestispora* and *Laevigatosporites ovalis* which appear in the Serpukhovian. Other spore species are spread in all sections of the Mississippian and only some of them pass into the Pennsylvanian. Such association of spores allows us to assign the primary coal-bearing rocks to the upper part of the Serpukhovian (Mississippian). In the Ukrainian Carpathians, Serpukhovian age of exotic rocks is determined for the first time.

The present study testified that the Carboniferous (Serpukhovian–Bashkirian) coal-bearing deposits may occur in the autochthonous basement of the Ukrainian Carpathians.

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Sedimentology, facies analysis

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Evidence of a depositional change on the Getic Carbonate Platform during the Early Cretaceous (Eastern Serbia)

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The Getic Carbonate Platform (GCP) represents a depositional system developed on the Neotethys northern margin during the Late Jurassic and Early Cretaceous. The shallow-water carbonate strata of the GCP are well preserved in Romania, Serbia and Bulgaria. During the past few decades only several studies were published regarding this shallow-water carbonate platform in the Serbian sector (Bucur *et al*., 2020). The characterization of facies types, the identification of depositional environments and their evolution through time as well as the correlation with Romanian and Bulgarian time-equivalent deposits remain open issues.

The two investigated sections, having total thickness of 100 m, comprise deposits of Berriasian–Valanginian age. They are located in the southeastern part of Serbia, near the town of Dimitrovgrad. Samples were collected and 60 petrographic thin sections, representative of different carbonate facies, were analyzed.

The lower part of the stratigraphic successions (~70 m of thickness) shows facies similar to the Upper Jurassic ones, rich in biota represented by *microproblematica* and microencrusters *(Bacinella*, *Lithocodium*, *Cayeuxia)*, calcareous and siliceous sponges, bivalves and rare corals. The identified facies are peloidal and skeletal packstone/rudstone and *Bacinella-Lithocodium* and sponge boundstone that are indicative of subtidal, moderate to low-energy, inner to outer platform environment with reef development. The platform interior facies consist of low-diversity packstone to grainstone with benthic foraminifera. The upper part of the stratigraphic succession (~30 m of thickness) shows an abrupt change to a mixed carbonate-siliciclastic depositional system with inner ramp ooidal packstone/grainstone with quartz grains, middle ramp bryozoan and brachiopod packstone with ooids and oncoids followed by basinal fine-grained sandstone. The rapid change from tropical photozoan biota to a heterozoan carbonate factory might have been driven by the siliciclastic input increasing the water turbidity and nutrient levels. Age equivalent mixed carbonate-siliciclastic facies were recognized by Bucur *et al*. (2020) in the Serbian part of the GCP.

The high diversity of facies that sharply change from tropical carbonate factory system to heterozoan carbonate deposits rich in terrigenous sediment provides insights into an important change of the depositional environments during the Early Cretaceous.

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Depositional settings of the Campanian–Maastrichtian carbonate deposits in section Komunari, Eastern Fore-Balkan, northeastern Bulgaria

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The Eastern Fore-Balkan Mts (north-eastern Bulgaria) consist of widely exposed shallow- to open-marine Upper Cretaceous–Paleogene carbonate/siliciclastic deposits, unconformably overlying Lower Cretaceous turbidite successions. The studied area is included in the Fore-Balkan Unit of the Balkan Tectonic Zone (after the tectonic scheme of Dabovski and Zagorchev, 2009). Sinnyovsky and Vangelov (2007) published the latest data on the litho- and biostratigraphy of these rocks, and their lithostratigraphic scheme and age assessments are followed in this work.

A detailed sedimentological study was carried out on the Upper Cretaceous deposits from section Komunari in order to reconstruct carbonate depositional paleoenvironments and evolution during the Late Campanian–Maastrichtian time interval. The studied succession corresponds to the Nikopol (Upper Campanian), Mezdra (Upper Campanian), Yankovo (Lower Maastrichtian), Dobrina (Lower Maastrichtian) and Kaylaka (Upper Maastrichtian) Formations and unconformably covers the Coniacian–Santonian limestones of the Murna Formation. The base of the section consists of massive, creamy grey bioclastic limestones (bioclastic and intraclastic-bioclastic packstones/grainstones) of the Nikopol Formation. Upward in the section, massive, light grey, silty limestones (glauconitic silty bioclastic wackestones and silty spiculite wackestones/packstones) of the Mezdra and Yankovo Formations are exposed. An erosive surface and a layer composed of *Pycnodonte vesicularis* (Lamarck) shell concentrations occur in the lower part of the Dobrina Formation. The latter continues with thick- to medium-bedded, creamy sandy limestones (sandy echinoderm packstones). The succession ends with massive creamy bioclastic limestones (bioclastic packstones and grainstones) of the Kaylaka Formation.

At the onset of the Late Campanian carbonate deposition occurred in a shallow-marine setting under agitated hydrodynamic conditions (Nikopol Formation). Later, during the Late Campanian and in the beginning of the Early Maastrichtian, the sedimentation continued in relatively deep-water environments (Mezdra and Yankovo Formations) below the storm wave base (SWB). A shallowing trend started during the Early Maastrichtian time when storm-related lag deposits with concentrations of *Pycnodonte vesicularis* (Lamarck) were formed. The deposition took place in an open-marine setting, most likely between the fair-weather wave base (FWWB) and SWB. The Late Maastrichtian sedimentation occurred in a high-energy shallow-marine environment near to or above the FWWB (Kaylaka Formation).

The studied Upper Campanian–Maastrichtian carbonate sediments in section Komunari are interpreted as shallow- to deep-water marine deposits. They were formed in various low- to high-energy settings below the SWB, between the SWB and FWWB, and near to or above the FWWB.

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Carbonate carbon isotope record of the Carnian Pluvial Episode in the western Balkanides (Bulgaria)

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The Carnian (early Late Triassic; 237–227 Ma) was marked by major biological changes. Marine and terrestrial fauna and flora experienced high extinction rates, while some groups (including the dinosaurs and the modern conifers) diversified explosively, forming new modern-like ecosystems. The biological turnover could have been triggered by the Carnian Pluvial Episode (CPE) a climate change marked by a widespread enhancement of the hydrological cycle. Evidence for more humid conditions is found in deep-water to terrestrial depositional environments. The CPE is synchronous with multiple negative C-isotope shifts and increases of seawater temperature, in a time interval of only ca. 1–2 million years (232–234 Ma). The CPE is coeval with the eruption of the Wrangellia large igneous province (LIP), an oceanic plateau that was active in the middle of the Panthalassa Ocean. Here we present the first record of the CPE C-isotope perturbation in successions of the western Balkanides (Bulgaria). The sampled sections encompass the late Middle to early Late Triassic Rusinovdel Formation, a sequence of shallow water and peritidal carbonates, up to the contact with the overlying continental siliciclastic units of the Moesian Group, which were interpreted as the sedimentological expression of the CPE in the area, with an abrupt influx of terrestrial material into the basin triggered by a more vigorous hydrological cycle. Bulk carbonate C-isotope analyses reveal multiple isotope shifts in the uppermost part of the Rusinovdel Formation, preceding the change from carbonate to terrigenous sedimentation. Paired C and O isotopes suggest little diagenetic overprint on the pristine signal, a fact also supported by the consistency of the isotope records between sections. The new record adds important information on the CPE in the western Tethys realm, and clarifies the temporal relationship between the C-cycle perturbation and the environmental changes recorded by shifts in the sedimentation style.

Depositional environment of the Silurian metalliferous sediments from section Asaritsa, West Balkan (Bulgaria)

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The Silurian sediments in section Asaritsa crop out in the western sector of the Stara Planina Mountains (Svoge Unit of the Srednogorie Zone). The interpretation of the depositional environment is based on the sedimentary structures, textures, geochemical and fossil characteristics.

Black and pale shales, siliceous shales, and lydites are the main lithological types in the succession. Aeronian graptolitic strata of black shales occur at the base of the section and pass upward into a graptolite-barren interval of pale-coloured shales as was described by Sachanski (2017). Telychian graptolitic strata cover the graptolite-barren interval in the upper part of the section. The Aeronian/Telychian boundary is assumed to lay at the base of the pale-coloured shale package, or within its lower part. The sediments show even parallel, horizontal bedding and lamination. Levels of different thickness and position bearing Mn carbonate nodules are a specific feature of the section. The main microscopic characteristics of the sediments define clast-poor silty mudstone to cherty mudstone. The XRD pattern showed quartz of low crystallinity and muscovite as main constituents, and clinochlore, vermiculite, siderite and goethite as subordinate minerals. Reflections of birnessite were also identified. The values of Al_2O_3/TiO_2 ratio, the most useful provenance indicator of sedimentary rocks, suggest mainly an intermediate to felsic igneous rock source. All samples plot in the fields of non-ferruginous wacke and litharenite according to the log (Fe_2O_3/K_2O) *vs.* log (SiO_2/Al_2O_3). The high content of Al_2O_3 (mean 12.6 wt.%) and Fe_2O_3 (mean 8.8 wt.%) indicate weathering and/or source rock alteration.

The grain-size, mineral composition and geochemical features of the studied Silurian sediments define a remote and weathered source land. Currents were most likely the main transport agent of the suspension. The different levels with carbonate nodules may indicate short periods of very low sedimentation rates. Overall, it is concluded that the sediments were deposited in an open-sea environment, away from the wave zone. The sharp lithological boundary between black and pale sediments suggests a rapid sea-level regression close to the Aeronian/Telychian boundary and transition from an oxygen-depleted to oxygen-rich environment. The graptolite assemblages provide a key to interpret the paleoenvironment. The determined graptolite species were planktonic, floating, and common where food was abundant, especially in upwelling currents, where deep water with nutrients was forced upwards into shallower waters in areas such as the tropics and at the edge of the continental shelf.

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Lithofacies characteristics and depositional environment of the Shavar Formation, SE Bulgaria

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The Shavar Formation (Maastrichtian–Ypresian) belongs to the lower part of the Krumovgrad Group in the eastern part of the Rhodopes, in SE Bulgaria. It is dominated by coarse terrigenous rocks deposited in half-graben basins, developed along the periphery of the Kesebir-Kardamos metamorphic dome. Recent mineral exploration drilling campaign, focused on low-temperature epithermal gold mineralization at the base of the Shavar Formation in the Krumovgrad area, has revealed significant differences in the thickness of the sedimentary sequence. Based on detailed lithological and facies analysis of drill cores from four exploration holes, we differentiate three major lithofacies groups: gravel-, sand- and mud-dominated, accompanied by one additional lithofacies group, related to carbonate deposition. These were further subdivided based on their structural and textural characteristics into lithofacies types, representing different depositional environments, as potential factor for localization of the ore mineralization in the area.

The gravel-dominated sediments typically constituting over 60 % of the sedimentary fill. *Lithofacies B* is the main component of the olistostrome units and is mostly represented by grain-supported, poorly sorted to unsorted angular or very poorly rounded pebbles to boulders of gneiss, schist, amphibolite, and marble from the underlying high-grade metamorphic core of the dome. *Lithofacies Gms* forms decimeter-thick units dominated by matrix-supported pebble- to cobble (breccia) conglomerate. Massive structure and angular to very well-rounded grains denote possible debris flow material deposited in a low-energy environment. *Lithofacies Gm* is represented by grain-supported granule- to cobble-dominated beds (centimeter to meters thick), typically alternating with lithofacies *Gms*, with features indicative of stream transport and washing out of finer particles. *Lithofacies Se*, which is dominated by pebble- to cobble-sized carbonaceous and/or carbonaceous-argillaceous intraclasts, shows evidence of soft sediment deformation processes, and is considered as result of flooding events, stream erosion and consequent channel lag deposition.

Six lithofacies types were recognized within the sand-dominated group – *Sms* (massive, matrix-supported), *Sm* (massive, grain-supported), *Sh* (fine laminated), *Sl* (low-angle cross-bedded), *Str* (trough cross-bedded), and *Sr* (small scale cross-bedded). These are composed of poorly- to well-sorted angular- to rounded extra- and intraclasts in varying proportions, and typically occur as interbeds (often in gradual transition) within the gravel- and/or mud-dominated intervals. They represent distal products of debris flows (*Sms*), crevasse-splay and/or overbank (*Sm*) and fluvial channel deposits (*Sh* - *Sr*).

Within the mud-dominated intervals 7 lithofacies types are defined and broadly subdivided into two sub-groups, based on their carbonate content. *Lithofacies Fms* (massive, with abundant poorly sorted extra- and intraclasts), *Fm* (massive, poor in siliciclastics), *Fh* (horizontally laminated), *Fl* (low-angle cross-bedded), and *Fsc* (sand-free) are characterized by low carbonate content, whereas lithofacies *Mm* (massive) and *Mh* (horizontally laminated) represent marlstone deposits. The mud-dominated sediments are common in the Shavar Formation, forming at least two units bellow and above the upper olistostrome unit. Their deposition most likely represents distal debris flow and/or overbank environments.

The carbonate-dominated lithofacies (*Pcc*) represents rocks of all types, displaying development of calcretes, paleosol and desiccation cracks, potentially linked to short-term climatic events.

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Introduction to the bulk rock chemistry of the Eocene hemipelagic/pelagic deposits in the Dinaric foreland basin

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The Eocene sediments along Adriatic coast deposited in the Dinaric foreland basin were processed sedimentologically, micropaleontologically, mineralogically and geochemically to assess the continuity of sedimentation, determine the age, composition of the foraminiferal assemblages and environmental conditions.

This work presents the bulk rock chemistry of hemipelagic/pelagic deposits (H/P sediments) collected in four geographically separated regions: Pićan-Pazin area on the Istrian Peninsula (Jakomići, Kožljak and Racani sections, 3 samples), Selce-Bribir (Kostelj section, 4 samples), Hvar Island (Zaraće Bay, 4 samples and Podstine Bay, 3 samples) and Krk Island (Baška beach section, 5 samples). These results were used to define the sediment maturity, the type of sources of deposited sediments and the geotectonic environment of marls deposition.

The analyzed samples show a wide range of SiO_2 contents. The values between 15 and 30 wt% were recorded in Istrian sediments, sediments from Podstine Bay and from the lower part of the Zaraće section, while significantly higher values (41–50 wt%) were measured for the Kostelj section, sediments from island of Krk and the upper part of the Zaraće Bay section. The Al_2O_3 wt% content is the lowest in the Podstine section (4–7 wt%). Sediments from Istria and the lower part of the Zaraće Bay section show the same alumina content (7–9 wt %). The samples from island of Krk have values between 8 and 13 wt%, while the samples from Kostelj and the upper part of the Zaraće section have the highest Al_2O_3 values (13–16 wt%). The lowest ICV values (Index of Compositional Variability (ICV = $[Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2)/Al_2O_2]$) have the samples from Kostelj section (1.40–2.09) and the upper part of the Zaraće section (1.75 and 1.90). Slightly higher values have the sediments from Baška beach (2.75–3.22). The samples from the Istrian peninsula and the samples from the lower parts of two sections on the island Hvar have similar ICV index values (from 4.08 to 6.48). The highest calculated ICV values (8.51 and 10.85) of the studied samples have the upper part of the Podstine Bay section on the island of Hvar, which can be ascribed to a high carbonate content.

The studied samples have the chemical index of weathering (CIA = $[Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$) between 62 and 76, which describes an intermediate weathering (Nesbitt and Young, 1982) and could be interpreted as conversion of feldspars, volcanic glass and other labile components to clay minerals. Clay mineral assemblage contains illite, illite-smectite, chlorite, dioctahedral vermiculite and sparse kaolinite and generally corresponds to ICV and CIA values. Low CN abundance of marls from Istria (< 11%), suggests a drop in marine carbonate productivity linked to climatic changes and/or a sea level rise.

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Lithofacies and depositional environments of the Paleocene deposits of Carpathian flaky (Skybova) cover within basins of the Stryi and Prut rivers

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Detailed study of the Yaremchan horizon make possible to emphasize its structure peculiarities. Stratigraphic sections of the Yaremchan horizon within basins of the Stryi and Prut rivers have been studied. In all sections the boundary between upper Cretaceous and Paleocene are Yaremchan horizon sandstones. Petrographic investigations of the clastic components among flysch rhythms in Yaremchan horizon testify about essentially heterogeneity within straton composition.

In southern-east part of the Skybova cover in sections along Prut and Pidbuzh rivers (river Stryi basin) up the profile thin-flysched deposits with well-sorted coarse-grained aleurolites transit at first into flysch cyclites with organeous-clastic limestones and then into cyclites with terrigenous psammites. Geological sections of the Yaremchan horizon along Rybnyk (river Stryi basin) have some other stratification character. Up to the section one can see here alteration of the well-sorted sandstones (Prut and Pidbuzh rivers) into coarse-grained clastic carbonate sandstones and fine-pebbled gravelites increased by inequigranular sometimes well-sorted terrigenous aleurolites and sandstones. In section of Yaremchan horizon rocks along river Prutets-Tchymyhovsky the right inflow of the Prut river – as well as in Pidbuzh river section one can see availability of the flysch deposits with clastic-carbonate sandstones. These differences correspond to the lower part of horizon in this section they overlap well-sorted coarse-grained aleurolites of the Paleocene lower part and after into fine-grained sorted terrigenous sandstones. The study of terrigenous lithotypes in Yaremchan horizon section along Zhenets river (the left tributary of the Prut river) gives an opportunity to examine gradual alteration up to the section from inequigranular sandstones to inequigranular aleurolites. Such section features are typical for Prytets-Tchymyhovsky river area. Thus in the Prut river basin according to alteration of the terrigenous petrotypes granulometric composition within flysch cyclites of Yaremchan horizon cyclite of the higher order is distinguished. It can correspond to mesocyclite according to the thickness or megacyclite due to rich content and occupy all chronological interval of the Yaremchan horizon. According to elementare cyclites lithotypes structure mentioned mesocyclite is transgressive. Lower elements of mesocyclite as well as ascertained as a rule are presented by clastic-carbonate sandstones or organeous-clastic limestones while upper elements consist of well-sorted sandstones and aleurolites.

Macroscopic occurrences of the sulphides, carbonates and oxides of copper are character for all sections of named above areas of Skybova cover. Different amounts of them are also present in the all rock types of the Yaremchan horizon. In aleuropelites and aleurolites in particular ore minerals as a rule are in cement of the rocks while in the sandstones, organeous-clastic limestones and clastic-carbonate sandstones ore mineral occur both in the rocks cement and its fragments.

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Cretaceous anoxic and oxic marine depositional intervals in the Romanian Carpathians: causes and consequences

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A significant change, from a Lower Cretaceous anoxic setting to an Upper Cretaceous oxic one, reflected in the deposition of red shales, took place in the Eastern Carpathians. This change might be related to the important palaeogeographic modifications, initiated by Albian tectonics, leading to a shift of the restricted circulation that characterized the anoxic basins of the Moldavian Trough to an open circulation among these semi-isolated basins.

The red shales (Cretaceous Oceanic Red Beds – CORB, Wagreich, 2009) are known to occur from the Lower-Upper Cretaceous boundary interval in the Tethyan and Boreal realms; in some areas, including the Romanian Carpathians, their deposition lasted up to end of the Cretaceous. Some of CORBs are seen as a consequence of the Lower Cretaceous anoxic events, which the appearance changed the geochemistry of the world ocean. Even the overall Upper Cretaceous marine setting was supposed to be oxic, temporally it was disrupted by the occurrence of thin rich-organic black shales, associated with high TOC content and enclosing significant excursion of the isotope $\delta^{13}C$, overprints of the Oceanic Anoxic Events (Jarvis *et al*., 2006).

Several OAEs are pointed out in the Eastern Carpathian Moldavide nappes, including the OAE1d (the Albian-Cenomanian Boundary Event) and the OAE2 (the Cenomanian-Turonian Boundary Event) in a depositional interval supposed to be an oxic one. This sandwiched occurrence probably mirror significant climate modifications, such as periodically and frequent replacement of the greenhouse related to the OAE setting by a cold climate of CORB intervals. This hypothesis may be true for deep marine basins, where red shales sedimented below the CCD. In such a setting, the oxic bottom conditions may be jointly caused by active bottom ocean circulation and modification in the ocean-atmosphere oxygen content. In contrast, some of the Upper Cretaceous CORBs were deposited in shallow water, well above CCD (*i.e*., within the Santonian-Campanian interval of the western Southern Carpathians); there, their presence suggests a warm arid climate, implying accumulation of red soils on emerged coastal plains, redeposited by transgressions in a marine environment. To conclude, the transition from an anoxic depositional regime to an oxic one seems to be a mid-Cretaceous worldwide event, but besides global changes, regional modifications may have a significant contribution.

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The Upper Jurassic-Lower Cretaceous evolution of the easternmost Getic Carbonate Platform (Southern Carpathians, Romania): insights from the Postăvaru and Piatra Mare massifs

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The studied deposits belong to the ,,Brașov Series,, (Patrulius, 1969). The sedimentary deposits from this geological unit form important outcrop areas in the eastern Getic Carbonate Platform (*e.g*., Piatra Craiului Massif, Dâmbovicioara Zone, Codlea Zone, Postăvaru and Piatra Mare Massif, western Bucegi Mountains) (Patrulius, 1969).

The bulk of the sedimentary successions from the studied areas contains Upper Jurassic (Kimmeridgian-Tithonian) Štramberk type limestones (Săndulescu, 1964). These limestones present nappe structures (in the Postăvaru Massif) or they occur as large scale olistoliths in the general mass of the upper Aptian Conglomerates (Piatra Mare Massif) (Săndulescu, 1964).

Approximately 1100 carbonate samples were collected from a total number of 37 sections located in the Postăvaru and Piatra Mare massifs. The facies analysis indicates the presence of nine major facies associations: bioclastic rudstone, coral-microbial boundstone, bioclastic intraclastic wackestone/floatstone, silicified wackestone to packstone, bioclastic grainstone with black pebbles, fenestral wackestone, homogeneous mudstone, ooidal bioclastic grainstone, wackestone with foraminifera and dasycladalean algae.

The micropaleontological assemblage consists of dasycladalean algae [*Cylpeina parasolkani* Farinacci and Radoičić, *Salpingoporella annulata* Carozzi, *Salpingoporella pygmaea* (Gümbel), *Seliporella neocomiensis* Radoičić, *Steinmanniporella kapelensis* (Sokač & Nikler), *Griphoporella jurassica* (Dragastan), *Petrascula bursiformis* Etallon, *Neoteutloporella socialis* (Praturlon), *Aloisalthella sulcata* (Alth)], encrusting organisms [*Bacinella* type structures, *Crescentiella morronensis* (Crescenti), *Iberopora bodeuri* Granier & Berthou, *Koskinobulina socialis* Cherchi & Schröder, *Pseudorothpletzella schmidi* Schlagintweit & Gawlick, *Radiomura cautica* Senowbari-Daryan & Schäfer, *Perturbatacrusta leini* Schlagintweit & Gawlick, *Taumathoporella parvovesiculifera* (Raineri)], calcareous sponges (*Calcistella jachenhausenensis* Reitner, *Neuropora lusitanica* Termier, Termier & Ramalho, *Thalamopora lusitanica* Termier), foraminifera [*Bramkampella arabica* Redmond, *Bulbobaculites felixi* Pleș *et al*., *Coscinoconus alpinus* (Leupold), *Coscinoconus cherchiae (*Arnaud-Vanneau *et al*.), *Coscinoconus delphinensis (*Arnaud-Vanneau *et al*.), *Coscinoconus sagittarius* (Arnaud-Vanneau *et al*.), *Coscinoconus campanellus (*Arnaud-Vanneau *et al*.), *Coscinoconus elongatus* Leupold, *Frentzenella involuta* (Mantsurova), *Meandrospira favrei* (Charollais *et al*.), *Nautiloculina brönimanni* Arnaud-Vanneau & Peybernès, *Protopeneroplis striata* Weynschenk, *Protopeneroplis ultragranulata* Gorbatchik] and pelagic microorganisms [*Calpionella alpina* Lorenz, *Calpionella eliptica* Cadish, *Calpionellopsis oblonga* (Cadish), *Crassicollaria parvula* Remane, *Crassicollaria intermedia* Durand-Delga, *Saccocoma* sp.].

This microfossil assemblage documents well the Upper Jurassic–Lower Cretaceous transition in the studied areas. Carbonate sediment accumulation was continuous during this interval, both in shallow and deep water depositional settings.

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Development of the Gosau-type wedge-top basins in the Western Carpathian Klippen Belt: inferences from the Pupov Formation (NW Slovakia)

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The Pieniny Klippen Belt (PKB) is a narrow zone with intricate internal structure spreading all-along the contact between the Cenozoic accretionary wedge of the External Carpathian Flysch Belt and the Cretaceous stack of the Central Western Carpathian (Austroalpine) basement-cover nappes. Being composed of the detached sedimentary units only, the PKB includes two different nappe groups: (1) the Oravic units (Jurassic–Eocene) derived from an independent palaeogeographic domain – an intra-oceanic (Penninic) continental fragment known as the Czorsztyn Ridge; (2) frontal elements of the Central Carpathian cover nappes, such as the Klape or Manín units in western Slovakia. The latter were incorporated in the rear of the nascent PKB accretionary wedge during the Late Cretaceous and then shared a common structural and partly also sedimentary history with the Oravic units located at their foreground. This evolution is recorded by various deposits of the syn-orogenic basins: foredeep trench-type in (1); and piggyback wedge-top Gosau basins in (2).

Due to strong backthrusting-related deformation, the structural position of the Pupov Fm. in the Varín PKB sector in NW Slovakia has not been fully understood yet; mostly it was assigned to the Klape Unit. It is composed of the Senonian, up to thousand meters thick sedimentary complex, which includes four members. The lower, Coniacian–Santonian Veľhora Mb. comprises a "flysch" sequence of turbiditic calcareous sandstones predominating over dark claystones and mudstones. The overlying Campanian variegated hemipelagic marlstones are designated as the Gbeľany Mb. The Maastrichtian Stage is represented by two distinct facies. In the Terchová village area, a very special local development is characterized by non-turbiditic, shallow-marine, thin-bedded gritty siltstones (Poľany Mb.). In contrast, deep-marine banded sequence of grey calcareous claystones and mudstones alternating in cm scale with distal turbiditic siltstones occurs a few km eastward in the Zázrivá village area (Campanian–Maastrichtian–Danian Zázrivka Mb.), while thick beds of graded turbiditic sandstones are rare.

We have carried out petrographic and heavy mineral analyses including geochemistry of detrital Cr-spinels, tourmalines and garnets. The sampled deposits include litho-quartzose to felspatho-litho-quartzose sandstones, fine-grained conglomerates and pebbly mudstones. They contain mostly lithoclasts of low- to medium-grade metamorphic rocks, basic volcanites and carbonates. Impoverished heavy mineral assemblage includes ultrastable tourmaline, zircon, rutile accompanied by Cr-spinel and apatite. Garnets, exclusively of almandine composition, are rare. Cr-spinels and complexly zoned tourmalines might have been derived from the southern Carpathian zones along the Meliata suture and transported within the mid-Cretaceous flysch formations of the Klape Unit to the PKB area, where they were resedimented into the Senonian deposits. Based on the specific structural position, age, lithological composition and impoverished heavy mineral assemblage, the Pupov Fm. is considered to represent a part of the wedge-top Gosau-type basin system.

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Phosphate-glauconite nodules and hardgrounds from the Cenomanian–Coniacian succession in NE Bulgaria – new data and interpretation

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The Upper Cretaceous is known for the occurrence of glauconite- and phosphate-rich sediments formed globally in marine basins. The present study reports some new data and interpretation of such deposits from the Cenomanian-Coniacian succession outcropping in the Eastern part of the Moesian Platform. The investigated units (Madara, Mogila and Dobrindol formations) consist of limestones having various textures, and locally of calcareous sandstones, deposited at the complex northern part of the Tethys Realm atop of a regional K1/K2 unconformity.

Previous authors have described "phosphorite concretion beds" in the sediments of Madara and Dobrindol formations giving some genetic interpretations (Sultanov, 1989). These deposits are defined herein as phosphate-glauconite nodule-bearing beds (PGNBB). The nodules are interpreted entirely as replaced lithoclasts and products of low sedimentation rate. Additionally, three mineralized hardgrounds (one of which – pre-K2) are identified and described.

PGNBB are found in six sections: Srednya, Provadia, Devnya, Povelyanovo, Padina and Beloslav. All beds cover scour surfaces (occasionally associated with hardgrounds) and in most cases are laterally discontinuous. The nodules are unevenly scattered and usually comprise <15–20% of the bulk rock volume, hence the term phosphate-glauconite bearing beds (Trappe, 2001). They show some common structural characteristics, association with glauconite pellets, and locally with abundant skeletal remains. The nodules often bear evidence for transportation, *i.e.*, have parautochthonous character. Stratigraphic condensation (upper Cenomanian–upper Turonian) is recognized in the second nodule-bearing bed of section Srednya.

The thin-section microscopy reveals that all nodules represent lithoclasts (mostly intraclasts) that have undergone complete or marginal replacement by glauconite, phosphates and iron oxyhydroxides. Many nodules record several mineralization events and reworking. Glauconite and phosphates are also present as filling burrows, biomolds, and microborings on bioclasts, and in some cases as intergranular cements.

Two phosphatized breccia-conglomerate beds occur in section Mogila-Kaspichan – at the base of the Madara Formation and at the base of the Dobrindol Formation (previously noted). These beds contain phosphatized/glauconitized and non-mineralized lithoclasts, abundant bioclasts, scarce concretions, and are cemented by phosphates. Some clasts show records of multi-cycle mineralization, and others have characteristics of former hardground lithoclasts. The early diagenetic cementation of these beds allows to define them as mineralized hardgrounds.

The described features of the phosphate-glauconite nodules suggest that the origin of these deposits was related to episodes of very low sedimentation rate (Föllmi, 2016). These episodes most likely resulted from sediment starvation due to the well-known transgressive events during the Late Cretaceous.

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The provenance of the green clasts from the Outer Carpathians: contributions to the understanding of the East European Platform edge architecture

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In the outermost tectonic units of the Eastern Carpathians, the Cretaceous – lower Miocene deposits contain low-grade metamorphic green clasts, whose origins are not fully understood. Previous petrographic studies support an eastern provenance, with respect to the Moldavide Basin (*i.e*., the Moesian Platform, the North Dobrogea Orogen, or the East European Platform) but also a western (Carpathian) source was postulated. The green clasts from conglomerate formations represented by the coarse Cretaceous and Oligocene turbidites, and Miocene fan deltas were petrographically analyzed and U-Pb dated to compare with potential eastern or western sources. The so-called anchimetamorphic "green-schists" forming the Ediacaran basement of the Dobrogea Moesian Platform are deformed sandstones, siltstones, and siliciclastic mudstones with a chlorite-rich matrix that preserves sedimentary features. Our study shows that a part of the green clasts from the Eastern Carpathian conglomerates look similar but the other are metamorphic rocks that reached greenschist to lower amphibolite facies conditions, with well-developed foliation where mineral neoformation involved blasthesis of chlorite, albite but also biotite and garnet. The U-Pb age distribution of the detrital zircons extracted from the green clasts of Eastern Carpathian conglomerates shows identical patterns. There is a dominant group in the 530–650 Ma range, while ages exceeding 1 Ga are almost insignificant. There is no similarity between the analyzed samples and the Bucovinic basement, and a western Alpine source is excluded. The East European Craton is over 1 Ga old, therefore not meeting the source-area quality. Similar peaks of 550–630 Ma are shown by the massifs located near the edge of the East European Craton (Tornquist-Teisseyre Zone-TTZ), like the Małopolska terrane in Poland, or North Dobrogea and Central Dobrogea (Moesia) in Romania, but these units also have secondary clusters > 1 Ga. We suggest that the green clasts of the Cretaceous-Miocene (Burdigalian) siliciclastic rocks of the Eastern Carpathians derive from a peri-Gondwanan Neoproterozoic-Cambrian arc. During its accretion to Baltica, zircon-bearing rocks were eroded and reworked in the forearc basin, with maximum depositional age of 520.3 ± 6.51 Ma. The sediments were buried, metamorphosed in greenschist to lower amphibolite facies, and uplifted probably during the Variscan orogeny. We consider that the source area for the green clasts of the East Carpathians was buried under the Alpine front of the Carpathian thrust line, near TTZ, during late Burdigalian since there are no post-Burdigalian green clast-rich formations.

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Session GT4

Magmatism

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Magmatism of the Sava Vardar Zone as an example of how complex tectonomagmatic divisions can be

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The Sava Vardar Zone (Pamić, 2002) or the Sava Zone (Schmid *et al*., 2008) is a discontinued belt of Late Cretaceous to Palaeogene variably metamorphosed flysch-like deposits associated with roughly contemporaneous magmatic rocks, varying in composition from basalt (gabbro) to rhyolite (granite). The belt can be followed along the Sava River, from Zagreb to Belgrade (WNW-ESE), and further south, towards the Gulf of Thessaloniki. Actual geotectonic reconstructions of the central Balkan Peninsula recognize the Sava Vardar Zone (SVZ) as the NW-dipping suture between the African (the Dinarides) and European (Tisza-Dacia) plates, however, its true tectonomagmatic history is still debatable.

Some authors (see Schmid *et al*., 2020) consider this zone remnants of an back-arc ocean that still existed in the latest Cretaceous; in this context, they regard the SVZ magmatic rocks as either ophiolites or/and products of forearc magmatism related to Late Cretaceous subduction, the very same one that was responsible for the formation of the Banatite-Timok-Srednogorie Belt. Other authors (*e.g*., Prelević *et al*., 2017) think that the Neotethys was completely closed in the earliest Cretaceous and that the SVZ is a (multiply?) reactivated suture between the African and European plates; they also argue that compositional variations shown by Upper Cretaceous magmatic rocks of the SVZ can be explained by intracontinental magmatism that involved the combination of extensional and compressional episodes.

This contribution is a brief petrogenetic overview of the Upper Cretaceous magmatic rocks that are so far known to occur along the SVZ, from Zagreb to Skopje. Three petrogenetically distinct groups are recognized: 1) olivine tholeiite to mildly alkaline basalts that are usually associated with rhyolites (± alkali feldspar granite) composing so-called bimodal suites, 2) mafic potassic/ultrapotassic volcanic rocks, and 3) andesite series.

1) Tholeiite to alkaline basalts and/or bimodal rock series crop out at the Kozara Mts. in northern Bosnia and Herzegovina, Požeška Gora and Papuk in Croatia, then near Krupanj (Rujevac), in Šumadija (Topola) and on the Jelica Mt. in Serbia and on the Klepa Mt. in North Macedonia. In addition, oil drilling has revealed the presence of similar rocks in the Sava-Drava Depression in Croatia as well as in southern Bačka and in the Kraljevo-Čačak Cenozoic Basin in Serbia.

Campanian pillow basalts and sheeted dolerite dykes of North Kozara have previously been regarded as ophiolites; however, Cvetković *et al*. (2014) ague that these rocks depart from all other Balkan ophiolites by their E-MORB signature and the close petrogenetic association with abundant glassy rhyolite to rhyodacite lavas. A similar petrochemical signature is confirmed for the SVZ bimodal suites in Croatia, for which an anorogenic setting is inferred mainly from data obtained on A-type granites. One of the largest basaltic masses in the SVZ occurs at Klepa Mt., ~10 km south of Veles in North Macedonia. Prelević *et al*. (2017) described pillow basalts, basaltic sheet flows and dykes and microgabbros as part of a shield volcano composed of subalkaline transitional to mildly alkaline basalts with a clear within-plate signature; the authors propose that the primary melts originated by partial melting of the mantle at the asthenosphere-lithosphere boundary; they also demonstrate that the lithospheric part of the magmatic source likely contained amphibole, apatite, ilmenite and garnet in the source, which implies intracontinental setting.

2) The SVZ potassic/ultrapotassic rocks are so far known only from Ripanj near Belgrade, where a late Coniacian–early Santonian (~87 Ma; phlogopite Ar-Ar) lamprophyre sill is found cutting Lower Cretaceous flysch sequences. The lamprophyre is strongly spilitized, but after necessary recalculations it is evident that this rock is ultrapotassic (K_2O>3 wt %; $K_2O/Na_2O > 2$), and belongs to the durbachite-vaugnerite series (*i.e*., the plutonic equivalents of minettes and kersantites) (Sokol *et al*., 2019). The authors suggest that the primary magma originated from a LREE- and K enriched, and garnet-bearing mantle source that is common in subcontinental lithospheres, which undergone orogenic processes.

3) The andesitic series represent the most peculiar and least known group among the SVZ Upper Cretaceous magmatic rocks. They are found in boreholes in south Bačka and southern and middle Banat as part of the Upper Cretaceous Karađorđevo Formation; new U-Pb zircon radiometric age determinations indicate that these andesites are Campanian (76.85 ± 1.28 Ma, 82.83 ± 2.22 Ma, and 84.42 ± 4.83 Ma). Very similar volcaniclastic andesites are found in the uppermost Senonian sandy, marly and clayey sedimentary series near Belgrade (Campanian?). Both rock suites likely represent accumulations of debris flows or submarine slumps from andesite volcanoes. They consist of fragments of hydrothermally altered andesite with albitized plagioclase, epidote and chlorite in the groundmass. Scarce XRF data indicate that these andesites have immobile trace element ratios (*e.g*., Nb/Y or Zr/Nb) similar to typical orogenic Upper Cretaceous andesites that occur in the Banatite-Timok-Srednogorje Belt and that their sodic character is most likely due to spilitization.

The above interpretation is based on a compilation of petrochemical and geochronological data that are extremely non-uniform in volume and quality concerning individual complexes, however, it still allows for highlighting three important constraints about the tectonomagmatic history of the SVZ:

The Late Cretaceous tectonic regime along the SVZ provided conditions for both orogenic (lamprophyres, andesites) and anorogenic (basalts, bimodal basalt-rhyolite suites) rocks.

The available age and stratigraphic data indicate that orogenic magmatism is slightly older (Coniacian-early Santonian) than the anorogenic one (Campanian-Maastrichtian).

There is solid evidence that the SVZ magmatic rocks occur not only on the Upper plate (Tisza-Dacia) but on the Lower plate (Dinarides) as well, which would be very difficult to explain in terms of active margin magmatism associated to a contemporaneous subduction.

In summary, with the present knowledge status it is much more likely that after the collision between the African and European plates, the SVZ acted as a diffuse transpressive-transtensional corridor where local tectonic regimes activated specific magmatic sources and, at least partly, controlled the subsequent partial melting and differentiation processes. Albeit with important variations, the SVZ continued to be tectonomagmatically active throughout the entire Cenozoic; therefore, this zone also hosts all the Oligo–Miocene volcano-plutonic complexes of the central part of the Balkan Peninsula and is the principal site of the formation of the most Miocene core complexes in this region.

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Granitic and pegmatitic rocks of Western Carpathians, Slovakia: a review of rare metal mineralization

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Granitic and pegmatitic rocks form the core mountain of the Tatric, Veporic, and uppermost Gemeric unit and the pre-Alpine Western Carpathian basement. Due to the arc-related character of the parental Variscan magmatism, only restricted pegmatite fields exist. The pegmatites form dike and lenticular bodies (usually < 5m thick) hosted by parental Variscan granites, granodiorites to leucotonalites (~360–340 Ma). Generally, the pegmatites show textural zoning including (from outside) aplitic, graphic, and coarse quartz-feldspar-muscovite border to intermediate zones to blocky K-feldspar and quartz core zones, locally with late albite replacements (saccharoidal albite, cleavelandite).

The largest and the most evolved granitic pegmatites from the Tatric unit are in Bratislava Massif and Žiar with the S-type affinity belonging to LCT-suite beryl-columbite rare element class. The primary rare-metal minerals consist of beryl, columbite-tantalite, zircon, monazite, pyrochlore, and gahnite. Other Be-phases like bertrandite and phenakite are alteration products of beryl I. The interesting phenomenon is the Bi-mineralization including bizmutocolumbite $BiNbO_4$, bizmutotantalite $BiTaO_4$, eulytite $Bi_4(SiO_4)_3$, bizmutinite Bi_2S_3, matildite $AgBiS_2$, and sulphosaltes of Bi (cosalite, emplektite, gladite, cobellite, lindströmite) and also Bi-enriched minerals from pyrochlore supergroup. The occurrence of these minerals is linked to subsolidus hydrothermal fluids during the late-stage magmatic evolution of granitic pegmatites. Geochemically these granitic pegmatites are enriched in Rb, Cs, Be, Nb, Ta, Sn, and W and depleted in Li, Sr, Ba, P, Zr, and REE's which resulted in the absence of Li- and B-rich phases. Such significantly low Li contents (only 23 ppm) are atypical for the LCT pegmatite suite. In Považský Inovec Mts., the 100–150 m long and 20 m thick muscovitic pegmatite body with rare-metal mineral association of garnet-gahnite-columbite-tantalite was identified. Granites from Nízke and Vysoké Tatry Mts. have I-type affinity. The pegmatitic dykes related to them are less frequent and display lower fractionation as documented by Na- and Mg-rich beryl from these pegmatites with dominant octahedral substitution.

Exceptional pegmatite dike with Li-schorl to elbaite and the Nb-Ta oxide minerals was recently discovered from Dobšiná in Gemeric unit. Fluorine-rich schorl-dravite was also identified in specialized Ss-type granite and late magmatic greissens from Betliar where it forms typical tourmaline "suns" in size up to 10 cm. The Gemeric unit is also characterized by small bodies of Permian (~ 270–250 Ma) rare metal granites (Li-Sn-W-Nb-Ta) evolved in the cupolas of larger hidden granite intrusions, where can be industrially interesting REE mineralization. Lithium phases were found in the Li-rich micas (siderophyllite-zinnwaldite) which were studied in detail from the Surovec leucogranite. Cassiterite, Nb-rich wolframite, columbite, Nb-Ta rutile, and microlite-pyrochlore occur as accessory minerals of the most evolved albite-topaz-Li-mica leucogranites (Gemerská Poloma, Hnilec granite occurrences). There were various Y-REE-U-Ti-Nb-Ta minerals including rutile, polycrase-(Y), uranpolycrase and pyrochlore identified in exocontact zones of granite from Dlhá Dolina and Čučma.

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Permian granite magmatism of the Western Carpathians: age, geochemical and mineralogical characteristics

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The Permian granites were described in the Veporic and Gemeric units of the Western Carpathians (Slovakia) but some occurrences were recognised also in the form of large granite boulders in the Paleogene sediments. In this way, we can recognise three types of occurrences of the Permian felsic magmatism in the Western Carpathians: *1*) A-type granite bodies in the Veporic and Gemeric units; *2*) small cupolas of S-type granite bodies as parts of a large hidden granite pluton with development of rare-metal granites in the Gemeric Unit; and *3*) S-(A) type granite exotic boulders within the Paleogene sediments in the northern Slovakia.

Ad 1. In general, the A-type granites are high in K, Rb, Y, REE, Zr, Th, Nb, Fe/Mg, Ga/Al; low Al, Mg, Ca, P, Sr, V and with a pronounced negative Eu anomaly. High iron biotite and increased amount of HFSE minerals are typical. Local hypersolvus alkali feldspars indicate their origin from hot melts. Zircon isotopic dating is in range from 267 Ma for the Hrončok body in the Veporic Unit to 262 Ma for the Turčok body in the Gemeric Unit. A-type granites preserved only as pebbles in the Klippen Belt show age of 264 Ma. The A-type granites were derived from the lower crust and are rift-related.

Ad 2. Rare-metal granites from cupolas of granite apexes in the Gemeric Unit are derived from large hidden granite body with S-type characteristics although in some locations A-type feature may be present, such as local very high Zr content. The specialized S-type granites were named based on their special mineralization of Sn-Nb-Ta-W in cupolas. Emplacements of the volatile rich leucocratic apexes were followed by intrusions of a barren porphyritic biotite granite and thus they formed composite magmatic bodies. Their geochemistry indicates a highly differentiated and fractionated character from a clay-rich source. The origin of the Gemeric granites at approximately 264 Ma was linked to a post-collisional extension in the initial Alpine rifting stage.

Ad 3. Large coarse-grained granite boulders, *e.g.,* the blocks from the Milotín, and Zábiedovo village are 3×2 m in size, are classified as peraluminous slightly porphyritic biotite granites. These granites were dated to 278 and 276 Ma, respectively. The deposition of granitic boulders within the Paleogene sediments is from an unknown source.

A-type granites and specialized S-type granites from the Veporic and Gemeric units are calk-alkaline and only partly alkaline and were formed during the Guadalupian stage – the Ss-type granites from the Gemeric Unit are much more fractionated showing different style of evolution and source. The older Cisuralian A-type granites are described in the more southern located Velence Mts. in Hungary. The Cisuralian granite boulders from the northern Slovakia show possible Permian age zoning which can be used in wider correlation research and consequently for the additional tectonic interpretation like determination of the shifted ALCAPA terrain in the frame of the present Central Europe.

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Late Paleozoic igneous episodes in the Pannonian Basin and the Apuseni Mts: petrology, zircon U–Pb dating, and regional correlations

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In the Carpathian–Pannonian region, the products of several Permo-Carboniferous magmatic episodes can be traced in outcrops (*e.g.*, Western Carpathians, Apuseni Mts) or in the basement of the Pannonian Basin well-explored by boreholes (*e.g.*, Southern and Central Transdanubia, Eastern Pannonian Basin). First descriptions and interpretations of the igneous rocks were associated with reports of uranium ore and hydrocarbon exploration (from the 1960–80s) that provided obsolete and/or incomplete information. Therefore, many of them were reexamined in the last decade in the light of modern petrological views (*e.g.*, trace element geochemistry and zircon dating). In the followings, the major outcomes of these investigations are summarized. In the Eastern Pannonian Basin (Tisza Mega-unit), S-type granitoids were drilled that most possibly represent crustal melts in an Early Carboniferous (~356 Ma) continental arc or collisional setting. Similar mineralogical compositions and major and trace element distributions refer to the genetic linkage of these rocks with the Codru granitoids (Apuseni Mts) and their feasible relationship with the S-type metagranites in the Papuk Mts (Slavonia). Many of these granitoids were affected by post-emplacement deformation and/or metamorphism. In Central Transdanubia (ALCAPA Mega-unit), an Early Permian (~281 Ma) dacitic volcanism was revealed, represented by lavas (boreholes in the Balaton Highland) and dykes in the Polgárdi limestone quarry (Szemerédi *et al*. 2020). Trace elements suggest that these rocks are associated with a post-orogenic environment and show similarity with the analogous formations of the Northern Veporic Unit, Western Carpathians. The youngest, Mid-Permian (~271–259 Ma) episode was revealed in a relatively large area of the Tisza Mega-unit (Szemerédi *et al*. 2020), represented dominantly by crystal-rich pyroclastic rocks or lavas in Southern Transdanubia, the Eastern Pannonian Basin and the Apuseni Mts. Trace element distributions suggest the rift-related (A-type) character of these rocks and, along with zircon ages, supported their plutonic–volcanic connection with the 267–260 Ma granitoids (Szemerédi *et al*. 2021) in the Highiş massif (SW Apuseni Mts). It is feasible that the large-volume Mid-Permian silicic magmatism of the Tisza Mega-unit formed a complex cogenetic suite together with mafic and intermediate melts that are prevalent in the Highiş massif (gabbros and diorites) and in the Codru-Moma Mts (basalts and andesites occurring with felsic ignimbrites). These A-type felsic rocks show similarity to some of the analogous formations in the Western Carpathians (*e.g.*, Gemeric, Silicic, and Veporic Units) and might represent similar anorogenic melts in the Paleo-Tethyan realm.

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The Late Cretaceous syenite from the Sava suture zone (eastern Croatia)

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The Sava suture zone represents a belt of igneous, metamorphic, and sedimentary rocks, stretching E-W from Zagreb to Belgrade and NNW-SSE along the Vardar River to the Aegean Sea. Only a minor part of the units is exposed at the surface as isolated outcrops, while the rest is covered by younger deposits. Igneous rocks of the Sava suture zone mainly belong to bimodal complex represented by basalt and rhyolite with gabbro and shallow A-type granite, covering the time span of 83.6–81.0 Ma.

In the Slavonia-Srijem Depression (SSD, eastern Croatia), boreholes drilled into the igneous rocks that belong to the pre-Neogene basement. The syenite is obtained as a core of the borehole in the vicinity of the town of Vinkovci. This rock represents the part of the pre-Neogene basement, covered by Upper Miocene deposits. The syenite is composed of K-feldspar and albite, followed by minor quartz, biotite, and hornblende, and accessory zircon, apatite, and opaque minerals. It is characterized by high $FeO_T/(FeO_T+MgO)$ ratio (0.81), high alkali content (K_2O+Na_2O=10.65 wt.%), accompanied by low CaO (2.07 wt.%) indicating an A-type affinity. The syenite displays similar trace element geochemistry as A-type granites recovered from the nearby boreholes, with enrichment in incompatible over compatible elements in primitive mantle-normalized pattern and light rare earth elements (REE) enrichment in chondrite-normalized REE pattern. The main difference between the A-type granites and the syenite is enrichment in Ba, K, Eu and Zr in the syenite. The possible cause of this difference is a fractionation of K-feldspar and zircon, indicative of cumulate origin for the syenite.

According to new zircon U-Pb LA-ICP-MS dating, the age of the syenite falls within the window of ~83.0–80.5 Ma. The age data and overall geochemistry point to an association with the Late Cretaceous magmatism of the Sava suture zone. This age is also overlapping with magmatism of the Apuseni–Banat–Timok–Srednogorie belt (ABTS), but ABTS magmatism is calc-alkaline, with typical subduction-related geochemistry. On the contrary, A-type signature with substantially higher Nb, Zr, and Hf along with lower Pb concentration of our SSD igneous rocks, along with the other Sava suture zone A-type granites, clearly differentiates them from ABTS magmatism.

Mid-Cretaceous adakite/TTG-like magmatism at the north Getic basement of the South Carpathians (Romania): origin on geochemical basis and age data review

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Mid-Cretaceous trondhjemites and granodiorites (TGSCF), forming a swarm of over 300 sills, dikes and small intrusive bodies along the Sibișel Shear Zone belonging to the Transcarpathian fault system at the north Getic basement of the South Carpathians (Sebeş-Cibin-NW Făgăraş Mountains), are revisited. The rocks are Na_2O-rich (4.5–7%), mainly peraluminous and exceptionally metaluminous in few cases, with I-S type characteristics. Variable Sr (250–900 ppm), low HREE (Yb of 0.05–1.9 ppm) and Y (3–16 ppm) contents, hence medium–high Sr/Y (43–447), $(LaYb)_N$ (6–40.27) ratios and REE trends with small to no Eu anomalies, approximate an adakitic signature. The rocks differ from the real adakites by lower #Mg (20–46), Ni (<7.5 ppm) and Cr (<25 ppm) contents, overlapping the characteristics of some rare tonalite-trondhjemite-granodiorite (TTG) suites formed in the thick lower crust or from slab melts at a low angle subduction. Trace-element behavior and comparison with experimental results indicate that TGSCF rocks crystallized from partial melts of garnet-bearing rocks (garnet amphibolites or eclogites) as part of the mafic crust. Completed with Sr and Nd isotope values [Sr_i of 0.7040–0.7045 and ε_{Nd} (T) from (–2.26) to (+1.22)], the main source may be estimated as EMI-OIB, as island arc tholeiites from a depleted mantle-like component enriched by crustal contaminant or an extension-related underplated mafic material in a region where mantle was previously enriched by subduction. The complex inner structure of the dated zircons (Dobrescu *et al.*, 2010) reveals inherited pre-magmatic zircons of several Proterozoic and early Paleozoic age ranges, meaning old crustal input. Our model for TGSCF genesis implies an asthenolite as a thermal trigger underplating the lower crust, with H_2O source in its hydrated components (phlogopite from garnet-peridotite) or in amphibolite/meta-gabbro dehydration from lower crust, affecting old crust materials. Enriched mantle influence could have induced melting (10–20%) on the hybrid source material at temperatures of 980–1150 °C and P>10 kbar, generating trondhjemite-granodiorite melt and leaving amphibole + garnet + clinopyroxene ± plagioclase residue. The presence of hypabissal textures with partial dissolution and resorption, corroded hornblende and magmatic epidote in trondhjemites and muscovite in granodiorites indicate crystallizing conditions of a deep-seated emplacement, followed by a rapid ascend, tectonic uplift and exhumation. U-Pb zircon ages of 109.8–104.8 Ma interpreted as an intrusion time (Dobrescu *et al.*, 2010) coincide with the supposed timing of the Ceahlău-Severin Ocean subduction/collision event. Rapid convergence and shallow subduction followed by tectonic underplating beneath Dacia, presumed by Ducea and Roban (2016) to have occurred at mid-Cretaceous time, provide a tectonic setting consistent with the adakite / TTG signature of the TGSCF rocks.

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Petrology and age of the Plovdiv pluton, Bulgaria

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The Plovdiv pluton is intruded along the Maritsa strike slip fault zone in the southern part of Central Srednogorie Zone, Bulgaria. Due to the erosion, several hills provide excellent outcrops for studying the pluton. Monzonites are the dominant igneous phase of the pluton. The presence of mafic enclaves and similar by composition intermediate dyke-like and irregular small bodies shows typical mingling structures with the hosting magmas. The latest phase is presented by aplitic and pegmatitic veins that crosscut all of the earlier phases.

Here we provide new geochronological, geochemical, isotope and petrologic data with the aim to constrain better the time of the intrusion, petrology, geochemistry, generation and magma sources.

The main intrusive phase of the Plovdiv pluton is presented by medium to coarse-grained massive rocks with typical monzonitic texture represented by poikilitically enclosed amphibole and plagioclase in K-feldspar. The rock-forming minerals are plagioclase, K-feldspar, quartz, amphibole, clinopyroxene and rarely biotite. The accessory minerals are well presented by titanite, apatite, zircon, magnetite and allanite. The mafic enclaves are of fine-grained gabbro to diorite with primary minerals of plagioclase and amphibole, but also rarely biotite and clinopyroxene. The accessory minerals are presented mostly by titanite, allanite and apatite. The small irregular and dyke-like bodies are quartz monzonite porphyries with porphyrocrysts of plagioclase, quartz, amphibole and rarely biotite and clinopyroxene set in fine-grained groundmass and accessories of apatite, titanite, zircon and magnetite. The aplitic veins are built predominantly of microcline and less quartz and plagioclase with minor biotite and muscovite and accessories of titanite, apatite and allanite.

Most of the rocks are metaluminous, high-K calc-alkaline to shoshonitic while some of the mafic enclaves are medium-K calc-alkaline. On a primitive-mantle normalized diagram, the rocks show peaks in LILE (U, Th, Pb) and troughs in Nb, Ta, Ti and P typical for orogenic magmas. They show high contents of LILE, decreasing MREE chondrite-normalized patterns and almost flat to listric-shaped HREE normalized profile. Some of the rocks exhibit geochemical adakite-like features with weak negative Eu (0.79 to 0.88) anomaly, high Sr (716 to 1667 ppm) and low Y (15 to 25 ppm) content. These feature along with decreasing Dy/Yb with increasing SiO_2 most probably are due to amphibole (and probably titanite) fractionation. The measured $^{87}Sr/^{86}Sr_{(80)}$ ratio in the quartz-monzonites of the Sahat tepe is 0.704254 and $\varepsilon Nd_{(80)}$ –0.38, while the isotopes of mafic enclave are slightly more primitive: 0.704143 and 1.90. The $\varepsilon Hf_{(80)}$ of the autocrystic zircons show variations in the range of +5 to +10.8 suggesting primitive magma source and magma mixing.

The P-T conditions of the amphiboles show continental depth of 6.6–4.8 km and 830–910 °C for the quartz-monzonites. The amphiboles from the mafic enclaves show similar conditions (6.9–4.8 km and 810–897 °C) probably due to re-equilibration. The amphiboles from the porphyritic dyke-like and irregular small bodies show three peaks of the crystallization: 6.4–6.8 km and 880–890 °C; 10–14 km and 900–940 °C; 17–22 km and 950–1000 °C.

The obtained LA-ICP-MS U-Pb zircon age from the Sahat Tepe hill is 80.02 ± 0.33 Ma.

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The Miocene granitic rocks of the Central Slovakian Neovolcanic Field: Isotopic constraints and dating

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The Alpine orogeny has produced granitic rocks during the Phanerozoic (Late Cretaceous–Eo-Alpine) and the Cenozoic (Miocene–Late Alpine) periods in the Western Carpathians. The youngest granitic rocks of the Western Carpathians – Miocene in age – are the focus of this study. The inner parts of the Western Carpathians were affected by extensive volcanism linked to the back arc rifting associated with asthenosphere updoming and/or formation of the Pannonian Basin in the Neogene/Quaternary. Neogene volcanic rocks form the so-called Central Slovakian Neovolcanic Field (CSNF). Studied diorites and granodiorites belong to the Hodruša-Štiavnica Intrusive Complex (HŠIC) which crops out in the central part of the CSNF and forms a resurgent horst that comprises a diorite subvolcanic intrusion and a younger granodiorite bell-jar pluton extending over an area of 100 km^2 (Konečný *et al.*, 1983). The diorites and diorite porphyries are medium to coarse-grained, dark grey, massive magmatic rocks with equigranular and porphyric texture. Petrographically, they consist of hypidiomorphic and/or phenocrystic basic plagioclase, orthopyroxene and amphibole, whereas quartz, orthoclase and rarely fine biotite form anhedral crystals and groundmass. Accessories include magnetite, apatite and zircon. The massive granodiorites ± granodiorite porphyries consist of intermediate plagioclase, quartz, K-feldspar, biotite, amphibole, and accessory magnetite, titanite, pyroxene, apatite and zircon. Their texture is equigranular and porphyric in marginal parts, locally with mafic microgranular enclaves. Geochemically, these granitoids belong to the High-K calc-alkaline magmatic series with metaluminous to partly subaluminous, and magnesian character. Whole-rock radiogenic isotopic compositions (Sr, Nd, Pb and Hf) together with stable isotopic characteristics (O, Li, Fe, Mg and ^{88}Sr) and/or zircon Hf isotopic composition suggest for their lower crustal/mantle source influenced by a mantle magma from SCLM. Extensive SHRIMP zircon dating proved the age of the diorite and diorite porphyry intrusions between ca. 15 and 13.6 Ma, whereas the granodiorites and granodiorite porphyries were emplaced before 13.6 and 12.8 Ma. This is in good agreement with the pilot SHRIMP zircon and ZHe & AHe dating by Kohút and Danišík (2017). The Carpathians Miocene mafic/felsic magmatism was a consequence of the complex multi-stage processes with the primary basaltic magma formed by melting of the lower crustal source at the mantle/crust boundary trigered by the upwelling of asthenospheric mantle. Due to delamination in the subducted lithospheric slab, younger granodiorite magma was mixed with a new melt generated from metasomatized lithospheric mantle. That is why it shows a more primitive mantle isotopic signature in comparison to the dioritic rocks in the HŠIC. Following formation of a melt reservoir in the middle crust, accompanied by secondary melting of the surrounding rocks, and/or repeated process of assimilation and fractionation produced a suite of chemically variable lithology from basalt to rhyolites and/or granitic rocks.

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Petrogenesis of calc-alkaline volcanic rocks of the Slanské Vrchy Mountains, eastern Slovakia: Constraints from Sr, Nd, and Hf isotopes, trace elements, and LA-ICP-MS U-Pb zircon geochronology

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The Carpathians are formed during the Oligocene to Miocene invasion of the ALCAPA and Tisia-Dacia crustal blocks into the Carpathian embayment, a landlocked basin with thinned continental and/or oceanic crust at the northern edge of the European platform. Related calc-alkaline and alkaline volcanism occurred between ~21 Ma and ~0.2 Ma and is commonly associated with subduction, extension, and upwelling of the asthenosphere (Pécskay *et al.*, 2006).

The ~50 km long, N-S trending Slanské Vrchy volcanic chain is located at the western flank of the Miocene Transcarpathian basin system in eastern Slovakia. Here, we present the first comprehensive geochemical dataset with state-of-the-art isotope (Sr, Nd, Hf) and LA-ICP-MS U-Pb zircon data for volcanics from Slanské Vrchy. The SiO_2 contents of studied volcanic rocks (n=21) range from 54 to 65 wt.%, and they are classified as basaltic andesite (one mafic enclave), andesite (n=14), and dacite (n=6) in the total alkali vs. silica (TAS) diagram. All samples show characteristic calc-alkaline signatures in mantle-normalized multi-element diagrams, *i.e*., strong enrichment of large ionic lithophile elements and Pb as well as negative Nb and Ta anomalies. The $^{87}Sr/^{86}Sr_{(12Ma)}$, $\varepsilon Nd_{(12Ma)}$ and $\varepsilon Hf_{(12Ma)}$ ratios of the basaltic andesite and andesites range from 0.7071 to 0.7096, –7.3 to –1.3, and –6.5 to 2.5, respectively. Similar isotope characteristics are observed for the dacites: $^{87}Sr/^{86}Sr_{(12Ma)}$, $\varepsilon Nd_{(12Ma)}$ and $\varepsilon Hf_{(12Ma)}$ ratios vary between 0.7078 to 0.7104, –7.2 to –3.1, and –6.5 to 0.0, respectively. Robust concordant U-Pb zircon ages are indistinguishable for the andesites (n=5) and dacites (n=3) and range from 12.2 ± 0.2 Ma to 11.8 ± 0.2 Ma.

Volcanism of Slanské Vrchy coincides with differential rotations of the ALCAPA and Tisia-Dacia crustal blocks. These block rotations are associated with the opening of the Transcarpathian basin system (commencing before 18 Ma), and led to the decoupling of the easternmost tip of ALCAPA from its host block along the Hernad detachment fault at ~12 Ma (Márton *et al.*, 2007). Magma generation was hence most likely related to mantle decompression melting, and the locations of magma ascent seem to be controlled by the stress regime of the Hernad fault, which runs parallel to the Slanské Vrchy chain. Furthermore, isotope data clearly indicate the importance of crust-mantle interactions for the genesis of calc-alkaline magmas. The most likely petrogenetic process is partial melting of mantle that was previously metasomatized by subduction-derived components (cf. Kovacs *et al.*, 2017). Such initial mantle melts were probably further modified by MASH processes (mixing, assimilation, storage, and hybridization) during storage at the lower crust and by AFC processes (assimilation and fractional crystallization) in the middle/upper crust.

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The Mogoşa volcano from the Miocene Gutâi Volcanic Zone, Eastern Carpathians (NW Romania). Petrological approach

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The Mogoşa composite volcano was built up in the second phase of the Miocene post-collisional intermediate volcanism from the Gutâi Volcanic Zone (GVZ), Eastern Carpathians, NW of Romania (Kovacs *et al.*, 2017). During its very long and mainly effusive activity (11.4–9.5 Ma), it has produced a remarkably homogeneous compositional range of products consisting of basaltic andesites. A distinct extrusive dome (Valea Morii, 10.1 Ma), composed of high-silica andesites/dacites with mafic microgranular enclaves (MME), arose on the western flank of the volcano. Associated dykes and sills of basaltic andesites occur especially in the area outside the volcano. Despite of the chemical homogeneity (51.5–56.4 wt.% SiO_2, 0.78–1.17 wt.% K_2O), rock types with different mineralogical and textural features are associated to temporally and spatially different volcanic events (*e.g.*, 11.4–11.3 Ma Piatra Şoimului pyroxene glomerocrystic mainly autoclastic lavas in SE; 10.3 Ma Baia Sprie pyroxene microporphyric glassy lava flows in SW; 9.5 Ma Mogoşa Peak pyroxene + macrocrystic amphibole lava flow around the summit of volcano).

The rock-forming mineral association mainly consists of plagioclases + pyroxenes (clinopyroxenes and orthopyroxenes) + Fe-Ti oxides. Amphiboles are presented only in the Valea Morii dome rocks and its amphibole-rich diktytaxitic MME, and in the Mogoşa Peak basaltic andesites. Plagioclases represent phenocrysts in the basaltic andesites (An_{65-84}), and phenocrysts and sieve-textured xenocrysts in the high-silica andesites/dacites ($An_{69–77}$). Clinopyroxenes (augite) are phenocrysts in the basaltic andesites (Mg#: 71–77) and MME (Mg#: 70–80) and xenocrysts in the acidic rocks of the Valea Morii dome (Mg#: 70–76). Orthopyroxene phenocrysts are enstatite ($En_{53–71}$) with higher Mg#: 65–77 in the basaltic andesites comparative with those of the Valea Morii acidic rocks (Mg#: 55–66). High Mg# (74-79) and high-Al (12.2–15.2 Al_2O_3) amphiboles occur as xenocrysts in the high-silica andesites/dacites, as phenocrysts in their MME and as macrocrysts (up to 4 cm) in the basaltic andesites from the top of the volcano.

The geochemistry indicates subalkaline, medium-K composition with typical subduction-related zone signatures (strong LILE and LREE enrichment and HFSE depletion) for the volcanic rocks. The MME from the Valea Morii dome display less LILE and LREE enrichment in the chondrite-normalized REE and NMORB-normalized diagrams. Positive correlation of the LILE/HFSE element ratios with differentiation indexes corroborated with the $^{87}Sr/^{86}Sr$ ratio values (0.7065–0.7076) shows the involvement of the crustal assimilation in the petrogenetic processes.

Recent P-T data acquired on amphiboles and clinopyroxenes from all the rock types have proven the presence of a complex volcanic plumbing system, consisting of deep lower crustal magmatic reservoirs where the generated magmas evolved (Kovacs *et al*., 2021), maintaining the long-lasting activity of the Mogoşa volcano.

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Sharp changes in magma evolution during the Quaternary volcanism of South Harghita, eastern-central Europe: constraints from bulk rock and zircon geochemistry and U-Pb dating

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The southernmost-end segment of the Călimani-Gurghiu-Harghita (CGH) chain (Eastern Carpathians, Romania) is represented by a succession of four aligned volcanoes (Luci-Lazu, Cucu, Pilişca and Ciomadul) formed by a postcollisional volcanism. The last three show distinct magma source characteristics and different petrogenetic evolution compared to the volcanic systems at the northern segment of the CGH.

The increasing Sr and Ba values in the bulk rocks, along with the changing Eu/Eu*, Hf content of zircon crystal with the calculated fO_2 from the Cucu volcano toward south is interpreted as distinct magma source regions with increasing metasomatized nature of the lithospheric mantle followed by fractional crystallization and mixing processes at crustal level. Two major sharp changes in the erupted magma composition are recognized at 2 Ma and 1 Ma, respectively, as revealed by zircon U-Pb ages. The last one occurred after an eruption gap between ~1.4–1 Ma when the activity of the Pilişca volcano terminated and the Ciomadul volcano dome field (CVDF) started to develop.

The Pilişca volcano with basaltic andesite evolved to dacite shows already a transition toward adakitic type magma composition. The CVDF volcanic activity started with a primitive shoshonitic magma derived by a low-degree partial melting of strongly metasomatized lithospheric mantle, whereas the more typical dacites were formed via multistage fractional crystallization and magma mixing. The adakitic character could be a result of various potential processes, from slab melting, interaction with peridotite mantle wedge, partial melting of mafic lower crust as well as magma mixing and fractional crystallization of garnet and/or amphibole. Trace element signatures of the magmas from Luci-Lazu to Ciomadul show a changing mantle source trend with various parental magma types and distinct fractional crystallization paths. Accumulation of mafic magmas beneath CVDF occurred at the base of the continental crust, where amphibole-dominated crystallization led to more evolved magmas. These differentiated magma batches built up a shallow crustal long standing felsic magma reservoir, where intermittent magma recharge events caused mixing in addition to a low pressure crystal fractionation, involving amphibole, biotite and plagioclase. Over time, the growing felsic magma reservoir below CVDF acted as a density filter and prevented the ascent of mafic mantle-derived magmas to the surface.

The sharp changes in the erupted magma composition can be related to changes in the geodynamic situation at the Southeast Carpathians during the Quaternary such as the distinct thermomechanical properties of the crustal blocks affecting the style of the collision as well as the geometry and asthenospheric mantle flow around the descending lithospheric slab. The associated geodynamic model could be a delamination process supporting magmatism generated in a highly hydrated lithospheric mantle below the Moesian Platform during the slab delamination rollback, although the alternative model of a near vertical slab as remnant of a former subduction cannot be unambiguously excluded as the source of adakitic and the ultrahydrous character of magmas via slab melting.

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Constraining the source of arc-like magmas in a post-subduction setting: the South Apuseni Mountains, Romania

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The post-subduction magmatism in the South Apuseni, containing numerous Au ± Te rich epithermal and porphyry deposits, was formed in extensional settings generated by the rotation of the underlying Dacia–Tisza crustal blocks during the Neogene and strike-slip tectonics during the Quaternary (*e.g.,* Seghedi *et al.*, 2021). The majority of rocks are andesitic in composition and exhibit subduction-like features such as enrichment in LREEs, LILEs and Pb and negative Nb, Ta and Ti anomalies. In addition, a small subset exhibits high Sr/Y ratios, similar to rocks named adakites. Currently, the two accepted explanations regarding the formation of the Neogene and Quaternary magmas in the South Apuseni involves either melting of an enriched SCLM modified during Mesozoic times (Harris *et al.*, 2013) or lower crustal melting followed by delamination and melting of the eclogizited delaminated lower crust, interacting with the asthenosphere (Seghedi *et al.*, 2007).

New geochemical and isotopic data allow a better reconstruction of the evolutionary history of the South Apuseni Mountains and highlight the role melting of lower crust played in the arc-like geochemistry displayed by the Neogene and Quaternary intrusions. Sr, Nd and Hf isotopic composition is mainly spatially controlled; however, in the two volcanic centres that exhibit a protracted evolution, younger magmas trend towards the juvenile end of the spectrum and exhibit higher Sr/Y values.

Our geochemical modelling indicates that both adakitic and normal calc-alkaline suites can be produced through a fluxed melting of gabbroic cumulates and OIB and MORB-like components, respectively. These cumulates, probably formed during the Jurassic and Cretaceous, exhibit arc-like geochemical signatures that are retained during melting.

The more enriched end members such as Uroi or Deva can be explained through 10% melting of a mixture composed of 90% lower crustal gabbro and 10% OIB-like melt. Melting was initiated by asthenospheric upwelling caused by the rollback of the Vrancea slab. This caused, in a first instance, melting in the DMM component of the mantle. This interacted with the lower crust, creating a hybrid source giving rise to normal calc-alkaline magmas. Where and when asthenospheric melts could interact with the lower crust, adakite-like rocks were generated.

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New data about volcanic rocks and forms from Hannah Point, Livingston Island, Antarctica

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Volcanic/magmatic activity in the South Shetland Islands occurred between Late Cretaceous on Livingston Island (Smellie *et al*., 1984) and up to the Quaternary in Deception Island. It shows a diverse compositional variation in response to a complex interplay of subduction with roll-back, back-arc extension, collision, strike-slip tectonics, as well as in response to further evolution of magmas in the crustal environment by processes of differentiation, crustal contamination, magma mixing, etc.

Most of the primary volcanic edifices and forms have been affected by erosion and tectonic processes. We can distinguish: (1) deeply eroded volcanic forms with secondary morphology and possible paleovolcanic reconstruction; (2) eroded volcanic forms with remnants of original morphology preserved; (3) the least eroded volcanic forms with original morphology quite well preserved.

Hannah Point is a small peninsula in the southern part of the island, and provide excellent rock outcrops. Pallàs *et al*. (1999) recognized five members within this succession, from base to top: (a) 120 m of polymictic volcaniclastic breccias, (b) 70 m of volcaniclastic breccias, (c) 65 m of basaltic lavas, (d) 65 m of volcaniclastic breccias, and (e) 150 m of andesitic lavas, suggesting that the rocks of this succession were emplaced as pyroclastic flows associated with explosive volcanic activity in a subaerial environment. In this research we provide new data about volcanic forms and rocks on Hannah Point.

The Upper Cretaceous volcanic succession of Hannah Point is composed of lava domes/dome-flows, lava flows, pyroclastic flow and flow deposits, resedimented volcaniclastic (epiclastic) products and dikes. All of the volcanic materials are products of activity of one, stratified, monogenetic volcano. Isolated simple-shaped lava dome/dome-flow occurs in the northern part of the area. It is conical dome shape and almost circular map outline. It is composed of basalts and basaltic-andesites. In the lower part of the cross-section are situated two basaltic-andesitic lava flows, separated each other by well-defined autobrecciated levels. Colonnade and entablature textures are common. Volcaniclastic rocks are the most common facies variety on Hannah Point. We can recognize pyroclastic flow and fall deposits and different epiclastic specimens. There are two types of pyroclastic fall rocks – block and bomb tuffs (pyroclastic breccia) and lapilli tuffs, and one type of pyroclastic flow rocks – ignimbrites. The rock succession is penetrated by some vertical dikes and sills with andesitic composition.

The volcanism at Hannah Point is a result of activity of one, monogenetic, stratified volcanic structure, which took place in several stages: *1*) effusive – generating of lava flows and lava domes; *2*) explosive – accumulating of pyroclastic fall deposits; *3*) collapse of eruption column – production of pyroclastic flow deposits.

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New U-Pb zircon ages of the Upper Cretaceous volcano-sedimentary deposits from the Haţeg Basin (Southern Carpathians) and temporal intrabasinal correlation

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Volcano-sedimentary deposits crop out in relatively small patches in the northwestern part of the Haţeg Basin (South Carpathians, Romania), around the villages of Densuş and Răchitova. They belong to the partly volcaniclastic continental beds deposited here during the Late Cretaceous, and are grouped into the Densuş-Ciula Formation. These units comprise primary volcanic and secondary epiclastic rocks of andesitic-dacitic composition.

Here we report new laser ablation ICP-MS U-Pb zircon ages of three volcaniclasts (from distinct outcrops) of andesito-dacitic composition from the Densuş area. There are no previous absolute age constraints on these rocks although earlier mapping assigned a Maastrichtian age. Our samples were collected from the Lower Member of the Densuş-Ciula Formation and belong to a debris flow deposit. The U-Pb analyses yielded crystallization ages of about 80–82 Ma for all three samples (80.44 ± 0.14, 80.22 ± 0.25, and 81.88 ± 0.17). Some (lower resolution) whole rock K-Ar and zircon fission track datings on volcaniclasts from the Răchitova outcrops yielded ages of 82.7 ± 1.5 Ma and 80 ± 9 Ma, respectively, and are consistent with our data. Our new ages also fall within the well documented range of the ~72–82 Ma subduction-related magmatism (Neo-Tethyan) in Banat and the Apuseni Mts. and sediments dispersed from it. Volcanic rocks sourcing these deposits were indubitably a part of this regionally significant magmatic arc.

The Densuş-Ciula Formation unconformably overlies the Răchitova Formation – grouping the youngest marine beds in this area, divided into Upper and Lower members. The Upper Member was formerly attributed to the upper Campanian due to two identified nannofossil events, the FO (first occurrence) of *Uniplanarius sissinghii* and *Uniplanarius trifidus*, both considered late Campanian events. More recently, the age of the Upper Member was biostratigraphically restricted to early late Campanian.

These ages conflict with our U-Pb zircon data, which suggest that subaerial volcanic activity was already taking place in this area by the middle Campanian. Either biostratigraphic ages are imprecise or the volcano-sedimentary deposition of the Densuş-Ciula Formation took place significantly later than the actual volcanism. More complicated scenarios, such as tectonic juxtaposition of older volcano-sedimentary rocks over younger marine deposits, are plausible but less likely. Further investigations of the ages and tectonic evolution of the uppermost Cretaceous in the Haţeg Basin are needed.

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Geochronology, geochemistry and geodynamic evolution of the Tatric granites from crystallization to exhumation (Tatra Mountains, Western Carpathians)

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The Western and High Tatra Mountains (northern Slovakia, southern Poland) contain the best-exposed rocks record within the Carpathian orogenic belt. They are a logical location to study arcuate orogenesis, exhumation rates of the deep crust, and magnitudes and rates involved in the transfer of heat and mass during mountain-building events. Understanding the timing and nature of tectonic events recorded in the Western Carpathian region is helpful for global plate reconstructions and linking the range to other locales that document the closure of the Tethyan oceans throughout Europe. Petrological, geochemical, and geochronological data from granitic assemblages across the Western (n=1) and High Tatra Mountains (n=19) were used to understand how they responded to an extended tectonic and magmatic history. Geochemical data from samples from the Western and High Tatra Mountains suggest they were emplaced in a volcanic arc setting at lower P (<5 kbar). Most have been derived from a mafic source, enriched mantle, non-garnet bearing source with some clay component. Two samples from the Western Tatra and High Tatra Mountains have HREE patterns and negative Eu anomalies consistent with a within-plate signature, suggesting the presence of melts from a collisional source are present in both regions.

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) zircon dating shows a dominant early Carboniferous (Tournaisian, TuffZirc age = 349.3 + 2.9/–1.5 Ma at 95% confidence, n=119 spots), but Paleoproterozoic/Neoarchean (2544 ± 33 Ma, ± 1σ) to late Carboniferous (Kasimovian, 305.8 ± 6.2 Ma) dates were also found. The age pattern is consistent with granitic assemblages within the European Variscan Belt and suggests an affinity with Armorican terranes derived from a northern Gondwanan Cadomian arc. The final stages of the Variscan orogenic collapse are timed at ~315 Ma based on the youngest zircon age population. Monazite dated in thin section are also Tournaisian, but the youngest age is Permian (Th-Pb, 270.0 ± 9.1 Ma, ± 1σ), consistent with the timing of a large-scale Pangean Permian extension.

High Tatra granite K-feldspar $^{40}Ar/^{39}Ar$ ages indicate slow post-magmatic cooling after the granite crystallization. The oldest $^{40}Ar/^{39}Ar$ ages from two samples near Lomnický štít (LS) suggest a thermal event in the Late Triassic (~220 Ma), but others from the sub-Tatra fault and near Gerlachovský štít (GS) are younger (Early Cretaceous, ~120 Ma). The thermal history from K-feldspar at the base of LS shows a pulsed exhumation at faster rates between 70–55 Ma (300–200 °C) and 45–35 Ma (200–100 °C). The results document the Paleo-Alpine tectonic imprint of the Western and High Tatra Mountains until the onset of more Neo-Alpine exhumation. The data point to uplift earlier than suggested by models of extrusion tectonics applied to the region. Early uplift is connected with the Eocene ALCAPA (ALps-CArpathians-Pannonia) escape leading later to the development of the Carpathian arc.

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Magma mixing in the Variscan granites (Malá Fatra Mts., Western Carpathians): evidence from the mineral compositions

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The Malá Fatra granitic massif shows zoning – transition from a tonalite (T) to granodiorite (GD) zone indicating a shallowing of the emplacement of magmas. The average zircon saturation temperature for the entire granodiorite zone is 752 °C; the tonalite zone shows relatively increased zircon saturation with average temperature of 780 °C. According to isotopic zircon datings, the granite massif was formed in short time span 347–342 Ma. The tonalites shows an average age of 346 ± 4 Ma but a wider spread of its age population from 350 to 341 Ma probably due to an intense heat input prolonging the melt stage. The compositional feature of feldspars, biotite and accessory minerals evidences mixing in this granite massif. Well-preserved plagioclase grains in the tonalite zone display a typical progressive zonal composition from $An_{33–30}$ in the cores to An_{26} in the rims. On the other hand, three type of plagioclase have been determined in the GD: (1) plagioclase I (core: $An_{24–36}$) displays oscillatory Ca zoning reflecting progressive magmatic crystallization but distinct lamellae show reverse zoning; (2) plagioclase II ($An_{22–17}$) is a product of subsolidus recrystallization during a post-magmatic low temperature overprint; (3) relic plagioclase with $An_{41–50}$ recognized in the core of plagioclase I is an evidence of very "hot" regime during origin. The hot high-T melt such as like is known for A-type granites indicates also the presence of antiperthite in plagioclase from the T. Two types of K-feldspar have been identified in GD: (1) K-feldspar I – primary magmatic, display internal Ba oscillatory progressive zoning with a bell shape magmatic trend in the central part, and a revers zoning on the rims; (2) K-feldspar II – from the rimes of K-feldspar I and in plagioclase joints contains low BaO content (<1.0 wt.%). Important is a finding of the relic sodium rich K-feldspar (Na_2O and BaO are up to 1.64 wt.% and 2.5 wt.%, respectively) what indicates mixing. Biotite in both tonalite and granodiorite are rarely preserved due to an intense chloritization. The biotite Mg/(Mg+Fe) ratio in tonalite and granodiorite is 0.50 and 0.45, respectively.

Apatite and allanite-(Ce), along with zircon, epidote, titanite, are typical primary accessory phases in the T, in contrary, monazite and Mn-rich apatite in GD documents the S-type character of the granodiorite. There is typical apatite with zircon zonal oriented inclusions. Ti-magnetite is abundant in both T and Gd zones. According to the Ti-magnetite – ilmenite oxythermometer, GD with mixing affiliation crystalized at 760 – 811 °C along FMQ buffer (fO_2 = -13.7 – -14.7).

Mixing of melts, derived from mantle and crustal components, in lower crustal MASH zone leads to homogenization of a melt and forming "granotonalite compositions". The transitional character of granodiorite/tonalite ("granotonalite") indicates also transition annite/phlogopite phases. The upper crustal emplacement of melts was favorable for a convective style of mixing, forming the mentioned multistage formation of plagioclases and K-feldspar, quartz ocelli and changes of zircon morphology and numerous, tiny zircon inclusions distributed concentrically inside the apatite.

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Orbicular gabbro from the northern part of the Plana Pluton, Bulgaria – new data

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Crystalline igneous rocks with orbicular textures are rare phenomena and always arouse the interest of geologists, especially in questions related to their genesis. The first outcrops of these types of rocks on the territory of Bulgaria have been found by the team of this study and the preliminary data are published by Pristavova *et al*. (2021).

The studied rocks with the orbicular structure are cropped out in the periphery of the Plana pluton, Sredna Gora Zone in the elongated zone with NW direction next to the contact with the host rocks from the Diabase-Phyllitoid Complex and the high-grade Thrace Unit. According to Georgiev *et al*. (2014) they are situated among the M1 - external facies of the pluton with diorite to quartz-diorite composition and trailed the Okol Shear Zone (OSZ) which marks the northern border of the pluton. The investigated orbicular rocks are built up by a core of mafic enclaves with a gabbro composition, consisting of amphibole /magnesio-hornblende/ and basic plagioclase /bytownite to anorthite/, mainly. The central core of the enclaves is surrounded by an encircling rhythmic pattern of clinopyroxene and plagioclase-rich "shells" or rims with a concentric-zonal texture. Each shell is built up by varying proportions of radially and/or tangentially arranged pyroxene and plagioclase aggregates with signs of high crystallization rate and superheating. The participation of the amphibole is limited, here and it is concentrated in the boundaries between the shells or along fracture "zones", related to extension conditions.

The new data about these orbicular rocks (core, shells, and hosted igneous matrix) referred to their geochemical characteristics (main oxides, REE), conditions of formation, and geotectonic setting. The geochemical results of the core and shells of these rocks show their typical gabbro composition where the igneous matrix is presented by quartz-monzonite to monzonite. The obtained thermodynamic conditions of shell formation are in the frame of T = 1000–1100 °C and pressure up to 3.0 kbar. According to the obtained data, we presume that the OSZ played the role of a superheating channel with undercooling conditions that promoted a rapid dendritic crystallization and the formation of orbicular structures around gabbro enclaves.

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New data on the U-Pb zircon age of rhyolite volcanoes in the Berehove-Byihan ore district, Ukraine

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The Berehove-Byihan ore district in the Ukrainian Transcarpathian hosts small gold-silver-base metal deposits and continues into Romania, where numerous industrial gold-silver and gold-base metal deposits occur. The age of the volcanic rocks in the Apuseni Mountains varies from 14.7 Ma to 7.4 Ma (Naumov *et al*., 2013). The gold-silver-bearing veins and stockworks are confined mainly to subvolcanic domes and stocks, partly being located in volcanic-sedimentary rocks nearby the volcanic bodies. In the Berehove-Byihan ore district, deposits are confined to the marginal fault zones that bound volcano-tectonic depressions or calderas filled with felsic volcanic or sedimentary and tuffaceous-sedimentary rocks varying in age from 16.4 Ma to 7.1 Ma. The gold-silver Muzhieve deposit and gold-base metal Berehove deposit in the Berehove ore field are confined to the rocks filling the paleocaldera. A set of smaller calderas or depressions (Ardov-Keretska and Zolotysta) occurs in the zone of the marginal fault of the Berehove paleocaldera. The caldera of the Zolotysta Mount is surrounded by rhyolitic domes and necks that were formed at the terminal stage of the volcanic activity. Drilling has revealed veins and an impregnated gold-base metal mineralization in the contact zone of the rhyolite dome structure. The K-Ar age of the rhyolite of the Ardov-Keretska depression was defined at 12.2 ± 0.7 Ma (Pécskay *et al*., 2000).

The Byihan ore field comprises a large volcano-tectonic depression and hosts a barite-base metal deposit with increased content of gold and silver. The K-Ar age of rhyolite is 12.6 ± 0.6 Ma (Pecskay *et al*., 2000). An S-N trending tectonic zone that hosts subvolcanic bodies of plagiorhyolites is located in the central part of the depression. The plagiorhyolite bodies are hydrothermally altered. In the Zastava area, the drill holes have revealed a 20 m-thick zone of barite mineralization and several zones of sulphide mineralization that contain up to 1% Pb and Zn and 0.6 ppm Au. The K-Ar age of the plagiorhyolites varies from 12.6 to 11.5 Ma (Pécskay *et al*., 2000).

We have carried our U-Pb zircon dating of rhyolites that occur in the Berehove (Zolotysta Mountain, sample 12K-04) and Byihan (Kosynska Mountain, sample 12K-05) ore fields. Zircons from sample 12K-04 are elongated-prismatic, euhedral, 50×200 µm in size, and bright in CL images with oscillatory zoning. Zircons from sample 12K-05 are bigger, up to 100×300–500 µm.

Three zircon grains dated in the sample 12K-04 yielded a weighted average $^{206}Pb/^{238}U$ age of 11.2 ± 1.9 Ma, whereas six grains dated in the sample 12K-06 yielded a weighted average $^{206}Pb/^{238}U$ age of 11.3 ± 0.5 Ma. Hence, the K-Ar and U-Pb ages of rhyolites in both ore fields are identical within an error. These ages are also close to the ages of ore-bearing felsic and intermediate subvolcanic bodies in the Baia Mare ore district and other parts of the Apuseni Mountains in Romania.

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Igneous origin of super-reduced mineral particles (spherules and native metals) in sediments of the Outer Zone of the Eastern Carpathians

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In the Earth sciences, the term "spherule" is used to refer to small spherical objects formed as a result of the solidification of silicate and/or metallic melt. Spherules discovered in kimberlites of the Ukrainian Shield, Yakutsk and Arkhangelsk diamondiferous provinces have been described in our previous works (Yatsenko, 2016). We found that spherules commonly occur together with other spherule-like high-reduced particles. We termed this group of particles as high-reduced mantle mineral associations (HRMMA). These associations include Ti-Mn-Fe-silicate (TMIS) spherules containing iron core; Ca-Al-silicate (CAS) spherules with iron inclusions; magnetite-wustite-iron spherules (MW-I); spherule-like metallic and intermetallic particles (Fe, Cu, Pb-Sn, Cu-Zn); the suite of oxygen-free minerals including diamond, moissanite, qusongite (WC); Ti-corundum with inclusions of Fe, Fe-Ti-Si, TiC and TiN phases. We hypothesized that the formation of HRMMA is associated with the processes in the lowermost mantle.

Further studies have shown that HRMMA particles are found in sedimentary rocks in some areas of Ukraine, including the Carpathian region. Earlier findings of two spherule varieties in the Mesozoic sediments of the Carpathian Basin were reported by Hungarian researchers (Uzonyi *et al*., 1998). The first one is similar to CAS spherules from kimberlites, the second variety is MW-I spherules.

The SEM/EDS method was used to study the composition and structure of the HRMMA particles collected at the Outer Zone of the Eastern Carpathians.

Natural outcrops of the Menilite Unit (Oligocene, Krosno structural zone) were studied at the Volosyanka site. MW-I spherules, glassy aluminum-iron-silicate (AIS) spherules, and native metal particles (Fe, Ni, Zn, Cu-Ni, Ni-Cu-Fe) were discovered here.

Samples of Upper Paleogene sediments obtained from the Borynya-3 borehole were studied at the Borynya site. MW-I and TMIS spherules were identified.

In the Dobromyl area, samples were taken from natural outcrops along the Pyatnychanka and Vyrva rivers. MW-I spherules and native Fe particles were found in clays of the Srtyi Unit, Skyba structural zone. Various varieties of HRMMA particles including TMIS, CAS, AIS, MW-I spherules, Ti-corundum, and native Fe particles were recognized in Neogene clay-sandy sediments (Dobromyl area, Boryslav-Pokuttia structural zone). In Ti-corundum inclusions of oxygen-free phases were recognized, which are made of TiN, TiC, Fe, Fe-Si, Ti-Zr and Fe-Ti-Cr-S phases.

The study showed that the studied HRMMA particles are similar to those from kimberlites. We believe that HRMMA was formed as a result of the explosive breakthrough of mantle gas streams. The studied HRMMA particles have no signs of mechanical abrasion and chemical weathering. Thus, these particles can be interpreted as pyroclastic rather than epiclastic (redeposited). This implies that their formation occurred synchronously with the deposition of the host rocks. Where the sources of the pyroclastic material eruption were located is still an open question.

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Trace elements content in some zeolitized pyroclastic rocks in Eastern Rhodopes (SE Bulgaria)

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Thick succession of Paleogene zeolitized pyroclastic rocks covers large areas in E Rhodopes (SE Bulgaria). They host several clinoptilolite and one mordenite deposits that were subject of increased interest in the last decades of the 20th century. However, the trace element geochemistry of these rocks remained largely undetermined. Only in recent years, data on trace and rare earth elements in zeolitized pyroclastic rocks in the E Rhodopes have been reported (Ivanova *et al*., 2018). In this study, nine samples were studied, which represent various secondary mineral associations: mordenitized tuff (Lyaskovets Village), analcimized tuff (SE of the town of Krumovgrad), samples with varied clinoptilolite/clay minerals ratio and different position in the pyroclastic section (SE of Krumovgrad, NW of the town of Dzhebel and near Silen, Dajdovnitsa, Dolno Cherkovishte and Mezek villages). One apatitized tuff (Bryagovo Village) was also analyzed.

The studied samples do not differ significantly in terms of their trace element contents. They all show down-sloping primitive mantle-normalized profiles with LILE enrichment, negative Ba and Ti anomalies and positive U-Th and Pb anomalies, typical of the acid lavas in the E Rhodopes (Yanev, 1998). The content of the compatible elements in the magma process, such as Ni, Cr, Co, Sc, *etc*., are very low. LIL elements behave as compatible in the studied rocks. Barium (118–902 ppm) and Sr (119–2934 ppm) are mainly incorporated in magmatic minerals and their contents in tuffs depend on the crystal and lithic clast abundance. Rubidium (76–339 ppm) and Cs (4–49 ppm) are concentrated in glass-replacing secondary minerals. HFS elements are controlled by the accessories and their presence in tuffs. An exception is U, which has highest contents (94 ppm) in the apatititized tuff. All studied samples are depleted in both light (Σ_{LREE} 99–182 ppm) and heavy REE ($\Sigma_{HREE+Y+Sc}$ 18–43 ppm).

In situ laser ablation inductively coupled plasma mass spectrometry analyses of clinoptilolite and associated phyllosilicates in one sample show that clinoptilolite contains only Rb (109–164 ppm), Sr (99–142 ppm), Zr (51–122 ppm), Nb (2–8 ppm), Cs (11–20 ppm), Ba (18–26 ppm), Hf (2–5 ppm) and Ta (1–3 ppm), whereas clays occurring as dark brown flakes within the clinoptilolite aggregates, contain more trace elements: V (20–54 ppm), Ni (13–37 ppm), Cu (15–23 ppm), Zn (216–960 ppm), Ga (8–90 ppm), Rb (2–1064 ppm), Sr (2-295 ppm), Zr (4-227 ppm), Nb (0-216 ppm), Cs (0-165 ppm), Ba (0-392 ppm), Hf (1-9 ppm), Pb (1–269 ppm), Th (0–61 ppm), U (0–75 ppm), Σ_{LREE} 0–14 ppm, Σ_{HREE} 30–47 ppm.

It can be concluded that the diversity in secondary mineral associations has relatively little influence on the trace element geochemistry of zeolitized pyroclastic rocks in E Rhodopes. In terms of their trace and rare earth element composition, they still show the main characteristics seen in the acid lava rocks of the area.

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Session GT5

Metamorphism

Conveners:

Gavril Săbău, Marian Janák, Philip Machev

Variscan metamorphic evolution of the Western Carpathians: a case study from the Tatra Mountains

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The Tatra Mountains of the Western Carpathians are a key area for the study of the eastern continuation of the Variscan basement within the Alpine-Carpathian orogenic belt in Central Europe. Metamorphic rocks are abundant in the western part (Western Tatra), whereas in the eastern part (the High Tatra) they occur as minor bodies in granites. Metamorphic zonation in the Tatra Mts. displays an inverted metamorphic sequence with high-grade rocks (gneiss, migmatite, amphibolite, eclogite) of kyanite and sillimanite zone in the hangingwall, and lower-grade rocks (micaschist) of staurolite-kyanite and kyanite-fibrolite zone in the footwall. The lower unit shows a prograde metamorphic sequence of Barrowian type. Metamorphic *P-T* conditions increase towards the contact with the upper unit, from 5–6 kbar/550–620 °C in the staurolite-kyanite zone to 6–8 kbar/620–660 °C in the kyanite-fibrolite zone. The upper unit shows the highest pressure conditions in the kyanite zone at the base of the unit. Eclogites, forming lenses and boudins in amphibolites, record the peak *P-T* conditions of ≥15 kbar/700 °C and overprint at 10–14 kbar/700–750 °C with formation of clinopyroxene + plagioclase symplectites. At higher levels of the upper unit (sillimanite zone) the pressure conditions are lower, without any relics of eclogite facies metamorphism in amphibolites. Paragneisses with prismatic sillimanite and rarely cordierite show migmatisation and partial melting due to dehydration reactions of biotite and formation of peritectic garnet at ~7–10 kbar and 760–770 °C. These rocks are intruded by a sheet-like granitoid pluton of leucogranite to biotite tonalite and amphibole diorite composition. Recent SIMS U–Pb zircon age data from the eclogite (Burda *et al*., 2021) recorded zircon forming event at 367 Ma, interpreted as a minimum age for subduction and high-pressure, eclogite facies metamorphism (M1) in Late Devonian. Medium-pressure/high-temperature metamorphism (M2) in Early Carboniferous (~350–340 Ma) is recorded by zircon and monazite ages in gneisses and migmatites (*e.g*., Moussallam *et al*., 2012), interpreted as a consequence of crustal thickening. Considering the age data there was the age gap at least 20 Myr between HP metamorphism (M1) and MP/HT metamorphism (M2). Decompression of high-grade rocks and partial melting of migmatites overlapped intrusion and emplacement of the granitoid pluton at ~350–340 Ma (*e.g*., Burda *et al*., 2013; Broska *et al*., 2022) accommodated in the upper unit. Exhumation and uplift of the high-grade metamorphic rocks and granite was accomplished by top-to-the-south-southeast thrusting over non-migmatised, lower-grade micaschists.

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Precambrian metamorphic complex in the Rhodope Massif – unified stratigraphic system

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The metamorphic complex of the Rhodope Massif has been subject of research for more than 100 years, but controversies over its structure and stratigraphy continue. The metamorphic basement of the Rhodope Massif is built of high-grade Precambrian metamorphic rocks divided into two groups with different age and petrographic composition named: Prarhodopian and Rhodopian.

The lower Prarhodopian group (PRG) shows features of an ancient infracrustal continental complex, which may have been a fragment from some supercontinent such as Rodinia. It consists of biotite, leptite, migmatic gneisses and granite-gneisses represented into three lithostratigraphic units up to top: Boykovo Formation, Bachkovo Formation and Punovo Formation. The absence of marbles is a specific feature of PRG. Cadomian, Hercynian and Alpine granitoid magmas, fluids and several generations of aplite-pegmatite veins penetrated the rocks, causing local migmatization and reheating. As a result the whole rock complex obtained geochemical signature of granite-granodiorite.

The upper Rhodopian group (RG) is an enough well stratified supracrustal variegated complex that has been transgressively deposited on the Prarhodopian one. It is represented by metamorphosed volcanogenic-sedimentary rocks: amphibolites, eclogites, garnet-lherzolites, mica schists, quartzites, marbles, and serpentinites, grouped in three parts, up to top: Lukovitsa Variegated Formation, Dobrostan Marble Formation and Belashtitsa Calc-silicate Formation. An Ophiolite association of Neoproterozoic age (610–566 Ma) occupies a clearly defined stratigraphic position in the lower levels of the Lukovitsa Variegated Formation and marks the boundary between the two groups. Subintrusive and volcanic basic magmatism cuts the rocks and connects the PRG and RG.

The PRG and RG were subjected to folding at least twice. In the general structural plan, the diapiric raised domes and linear positive structures are clearly outlined by layers of the RG. The cores of anticlines are built of the Prarhodopian gneisses. The spaces between them are occupied by deeply sunk subvertical, inclined or lying synclines, filled by the rocks of the Variegated and Marble Formations. The stratigraphic sequence is relatively well preserved, which allows through systematic study to restore the structure of the entire metamorphic complex.

The hypothetical ideas, launched 30 years ago that the metamorphic complex in the Rhodope massif is an Alpine building, made of “pile of thrusts”, discordant plates separated by Mesozoic fossil bearing sediments or 3–4 allochthones, were not confirmed by the additional field studies and observed spatial relationships between lithological units.

The same stratigraphic sequence in all parts of the Rhodopes, the normal transgressive contact between PRG and RG as well as the ophiolite magmatism connecting the two groups, determine the Rhodope Massif as a unified lithostratigraphic system of Proterozoic age. The long-term field research, documented in multiple maps, sections, stratigraphic columns, petrographic correlations and analyzes at different scales, provided the factual and reliable basis of the concept.

Rutile U-Pb age and trace element composition from medium-grade metasedimentary rocks of the Sakar Unit, Sakar-Strandzha Zone (SE Bulgaria)

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The presence of abundant rutile in calcite-biotite schist and metaconglomerate from the Sakar Unit (Sakar-Strandzha Zone) provoked our interest on its origin and age. Two samples were collected from the Paleocastro and Ustrem formations to the south of Srem Village (N 42°01′43.30″, E 26°29′37.60″). In calcite-biotite schist, rutile is found as inclusions in biotite porphyroblasts and in the matrix. Rutile in metaconglomerate occurs as big angular grains (up to 200 μm) or clusters of rounded grains rimed by magnetite, possibly detrital in origin. Much smaller euhedral grains to rutile needles are present in biotite. Rutile grains displayed homogenous structure with captured numerous microinclusions from matrix minerals (*e.g*., calcite, albite, muscovite, quartz, apatite, titanite).

Trace elements were analyzed by LA-ICP-MS in separated rutile grains. Despite the varying compositions and often overlapping ranges, rutiles from carbonate-biotite schist have higher average content of Y, Nb, Ta, Zr, Th, while those in metaconglomerate are enriched in V, Cr, Hf, and U. High Nb (833–9068 ppm) and low Cr concentrations (< 1000 ppm) plotted in discrimination diagram of Meinhold *et al*. (2008) suggest a felsic source for studied rutiles. High Nb and Ta concentrations are typical for metamorphic rutiles (Luvizotto and Zack, 2009) from biotite-bearing mineral assemblages, where biotite incorporates Ti over Nb (Zack *et al*., 2004).

The Zr-in-rutile thermometer of Zack *et al*. (2004) (57–203 ppm for metaconglomerate, and 88–153 ppm for calcite-biotite schist), give temperature in the range of 506–669 °C and 524–607 °C, respectively. In both samples, detrital zircons with magmatic textures yielded late Palaeozoic ages and have darker (probably metamorphic) overgrowths. The Ti-in-biotite thermometer (Henry *et al*., 2005) produced temperatures ranging between 505 °C and 650 °C. The similar temperature ranges for matrix biotite and rutiles suggests reequilibration and crystallization of rutile at metamorphic conditions.

The lower U content (0.60–1.43 ppm) in rutiles from calcite-biotite schist prevents the age determination. Rutiles from metaconglomerate with higher U content (2.26–33.37 ppm) allowed LA-ICP-MS $^{206}Pb/^{238}U$ ages to be obtained. All analyzes plot on a discordia line with a lower intercept age of 167 ± 35 Ma (2σ error uncertainties; MSWD = 0.92, n=12). We consider this age as time of Middle Jurassic regional metamorphic event that caused rutile growth and re-equilibration of detrital grains under lower amphibolite facies metamorphism.

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Contact-metamorphic rocks on the Europe-Adria suture zone in central Serbia

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The Rudnik Mts, Serbia, is a volcano-intrusive complex and is located on the suture between passive Adria and active Europa margin zone. This northwest-southeast elongated area is composed mostly of the Albian-Cenomanian laminated clastics and carbonates in a proximal shelf environment and Cenozoic volcanics, as well. The sediments are metamorphosed on contact with different extrusive volcanic facies, quartzlatitic in composition.

U/Pb zircon dating from quartzlatite dykes shows 23.9 Ma age on the Oligocene–Miocene boundary. Contact-metamorphic rocks are investigated from the boreholes and include meta-conglomerates and meta-sandstones to skarn and hornfels facies. The intensity of metamorphism is in close relationship with protolith rock, hence metaclastic rocks have mineral associations composed of quartz, feldspars, sericite, actinolite-tremolite and epidote. More skarnized carbonate rocks contain calcite, epidote, zoisite, grossular/andradite/uvarovite garnets, pyroxene and vesuvianite. Grossular/andradite garnets show zonation from the core to the rim. The core composition is $Grs_{36.4}$ and $Adr_{61.8}$, while the rim is formed of Adr_{100}. The grossular/uvarovite garnets composed of $Grs_{61.7}$ and $Uvt_{31.1}$ together with a slight content of andradite component zonation is absent. This skarnized zone is also a host rock for Pb/Zn mineralization with a small amount of scheelite, magnetite and cassiterite. The mineral assemblage with the occurrence of Ca garnets and vesuvianite indicate that the skarnization of calc-silicate rock was at 450 °C. Microthermometric measurements of temperature homogenization in garnet fluid inclusion reveals a temperature range of 373–392 °C. The hydrothermal phase overprint can be locally observed on contact between the ore vein-skarn and it is manifested by the increased quartz content and rock bleaching.

The appearance of rare uvarovite-like garnets is of special importance that allows the determination of a chromium source in this contact-metamorphism system. Proximity to the Vardar ophiolitic complex, geotectonic regime on a local scale and development of Cenozoic magmatism requires further investigation to better understand the evolution history of the Rudnik Mts. contact-metamorphic complex.

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Decoding metamorphic evolution of metaeclogites from Devisil lithotectonic unit (East Rhodopes, Bulgaria)

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The Rhodopes represent an area of Alpine successive stages of nappe-stacking and post-collisional extension in terranes with different composition, age and metamorphic evolution. Numerous eclogitic boudins and slivers are scattered throughout these terranes. Dating of these rocks provides information for ancient oceanic lithosphere in the Bulgarian part of the Alpine collisional belt.

The eclogitic rocks under study belong to the Devisil Lithotectonic Unit (DLU) which crops out in the Eastern Rhodopes (Bulgaria). It is built of metagabbro associated with metaplagiogranites, marbles, metapelites with sporadic thin intercalations of quartzites, and lense-like bodies of amphibolized eclogites. The unit is limited at the bottom and top by ductile shear zones – Kesebir and Devisil zones, separating it from Kesebir and Krumovitsa Units, respectively.

The metaeclogites form small lenses in the lower section of the Devisil Unit enclosed in garnet-two mica schists. They are dark green with massive structure. In the strongly deformed parts thin fine grained garnet stripes were formed. The protoliths of metaeclogites are basic magmatic rocks with MORB characteristics (SiO_2 = 44.8–48.9% and MgO = 5.7–6.7%).

The high-pressure (HP) mineral assemblage is presented by garnet (Grt1) + omphacite(Omp) + rutile (Rt). Grt1 shows progressive zoning with increase of almandine and pyrope from core to rim up to 66.4 and 21.3%, respectively and decrease of grossular in the same direction. Spessartine remains relatively constant rapidly increasing at the rims, whereas Grt2 is homogenous, spessartine-rich (up to 23%) and depleted in pyrope (max. 11%). Omphacite is preserved in the garnet whereas in the matrix it is partly or completely replaced by albite-clinopyroxene symplectites. The Jadeite-component of clinopyroxene varies in the range of 42.8–56.70%. Rutile occurs as numerous small grains in garnet porphyroblasts or in symplectitized matrix being partially replaced by ilmenite. The symplectitic pyroxene is almost pure diopside with Jd component 2.4–3.3% and plagioclase composition is $An_{4–10.7}$. During the early high-temperature amphibolite facies overprint porphyroblasts of large green-yellow Mg-hornblende are formed containing inclusions of garnet, clinopyroxene-albite symplectites and rutile. The P-T conditions of the HP metamorphism are in the range 620–665 °C and 1.8–2.0 GPa.

Zircon crystals separated for U-Pb dating are pale yellow, transparent, partially rounded short prismatic. CL images of the grains reveal their complex zoning with a broad homogenous dark domains and bright irregular shell and domains with sector and fir-tree zoning. Some grains show partially resorbed irregular outlines around which thin dark rims are formed. CO_2, omphacite, rutile, mono- and polycrystalline quartz etc. high pressure inclusions are preserved in the core and outer parts of zircon grains. Low Th, U and Th/U ratio as well as chondrite-normalized REE patterns suggest metamorphic origin of the zircon and possible Triassic age (246 ± 5.6 Ma). Because of the low U contents of zircon we accept this age with caution and suppose that more precise dating is necessary.

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Early Cambrian magmatism in the Vlahina Mountain (SW Bulgaria) questioning the affinity with the Vertiskos Unit (Serbo-Macedonian Massif)

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The Rhodope and Serbo-Macedonian provinces of southern Bulgaria and northeastern Greece comprise a structurally complicated domain of tectonically intercalated high- and low-grade metamorphic rocks and igneous bodies separated by Struma (Strymon) Valley detachment fault. The rocks of the Serbo-Macedonian Massif were subdivided in two series – Vertiskos and Kerdilion as on the territory of Bulgaria only the rocks of the Vertiskos Unit crop out.

The investigated rocks (metadiorite-metagabbro) are exposed in an area of about 60 km^2 in the central part of the Vlahina Mountain. On all geological maps they were separated as part of the Vertiskos Unit. Mafic dykes with sharp intrusive contacts crosscut these orthogneisses and contain large idioblastic garnet porphyroblasts. Mafic enclaves, which are usually elongated into the foliation plane and which are structurally and texturally similar to the dykes, are helpful to deduce the bulk strain by which the intrusive body was affected under solid state conditions. They also indicate a coeval magmatism and magma mingling.

The metamorphic mineral assemblage is presented by plagioclase ($An_{21–34}$) + biotite (XFe = 0.44–0.56) + epidote + garnet (Alm = 57–58.3%; Gross = 27.7–29.3%; Pyr = 7.6–9.3%; Spess = 3.9–6.7%) + amphibole + quartz + rutile + zircon. Small xenomorphic clinopyroxene (pigeonite) grains (predominantly replaced by amphibole) in the matrix of the rocks represent relicts from the original magmatic mineral assemblage. The retrogressive greenschist facies assemblage is presented by chlorite + actinolite + albite + calcite. P-T conditions of peak metamorphism are in the range T = 630–670 °C and P = 8.5–10.5 kbar.

The orthogneisses from the Vlahina Mountain are classified as metagabbro-metadiorites with SiO_2 = 51.7–56.2%. The croscutting mafic dykes have a more basic composition (metagabbro). The investigated rocks are calc-alkaline, metaluminous, K-enriched and therefore are classified as subalkaline potassic. They have a poorly marked tholeiitic trend and on the TiO_2-MnO-P_2O_5 discrimination diagram they plot mainly in the IAT (island arc tholeiites) field. Such contrasting geochemical chracteristics are typical of island arc magmatism. Therefore we assume that the protoliths of the orthogneisses had an island arc origin.

To determine protolithic age of the metadiorites we used LA-ICP-MS method for zircons. The obtained concordant age of 541 ± 2.6 Ma is older than the known ages of orthometamorphic rocks from the Vertiskos unit in Bulgaria and Greece. But it is in good agreement with the data from the basement of Struma Unit (the autochthon of the Kraishte Zone) – 557 ± 3.5 Ma for metagabbro of Razhdavitsa and 569 ± 11 Ma for diorites from Struma diorite formation. Similar ages were reported by Zagorchev. This circumstance along with the grade of metamorphism (lower that in Vertiskos Unit) allow us to conclude that these rocks belong to the basement of Kraishte Zone (Struma Unit) not to the Serbo-Macedonian Massif.

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Session GT6

Mineralogy and applied mineralogy

Conveners:

Călin Tămaș, Mihail Tarassov, Thomas Kerestedjian

Mineral diversity on the northern slopes of Vâlcan Mountains, South Carpathians, Romania

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Mineral diversity of four segments of the northern slopes of Vâlcan Mountains are studied using X-ray powder diffraction (XRD), infrared spectroscopy (FTIR), Raman spectroscopy, scanning electron microscopy with energy dispersion spectrometry (SEM–EDS) and optical microscopy.

The Vâlcan Mountains mostly belong to the Danubian domain and some intrusions of the Getic Nape. The geology of the area shows mainly a "metamorphic terrain" composed of quartzites, biotite gneisses, marbles and graphitic gneisses belonging to the Lainici-Păiuș series with bodies of leucogranitoid intrusions. Amphibolites, ultramafic bodies and gneisses, with intrusive bodies of the Retezat pluton composed of granodiorites and tonalites with some quartz diorites belong to the Drăgșan series. Both of these rock formations are considered by recent studies being of late Precambrian age.

The „Braia" Valley – „Tusu" Valley is distinguished by the newly determined associations of carbonate minerals found in middle Jurassic limestones and dolomitic marbles: calcite, dolomite, aragonite and siderite. The illite group of minerals and a small amount of gaspeite, probably as a relic mineral, were also detected using SEM-EDS.

„Șiglăul Mare" Mountain – „Valea de pești" Valley stands out with the existence of quartz veins in metamorphic rocks: amphibolites, amphibolitic, quartz-feldspar and biotitic gneisses. Also migmatites, phyllites, quartzites with chlorites are observed. The quartz has a variety of colours: white, green, yellow, smokey. Important for this sector is the green shade of quartz associated with the presence of dispersed micro-granular malachite. Important for this sector are the copper minerals, formed in secondary processes, such as: cuprite Cu_2O, malachite $Cu_2(CO_3)(OH)_2$, dioptase $CuSiO_3 \cdot H_2O$, cuprospinel (Cu, Mg)$Fe^{3+}2O_4$.

In the „Jiul de Vest" Gorge – „Gărbovu" Valley sector, the upper layers consist of dolomitic marbles of Jurassic age and below them are the amphibolites of precambrian age. The outcrops show small veins of pyrites crossing the bodies of the lower rock formation. Alteration caused by meteoric water and weather conditions led to the formation of hydrated sulphates. Pickeringite $(MgAl_2SO_4)\cdot 22H_2O$, is associated with halotrichite $(Fe^{2+}Al_2(SO_4)_4\cdot 22H_2O)$. The two minerals form an isomorphic series and are accompanied by gypsum and alunogene. A complete separation between pickeringite and halotrichite is difficult; Raman and FTIR spectroscopy shows that the two minerals are found together in all the analyzed samples.

„Câmpu Mielului" – „Oslea" Mountain sector presents a diverse mineralization based on ferrous and titaniferous minerals such as magnetite, hematite, lepidocrocite (γ–$Fe^{3+}O(OH)$, rutile, anatase, and ilmenite found in amphibolytic gneisses and micaceous gneisses, with ulvospinel $TiFe^{2+}{}_2O_4$ as a novelty. Phosphate like fluorapatite $(Ca_5(PO_4)_3F)$, monazite (Ce, La, Nd, Th) PO_4 and xenotime (YPO_4), not mentioned till the present study, were also identified.

Study of Cd uptake onto modified forms of natural clinoptilolite tuff

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Environmental pollution is important problem, raising serious concerns about human health and the state of ecosystems. Cadmium is one of the most toxic heavy metals even at low concentrations. The variability of the exchange properties of clinoptilolite depends on the Si/Al ratio, the contents and the type of the extra-framework cations within the structure and their coordination by H_2O molecules.

In this study, we focus on sorption characteristics of modified forms of natural clinoptilolite tuff as exchanger for cadmium from solutions at room temperature and at different initial pH. The main objective is to compare the sorption properties of the modified forms obtained by different techniques with regard to be used as a sorbents for detoxification of living organisms.

The studied clinoptilolite-rich tuff was collected from the Beli Plast deposit (Eastern Rhodopes). Fraction of particle size 0.15 mm was chosen for these investigations.

The whole-rock major element contents were obtained using ICP-OES analysis. Powder XRD measurements were carried out using PANanalytical EMPYREAN Diffractometer system, operating at 40 kV and 30 mA, with Cu Kα radiation. XRD patterns were recorded at room temperature from 3 to 100 °2θ with a scanning resolution of 0.013°/80 s. Two types of modified forms were prepared: Na-exchanged clinoptilolite tuff and H-form. The clinoptilolite sample was exchanged into sodium form by stirring 50 g of the natural sample and 500 ml of 1 M NaCl solution at 80 °C. The H-form was obtained using the NH_4-form. The natural sample was treated with 1 M of NH_4NO_3 for 6 days at 60 °C. Then, the washed and dried sample was heated for 24 h at 400 °C in a muffle furnace. Cadmium stock solution of a concentration 0.005 M was prepared from $Cd(NO_3)_2 \cdot 4H_2O$.

The mineral composition (wt.%) (obtained by quantitative XRD analysis) is: clinoptilolite 88.5, smectite 2, opal-CT 7.5, and plagioclase 2.

The rate of Cd^{2+} uptake by the modified clinoptilolite forms as a function of contact time was studied. The Cd^{2+} amount sorbed by the Na-form increases rapidly and reaches an equilibrium value after 40 min with 80–94% effectiveness. For the H-form the amount of Cd^{2+} uptake is lower, being equal to about 4–5% after 50 min. The experimental data for kinetics of Na-form fit well with the pseudo-second-order model with q_e (amount of sorbed Cd at equilibrium, meq/g) and k_2 (rate constant, g/meq.min) for pH 2.6, respectively 0.451 and 0.098, and for pH 4.94 the values are 0.474 and 0.339. For the H-form, the initial pH=4.94 decreases with time, changing between 4.1 and 4.3, while for the Na-form there is an increase up to 5.8. The initial pH=2.6 remains almost the same between 2.7 and 3.1 for both clinoptilolite forms. Comparing the XRD patterns of the initial and Cd-exchanged forms, a decrease of the intensity of 020 diffraction peak is registered, indicating that Cd^{2+} cation is sorbed by the studied forms.

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Mineral surface Science and Nanogeoscience

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Mineral Surface Science has contributed to the establishment of Nanogeoscience, concerning the study of nanoparticles in nature and the investigation of geological processes on nanoscale (1 nm–100 nm) (*e.g.*, Hochella, 2008a). Nanogeoscience is based on advanced microscopic and surface-spectroscopic techniques, such as AFM, TEM/STEM-EELS, and XPS. Accelerator-/Synchrotron-based techniques, including PIXE, NRRA, RBS, SR-(μ)XRF, -(μ)XRD, and (μ)XANES/EXAFS fortify the entire field. Of particular interest is the study of nanometer-sized crystalline minerals or even poorly-, non-crystalline minerals, *i.e.*, mineral nanoparticles, and nanominerals (*e.g.*, Hochella *et al.*, 2008b; Caraballo *et al.*, 2015). Besides, natural nanoparticles or nanomaterials (NNP) are frequently associated to anthropogenic nanoparticles (ANP), such as incidental nanoparticles (INP) and engineered nanoparticles (ENP) in Earth Systems (*e.g.*, Hochella *et al.*, 2019). Nanoporous minerals (having micro-/nano-pores or channels, hosting ions and H_2O-molecules, in their structure) are important materials when studying the Earth and developing environmental technology and industrial applications. In addition to zeolites (*e.g.*, Godelitsas and Armbruster, 2003), todorokite-type minerals exhibit ion-exchange and catalytic properties (*e.g.*, Katranas *et al.*, 2001). Clay minerals and nanominerals are also crucial in the study of ores and related metallurgical products and wastes (*e.g.*, Gamaletsos *et al.*, 2016, 2017; Samouhos *et al.*, 2019). Finally, the environmental importance of mineral nanoparticles and nanominerals, either crystalline or amorphous, is attributed to their vital role to mobility and (bio)geochemical cycles of hazardous elements and compounds in nature (*e.g.*, Godelitsas *et al.*, 2015; Kollias *et al.*, 2021; Kotopoulou *et al.*, 2022).

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Development of proximal sensing in Goldeneye Project "Earth observation and Earth GNSS data acquisition and processing platform for safe, sustainable and cost-efficient mining operations"

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Goldeneye project combines remote sensing with proximal sensing to produce reference calibrated mineralogical maps. The project brings together satellite sensor data, drone sensor data both as well as ground sensor data. Satellite data offers spectral signatures of large areas but suffers from limited spatial resolution and blind spots of high-resolution data. The amount of available wavelengths is often limited in the interesting SWIR range. Drone aerial data can provide a spectral mapping of smaller areas with higher resolution to cover specific interesting locations but is often limited to VIS-NIR wavelength range as mineralogically more interesting SWIR range has very limited and expensive sensor selection. Due to these challenges with aerial data, it is important to produce reference information for the calibration of the satellite and drone data. The conventionally used analyses for producing mineralogical information are mineral liberation analysis (MLA) and X-Ray diffraction (XRD) which require extensive sample preparations and are laborious. Goldeneye project has applied two new spectral sensors for easier production of reference data at the field sites as well as from field-collected rock samples. Hyperspectral (HS) imaging is an interesting option for imaging loose rock samples and rock wall structures in field conditions. However, there are challenges with conventional HS cameras related to changing light conditions outdoors. Active hyperspectral sensing (AHS) is overcoming these issues with active laser illumination and compact sensor size enabling field use and providing indicative information on the mineralogy of the measured locations. This information can be used to focus the exploration into interesting areas. Another novel sensor development is the time-gated (TG) Raman spectroscopy. Raman spectroscopy can provide accurate fingerprint information on the measured rock samples. There are continuous-wave Raman spectrometers, which are already field deployable. However, conventional Raman suffers from the auto-fluorescence emission triggered by laser illumination. TG-Raman has the benefit of time-resolved sensing, where the Raman scattering is recorded before the fluorescence signal is over-powering the weaker scattered Raman signal. TG-Raman can thus offer information from a wider variety of geological specimens. The benefit of Raman is the accurate spectral fingerprint and the ability to distinguish small mineralogical features as the detection spot is in the range of hundreds of microns. It can be used to scan geological specimens to give an overview of the mineral selection detected on the rock sample. However, it cannot provide an image covering large sample areas as it measures very small points and looks at the finer features. The benefit of having two distinguishably different sensor methods gives Goldeneye project the benefit of both systems. The AHS sensor can provide indicative data from large areas at the field conditions, whereas the TG Raman can be used to determine more accurately the existing mineral selection. This data can be combined to offer the Goldeneye-platform reference information for the calibration of the satellite and aerial drone data for creating mineralogical maps of large areas.

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Trace elements in pyrite and marcasite formed in silty clay from the Maritsa East lignite basin, Bulgaria

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Pyrite and marcasite aggregates were found in a sample of blue-green silty clay from an exploration drill core at the northern edge of the Troyanovo North mine, Maritsa East lignite basin, Bulgaria. The clay sample is taken from the bottommost part of the drill core (109.4 m depth), and is associated with the underlying clays below the Maritsa Formation (Nedyalkov, 1985). The silty clay contains quartz, plagioclase, mica, montmorillonite, pyrite and marcasite aggregates, as well as insignificant quantity of organic matter. Optical (binocular and reflected light) and scanning electron microscopy were used to examine the morphology, size, and internal texture of the aggregates. Chemical composition was determined by electron microprobe and in situ laser ablation inductively coupled plasma mass spectrometry.

Pyrite and marcasite aggregates have various sizes, from 50 µm (single crystal twins) to 0.5 cm (large twinned aggregates). Pyrite occurs as single cubic and cuboctahedral crystals, penetrative twins, complex overgrown oval-shaped twinned aggregates with visible cubic to truncated octahedral habits. Marcasite occurs as single tabular, pyramidal crystals, but often as twinned (penetrative, parallel, contact) composite oval-shaped aggregates. Pyrite is often overgrown by marcasite. Pyrite and marcasite aggregates contain overgrown quartz and plagioclase grains.

Marcasite contains higher trace element contents than pyrite (in ppm): Mn (113–29630), As (6.5–2150), Zn (7.5–483), Cu (4.5–480), Ni (7–360), Mo (1.3–150), Co (0.8–57), Pb (0.3–12.6). Several analyses detected Ag, Sb, Tl, Hg, and V. Pyrite contains less trace element impurities. Most common are (in ppm): Mn (66–280), As (21–750), Ni (9.8–114), Co (3.3–46), Mo (6–92), Zn (7.6–14.6), and Pb (1–28). Elements such as Cu, Sb, Hg, Tl and V, were sporadically detected. The higher enrichment with impurities in marcasite could be related to conditions of its formation. Usually, the formation of marcasite occurs later than pyrite and at lower pH (<4), and can be a result of the oxidation of pyrite exposed to oxygenated water (Rickard, 2012), or in this case, acidic water infiltration from the overlying organic matter containing layers (black clay partings and coal layers). This percolation decreases the pH and sustains the pore water saturation with metal complexes. Some of these metals (Cu, Zn, and Mo) are related to the decomposition of organic matter. Both organic matter (coal) and clays sorb/desorb elements from/into the pore waters. The formation of pyrite and marcasite involves the nucleation and subsequent sulfidation of an iron monosulfide precursor, as well as the nucleation from pore water solution (Schoonen and Barnes, 1991). The aggregate growth is slow in low supersaturation and variable hydrodynamic regime, which sometimes leads to partial dissolution (traces on the pyrite crystal faces) (Rickard, 2012).

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Further on the choice of space group for scapolite group members

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Scapolites are rock-forming minerals with well-pronounced crystal chemical complexity. The interest in such compounds is determined by the possibility of their use as geothermometers, as well as by their potential for greenhouse gas storage. Their crystal structure is composed of a $[(Si,Al)_nO_{2n}]$ framework containing eight- and four-membered rings. Calcium and sodium cations are located in the channels formed by the eight-membered rings, and carbonate, sulphate and chlorine anions are located in those formed by the four-membered rings. There are three types of heterovalent isomorphism for group members, which can generally be represented as follows: Si↔Al (framework cations); Ca↔Na and CO_3↔SO_4↔Cl (extra-framework species). Relations between the three schemes are not always explicit and unambiguous, but in general their joint manifestation leads to electroneutrality. The use of routine practices applicable to other aluminosilicates are often resorted during investigations of the crystal chemical peculiarities of scapolites, especially regarding their framework construction. These are: Lowenstein's rule referring to the aluminium and silicon order; the dependence of size of the framework tetrahedra on the type of their central cations (Si, Al). The latter indicates the preferred population in the tetrahedral positions. The highest symmetry space group used in solving crystal structures in the marialite-meyonite series $Na_4Al_3Si_9O_{24}Cl$ (Me0) – $Ca_4Al_6Si_6O_{24}CO_3$ (Me100), is the tetragonal *I*4/*m*. It is applicable to the representatives falling within the compositional range of the two end members. In the middle region, however, additional reflexes are observed in the diffraction patterns, which require the use of the primitive *P*42/*n* of the tetragonal syngony. Drawing boundaries between the representatives of the two space groups, especially those with high calcium content, is still controversial.

This work presents results of single-crystal X-ray investigations of scapolites from three localities, two of which are reported for the first time. The studies samples have been identified as Me71; Me75, and Me80. Their crystal chemical characteristics relate them to the disputed area for selection of a space group. In search of an opportunity to refine the arrangement of framework cations, the structure of each phase has been solved in three space groups: *I*4/*m*, *P*42/*n*, and the monoclinic *I*2/*m*. The obtained results shed new light on the choice of space group for description of scapolite crystal structures, as well as on the positions preferred by silicon and aluminium ions, and hence for their ordering in the framework construction.

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Low-crystalline secondary tungsten trioxides hydrates in the geochemical and phase evolution of tungsten in the oxidation zone: an example from the Grantcharitsa tungsten deposit, Bulgaria

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In the present work, the emphasis is on the significance and place of amorphous or low-crystalline secondary tungsten trioxide hydrates, formed after scheelite and minerals of the wolframite group, in the geochemical and phase evolution of tungsten in the oxidation zone. A historical retrospective of studies of amorphous secondary tungsten products is given and compared with data obtained for the oxidation zone of the scheelite-pyrite deposit Grantcharitsa (Western Rhodopes, Bulgaria) (Tarassov and Tarassova, 2018).

It is shown that although meymacite is the only amorphous secondary tungsten mineral approved by IMA with the accepted formula $WO_3.2H_2O$, the composition of this type of mineral is more diverse. This contradiction can be explained by the level of available analytical methods used in the past, as well as by the views of some authors and historical misunderstandings. The name “meymacite” was introduced by Carnot in 1874 (Pierrot & Van Tassel, 1965) to describe a brown resinous secondary mineral which forms pseudomorphs after scheelite $CaWO_4$ from the Meymac mine (Corrèze, France) and which was considered to be trioxide hydrate (or tungstic acid). Much later, Pierrot and Van Tassel (1965) found that the original Carnot samples contain about 6 wt.% Fe_2O_3, and attributed the samples to fine-crystalline ferritungstite $((W,Fe)_2(O,OH)_6.H_2O$, “hydrokenoelsmoreite” – according to the actual nomenclature, and a pyrochlore-type mineral).

The low-crystalline secondary tungsten material found by us in the oxidation zone of the Grantcharitsa deposit in appearance and chemical composition (Fe_2O_3 – 6.7–12.1 wt.%) well resembles Carnot meymacite and is not fine-crystalline “ferritungstite”. Its XRD pattern consists of two distinct peaks at 3.85 and 1.925Å and asymmetric amorphous halos. These data as well as the Raman spectra of the material are in good agreement with the $WO_3.1/3H_2O$ phase with a structure consisting of alternating layers of hexagonal tungsten bronze. The iron-containing meymacite, $WO_3.xFe_2O_3.nH_2O$, is the most widespread supergene mineral of W in the Grantcharitsa deposit and the earliest product of scheelite alteration, and occurs as full or partial pseudomorphs after scheelite. All other secondary tungsten minerals found in the deposit – tungstite $WO_3.H_2O$, hydrotungstite $WO_3.2H_2O$, iron-containing hydrokenoelsmoreite $(W,Fe)_2(O,OH)_6.H_2O$, stolzite $PbWO_4$ as well as tungsten-bearing goethite and hematite are formed due to iron-containing meymacite and nowhere directly replace primary scheelite.

It is assumed that in other tungsten deposits the formation of such minerals as hydrokenoelsmoreite with a pyrochlore type of structure, and pittongite and phyllotungstite with combined pyrochlore and tungsten bronze types of structure, also require the presence of a low crystalline tungsten trioxide hydrate precursor, containing iron, aluminum and other impurities.

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Mineralogy and geochemistry of gold from the Babyak Mo-Ag-Au-W-Bi-base metal deposit, Western Rhodopes, Bulgaria

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Gold in Bulgaria is presented in diverse types of ore mineralizations, related mainly to magmatic-hydrothermal systems. Important gold deposits and occurrences, including those already closed for production, are located in the Srednogorie Zone (Chelopech, Elatsite, Assarel, Radka, Elshitsa, Zidarovo, Milin Kamak), in the Kraishte Zone (Zlata, Krushev Dol) and in the Rhodopes (Chala, Ada Tepe, Srebren).

Gold is one of the main ore components in the Babyak Mo-Ag-Au-W-Bi-base metal deposit. The mineralization is hosted by the Upper Cretaceous (~70 Ma) granites (±pegmatites and aplites) and partly by the brittle contacts with the Jurassic metamorphic basement in the Western Rhodopes. Based on Re-Os age dating of molybdenite, an Early Eocene age (~53 Ma) of the ore mineralization is suggested. Ore mineralization style includes sulfide and sulfosalt veinlets, disseminations and nests mainly within brittle to brecciated veins with quartz to quartz-feldspar composition. Major ore minerals for the deposit are pyrite and molybdenite, whereas sphalerite, galena, chalcopyrite, bismuthinite, Pb-Bi sulfosalts, magnetite, hübnerite, scheelite, arsenopyrite and rutile are minor. The ore-forming process is accompanied by moderate to strong wall-rock hydrothermal alterations, comprising mostly phyllic, silicification and greisen-like types.

Here, we present new mineralogical and geochemical data of gold from the Babyak deposit. The study is based on field observations and optical microscopy in combination with SEM-EDS analytical studies. Gold in the analyzed samples occurs usually as microscopic aggregates with particle size between 1 and 80 µm. The gold grains are irregularly shaped, elongated and/or teardrop-shaped. Gold mainly occurs as enclosed microinclusions, intergranular and/or cracks filling in well-crystallized coarse-grained pyrite. Most often gold appears as clusters of multiple particles and rarely as single grains. Some of the gold grains have a porous sponge-like view. In the host pyrite, gold is closely associated with microinclusions of galena and less with sphalerite, chalcopyrite, covellite, bornite and tetrahedrite. According to its chemical composition, gold in the ore mineralization of the Babyak deposit is considered electrum. The SEM-EDS data show variation in Au content between 66.53 and 78.66 wt% (av. 74.80 wt%), while Ag content is from 17.99 wt% up to 27.66 wt% (av. 22.77 wt%). Other typical impurity elements in gold aggregates are Fe (0.26–3.90 wt%, avg. 0.81 wt%) and Cu (0.16–2.20 wt%, avg. 0.95 wt%). In some analyses, S is also established (3.33–7.25 wt%, avg. 5.33 wt%) coming most probably from the host pyrite. Regarding the chemical composition of the studied gold, there is no clear zonation in the distribution of the elements between the central parts of the particles and their peripheries, except the sponge-like grains. The latter represent aggregates of gold grains, light in BSE images and enriched in Au, Ag and depleted in Fe, Cu, S, and darker areas enriched in Fe, Cu and S most likely composed of Fe and Cu sulfides.

Further studies on gold and associated ore and alteration minerals are required to better clarifying their relationships and morphological features as well as the physical-chemical conditions of the multistage hydrothermal ore-forming process in the Babyak area.

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The 'manganese event' in the byproducts of hydrothermal speleogenesis

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The byproducts of hydrothermal speleogenesis are mainly calcite mammillaries and spar. In this study 7 sub-samples from four caves in three areas of Greece are investigated. Morphological evidence along with fluid inclusion study and geochemical data indicate the hydrothermal origin of the sampled caves and the corresponding deposits. The analyzed calcite deposits contain black layers with a chemical composition dominated by manganese that was investigated by Scanning Electron Microscopy in combination with an Energy Dispersive Spectrometer. Other elements such as Fe, Ca, Ni, Mg, Al, Zn and Ba have been identified in the samples from mammillaries. Their content is differentiated according to the geographical origin of the samples. In one case, a double-terminated phantom calcite crystal displays two repetitions of Mn-oxide layers along the growth surfaces. The rest of the samples are mammillaries with one to four occurrences of Mn-oxide layers. In one case the manganese layer is formed along with partial dissolution that resulted in small pits on the calcite growth surface. These Mn-rich layers in both the phantom crystals and the mammillaries are interpreted as the result of changes in the fluid conditions and fluctuations (common in phantom crystals) that lead to deposition of the Mn-oxides along or without contemporary dissolution. In order to mark the changes in conditions, these layers are considered and described as the 'manganese event'. Because of the low deposition rate of the mammillaries, the repetition of 'manganese events' are plausibly independent of exogenous factors, such as seeping water. This event can be found in the byproducts of both shallow and deep phreatic setting of hydrothermal speleogenesis that correspond to mammillaries and spar speleothems, respectively (*e.g.* Polyak *et al.*, 2008; 2014). The available data set show that the 'manganese event' is part of a repetitive depositional pattern that appears in at least 15% carbonate byproducts of hydrothermal speleogenesis.

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Mineralogical and physicochemical characterization of bentonite clay from Svrljig, Serbia

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This study focuses on the mineralogical characterization of bentonite clay from Svrljig, Serbia. It has been found that the bentonite clay is the most abundant clay in this region, therefore an adequate identification of their mineralogy and physicochemical properties is an important step to a potential technical application in the future.

Characteristic properties of the sample were determined by chemical analysis, infrared spectrophotometry (Milošević and Logar, 2014; Milošević, 2011), differential thermal analysis (DTA) and X-ray diffraction (powder, oriented, saturated and heated). The physical properties were determined by granulometry (pipette method), cation exchange capacity (CEC) and specific surface area (SSA) measurements. The sample consists mostly of a fraction <1 µm (56.1%) with a 9.5% <2 µm, representing a total clay content (65.5%). Coarse grain fraction (>20 µm) is present in a total of 10.5%. When the clay, silt and sand content were plotted on the triangular diagram, it was concluded that the sample is sandy clay with low porosity and low permeability. Chemical analysis showed that the sample mainly consists of 52.95% SiO_2, 17.79% Al_2O_3, 1.02% K_2O, 2.92% FeO, 6.34% CaO and 1.17% MgO, with a lower content of MnO (0.70%), Na_2O (0.08%), TiO_2 (0.35%) and BaO (0.03%). Higher values of the SiO_2/Al_2O_3 mass ratios (2.97) together with LOI of 16%, CEC (84.5 mmol/100g) and SSA (661.8 m^2*g^{-1}) indicate a higher content of montmorillonite. Infrared spectrophotometry determined that the composition corresponds to a high content of montmorillonite clay with peaks at 3620 cm^{-1}, 3420 cm^{-1}, 1632 cm^{-1} and 1018 cm^{-1}. The peaks at 1444 cm^{-1} and 873 cm^{-1} correspond to carbonate minerals, although in a very small quantity. X-ray diffraction indicates that the bentonite sample is a mixture of montmorillonite as major component, identified by d001 basal spacing value of 15.11 Å at 5.86 (2θ) and less frequent minerals such as quartz, carbonates and feldspars. This mineralogy was confirmed by XRD for oriented, saturated and heated samples. DTA curve, in addition to the typical peaks related to montmorillonite (≈ 140 °C and 600 °C), also contains two smaller endothermic peaks at approximately 900 °C and 300 °C corresponding to carbonates and iron oxy/hydroxides, respectively.

The clay from Svrljig (Serbia) was characterized by chemical, mineralogical and thermal analysis. All applied methods were in good agreement indicating that the studied clay has a high content of montmorillonite and a smaller amount of quartz, carbonates, iron oxy/hydroxides and feldspars.

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Mineralogical and chemical characterization of sphalerite and wurtzite from Săcărâmb Au-Ag-Te ore deposit

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The composition of sphalerite from Romanian hydrothermal deposits is relatively well established Buzatu *et al*. (2013), Tămaș *et al*. (2021) and Damian *et al*. (2021), however, the composition of sphalerite from the Săcărâmb Au-Ag-Te epithermal ore deposit isn't well documented. In this study, we observe three genetic types of sphalerite: from ferroan $(Zn_{0.87}Fe_{0.16})_{\Sigma=1.03}S_{0.97}$ to manganoferroan $(Zn_{0.77}Mn_{0.14}Fe_{0.06})_{\Sigma=0.97}S_{1.03}$ and lately manganese-rich $(Zn_{0.8}Mn_{0.25})_{\Sigma=1.05}S_{0.95}$ compositions. Samples of sphalerite were investigated by Raman spectroscopy in correlation with SEM-EDS. The results obtained show a systematic peak-position shift towards lower wavenumbers with increasing Mn content, mainly linked to the smaller ionic radius of Mn^{2+} and polyhedral distortions in tetrahedral sites (MnS_4). Wurtzite was observed in the studied samples, presenting skeletal and radial micro textures, with a complex composition $(Zn_{0.8}Fe_{0.01}Cu_{0.08}Mn_{0.01}Ag_{0.02}Sb_{0.03}As_{0.02})_{\Sigma=0.97}S_{1.03}$. Wurtzite is associated with the late stage Cu-Ag sulfosalt mineralization, in alabandite rich samples. It is known that wurtzite occurs frequently in high temperature polymetallic mineralization (>400 °C) but numerous experimental studies have shown that wurtzite can form at temperatures below 250 °C up to room temperature (Zhang and Qi, 2006). Radial aggregates of submicron prismatic crystals were experimentally obtained by Zhang and Qi (2006) in hydrothermal solutions with temperatures below 100 °C. The presence of radiant wurtzite indicates that it crystallized rapidly from a supersaturated hydrothermal solution below 200 °C, in a non-turbulent and reducing environment. Enrichment in Cu, Ag and Sb cations has also been described in Beaudoin (2000) study of zoned sphalerite containing inclusions of pseudomorphic sphalerite acicular crystals after wurtzite in the Kokanee Mountains, British Columbia, Canada. However, the presence of As and Sb can also be attributed to luzonite and famatinite inclusions This assumption is based on the frequently association in the studied samples of these sulphosalts with wurtzite. The formation of Mn-rich sphalerites and radiant wurtzite is likely caused by the succession of low temperature supersaturated hydrothermal fluids and the interaction with the previous mineral stages.

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XRD crystallinity degrees and formation temperature of graphite in some regional metamorphic rocks from the Central and Eastern Rhodopes, Bulgaria: test of the new $GD_{(0–30)}$ scale

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Graphitization degrees and temperature of regional metamorphism in the Central and Eastern Rhodopes are determined by value of the parameter d_{002} (Å) of graphite in graphite-bearing marbles and schists from Vacha area, Madan-Erma River area (Madan lithotectonic unit), Ardino-Nedelino area (Startsevo lithotectonic unit) and Chernichevo-Boturche area (Byala Reka lithotectonic unit). Equations of different authors, formulated between 1951 and 2021, were used. They are integrated in one system (Vlahov, 2021), allowing a conversion of the results and deriving new quantitative correlations between temperature of metamorphism, structural parameter d_{002} (Å) and degree of structural order of semi-graphite and graphite. The comparison of the data allows creation of a new scheme – $GD_{(0–30)}$. The real range of this geothermometer is large − from 84 °C to 804 °C (from zeolite to granulite facies of regional metamorphism). The temperature peak of metamorphism in the studied areas is 660 °C ($GD_{(0–30)}$ = 24, well-crystallized graphite) which is the upper limit of the amphibolite facies, and the lowest temperature is 468 °C ($GD_{(0–30)}$ = 16, graphite) which is characteristic for the lower part of greenschist facies PT field. The calculated temperatures of metamorphism in the Central and Eastern Rhodopes by all published equations (1951-2021) correspond to the conditions of metamorphism established by other methods without using of structural parameter d_{002} (Å) of graphite. The tested new $GD_{(0–30)}$ scale is convenient to operate because: 1) the degrees of graphitization form a regular continuous numerical order from 0 to 30; 2) the change with one degree of graphitization corresponds to a change in the temperature of metamorphism by 24 °C and by 0.001 Å of the structural parameter d_{002} (Å). This accuracy is sufficient for the purposes of mineralogical research, facial diagnostics of metamorphic rocks, and forecasting the industrial properties of graphite; 3) the $GD_{(0–30)}$ system is based on equations, which can be easily transformed for another initial temperature, without changing the calculation principle; 4) the calculated temperatures of metamorphism in the Central and Eastern Rhodopes by new $GD_{(0–30)}$ system corresponds to conditions of metamorphism established by other methods without using of structural parameter d_{002} (Å) of graphite; 5) in addition to the influence of temperature, the values of the graphitization degrees also include the effect of all secondary factors on the graphitization processes; 6) all structural data must be confirmed by the mineral composition and the order of mineral formation in the rocks; 7) the study of contradictions between the instrumental data ($GD_{(0–30)}$ system) of the carbon material and the mineral composition of the host rocks leads to the discovery of new facts about the metamorphic history of carbon-bearing rocks.

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Propylitic vs sodium-calcium alterations: comparative analysis of hydrothermal epidote and chlorite into the Elatsite porphyry Cu-Au deposit, Bulgaria

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The Elatsite porphyry Cu-Au deposit is one of the biggest deposits in Bulgaria and is situated at the northern most part of the Panagyurishte ore region, which is part of the Apuseni–Banat–Timok–Srednogorie (ABTS) copper belt. The geology of the Elatsite deposit consists of a basement intruded by the Late Cretaceous magmatic subvolcanic to hypabyssal bodies. The main porphyritic rocks consist of quartz-monzodiorites and granodiorites as well as quartz-diorites. The basement comprises low-grade Paleozoic schists intruded by the Variscan Vezhen granitoid pluton. At the contact of the Vezhen pluton with the metamorphic rocks are formed varieties of hornfelses. The hydrothermal alteration assemblages describe at the deposit are propylitic, K-silicate, K-silicate-sericitic, sericitic, quartz–adularia–carbonate alterations and newly identified for the deposit Na–Ca, Na–Ca–K-silicate alterations and skarns.

Na–Ca alteration is minor in the deposit and affects mostly the Late Cretaceous porphyritic rocks and less the Variscan granodiorites. The mineral composition (association), of the different types of manifestations, is represented by amphibole, epidote, plagioclase, albite, chlorite, rarely clinopyroxene, rutile, magnetite, apatite, small amounts of hematite and quartz. Impressive manifestations of Na-Ca alteration are the amphibole veins and the yellow-green clusters formed only in the hornfelses sequence. The propylitic alteration is relatively rare in the open pit, developed mainly outside the pit. The mineral association includes variety of epidote, chlorite, albite, actinolite, sericite, calcite, apatite, zeolite, pyrite.

The trace elements content of the propylitic altered rocks is similar to those of the equivalent fresh rocks. The trace elements content of the Na-Ca altered rocks is lower. The epidote from the propylitic alteration shows lower contents of Fe and Ca, and higher contents of Mn, K and Cl than the epidote from the Na-Ca alteration. Higher contents for all REE and the other trace elements (except Rb) were measured for the epidote from the propylitic alteration. The chlorite from Na-Ca alteration is relatively rare at the deposit. It occurs mainly in veinlets and replaced secondary hydrothermal mafic minerals with epidote and significant amounts of sulfides. It is determined as ripidolite. The chlorites from the propylitic alteration occur as pseudomorphosis on primary (magmatic) minerals. The chlorite is determined as clinochlorite to pycnochlorite, and single analyses as ripidolite. The estimated temperatures for chlorite from propylitic alteration are around 140–340 °C and for chlorite from Na-Ca alteration are 294–330 °C.

The geochemical characteristics of the two minerals maintain the view of the two different alterations. The morphologic peculiarities and the similarities of the temperature for the chlorites of the two alterations suggest that chlorite is not part of Na-Ca mineral alteration. The higher in temperature mineral assemblage is pyroxenes, amphiboles and more Ca-epidotes, formed around 450 °C (Seedorff *et al*., 2008). The studied chlorites could be formed later by different fluids.

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Session GT7

Tectonics

Conveners:

László Fodor, Franz Neubauer

Thrace Basin – a major Oligocene clastic depocentre

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The Thrace Basin is a large hydrocarbon-bearing Cenozoic depocentre located between the Strandja massif in the northeast, the Rhodope Massif in the west, and the Sakarya Zone in the south. The sedimentary infill in the centre of the Thrace Basin exceeds 9 km. The major part of the Thrace basin lies in Turkey and its margins extend into Bulgaria and Greece. The sedimentary sequence in the Thrace Basin starts with shallow marine Eocene limestones, which are overlain by a very thick, regressive siliciclastic sequence. The clastic sequence begins with distal turbidites, which pass up into proximal turbidites, deltaic sandstones-shales and into lignite-bearing paralic sandstones.

The Thrace basin is usually regarded as an Eocene–Oligocene depocentre. However, new zircon U-Pb ages from tuffs within the silicilastics show that more than 90% of the sequence is Early Oligocene in age. New paleontological data also indicate that the basal shallow marine limestones are Late or late Middle Eocene (Bartonian–Priabonian) rather than early Middle Eocene (Lutetian) in age.

The Thrace Basin was inverted during the Late Oligocene – Early Miocene by north-northwest – south-southeast shortening, which led to interruption of sedimentation and formation of large-scale folds, such as the Korudağ anticline and Ganos monocline. Continental sedimentation commenced later in the Miocene. The sedimentary sequence in the Thrace Basin indicates extremely rapid clastic sedimentation during the Early Oligocene, related to the coeval exhumation of the Rhodope Massif.

Holyatyn Structure as the fragment of the Subsilesian Unit in the Ukrainian Outer Carpathians

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The Outer Carpathians are described as the Cretaceous–Neogene accretionary prism formed as a result of subduction of the Carpathian sedimentary flysch basin substratum beneath the Alcapa and Tisza-Dacia (micro)continental terranes, which are now located in the Central Carpathians. Main nappes of this prism show different lithostratigraphy and tectonic structure and therefore are often considered as structural-facies units derived from the different subbasins divided by the intrabasinal uplifts.

The author's detailed geological mapping works suggest that the Holyatyn Structure (located near the villages of Holyatyn and Maidan in the Rika River basin, Ukrainian Carpathians, Transcarpathian administrative region) is a destructured fragment of the Subsilesian Unit located in the Outer Carpathians between the Silesian and Skyba units. Its stratigraphic succession begins with the Early Cretaceous quartzitic medium-bedded black flysch (Shypot Formation, a few tens of meters in thickness) as well as green mudstone and chert in the top of the formation. It is normally overlain by the Upper Cretaceous-Paleocene variegated shales and marls (Holyatyn Beds, up to 100 m in thickness). A dark-gray and black flysch (so-called "Black Eocene", up to 400 m in thickness) lies above. This flysch ends with the late Eocene '*Globigerina* Marl Horizon'. Oligocene black-shale deposits and the gray flysch with black-shale intercalations (Menilite Formation and the transitional Menilite-Krosno beds, a few tens of meters in thickness) complete the succession of the Holyatyn Structure.

The *Uvigerinammina jankoi* Zone, *Spiropiectinella costata* Zone, *Caudammina gigantean* Zone, *Rzehakina inclusa* Zone and *Rzehakina fissistomata* Zone, based on benthic foraminifera and having a total extent from the Late Cretaceous to the Paleocene, have been identified in the Holyatyn Beds (Ponomaryova, 2007).

The anticline core of the Holyatyn Structure is composed of deformed Lower Cretaceous flysch and ductile Upper Cretaceous clay-marly Holyatyn Beds which were extruded into the Oligocene flysch. This extrusion apparently was caused by transpressive movements. The Holyatyn Structure is similar to the flower structure.

The geological setting, stratigraphy, sedimentological features and the age of the Holyatyn Beds suggest that the Holyatyn Beds corresponds to the variegated Weglówka marls developed in the Polish part of the Subsilesian Unit and marks the Subsilesian intrabasinal uplift (see Ponomaryova, 2007; Hnylko and Hnylko, 2019, and references therein). The uplift can be compared to the fore-bulge formed ahead of the accretionary prism front. Subsilesian uplift was buried in the Eocene due to the subduction and accretionary prism progradation.

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Structural reconsiderations in the southwestern part of South Carpathians

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Motto: „En quelle mesure la conception de Murgoci est-elle restée valable?"
(A. Streckeisen, 1931, Sur la structure tectonique des Carpates Méridionales)

The overall structural picture of the western part of the South Carpathians, dominated by the so-called "Getic Nappe" proposed at the beginning of the twentieth century by Murgoci (1905, 1910) does not seem to correspond to reality. Increasingly detailed cartographic works published later, over time, gradually led to structural images that were no longer in line with the original version of the interpretation. Especially these works highlighted the existence of many significant dislocations with various orientations that replaced, on different segments, the old trace of overthrust lines previously imagined, especially in the so-called Bahna and Godeanu outliers (klippen) areas. However, in the reference years 1961 (CBGA Congress, Bucharest), 1968 (Geological map 1:200,000 Baia de Aramă and International Geological Congress, Prague) and 1977 (Geological map 1:50,000 Obârşia Cloşani) this old structural image was maintained. During this time, some drilling data also infirmed this initial structural image in different places. Also, starting with 1954, other field observations contradicted the old structural interpretation. From 1967 (Mircea Ilie) dates the idea of "autochthonous overthrust" of the Godeanu Mountain. Our unpublished field works in the Mehedinţi Plateau area, at a scale of 1:5,000, infirmed the existence of the "Bahna outlier" and highlighted numerous faults with very different orientations, grouped in distinct systems. In particular, our very detailed cartographic works in the Balta-Baia de Aramă Neogene Graben area and in the Coşuştea Zone allowed the reinterpretation of a significant reference drilling (1411 ISEM) in this plateau. But the most conclusive data on the non-existence of an overthrust can be obtained by structural reinterpretation of many geological maps; with these reinterpretations, a completely new structural image is highlighted compared to the one imagined by Murgoci in his time. From the above, it would follow that in fact, the areas of development of crystalline schists attributed to the "Getic Realm" from the so-called nappe in the SW part of South Carpathians are the subbasement of crystalline schists and Mesozoic deposits attributed to the "Danubian Realm". Also, geomorphological data invalidate the overthrust position of the "Getic Crystalline" in the "Bahna outlier" or in the Cerna Graben areas. The ultramobilist idea of the large-scale nappes was initially promoted by French (Bertrand, Lugeon, Termier, Haug) and Swiss (Schardt, Streckeisen) geologists and was applied to the Carpathians by Uhlig (Austria) and by Romanian (Mrazec, Murgoci, Ghica-Budeşti, Popescu-Voiteşti, Drăghiceanu and later by Codarcea, I. Dumitrescu, Săndulescu, Năstăseanu, Stănoiu) geologists. However, the structure in nappes imagined in different distinct regions of the Carpathians was not unanimously accepted over time and found most famous opponents, among which can be mentioned especially Macovei, Atanasiu, Preda, and Grozescu. Already in 1922, Macovei strongly rejected the idea of a Getic overthrust and used syntagms such as "supposed nappe" or "alleged Getic Nappe". Instead, he believed that in reality there was a series of "crystalline scales" that "thrust from the Getic Depression" to the north and west.

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The Roboré microcontinent, SW Amazonian Craton: new insights on the Orosirian-Ectasian crustal evolution from U-Pb geochronology

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New U-Pb zircon ages and Nd and Hf zircon constraints of rocks from the Roboré microcontinent, the Eastern Precambrian Shield of Bolivia, in the SW of the Amazonian Craton, are proposed. This microcontinent is subdivided into the San Diablo and Paraguá terranes. Zircon U-Pb dating determines that the continental crust underwent a long-lived tectonic-magmatic history, during three successive events: 1941–1849 Ma, 1690–1610 Ma, and 1430–1340 Ma. The Roboré microcontinent experienced crustal shortening, magmatism, and overprints due to the Sunsás/Greenville (1100–1000 Ma) orogeny that marks the Amazonia-eastern Laurentia collage. The oldest San Diablo terrane comprises amphibolite facies gneissic rocks (1941 ± 40 Ma), which were intruded by plutonic bodies of 1874 Ma and 1849 Ma. The country rocks yield Sm-Nd T_{DM} ages and εNdt values from 1.96 Ga to 2.29 Ga and 1.76 to –2.73 respectively, suggestive of derivation from short-lived, juvenile protoliths. The Correreca intrusion is as young as 1874–1862 Ma with zircon Hf model ages of 2.68 Ga and 2.29 Ga with εHft values varying from – 4.63 to +2.76. The isotopic signatures for the San Diablo crust are consistent with magma genesis in a juvenile-like accretionary arc, have a calc-alkaline character, and show a subduction-related tectonic setting. The Paraguá terrane contains granulitic crust dated at 1820 Ma. The available Sm-Nd T_{DM} model ages spread from ~1.7 Ga to ~2.2 Ga and εNdt values range from +3.0 to –2.9, with Paleoproterozoic protoliths. The basement rocks are crosscut by the Yarituses Suite (1683–1610 Ma) located to the west, which includes the following granites: La Cruz, Refugio, San Pablo, San Miguel, and Rosario. These granites exhibit Sm-Nd T_{DM} model ages of 1.8 Ga to 2.5 Ga and εNdt of +4.06 to –3.8. These units characterize the Suruquiso accretionary orogeny characterized here by coalescence of the San Diablo and Paraguá terranes. Eventually, the Paraguá crust is crosscut by the San Ignacio granitoids, known as the Pensamiento Granitoid Complex (1440–1270 Ma). These rocks show Sm-Nd T_{DM} model ages between 1.6 Ga and 2.4 Ga, and predominantly crustal-like isotopic signatures of +5.2 to –4.0 akin to a convergent arc setting. The granitoids are products of the Alto Guaporé orogeny in the Brazilian counterpart, distinguished by an accretionary phase (~1440 Ma) and a collisional one (~1330 Ma). The San Ramón and Coronación granodiorites (1429–1423 Ma) are pre- to synkinematic to the collisional phase, whereas the La Junta (~1380 ± 17 Ma) and San Martin (1409 ± 17 Ma) granites are syn- to late kinematic. The Diamantina granite (1357 ± 19 Ma) is coeval with the collisional phase, while the San Andrés granite (1289–1275 Ma) is a post-kinematic pluton. The Pensamiento Granitoid Complex documents the Roboré microcontinent collision with the active margin of the proto-Amazonia at the Ectasian. The microcontinent ends with the Sunsás/Grenville collision leading to the tectonic stabilization of the Amazonian Craton.

Geological and geophysical mapping within the Samaria Gorge, Lefka Ori, Western Crete, Greece and new insights by 3D visualization

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The Crete Island is one of the tectonically most active regions globally, where the African plate converges beneath the Eurasian one. Throughout this convergence, Crete has been characterized as the accretionary wedge of the Aegean region, consisting of superimposed tectonic units. These units highlight deformation mechanisms that affected the geological formations during the Hellenic Orogeny evolution, while their geometry and kinematics indicate the spatial stress distribution.

The dominant geological formation forming the largest mountains of Crete belongs to the Plattenkalk Group, which consists of metamorphic carbonates with chert intercalations and metaclastic formations. Regarding the stratigraphic column of Crete, different interpretations have been proposed about the tectonic position of the Mandara Limestone Formation and the Trypali Unit. The interaction between metaclastics and metamorphic carbonates with chert formations is decisive, as the contact between them defines the spatial distribution of springs. These springs supply the Samaria Gorge and Agia Roumeli Village, visited by thousands of people every summer.

Considering that the Mt. Gigilos is the core of a NNE–SSW-striking anticline megastructure (Soujon *et al*., 1998; Manutsoglu *et al*., 2001), detailed geological mapping will provide the opportunity to develop conceptual models about the formation and the water discharge of aquifers through the springs. The geological mapping data will be further supported by geophysical surveys, which will be implemented within the Samaria Gorge region.

Moreover, apart from the 2D geological mapping, a 3D visualization will be performed, implemented by the ArcGIS software package, while additional geological cross-sections showing the detailed lithologic and tectonic properties of eological formations from the Samaria Gorge will be constructed.

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Geodynamics of coal-bearing formation of Transcarpathia

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The Transcarpathian deflection is adjacent to the Pannonian massif in the south-west and bordered by folded structures of the Inner Carpathians. In the north-east, the deflection is separated from the Folded Carpathians by the Transcarpathian (Peripennine) deep fault, in the south-west of the Pannonian Basin it is separated by the Prypannon deep fault. The generation of the Carpathian coal formation is associated with the final stages of Alpine tectogenesis, which led up to the rise of the intra-Carpathian territory and the block-folding dislocations of the Mesozoic and Paleogene successions. Within the boundaries of deflection of the incision is represented by the Alpine structural units. The upper structural floor is composed of Neogene molasse, which inconsistently overlaps the fold-block of the Mesozoic–Paleogene foundation. The maximum depth of the Neogene is 3.0–3.5 km. On most of the deflection under the Neogene surface, Paleogene sediments, Upper Cretaceous terrigenous layers, Jurassic terrigenous-carbonate rocks, Triassic limestone and dolomite occur and in the Uzh River basin of various Paleozoic metamorphic rocks are exposed.

Thick coal accumulated on the deflection during volcanic and post-volcanic activity, which began in the late Sarmatian and ended in late Pliocene. Complex geodynamic conditions, influence of volcanism and climate features were not conducive to the accumulation and conservation of large volumes of plant material. Transcarpathian coal deposits are represented mainly by thin layers and coal lenses, often clogged with volcanogenic material.

At the beginning of the Miocene, as a result of the Sava phase, the process of the earth's crust along the suture zones of the Transcarpathian and Prypannon deep faults was sharply activated, to which volcanic activity was restricted. Effusive and intrusive basic and acidic magmatism appeared during the Badenian times.

Two stages of Transcarpathian Neogene volcanism, an early stage (with two phases), and a late stage, were recognized by Radzivill *et al.* (1986). The first phase of the early stage took place in early Tortonian, whereas the second phase was in the late Tortonian–early Sarmatian. The latter stage occurred from the mid-Sarmatian to the Pliocene. The peak of volcanic activity was observed in the Levantine stage.

The coal-bearing layer is represented by layering of marls, tuffs, tuffites, clays and separate lenses of brown coal. The width of layer varies from 100 m or more in the central part of the area to almost complete thinning in southward direction. Five or six coal layers with complex and simple structures have been identified, their occurrence is close to horizontal, the thickness does not exceed 3.0 m. The depth of coal layers varies from 120 m to 350 m. The characteristic feature is the presence tuffogenic rocks at the base of most coal layers.

The coal deposits are composed of matte, semi-matte and semi-glossy humus coal of dark brown, black, sometimes of light brown color. Coal deposits of the Transcarpathian area contain up to 29% of rare and scattered mineral elements.

The Transcarpathian coal-bearing formation of Miocene-Pliocene age includes more than 20 coal deposits. The largest deposits are Behanske, Ilnytske, Gorbske, Berezynske. The processes of peat accumulation and coal formation of Transcarpathia were significantly influenced by volcanic and post-volcanic processes.

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Migration of basin formation and contrasting deformation style in the western and southern Pannonian Basin (central Europe)

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The Pannonian Basin is a continental extensional basin system with various depocentres within the Alpine–Carpathian–Dinaridic orogenic belt. Along the western basin margin, exhumation along the Rechnitz, Pohorje, Kozjak, and Baján detachments resulted in cooling of variable units of the Alpine nappe stack. This process is constrained by thermochronological data between ~25–23 Ma to ~15 Ma (Fodor *et al.*, 2021). Rapid subsidence in supradetachment sub-basins indicates the onset of sedimentation in the late Early Miocene from ~19 Ma or 17.2 Ma. In addition to extensional structures, strike-slip faults mostly accommodated differential extension; branches of the Mid-Hungarian Shear Zone (MHZ) could also play the role of transfer faults.

During this period, the hanging wall margin of the detachment system, *i.e.*, the pre-Miocene rocks of the Transdanubian Range (TR) experienced surface exposure, karstification, and terrestrial sedimentation. After ~14.5 Ma faulting, subsidence and basin formation shifted north-eastward and reached the TR where fault-controlled basin subsidence lasted until ~8 Ma. 3D thermo-mechanical forward models analyze this depocenter migration and predict the subsidence and heat flow evolution that fits observational data. These models consider fast lithospheric thinning, mantle melting, lower crustal viscous flow and upper crustal brittle deformation. Simultaneously with depocenter migration, the southern part of the former rift system, near or within the MHZ, underwent ~N–S shortening; the early syn-rift basin fill was folded and their boundary faults were inverted. Deformation was dated to ~15–14 Ma („middle" Badenian) and continued locally to ~9.7 Ma while north of the MHZ the TR was still affected by modest extensional faulting. The particularity of this shortening is that it happened during the post-rift thermal cooling stage. The low-rate contraction and related uplift rarely exceeded this regional thermal subsidence.

The depocenter migration extended in large parts of the Pannonian basin, as demonstrated by earlier studies (*e.g.*, Balázs *et al.* 2016). The southern and western margin of the basin is marked by core complex formation, low-angle detachment formation, and depocenter migration from the margin toward the basin center. The spatial shift can reach 150–200km and the temporal shift of core complex extension to latest hanging wall basin formation is in the range of ~9–14 Ma. All the deformation could be connected to the presence of inherited lithospheric weak zones, namely former plate boundaries/subduction channels, which localised extension.

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Structural and lithological settings controlling ore mineralization of Chelopech Au–Cu deposit, Bulgaria

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The Chelopech deposit is part of the Elatsite-Chelopech ore field located in the Upper Cretaceous andesite/diorite, breccia sequence just below covering sediments forming syncline. Most researchers dealing with the genesis and mineralization are of the opinion that in the Chelopech deposit there is a complex system of factors influencing the ore deposition process. Ore mineralization is associated with hydrothermal system connected with Upper Cretaceous magmatism in the area. Some of the factors controlling ore deposition are temperature, pressure, acidity, structural settings and lithological characteristics of the rocks containing the deposit. This abstract is focused on the lithological and structural preconditions that contributed to the formation of the deposit. Information from the underground mapping, drilling data and modern surface surveys were used to support geological lineation and interpretation.

There are several hypotheses about the genesis of the deposit and the geological evolution in the area. The mechanics of the emplacement of the igneous rocks containing the deposit still remain unclear. Further research in this direction would expand our understanding of lithological control over the mineralization. The abstract aims to suggest some structural and lithological additions to the genetic model associated with the formation of “pull-apart basin” in transtension mode proposed by Zhelev and Antonov in 2003.

Host rocks are located between “Sub-Balkan” and “Petrovden” faults. The volume of the enclosed rocks is geometrically limited by the opening and blocking of the basement through the Upper Cretaceous extension event. The direction of rupture in the basement is most likely controlled by an earlier inhomogeneity of the foliation in basement, which was observed during the surface mapping and corresponds to the major fault zones. Created volume gap was infilled by Upper Cretaceous magmatic rocks in an underwater environment. Local negative “flower” structure is formed and sin- to post- magmatic sedimentation very quickly covers the host rocks. As possible conclusion is that syncline structure above the deposit has genetic connection with this event. The direction of opening in the basement is of great importance for the linear distribution and continuity of the magmatic sequence. Magmatic rocks were developed along several en-echelon pull-apart basins. The proposed concept relays on defined continuity in magmatic bodies and the relationship with the major fault zones. In the present terrain the Sub-Balkan fault stands out most clearly. In the area of Chelopech deposit it has two N–E segments (Mirkovo-Chelopech and Tsarkvishte-Zlatitsa), as well as one transitional zone with direction SW–NE in Chelopech area. According to the proposed concept, all segments referencing well with basement fabric and show initial fault trace. Extension event over the basement generated elongated magmatic zone with direction of the long axis at 120° (along the Chelopech-Mirkovo segment), as the northern block has moved to the NE and the southern block to the SW. The transition zone between the two SW-NE trending segments (Chelopech-Tsarkvishte) is characterized as a moderately dipping right lateral strike-slip zone (dip direction/dip: 135/45). Judging by the distance between the Petrovden and Sub-Balkan faults, the displacement along the transitional zone can be estimated as ≈ 2 km. During the displacement, gaps in transition fault zone were quickly filled with tectonic clay, which leads to significant thickness of this segment.

The suggested model for the development of the Chelopech formation explains the NW-SE and SW-NE linear distribution of magmatic sequence. The linearity in the host rocks directly affects the spatial position of the ore bodies forming L-shape volume and referencing good with major fault zones. This interpretation suggests possible existence of covered magmatic host rocks NE from Chelopech formed in very similar environment. The “pull-apart” model with basement opening in direction of ≈ 045° can be applied as possible ore controlling factor not only in the Chelopech area but in all bodies of the Panagyurishte ore district as well.

The Gorce Mountains lineaments network geometry and topology

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Topological analyses of geological structural networks are quite new approach to the tectonic studies, based on a graph theory (Sanderson *et al*., 2018). This methodology, combined with modern remote sensing data like laser scanning, presents new ways to resolve structural problems. To test the applicability of this approach, we analysed network of lineaments in the Gorce Mountains.

The Gorce Mountains are located in the Outer Carpathians and formed of Magura Nappe flysh deposits, forming Krynica, Bystrica, Raca and Siary subunits, of which Krynica and Bystrica subunits are present in the study area (Kania and Szczęch, 2020).

The lineament network was extracted manually from the 1m resolution airborne LiDAR digital elevation model and analyzed with the NetworkGT toolset for ArcGIS software (Nyberg *et al*., 2018). Most of the lineaments studied were confirmed in the field as related to the fault zones. The study was focused on topological properties of the network, such as: 1D intensity, 2D intensity, nodes, lines, and branch frequency, connect types. Parameters were analyzed for the whole area, as well as in a regular 250 m grid, as well as in the zones built of different litostratigraphic units.

The tectonic-related lineament network of the Gorce Mountains was found in general to be of isolated type. However, in some of lithostratigraphic units (*i.e*., these ones built of medium to thick bedded sandstones, like Poprad and Piwniczna Sandstone members) the network is significantly more interconnected.

Despite the general trend of spatial variability related to the lithostratigraphy, the E-W trend was found, which is related to the major shear zones cutting study area in its eastern part. In some places, splay-ends of strike-slip faults were confirmed on the digital elevation model.

As for the geometry, the azimuths of the lineaments are concordant with the general Western Carpathian system, with some local deviations expressed by presence of secondary sets of lineaments.

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Linking long-term erosion and denudation with climate-change induced drainage and basin evolution at the Dinaric-Hellenic junction

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The Dinaric-Hellenic junction, marked by the Shkoder Peja Normal Fault system (SPNF), accommodated Oligo-Miocene extension and clockwise rotation of the Hellenides with respect to the Dinarides, probably in response to Hellenic rollback subduction. The SPNF bounds the Mid-Miocene to Pleistocene Western Kosovo Basin (WKB) and the Plio-Pleistocene Tropoja Basin (TB) and coincides with a marked change in relief. The main drainage divide of the Dinaric-Hellenic orogen is arcuate in the footwall of the SPNF and borders the Drin river catchment.

To investigate the history of cooling and normal faulting at the Dinaric-Hellenic junction, we applied thermochronology (ZFT, ZHe, AFT) and thermometry (RSCM) on samples across and along the SPNF. Peak temperatures of ~180–280 °C in the external Dinaric nappes are interpreted to have been attained during nappe stacking to ~10 km burial depth. The internal Dinaric nappes experienced higher peak temperatures (~320–460 °C) than the external Dinaric nappes, where cooling to below ~240 °C began at ~70 Ma. Cooling of both the internal and external Dinaric nappes below ~180 °C in Eocene time was followed by simultaneous cooling of these units to below ~110 °C in Oligo-Miocene time, with no differential cooling across and along strike of the SPNF during this period. Cooling rates of ~3.2–3.0 °C/ Ma at the Dinaric-Hellenic junction indicate long-term erosion and denudation rates of 0.1–0.2 mm/a since ~70 Ma in the internal Dinarides and since ~50 Ma in the external Dinarides.

To determine if there is a relationship of fault activity with drainage basin evolution and climatic variability, we analyzed the present-day geomorphology using fluvial channel steepness morphology (k_{sn}) and χ (Chi) as a proxy for fluvial-morphological stability. We found that higher values of k_{sn} and χ occur in the footwall of the SPNF towards the main drainage divide. ^{36}Cl-cosmogenic-nuclide depth-profile ages of the two youngest terraces in the TB (~12, ~8 ka) correlate with periods of wetter climate and increased sediment transport in post-LGM time. This period postdates the demise of two internally drained basins, which are preserved in the Late Pliocene stratigraphy of the basins. Post-LGM fluvial incision rates of ~12 mm/yr are significantly greater than reported in central and southern Albania for the same period and are interpreted to reflect autogenic fluvial incision. Thus, short-term glacial/interglacial climatic variability, hinterland erosion and base- level changes appear to have regulated basin filling and excavation cycles when the rivers draining the WKB and TB became part of the Drin River network.

These significant morphological changes occurred over much shorter periods than cooling, long-term exhumation, and clockwise rotation on the SPNF, which initiated already in Oligo-Miocene time. Nevertheless, the SPNF system provided a structural and erosional framework upon which climate-change induced erosion in Holocene time effected reorganization of the regional drainage pattern, including the formation and partial emptying of lakes and basins.

Third-order mélange: preliminary concept of the problematic internal structure of the Meliata Unit *s.s.* in Bohúňovo locality (Western Carpathians, Slovakia)

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In general, mélanges represent mixed geological complexes including blocks or bodies of different ages and origin that are commonly embedded in a pelagic or ophiolitic matrix. Mélanges are significant constituents of collisional- and accretionary-type orogens. Their chaotic internal fabric can be a result of various processes, such as tectonic disruption, mass transport, *etc*. The Meliata Unit represents remains of a suture zone after closure of the Meliata Ocean in the southern Carpathian zones. The studied Meliata Unit in the lowermost structural position is part of the Inner Western Carpathian cover nappes which overlie Austroalpine Gemer basement Superunit. The Meliata Unit is divided into the blueschists-facies metamorphosed Bôrka Nappe (composed of Permian–Jurassic stratigraphic units) and the low-grade Jurassic mélange complex including olistostrome bodies with various Triassic components; the Meliata Unit *s.s.* This work is focused on mélange complexes of the Meliata Unit *s.s.* at the locality between Bohúňovo and Čoltovo villages on the southwest border of the Slovak Karst National Park. This locality is characterised by the contact of two separate bodies differing in lithology and metamorphic grade. The first body is represented by a huge block of crystalline limestone (equivalent to the Middle Triassic Wetterstein Limestone). The marble shows considerable signs of multiple recrystallization processes and tectonic overprint. The second block is completely different. It is an independent olistostrome body and it is defined by the term third-order mélange. This olistostrome is composed of red siltstones with blocks of light grey carbonate microbreccias containing lithoclasts of older limestones with foraminifera microfauna of Triassic age (most probably middle to upper Anisian), which is the first piece of the mélange puzzle. Thus, the blocks of the Triassic carbonate microbreccias themselves represent a sedimentary mélange in a sedimentary mélange of higher order, which is composed of red siltstones. These siltstones contain radiolarian microfauna of Middle Triassic age (late Ladinian) and together with blocks of carbonate breccias had formed an olistostrome body of Triassic age before having incorporated into the Jurassic matrix and as a part of the Meliata Unit *s.s.* tectonic mélange. The position and structure of the investigated sedimentary body on the direct contact with the block of higher metamorphosed marble at this locality records the influence of dynamic Mesozoic sedimentation and the complex tectonic processes, which resulted in the emergence of the 3rd generation of mélange.

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Spatio-temporal correlation of speleogenesis with active tectonics in Asprorema Cave (Mt. Pinovo, Greece)

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The Asprorema Cave (also known as Gardanska Cave) in Northern Greece is a typical example of a fracture-guided cave. The cave is formed in Cretaceous limestones of the Pinovo nappe in the Almopia sub-Zone of the Axios geotectonic Zone. The geometry of the passages is affected by relative movements of the sidewalls revealing that these discontinuities are faults. The cave entrance is located at the escarpment of a NNW–SSE striking fault that also defines the valley of Asprorema stream.

Methods include correlation of the cave development with the active tectonic regime of the area and the orientation of the main stress field. Fault geometries and past activations are studied and correlated to the known deformational events in the broader area, temporally delimiting the speleogenesis. Microscale and mesoscale cave morphology, such as scallops and symmetrical passages, has been formed by syntectonic to post-tectonic speleogenesis. These dissolutional features are indicative of phreatic/epiphreatic conditions. The slip surfaces of the faults are not corroded suggesting that at least the most recent activations took place after the cave's shifting from the phreatic/epiphreatic zone to the vadose zone. Various speleogenetic and tectonic events are cross-correlated and discussed in order to interpret the evolution history of the cave.

Based on the structural analysis of conjugated faults and striations three main neotectonic phases are recognized. The first group of structures is faults oriented NNW–SSE, the striations of which show a dextral strike-slip movement. Cave passages along these faults are not affected by activations, setting them the oldest group of structures. The second group includes NE–SW striking faults with a dextral strike-slip movement, according to the striation analysis. The final group comprises NE–SW striking normal faults that reveal an extensional stress-regime. The $\sigma1$ stress-axis standing almost vertical and the $\sigma3$ orientation is sub-horizontal, showing NW–SE extension. These structures affect the shape of cave passages causing displacement of cave walls. Previous neotectonic studies in the broader region consider the above deformation phases as post-middle Miocene, while the youngest deformation phase described above is placed to the Quaternary. The results strengthen the significance of caves in preserving the neotectonic history that may be difficult to be observed on the surface.

New methodology for lithotectonic units defining, applicable for orogenic belts world-wide: The results of its testing in the Western Carpathians

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New methodology of XD labelling for defining of lithotectonic units, tested in the W Carpathians at a general scale of 1:2 000 000, as well as in the innermost W. Carpathians (Gemericum and adjacent units) at the detail scale of 1:50 000, has a uniform applicability for orogenic belts world-wide. Lithotectonic classification is based on orogenic (Wilson) cycles, being indicated in XD designation by the prefix X, as well as an affiliation of individual lithological unit to particular orogenic phases D of these cycles: D0 – divergent process of riftogenesis; D1 – convergent processes of subduction, obduction and closure of elongated oceanic space by collision; D2 – post-collisional thermal / deformation processes, unroofing and metamorphic core complex evolution; D3 – intraplate consolidation (strike-slips, transpression, transtension, rotation of blocks, *etc*.); and D4 – regional extension (pure shear-type regional faults, Basin and Range-type tectonics). In practice, there a more detail classification using the designation of sub-phases – *e.g*., D1a, D1b, is usually applied.

We recommend following X prefixes for orogenic belts / processes within Europe: Sv – Svecofennian, Go – Gothian, Sn – Sveconorwegian, Ti – Timanide, Cd – Cadomian, Cl – Caledonian, V – Variscan, Ur – Uralian, A – Alpine (in the case of W. Carpathians: Ap – Paleo-Alpine of Mesozoic evolution and An – Neo-Alpine – dominantly Cenozoic evolution; both represent complete orogenic cycles), He – Hellenic orogeny. The use of extended set of prefixes for orogenic cycles besides Europe makes proposed methodology universal.

The W Carpathians, as a segment of Alpine-Himalayan orogenic belt, developed in Phanerozoic times during multiple orogenic (Wilson) cycles of Intra-Pangea type (cf. Németh *et al*., 2016; Németh, 2021). The Variscan (V; Paleozoic), Paleo-Alpine (Ap; Mesozoic) and Neo-Alpine (An; dominantly Cenozoic) orogenic cycles in this territory were proved by exact geological data, including revealed three suture zones (V; Ap; An) after elongated basins with oceanic crust in their axial zones and three generations of high-pressure rocks of subduction metamorphism (V; Ap; An). Two generations of dismembered ophiolite suite remains (V; Ap) and two proved metamorphic core complexes related to post-collisional evolution of Variscan and Paleo-Alpine orogenic cycles (V; Ap) complete the geodynamic interpretation of W. Carpathians. The youngest – Neo-Alpine (Cenozoic) – orogenic cycle (An) has besides an interpreted suture zone and accretionary prism also well-defined related volcano-sedimentary sequences.

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Indentor mechanism of formation and development of the geodynamic system of the Caucasus

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The Caucasus is one of the geodynamically active regions of the Alpine–Himalayan belt. It forms an elongated mountain system between the Black and Caspian Seas with a total length of more than 1300 km. The peculiarities of the regional geodynamics are due to the interaction of two large lithospheric plates, the Eurasian and Arabian plates. The region is a typical example of collisional tectonics characterized by compressional strain in the submeridional direction, extension in the sublatitudinal direction, and overall uplift of the Greater Caucasus mountain system (Khain, 1975).

The geological and geophysical data on the tectonic structure of the Caucasus region are analyzed in order to identify a common cause of the geodynamic activity and related seismic activity in the Caucasus, link it to the tectonic zoning, and compare the structure of the crust with structural inhomogeneities of the sublithospheric upper mantle, determined from seismic tomography data (Li *et al*., 2008; Koulakov *et al*., 2012).

Summarizing the regional and local seismic tomography data and comparing them with geodetic data on modern movements and deformation of the crust in the Caucasus region, the geodynamics of the region can presumably be represented by the following processes. The ascending hot mantle flow from the Afar plume, in its movement to the north, entrains lithospheric plates – African and Arabian – creating part of the global Alpine–Himalayan fold region. When they collide with the southeastern margin of the East European Platform (Scythian Plate) and, on a larger scale, with the central margin of the Eurasian Plate, a collision zone is formed. Over the entire collision front, the pressure of the lithospheric plates from the south is nonuniformly distributed. Nonuniform pressure creates compression zones, where the force applied by the indenter onto the edge of the platform is maximum, and decompression (relaxation, stretching), where the overpressure created in compression zones is released.

The results of analyzing seismogeological and geodetic satellite observations and solutions for earthquake focal mechanisms in the lower part of the lithospheric layer revealed certain features of the geodynamics of the Caucasus region. The main organizing factor of influence on the regional geodynamic and tectonic regimes is the mantle flow. These flows form an upward trend of high-temperature mantle coming from the Afar plume, which drives the Arabian indenter and, as a result of contact with the high-velocity (cold) lithospheric layer of the East European Platform, forms the collision zone between the lithospheric layers of the indenter and East European Platform. The interaction zone of the two lithospheres is the Scythian Plate. The Afar mantle flow, as a result of a collision with the mantle under the margin of the East European Platform, is divided into three branches – the western, central, and eastern-forming and organizing the dynamics of blocks of the broken lithosphere and crust. The dynamics of these blocks could be described by the scheme of indenter action on the host rocks. Three phases of indenter penetration were identified with the features of the dynamics of blocks of crust and lithosphere corresponding to each phase.

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Post-Eocene backthrusting in marginal units of the Central Western Carpathians: tectono-sedimentary mélanges and inverted thrust sheets

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Backthrust stacking of the frontal part of the Central Western Carpathian units has been found in the Malá Fatra Mts and Strážovské vrchy Mts. Such backthrusts, which in some places affected also the Paleogene sediments, were recognized as internal nappe duplexes or south-verging reverse faults of Fatric-Hronic nappes. A new zone of backthusting has been located in northern part of the Veľká Fatra Mts., in several drills throughout the Korbeľka Structure. Moreover, these thrust sheets of the Krížna Unit are tectonically superposed on the Paleogene sediments providing a good opportunity to study their stratigraphic and structural discordances. Middle Triassic dolomites of the Choč Nappe are overlapped by the Paleogene sediments, represented by basal carbonate breccias, passing into pelagic sequence of grey marlstones, occasionally with coralgal limestones and nummulitic-rich intervals. Paleogene formations are overthrust by Lower Cretaceous shales, which markedly differ from underlying marlstones by ductile/brittle deformation, refolding, parallel-bedding shearing, veining, etc. Lower Cretaceous shales are intercalated by volcanic bodies (hyaloclastites, greenish limburgites), which in some drill sections directly overlay the Paleogene marlstones. Tectonic superposition is clearly proved by occurrence of Middle Eocene microfauna in underlying marlstones (*e.g.*, *Hantkenina*, *Acarinina*) and lower Aptian microfauna in overlying shales (*e.g.*, *Paraticinella*, *Hedbergella*). Their overturned position is also indicated by inverse zonality of illitization with a higher alteration of the Cretaceous shales (130–170 °C) and lower alteration of the Paleogene marlstones (90–120 °C). The structural discordance between strongly affected overlying sequence and undeformed footwall sequence is typical for thrust faults. These data allow to interpret post-Lutetian stacking of backthrusts, meaning before the Sub-Tatra group of the Central Carpathian Paleogene Basin (CCPB). This is also indicated by discordance between Lutetian and Priabonian-Oligocene sequences in northern part of the Turiec Basin.

In the Orava Highlands, the backthrust zones along the Pieniny Klippen Belt (PKB) are accommodated by tectono-sedimentary mélange (Záskalie Beds). The Záskalie Beds comprises of disrupted strata of Upper Cretaceous and Paleocene sediments with block-in-matrix fabrics. Large-sized blocks are represented by lithoclasts, detached slumps and broken beds, embedded in shaly matrix. The Záskalie Beds represent a syntectonic accumulation derived from the PKB units, southwardly thrusted over the footwall unit of the Oligocene flysch formations of the CCPB. This overthrust structure of the Upper Cretaceous – Paleocene deposits of the PKB is also visible after a recent landslide on a well-known locality in the Záskalie Beds, near Dolný Kubín. The primarily north-vergent nappe structure of the youngest synsedimentary formations of the PKB was clearly overprinted by south-vergent backthrusting, which is verified by shear deformation elements, strata in overturned position and dipping of the beds to the north. The backthrusting in the marginal mountain belt imply an important role of backstop orogenic wedging of the Western Carpathians.

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Features of earthquake source mechanisms in the subcrustal lithosphere of the Caucasus region

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The source mechanisms of earthquakes with hypocenters in the deep part of the lithospheric layer were analyzed. Of all the earthquakes presented in the Seismological Bulletin of the Caucasian Branch of the Russian Academy of Sciences for the period 1971–2016, 30 events met the necessary requirements: the foci were located below the crust, and there were also signs of the phases of the first arrivals of P-waves at no fewer than five stations that recorded the event. To construct the earthquake mechanisms, A.V. Lander's FA program is used (Lander, 2018).

Lack of information about the signs of the first phases of P-waves in the Seismological Bulletin limited the number of processed earthquakes and their geographical scatter. It turned out that deep earthquakes available for research are concentrated mainly in the North and Central Caucasus.

Analysis of the obtained earthquake mechanisms shows their division into several groups depending on depth and location. In terms of depth, a group is distinguished, which includes mechanisms of earthquakes with depths of up to 88 km. In this depth interval, the mechanisms obey the processes which occur under the influence of penetration of the indenting Arabian platform. In accordance with the location of the hypocenter, the mechanisms follow the guiding pressure vector both from the indenter and from neighboring blocks, which undergo compression when moving to north under action of the indenter, which initiates both normal and reverse movements of the blocks.

The mechanisms of deep earthquakes corresponding to the lithospheric layer have shear components; the points of application of compression forces correspond to the directions of application of forces from the indenter. Several earthquakes are exceptions, for which the focal mechanisms show normal-fault components; geographically, these foci are attributed to a plunging high-velocity layer recorded by seismic tomography (Koulakov *et al*., 2012). The shear components of the mechanisms of deep earthquakes indicate that the mantle moves in the lower part of the lithosphere, while earthquakes occur in a viscous medium. Several reasons for subcrustal earthquakes are cited: decompaction of the upper mantle (Trifonov *et al*., 2012), which leads to detachment and subsidence of dense and cold metabasite slabs into the asthenosphere; slab loads on host rocks; phase transformations of rocks, deserpentinization, eclogitization of the remnants of less metamorphosed basic rocks, and transition of quartz to coesite; the cause of seismogenic movements may not be so much the high deviatoric stresses as a decrease in rock strength in mylonitization zones with the increased action of fluids (Rodkin *et al*., 2009). The subsidence of seismogenic slabs and intense uplift of mountains occurred simultaneously and had a single caused: deconsolidation of the upper mantle under the action of the asthenosphere.

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The Pokuttya deep fault of the Ukrainian Carpathians

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The influence in the Pokuttia deep fault on the flysch structure has been revealed in the Boryslav-Pokuttia nappe as a series of dislocations with a break of continuity of the north-eastern orientation at the boundary between the Hutsulkyi and Boikivskyi segments. The structure has a horizontal displacement of 10 km and an up to 1.5 km vertical displacement; it is considered as a left-lateral strike-slip fault. In the Skyba nappe this fault truncatesion of its front part of the Hutsulskyi segment. In the Dukla-Chornohora nappe and the Bitlya-Svydovets sub-nappe the deformation features are sigmoidal curvatures of their parts in the fault zone with amplitudes of horizontal displacements of up to 10 km. As a result, the Krasnoshora and Hoverla units are joined into a single sub-nappe, and the thrusts and folds of the Bitlya-Svydovets sub-nappe are overlapped, to a considerable extent, by it and by the Skupiv sub-nappe. Owing to post-thrust vertical movements the Hutsulskyi segment was uplifted during Pliocene-Pleistocene. The rise of the area of the Duklya – Chornohora nappe was the most intensive. The structures of the Bitlya-Svydovets sub-nappe are only fragmentally outcropping from under it.

In the territory of Romania structurally correspond to them from the north – the thrust-sheet with olistostrome Slon in the Lower Verkhovyna deposits of Oligocene, and from the south – tectonic units Toroklezh and Makla. The Pokuttia fault displaces the Precarpathian regional minimum (amplitude of about 10 km), and the Uzhok deep fault with the signs of right-lateral displacement. This is a perceptible impact of the Pokuttia fault on the sub-meridional Radekhiv-Viktoriv fault. Sites of intersections of the mentioned faults, so-called knots, if the traps are available, are known to be favorable zones for hydrocarbon accumulation on commercial scales. In the light of new data on the geological structure of the region the hydrocarbon perspective is raised for the separated structures of Vorohta-Yasynia (Lazeshchynska, Yasynska and Voronenkivska), as well as Semakivska and Hryniavska, where commercial influxes of hydrocarbons were obtained. This observation also concerns the structures of the basement of the Lopushna subzone of the outer zone of the Carpathian Foredeep under the overthrust of the Carpathians. For the first time, using new geological data it was possible to prove the influence of the Pokuttia fault in a form of the left-lateral strike-slip on the structures of the flysch cover. The structural parallelization of the Bitlya-Svydovets sub-nappe of the Krosno nappe of the Ukrainian Carpathians was carried out with the tectonic units of the Romanian Eastern Carpathians. Interaction of the given fault with the Pre-Carpathian regional minimum and the Uzhok deep fault has a character of the right-lateral shift. Areas connected with these dislocations are prospective for hydrocarbon accumulations of commercial value. As a result of investigations essential corrections have been inserted concerning the geological structure of the south-eastern part of the Ukrainian Carpathians. Together with geochemical indications this presents new possibilities in searching for hydrocarbon deposits here.

New data from the mélange complexes of the Meliata Unit *s.s.* in a freshly excavated section, Čoltovo Village (Western Carpathians, Slovakia)

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The Čoltovo gorge and its surroundings are a well-known locality in connection with the Meliata Unit (specifically with the Meliata Unit *s.s.*). The Meliata Unit is represented by obscure mélange complexes of the southern part in the Western Carpathians, linked with the closure of the ancient Meliata Ocean. In general, it is divided into HP/LT Permian to Jurassic metamorphosed clastic sediments and carbonates, in association with basic volcanics and sediments (Bôrka Nappe) and low-grade chaotic Jurassic mélange complexes with huge olistostrome bodies with various Triassic components (Meliata Unit *s.s.*), the latter being the main subject of this work. Recently, new outcrops were excavated near Čoltovo Village along foots of the W–E trending slope of the Slaná riverbank, where previous outcrops provided only scarce information. After removal of the debris and soil, the very complicated internal structure of the Meliata mélange is clearly visible. The new Čoltovo section (composed of 6 individual dig outs, ČLP1 to ČLP6) is divided into two lithologically somewhat different parts. The eastern part is characterized mostly by strongly weathered dark-colored fine-grained shales and light grey to green sandstones containing blocks of various rocks tens of centimeters in diameter. Blocks are mostly represented by basic volcanics and dark coarse-grained crinoidal limestones. In contrast, the western part of the section consists of red and white cherty siltstones containing basic volcanic matter, and dark red, green and purple radiolarites. As a part of the mélange complexes, we also consider a thin set of dark crinoidal limestones, shales and conglomerates containing foraminifers of yet unknown age. The affiliation of these beds with the Meliata Unit is documented by their presence as blocks and clasts in the shales and sandstones in the new outcrops. The mélange complexes are overstepped by the Lower Miocene coarse-grained limestones and sandstones. Thirty new samples were collected from the Čoltovo section, of which 3 yielded identifiable radiolarians of the Middle Triassic age. In addition, to the east of the newly excavated outcrops, we formerly obtained one productive sample with radiolarian microfauna of the Upper Triassic age, too. Up to this date, on this locality, the presence of Jurassic flysch sediments (matrix of the mélange) was biostratigraphically not determined. In order to resolve the dynamic tectono-sedimentary history of the Meliata Unit, detailed investigations of the rock composition (mainly blocks), the character of the contact with the surrounding ensembles and further paleontological research are in progress.

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Session GT8

Quaternary geology and landscape evolution

Conveners:

Lidija Galović, Ljupko Rundić, Marlena Yaneva

Abrupt climate changes – Evidence from Quaternary sedimentological sequences in Croatia (ACCENT)

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A fundamental and interdisciplinary approach to investigate abrupt climate change enables us to obtain valuable data and interpret the dynamics of these changes. These data and their interpretation can form the basis for both comparing paleoclimate changes with modern ones and predicting the dynamics of these changes in the future. These insights can make it easier for humankind to adapt to changes that will affect all aspects of life on Earth. Because of the fast and unquestionable climate change and threats that have emerged, geologists have been trying, based on records in Quaternary sediments, to identify the process of change.

The exploration is focused on loess/paleosoil sequences and the Đurđevac Sands in the Pannonian area (continental climate) and fluvioglacial sediments in the foothills of the Velebit Mt. and lake sediments from Lake Vrgorac in the Dinaric area (Mediterranean climate).

Firstly, explorations of loess-paleosoil sequences revealed the existence of 14 cumulic horizons, which evolved just above well-developed paleosoils. They represent paleoclimate archives of the dynamics of 14 climate changes. The research is focused on analyzing cumulic horizons in NE Croatia, providing detailed descriptions of transitions from the warm to the glacial period in the Late Pleistocene. Next, the investigation of paleosoils and geomorphological/sedimentological features in the dunes of the Đurđevac Sands may help to determine the nature of the Pleistocene-Holocene transition in this area, as well as potential Holocene climate-related paleoenvironmental changes. Those terrestrial archives in the south of the Carpathian Basin provide insight into the magnitude, timing, and spatial variability of climate changes.

In addition, fluvioglacial sediment successions in the foothill of the Velebit Mt. are crucial for describing abrupt climate change during the Late Pleistocene, as it will reveal the magnitude, timing, and spatial variability of climatic transitions and correlate them with transitions in a continental climate as based on the other archives outlined above. Finally, the depositional environments and sediment facies found in Vrgoračko polje are considered to represent a typical Quaternary lacustrine sedimentation pattern for other Dinaric karst fields in a Mediterranean climate. The dynamics of all mentioned facies transitions in all proposed sections are a consequence of past climate change.

The specific geological and pedological diversity, geographical position, geomorphology and climate diversity of Croatia enable the parallel high-resolution study of the development of abrupt climate changes at locations only 300 km apart. This research will improve our understanding of the spatial extent and differences in occurrence of paleoclimatic events in the Pannonian and Dinaric areas. That will yield insight into eolian-fluvioglacial-lacustrine teleconnections in SE Europe. In turn, this forms the basis for supraregional correlations with the European Sand Belt (NW Europe) and the Adriatic Sea.

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Transient metamorphosis of the Stob terrace riser

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Since the onset of the Early–Middle Pleistocene transition, during which the glacial-interglacial oscillations shifted from a period of 41 kyr to 100 kyr, a great regional degradation has affected the Rila region in SW Bulgaria. Streams have incised more than 85 m. The Rila River is a large tributary of the main Struma River. Since the Chibanian, the tributary reach across the piedmont shaped an asymmetric valley downcutting in the fluvial deposits of Neogene and Quaternary ages. The Struma flow direction governed a steady southward avulsion of the Rila River that resulted in a set of strath terraces on the northern side, a wide Holocene floodplain, and a high riser along the southern margin. This terrace riser turned into a fault when satellite imagery became available for widespread use. Moreover, an observation of a stream channel near Stob Village was interpreted as a colluvial wedge that originated from a surface-rupturing earthquake (Tranos *et al*., 2006). The channel depth was associated with a vertical fault displacement. It was then used to estimate the fault slip rate during the Holocene. In that way, a lineament in imagery half-tones emerged as a seismic source and, consequently, it became a factor in seismic hazard assessments (SHAs). We began to study the Stob fault, aiming to provide the fault parameters that are required for SHA. Routine approaches were implemented: tectonic geomorphology, field observations, and geophysical imaging of the shallow subsurface.

One of our working hypotheses stated that topography results from fault displacement field plus degradation minus aggradation. We found that the modeled deformations for the Stob fault due to shear faults in an elastic half-space are incompatible with the common dimensions of the continental upper crust. Swath elevation profiles show that the regional base-level drop only controls the drainage network in the region surrounding the Stob lineament. The topographic relief across and along the steeper riverside is unaffected by a local tectonic factor. An assumed fault displacement field during the Chibanian and Late Pleistocene would influence the lateral position of the Struma channels. Instead of tectonic control, the Struma River guides its tributary. Field observations failed to identify small tectonic landforms, ruptured Quaternary sediment, or fault traces at all. Electrical resistivity profiling proceeded across the riverside at the Stob locality. The tomograms image Quaternary fluvial deposits that transit gradually toward the Holocene floodplain. Our research attempt did not succeed to contribute the fault parameters for SHA. We encourage further studies, employing more appropriate methods or alternative hypotheses on fault interaction with the Earth's surface in finding the Stob fault traces. Until then, the notion that the Stob terrace riser is a fault could be avoided, at least to improve the SHA.

Acknowledgements. The resistivity survey was supported by BAS Project Thracians: ethnic genesis and evolution, cultural identities, civilization interactions, and ancient heritage. Theme: Variants of adaptation to environmental change in the past: geoarchaeological, zooarchaeological, and archaeobotanical aspects.

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Quaternary submerged landscapes in the NW Black Sea

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The NW Black Sea experienced during the Quaternary several transgression–regression phases, mainly related to sea-level variations. The associated phenomena produced specific submerged landscapes that testify in a complex way to this variability.

The sea-level variations of the Black Sea during the Quaternary are still a debatable topic in many papers. These variations of the Black Sea basin in terms of coastal migration and water depths had an important impact, especially in the NW part, where the continental platform is the widest of this marine basin. During the Last Glacial Maximum (LGM), the Black Sea level lowered to about –150 m compared to the present level of the sea. The entire NW shelf of the Black Sea has been subaerial for several thousands of years; during the lowstand level, a network of rivers developed on the present shelf area. Besides these rivers, other features have developed at the level of the present seafloor but also as buried features, below the present sea bottom.

Some of these features are very important for mapping the former paleoshorelines corresponding to different stages of transgressions–regressions that lasted long enough at a stable water level. The most common submerged feature that indicates a paleoshoreline is the wavecut terrace. Due to subsequent sweeping of the continental platform as the result of other variations, smaller than that corresponding to the LGM, not all of the wavecut terraces are preserved on the shelf area. Besides the wavecut terraces, other features prone to suggest paleoshorelines, as are the dune fields, have been mapped, mainly on the external shelf area.

Close to the shelf break, it is quite common to have alignments or fields of pockmarks; the pockmarks are submerged features, shaped as funnels formed on the seafloor as local depressions of circular or ellipsoidal shape; these features testify to active, dormant or paleofluid seeps, rooted in the shallow sediments, but sometimes with deeper origins.

Some linear features indicating neotectonic lines have been mapped; these features usually have a local development and are expressed at the level of the sea bottom as a sudden variation of the local altitude of the seafloor and affect the bottom morphologies.

Sand ridges and other nearshore specific features have been followed on the detailed Digital Terrain Models (DTMs) of the seafloor.

Paleovalleys and local swamps have been mapped on large areas on the NW shelf of the Black Sea.

The geological interpretation of the submerged features is not straightforward, mainly due to the palimpsestic character of the evolution of the NW Black Sea shelf area during the Quaternary.

To map and characterize the submerged structures, the Multibeam Echosounding (MBES) equipment was most commonly used, but sometimes side-scan sonar and sub-bottom profiling techniques were applied.

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Functional role of the Mikri Gourna Cave in the karst system of Mt. Olympus (Greece)

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Mikri Gourna is a cave located, on the NW slope of the mountain Olympus (40°4′8.05″N; 22°19′58.47″E), at an altitude of 2,386 m above sea level (asl), in the surroundings of the Christaki refuge. The cave is part of a karst depression in a cirque valley that feeds the Xerolakki drainage. The Mikri Gourna Cave was investigated and monitored for four successive years. Although the cave was considered an ice cave (Lazaridis *et al*., 2018), the fieldwork has shown that firn accumulation at its deepest part melts in early autumn. This excludes it from the list of ice caves in Greece and supports the assumption that the firn accumulation is just a modern pattern. Karst dissolution forms from cave interior, such as scallops, exhibit an inward flow direction. The maximum velocity obtained by scallops' analysis is 1.57 m/s. This corresponds to the maximum discharge/recharge velocities that occur in a conduit (*e.g*., Lauritzen, 1989).

The geomorphology of the landscape reveals that the area was a glacier with different retreat phases. The Mikri Gourna Cave has been developed horizontally, with a slightly downward-sloping entrance, located on the edge at the lowest point of a spacious karst depression. New evidence reclassifies it as a "dynamic" periglacial cave with firn, active during the glacier retreat in the Pleistocene. The term "dynamic" has been derived from Luetscher and Jeannin's (2004) process-based classification scheme of alpine ice caves, while the term "periglacial cave" is used herein to describe both the functional role and the relative position of the cave in the karst depression. Mikri Gourna's significance, as a recharge point to the karst system of the mountain mainly during periglacial periods, is strengthened by the estimated flow velocity and the inward flow direction.

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Morphometric and statistical analyses of caves in the Lefka Ori massif (Crete, Greece)

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Morphometric and statistical analyses have been conducted on a dataset comprising over 500 caves in the Lefka Ori mountain range in Crete. Crete is one of the southernmost Greek islands, located in the eastern Mediterranean Sea at the margin of the Aegean subduction zone. The tectonic history of the island includes the HP/LT zone formation by the Oligocene Alpine compressional episode, which was followed by the extensional episode of the Miocene–Pliocene related to the African plate subduction under the Eurasian plate (Fassoulas, 2017). The extension led to the formation of tectonic windows, revealing a limestone sequence that resulted in the development of an extensive karst landscape, distinguished for its high cave density. The Lefka Ori massif includes numerous peaks rising to over 2,000 m. Pachnes is the highest at 2,452 m. Gorges and the regional karstification patterns are forming in the area due to the uplift of the massif.

The dataset includes cross-sections, longitudinal sections, and plan views of caves, collected from various reports and publications of cave explorations carried out in Lefka Ori during the last half-century. The maps are processed to quantify the cave shape by measures, such as plan length, traverse length, verticality index, etc. The results are used to investigate the distribution of the cave sizes and shapes in Lefka Ori. Statistical analysis identifies caves of significant extent in both vertical and horizontal dimensions (*e.g.*, Pralina, The Lion, Sternes), as outliers. Caves corresponding to outliers are being further scrutinized in terms of their morphometry, and the methods used include both Euclidean and fractal geometry. The altimetric distribution of cave entrances is investigated in terms of both quantitative and qualitative parameters, such as cave depth and rock type. The qualitative morphological characteristics of the caves and the morphometric data indicate that vadose speleogenesis predominates in Lefka Ori. According to Ford and Williams's (2007) vadose cave type classification (primary, drawdown, and invasion), the caves of Lefka Ori fall in the category of primary vadose caves. Gourgouthakas (1,208 m depth), the deepest cave in Greece and located in the Lefka Ori massif, is a characteristic example of this cave type. Primary vadose caves are related to an initially deep water table, combined with the occurrence of deep and open fissuring. Both conditions are met in areas characterized by rapid tectonic uplift, which is consistent with the evolution of Lefka Ori.

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Effects of climate change on lakes' biotic response in the cirque "Seven Rila Lakes", Bulgaria

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Remote mountain lakes are usually located in pristine places, often in protected areas without intensive anthropogenic activity, forestry practices or agriculture pressure. However, in the 20th century, human-induced changes, such as an increase in airborne pollution and climate warming after the Little Ice Age (LIA), caused a higher trophic level, which affected diatoms' distribution.

The Rila Mt., the highest mountain on the Balkan Peninsula (peak Musala is 2925 m a.s.l.), are situated in Southwest Bulgaria. The total number of lakes in Rila is 140. All these lakes are of glacial origin. They are considered to be between 13,000 and 14,000 years old, formed when the ice masses covering the high altitudinal zones during the Pleistocene began to thaw. Most numerous are the lakes located at 2200 m to 2500 m a.s.l. To explore the effects of climate change on mountain lakes, we examine paleolimnological records from seven lakes located in the cirque "Seven Rila Lakes". Sediment short cores (14–17 cm) were collected from the lakes. Diatoms were analyzed from the top (present-day) and the bottom (pre-industrial) sediment samples. This "top/bottom" comparison approach is commonly used in the paleolimnological studies for presenting a "snapshot" of the environmental changes and for the assessment of limnological conditions before the identified effects of industrialization, recent climate change and extensive catchment land-use changes. Living diatom communities (epilithon) were also collected from all seven lakes in the last 20 years. The lakes in this realm hold not only aesthetic and recreational values, but also spiritual values. In August, every year, thousands of people gather to perform their sacred dance. The first synthesis of the knowledge on diatom biodiversity in this high-mountain region was published previously (Ognjanova-Rumenova *et al*., 2019). There is a serious change in the values of the Shannon-Weaver index and species richness in the diatom epilithon assemblages over the last 20 years in the studied lakes.

To determine the potential sensitivity of lakes to climate change, with sensitivity defined by the degree of change in climate-linked indicators, we propose the ordination technique – Detrended Correspondence Analysis (DCA), to assess the variations in diatom epilithon assemblages, separately in the samples 2000/2015. Percent abundance change in four diatom species and species groups from pre-industrial to present times showed varying patterns of increase and decrease among species in the studied lakes.

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Session GT9

Geophysics and seismology

Conveners:

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Density model of the Earth's crust on the Pancake profile

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This report presents the results of geological and tectonic nature research of the Bouguer gravity anomalies and presents the constructed deep 2D density model on the Pancake profile.

The use of gravity fields in combination with seismic data significantly increases the reliability construction of complex geological and geophysical models, which is important both in studying the nature of deep inhomogeneities in the Earth's crust and upper mantle, and in solving applied problems of geophysics.

The international Pancake profile, which in 2008 carried out seismic surveys using wide-angle seismic sounding, begins in the central part of the Pannonian Basin in Hungary, passes through the Ukrainian part of the Eastern Carpathians and reaches the southwestern slope of the East European Craton (EEC). Based on the results of seismic surveys on the Pancake profile (650 km), deep velocity models of the earth's crust and upper mantle were built (Starostenko *et al*., 2013; Verpakhovska *et al*., 2018).

The need to build a density model along the Pancake profile is due to the fact that the results of seismic surveys on this profile have piqued considerable interest among a wide range of geologists and geophysicists, as well as due to certain differences in deep seismic models of various authors.

The main feature of the Bouguer gravity field on the Pancake profile is the intensive Carpathian gravity minimum (up to –90 mGal), a large positive anomaly covering the Transcarpathian Trough and a number of smaller anomalies of different sign against the background of increasing field intensity in the northeast direction within the EEC.

The gravity modeling technique (Anikeyev *et al*., 2017) includes careful analysis of depths and geometry of seismic boundaries, analysis of geological and geophysical maps and models related to the geological and tectonic structure of the study region, creating the structural part of the model and determining the densities of the layers and blocks of the model. The refinement of the geometry and densities of the model is performed by the method of selection, which is based on the interactive solution of the gravity direct and the analysis of the reasons for the inconsistency of the calculated gravity field and Bouguer anomalies.

According to the gravity modeling results, it is shown that the features of the Bouguer anomalies within the EEC are due to the decrease in the thickness of the earth's crust, the approach of the basement to the day surface and the complex geometry of its surface. A positive anomaly over the Transcarpathian Trough is due to a sharp rise in the surfaces of the basement and MOHO. The deep Carpathian gravity minimum in the front of the Outer Ukrainian Carpathians (OUC) is probably due to the presence of low-density zones in the Earth's crust and the deepening of the MOHO.

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Filtering and smoothing of geophysical dataset regarding anomalies' regionality and depth of the geological model

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Geophysical methods are indirect methods of investigating the subsoil that have different depths of investigation. In order to corroborate the information coming from geophysical surveys, it is necessary to filter and smooth the data, with the aim of separating anomalies based on the regionality and the depth of investigation specific to each method. We used the primary gravimetric data (from the International Gravimetric Bureau) and the magnetic data (from the archive of the Geological Institute of Romania), which were filtered and processed according to the algorithms specific to each geophysical method. The Bouguer anomaly and its residue reflect the effect of geological structures extending from the surface to great depths, which corresponds to a low density of sedimentary deposits above volcanic rocks. The areas of intramountain depressions are manifested by minimal Bouguer anomalies. These reflect the presence of high-density geological structures (potential subvolcanic intrusions). The magnetic anomalies recorded at the surface of the land represent the cumulative and weighted effect of the sources from the surface to the depth of the Curie surface, where the rocks lose their magnetic properties.

The operation of separating gravitational and magnetic anomalies consists in determining the number of sources, the characteristics of each (depth, density, shape and dimensions) so as to result in a cumulative total anomaly, measured at the Earth's surface. There are different ways to achieve this separation of anomalies. In this study are some examples of using the moving average method and polynomial trending surfaces. Also, we present the results of the moving average with different windows compared to the trending surfaces with different degrees, for a case study in the mountains of the Eastern Carpathians. For the study of deep tectonics based on all the data used, we used the correlation coefficient between different parameters, calculated in movable windows of different sizes both in plan and in space. For this, we have developed specific calculation programs. The analysis of polynomial trend surfaces contributes to the recognition, isolation and measurement of trends that can be calculated and represented by analytical equations, thus achieving a separation in regional and local variations. Analytical expressions of polynomial trends were calculated based on the least squares' method, highlighting the regional trend caused by deep structures. We also compared the results of these filtering methods with the results of analytical continuations in the upper half-space, according to the Laplace equation and with the spectral methods, according to the 2D and 3D Fourier transform.

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Characterization of the contact between Adriatic and Pannonian lithosphere based on the 3D velocity model from local earthquake tomography

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The study area represents the contact between the Adriatic microplate as part of the African plate and the Pannonian Basin as part of the Eurasian plate. This investigation is a continuation of the geophysical studies focused on the Dinarides and its adjacent areas. So far, several structural models based on 3D geophysical models of the upper mantle have been proposed, while there is no complete high-resolution geophysical model of the crust and the transition zone to the upper mantle. Our goal is to provide the first high-resolution 3D velocity model of the crust and the uppermost mantle in the broader Dinarides region.

We applied the method of Local Earthquake Tomography (LET). The data sets of P-wave propagation times, calculated from earthquakes recorded by temporary and permanent seismic stations in the study area, were inverted to obtain a three-dimensional P-wave velocity model. The new geophysical model provided the best resolution of the uppermost mantle yet achieved in this study area and in a model of this scale. We assumed that the model would better reveal the structures of the crust. However, our model revealed features at the level of the lowermost crust and upper mantle that had previously been considered only on the basis of geologic relationships at the surface or structures within the crust projected to the level of the mantle. To date, there's no structural model of the crust-mantle transition based on 3D geophysical data that directly samples the lower crust and upper mantle. The resolution documented by the resolution tests is less than a hundred kilometers in the horizontal direction and a few kilometers in the vertical direction in the area with good ray coverage. The most reliable feature of the model concerns the structure of the lower crust and uppermost mantle.

The model confirms previous findings of crustal thickening beneath the Dinarides and crustal thinning beneath the Pannonian Basin. The Moho shape is based on the highest vertical velocity gradient in the lower crust, and the depth of the boundary corresponds to the velocity surface of about 7 km/s. Under the Dinarides, there is a deep low velocity zone that extends to depths greater than 55 km and has a characteristic NW–SE trend. The pronounced low velocity anomaly ($Vp < 7.5$ km/s) is surrounded by higher velocities typical of the uppermost mantle. The deep, low-velocity anomaly occurring in the uppermost mantle and traced along the Dinarides can be explained by two models: a broad shear zone at the contact between two mantles or a subsided part of the lower Adriatic crust beneath the Pannonian lithospheric mantle. Therefore, we performed two-dimensional forward gravimetric modeling to reduce the ambiguity of interpretation. The anomaly is interpreted as fragmentation in the uppermost mantle. The high and low velocity alteration in the narrow region below the Dinarides may be the first geophysical evidence of contact between the Adriatic and Pannonian mantles. According to the velocity pattern, the contact zone can be located at the NE flank of the Dinarides.

Seismicity of the Transcarpathia Depression in the 21st century

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The Ukrainian Carpathians are located in the Alpine–Himalayan seismic and orogenic belt. The seismicity of the Carpathian region of Ukraine is determined by the earthquakes of Transcarpathia, the Flysch Carpathians, Precarpathians as well as the influence of seismically active zones of Poland, Slovakia, Hungary and Romania, including the powerful seismically active zone Vrancea. The most active in the territory of Western Ukraine is Transcarpathia. According to the MSK-64 scale of Ukraine, Transcarpathia is classified as a seven-point zone.

For carrying out the analysis of the seismicity features of the Transcarpathian Depression at the beginning of the 21st century and its links with the tectonic structure were used instrumental data of the Carpathian seismic network of Ukraine during 2000–2020. During the review period, 306 earthquakes with a magnitude M from 1.3 to 4.2 were registered on the territory of Transcarpathia. It was established that the highest seismicity during the considered period was characteristic of the Transcarpathian (Pieninic) and Pannonian faults, in the zones of which significant earthquakes occurred, in particular, near the city of Beregove (23 November 2006; M = 4.2) and near the village of Uglya (14 December 2010; M=3.2). A series of earthquakes (71 events) took place near the city of Tyachiv on 19 July 2015, the most significant of which were with magnitude from 2.1 to 3.5; and near the village of Zabrod in the area of the Transcarpathian deep fault on 6 June 2017 (M = 2.6). Two earthquakes were recorded in the north-western part of Transcarpathia (near the city of Uzhhorod) on 19 April 2020 (M = 2.4) and on 27 April 2020 (M = 2.3). Among the transverse faults, according to the level of seismicity, the Latoritsky, Borzhavsky, Vinogradovsky, Oashsky faults, the Tyachyv lineament, as well as intersection points with the Transcarpathian and Panonian deep faults are distinguished.

In the distribution of earthquake sources with depth in the Transcarpathian Depression, three levels of their concentration are distinguished: the thickness of the sedimentary layer and the basement to the depth of the granite layer (2–10 km), the upper part of the basalt layer (15–22 km) and the layer near the Moho surface (25–35 km). The Transcarpathian fault appears as a subvertical zone and is marked by earthquake hypocenters in the depth range from 2–3 km to 30–35 km (Moho surface). Earthquake hypocenters create a V-shaped field with a maximum concentration in the zone of the Transcarpathian deep fault: the number of hypocenters decreases with depth, and the boundaries of their distribution narrow.

The seismicity of the Transcarpathian Depression reflects the geodynamics of the Carpathian region at the present stage of geological development of the Carpathians and is due to the interaction of the Carpathian folded structure with the ALCAPA and Tisia-Dacia terrains.

Geophysical characteristics of the Eastern (Ukrainian) Carpathians lithosphere: oil and gas potential aspect

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The study area is part of the Eastern Carpathian structure, in which there are large-scale geophysical inhomogeneities of the Earth's crust and lithosphere, which reflect the complex processes of formation of the Carpathian structure and the transition zone between the Eastern European craton, the Western European platform and the Pannonian depression.

The report presents the results of the analysis of geomagnetic and gravitational fields and the heat flow density map in relation to oil and gas potential, taking into account the results of seismic surveys along the PANCAKE and RomUkrSeis geotravers (Kutas, 2021; Orlyuk *et al*., 2021; Starostenko *et al*., 2021). Transformants of geophysical fields were calculated, namely: their regional and local components and horizontal gradient to clarify the structure of different layers of the Earth's crust, the selection of major faults and the connection with oil and gas deposits. A significant connection between the locations of oil and gas deposits with regional and local features of magnetic and gravitational fields and anomalies of the heat flow density was found.

Oil and oil and gas deposits of the Pre-Carpathian Foredeep are in the zone of the regional minimum of the gravitational field and, accordingly, the minimum of its horizontal gradient and the increased horizontal gradient of the magnetic field. Gas deposits are located in the region of minimum horizontal gradient of geomagnetic field and elevated values of gravitational field gradient. The spatial relationship of oil deposits with local positive anomalies of magnetic and thermal fields and relative minima of the gravitational field was also found.

Comprehensive analysis of geophysical data, including magnetic models of geotravers PANCAKE and RomUkrSeis, revealed the location of the main faults of the Carpathian region on the surface and in the deep crust, as well as show the potential relationship with hydrocarbon deposits.

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On the possible mantle nature of the long-wave Central European magnetic anomaly

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This report presents the results of a comprehensive analysis of geological and geophysical data, carried out to substantiate the existence and nature of transition class of magnetic anomalies produced by the Earth's core and the lithosphere. This class of anomalies with a wavelength of 2000–4000 km belongs to the overlap region of the geomagnetic field spectra of the core and the lithosphere, and therefore their separation is arbitrary. The original technology of identifying the lithospheric component developed by the authors is based on one of the fundamental principles of geomagnetism – the change in time and space of the Earth's core field and the stable position of the lithospheric anomalies.

The lithospheric component containing anomalies with a wavelength of more than 2400 km was separated from the main geomagnetic field B_{IGRF}-12. The subject of our research is the submeridional Central European magnetic anomaly of this class, traced from the northern coast of Europe to the edge of the East Saharan mesocraton in Africa. To substantiate its mantle nature information was analyzed on tectonic position of the anomaly and distribution of local magnetic anomalies in the crust, relief of the Moho discontinuity, thickness of the lower (mafic) crust, average velocities V_P of the crystalline crust. The inhomogeneity of the Earth's crust cannot explain the anomaly under study, and therefore it is mantle in nature. The distribution of the physical parameters of the crust and the tectonic position of the anomaly indicate the possible presence of a long-lived transregional lithospheric lineament such as a suture zone along its axis.

Generalization of theoretical and experimental data suggests that, under certain thermodynamic, reductive-oxidative, and tectonic conditions of the upper mantle, ferrimagnetic minerals (magnetite, hematite, native iron, and alloys of iron with nickel and cobalt) can exist, transform and form again within a wide range of Curie temperatures from 580 °C to 1100 °C. It limits the lower boundary of the magnetization stability at a depth of 600–640 km. The most favorable conditions for the origin of such sources are areas of subduction and relics of relatively cold slabs, suture zones and associated with them present-day fluids and plumes. In the area of the anomaly under study, fluids and the Iberian plume were identified from seismic tomographic data, which, in combination with the rise of the bottom of the upper mantle and the presence of inclined high-velocity layers in its low-velocity part, characterize the excited mantle. Thus, the Central European long-wave magnetic anomaly can be interpreted as the total effect of the relicts of primary ferrimagnets formed under the influence of fluidization of the mantle.

An interdisciplinary approach to studying Pre-Earthquake processes

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Over the past 15–20 years, there has been a significant revival of interest in pre-earthquake studies in Japan, Russia, China, the EU, and elsewhere. We will summarize a multi-year research effort on wide-ranging observations of pre-earthquake processes. Based on space and ground data, we present some new results relevant to the existence of pre-earthquake signals. Some recent results were obtained from modeling the atmosphere-ionosphere connection and analyses of seismic records (foreshocks /aftershocks), geochemical, electromagnetic, and thermodynamic processes related to stress changes in the lithosphere, along with their statistical and physical validation. In this study, we are exploring retrospectively/prospectively the potential of atmospheric and ionospheric signals to alert for large earthquakes. A new R&D geospace approach has been developed to study specific physical parameters variation in the atmosphere and ionosphere that we found to be connected with the earthquake preparation processes. We study the near-Earth space plasma dynamics and the electromagnetic environment by multi-parameter analysis from a variety of space-based missions and validation of the physical concept of Lithosphere- Atmosphere- Ionosphere -Magnetosphere coupling (LAIMC), which links the chain of processes initiated by atmospheric boundary layer modification by the preparation of major earthquakes. We also present the potential impact of these interdisciplinary studies on earthquake predictability. This cross-disciplinary approach could impact our further understanding of the physics of earthquakes and the phenomena that precede their energy release. Summaries of our approach were published in two new books by AGU/Wiley and IOP (Ouzounov *et al*., 2018, Pulinets and Ouzounov, 2018). These books are intended to show the variety of seismic, atmospheric, electromagnetic, and geochemical pre-earthquake processes parameters and will bring this knowledge and awareness to a broader geoscience community.

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Modeling of seismicity on the territory of Bulgaria

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Bulgaria is located in the eastern part of the Balkan Peninsula, the modern geodynamics of which is determined by active tectonic processes in the Eastern Mediterranean. In Bulgaria, the spatial distribution of seismicity across the country is uneven. Most of the strong events are concentrated in the southwestern part of Bulgaria. To better understand the seismic hazard in the region, we apply a block and fault dynamics (BAFD) model for the Bulgarian region to model regional earthquakes. The structure of the model is based on the results of morphostructural analysis to identify blocks of the Earth's crust and the available GPS observations of the movements of the Earth's crust in the region. This study presents preliminary results obtained in the course of numerical experiments carried out to determine the areas of occurrence of strong earthquakes and the time of their repetition. As a result, we have created a synthetic catalog of earthquakes. The main characteristics of the computed artificial seismicity are in good agreement with the features of real seismicity reported by Bulgarian catalogs.

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Three-dimensional crustal model of the Dinarides and marginal areas based on gravity and seismic models

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The survey area includes the Dinarides and the peripheral areas of the Pannonian Basin and the Adriatic Sea, and is located at the collision of the Adriatic microplate and the Pannonian tectonic segment of Eurasia. The basic goal of the research is to determine a three-dimensional geological model of the crust and the uppermost mantle based on three-dimensional gravity and seismic models.

The density model was determined based on 2D-gravity modelling according to the methodology applied by Šumanovac (2010). Gravity modelling is characterized by relatively wide ambiguity limits, but using the so-called ‘calibrated density set’, they can be significantly constricted. The modelling was performed on the Alp07 profile and five gravity profiles placed approximately perpendicular to the Dinarides extension. The basic assumption is that the structure of the Dinarides is generally two-dimensional. This would mean that the geological properties along the Dinarides do not change, so the calibration of the density set is made on the Alp07 profile in the northern Dinarides. The two-dimensionality of the geological structure is clearly evident on regional geological and gravity maps, especially the Bouguer anomaly map. Based on two-dimensional density models of gravity profiles, a three-dimensional density model was developed, which clearly presents the relationships in the survey area.

Two velocity models were constructed. The first model was constructed by converting the density model into velocities. The procedure opposite to the determination of the calibrated density set is now used. However, this transfer is now made on a 3D-density model, so a 3D-velocity model has been constructed in order to correlate with the velocity model obtained by seismic method. The second velocity model of the Dinarides and marginal areas was determined by local earthquake tomography by means of inverse seismic modelling.

By correlating all geophysical models, the first three-dimensional geological model in the area of the Dinarides and marginal areas was determined. The smallest thicknesses of the crust, only about 20 km, are located below the Pannonian Basin, and the crust is apparently single-layered. Small crust thicknesses, 25–30 km, are also found in the Adriatic Sea, the area of the undeformed Adriatic microplate. Beneath the Dinarides, the crust thickens abruptly, and the greatest thicknesses lie below the centre of the Dinarides in a narrow and regular zone with a Dinaridic extension. The width of the Moho depression along the Dinarides is largely similar, but the maximum depths of the Moho changing from 45 km in the northern to 50 km in the southern Dinarides. Between the two-layer Dinaridic crust, which includes the Adriatic units, and the single-layer Pannonian crust, which includes European units, there is a wide Transitional Zone. It plays the role of a suture zone of two continents, Africa and Europe. The most prominent phenomenon is the high density body below the Sava Depression, which can be interpreted as a larger block of oceanic crust rocks.

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Drone based alteration mapping and trace-elements vectors toward gold mineralization in the Pesovets epithermal system, Panagyurishte ore district, Bulgaria

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Drone based photogrammetry approach by means of *DJI Matrice 300 RTK Combo* with combined RGB and TIR camera *Zenmuse H20T* was utilized for hydrothermal alterations mapping and targeting for gold mineral exploration in Pesovets epithermal system, located in the Panagyurishte ore district, Bulgaria. Mineral alterations map was assembled using orthophoto model and TIR 3D mapping to utilize the time and cost efficiency of the subsequent field work. Geological mapping and rock sampling was carried for classification and verification of drone orthophoto mosaic in addition to XRF and XRD mapping and stream sediments sampling. 3D drone supported remote sensing and field mapping outlined clearly the Pesovets paleovolcano center with very well defined volcanic neck, radial and concentric fault structures and some regional fault zones. Well distinguished hydrothermal alterations styles such as massive and vuggy silica, advanced argillic (Na-alunite, goyazite, svanbergite, dickite, topaz), argillic (kaolinite-alunite) and more distal intermediate argillic (illite-smectite) and propylitic (chlorite-epidote) domains were mapped (Bogdanov *et al*., 2021). Svanbrgite and goyazite seem to be the source for Sr enrichment in the advanced argillic domains. The drone based TIR alteration mapping of Pesovets silica cap has demonstrated much better mapping resolution and more detailed outline of the advanced argillic kaolinite-alunite alterations as compared with the ASTER (Amin and Mazlam, 2012) and WordView-3 surface mineral alteration mapping.

Ore petrography study indicates submicroscopic, rounded 5–50 µm in size native gold blebs with high fineness (>850‰) grains in an assemblage with vuggy silica, alunite, kaolinite and goethite. Stream sediment sampling of the Luda Yana River at the foot of the Pesovets hill has resulted in discovery of angular, thick bladed and rounded visible native gold grains ranging in size from 250 × 144 µm to 625 × 416 µm, indicating for promising high-sulfidation epithermal gold exploration target in the studied area. Rutile and anatase enrichment have been recognized by increasing Ti concentrations from 290 ppm to 2400 ppm as indicated by field *Skyray Explorer 7000* XRF study. The Co (0.28–0.70 ppm), V (4.7–51 ppm), and As (20–50 ppm) concentrations increased in correlation with Cu (6.4–50 ppm) from argillic to advanced argillic alteration zone at least twice and could be used as trace-elements vectors toward epithermal gold enrichment of the Pesovets silica cap.

The recent study example demonstrates time- and cost-efficient, drone-based mineral mapping approach for sustainable mineral exploration targeting and evaluation.

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Miocene Western Balkan lithium-borates metallogenic zone

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A series of new lithium-boron discoveries within Western Balkan countries in the last two decade significantly increased level of geological knowledge allowing us to summarise for the first time joint geological features of these new and peculiar metallogenic zone: *1*) lithium-boron mineralization is hosted within Miocene extensional lacustrine basins, usually at depth >200 m; *2*) lacustrine serial consist of fine-grained siliciclastic sediments (marls, clays, shales, fine-grained sandstone) and scarce evaporites with intercalations of volcaniclastic, tuff, ash-flow or travertine pointing to the adjoining volcanic activity, whereas geophysical research sometimes reveal shallow intrusions; *3*) lacustrine basins are usually normal faults-controlled extensional grabens, with fault system probably acting as a major magma/fluid-pathway; *4*) northernmost (Jadar, Valjevo, Rekovac) sodium borate/borosilicate deposits (jadarite, borax, probertite, searlesite) gradually transition to calcium borate southward (Jarando – Piskanja, Pobrđe; colemanite±ulexite); *5*) contemporaneous(?) granitoid rocks from the westernmost part of the zone hosts pegmatite and greisen with surface lithium anomalies of 0.02–0.08% Li_2O extending several km^2; *6*) geochemistry of granitoid rocks points to high-K calc-alkaline - shoshonite magma series with sum of alkalis 6.9% to 12.5%; SiO_2 of 64.7% to 82.4%; Fe_2O_3 of <0.5% to 4.5%, very low CaO (<1%), MgO (<0.4%), MnO (<0.03%), with high Th, U, Pb, negative Nb, Ti and general Rare Earth Elements (REE) trend as of La, Ce > MREE > HREE, pronounced negative Eu; *6*) the Western Balkan lithium-borate metallogenic zone can be traced for 1500 km, spreading subparallel to the Sava-Vardar and Western Vardar zone toward its Turkey counterpart, the Izmir-Ankara-Erzincan Zone.

Geodynamically (but not radiometrically) related high-K calc-alkaline to shoshonite metaluminous I-type plutons, as well as part of peraluminous S-type plutons from the westernmost part of the WB LiB, contain weak lithium anomalies and could serve as potential source for lithium (and boron) mineralization in neighboring Miocene lacustrine basins. Existing geological and mineralogical dataset points to Miocene lacustrine basins reheating by magmatic/shallow volcanic intrusions and discharge of hydrothermal Li/B fluids to lake water (Ercegovac *et al.*, 1991; Obradović *et al.*, 1992). Miocene lake system of the WB LiB therefore has served as geological traps for syngenetic hydrothermal lithium and boron mineralization during lower and middle Miocene.

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Cosmic-ray muography applied to porphyry copper environments

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Cosmic-ray muography (or just muography) is a novel geophysical method based on the repeated directional measurements of particle flux of the elementary particle muon underneath or sideways of the volume of interest. Muons lose energy in the matter until they are stopped (attenuated). The only major contributor to the energy loss is the material density, and a higher average density leads to quicker energy loss. This is the basis exploited in muography to reconstruct two- or three-dimensional density images of the interesting volume, such as a rock formation or orebody. Attenuation of muons in different directions works similarly to attenuation of man-made X-rays in the material. However, muography is a totally passive method without the need to generate muons. Instead, muons are constantly regenerated in the upper atmosphere via air molecule interaction with primary cosmic radiation. The most energetic muons can reach hundreds of meters depths in rocks, some even up to a few kilometers.

Muography applied to mineral deposit exploration and research is an emerging tool for those who are looking for alternatives to gravity and seismics. The benefits of muography include controllable resolution and independence of the contact directions of geological boundaries. While muons attenuate, they do not bend like seismic waves. Considering physical appearance, two detector types stand out: borehole probes and box-like “telescopes”. These could be used separately or as combined arrays in porphyry copper environments. Joint inversions with gravity and seismic data are also possible.

Regarding muon telescopes, they must be located either in open pits or inside underground tunnels unless the local topography allows direct surface-based surveying of high landforms. The key is to position the detector behind the rock volume of interest. Moreover, muography can be used in all stages, from early field research to post-closure monitoring. Specific applications include drilling targeting and optimization, resource delineation, lithological mapping, structural geology, tunnel planning and optimization, and heap scanning. In addition, muography can be applied even for time-lapse-based density-change monitoring of embankments, slopes and the environment.

Conventional geophysical methods applied in porphyry copper environments may, at least occasionally, have undesirable resolution capabilities for the task at hand. Muography is fundamentally different in that it is a statistical imaging method. While there is always an upper limit to image resolution, muographic data acquisition is flexible, and image resolutions can be improved by recording larger sets of muons or from more locations. If data reliability is an important issue, reliability can be improved by measuring longer.

On the above basis, porphyry copper environments offer many opportunities for muography. These include hydrothermal alteration zones, primary lithological mapping, and structural geological targeting. If there is a known or expected relationship between rock density and mineralization features, they may well be feasible targets for muography, assuming the density contrasts are in the range of a few percentages or more. Magnetic or conductive properties of rocks are not a hindrance either, as muography is primarily sensitive to only density (and to a minor extent to rock chemistry).

Porphyry copper systems II: The role of magmatic sulfides in the process chain of metal enrichment

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Loss of magmatic sulfides to the mantle is posited to explain the Cu deficit of evolved arc magmas and the depleted Cu/Ag ratio of the continental crust. We analyse the question whether saturating sulfides may instead be mechanically entrained with rising magmas and how this would affect their geochemical fate in the upper crust.

Entrainment is plausible considering sulfide wetting properties and settling velocities relative to magma ascent velocities. Multicomponent thermodynamic analysis based on a model composition of hydrous arc basalt shows that entrained sulfide increases the pressure at which magmas become saturated with respect to H-O-S fluids in the upper crust. This pressure increase is on the order of 100–1000 bars, increasing with temperature, water content and oxidation. As a result, sulfides decompose in a rapidly ascending hot magma within a small pressure - temperature interval after the magma becomes saturated with hydrous fluid. Surface kinetics indicates that bubbles are likely to nucleate on sulfide particles, allowing wholesale transfer of S and chalcophile metals including Cu from the sulfide to the fluid, over a small crystallization interval and without limitations by diffusion through the silicate melt.

This sequence of processes gives magmatic sulfides an active role in ore metal transport and enrichment to form porphyry copper deposits, rather than a step of partial metal depletion. It may also have consequences for global Cu budgets. Magmas reach high water contents by fractionation in the lower or middle crust, so that later sulfide decomposition is most effective above thick continental crust. This may lead to loss of chalcophile metals by dispersal through the hydrosphere and their recycling by sediment subduction, and not only by recycling of sulfide-bearing lower-crustal cumulates to the mantle as commonly posited.

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New fluid inclusion data from the Krumovgrad goldfield, SE Bulgaria

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Fluid inclusion petrography and microthermometric study presented here were conducted on ore samples from the Ada Tepe, Synap and Surnak deposits (Krumovgrad goldfield), Eastern Rhodope Mountains. The aim is to present first fluid inclusion data on the Synap deposit, and new data on the palaeofluid characteristics in the Ada Tepe and Surnak deposits.

Over 25 hand specimens from surface outcrops in the Ada Tepe, Synap and Surnak deposits were selected for a fluid inclusion study. The hand specimens comprise silicified both breccia-conglomerate and high-grade metamorphic rocks cross-cut by pyrite/marcasite veinlets. Fluid inclusion petrography and microthermometry were carried out using a Linkam THMS 600 heating–cooling stage at the Fluid Inclusion Laboratory of the Department of Geological Engineering, Pamukkale University, Turkey. Fluid inclusion assemblages (FIAs) were classified at room temperature, and the ice-melting temperatures were converted to salinities assuming the fluid composition is represented by the H_2O – NaCl system. The fluid inclusion study was performed in quartz and calcite from the three deposits.

Fluid inclusions in the three deposits mentioned have similar characteristics. Although the fluid inclusions are very small in the wafers prepared, FIAs are abundant in both quartz and calcite. There is strong evidence for boiling in the samples studied, which included FIAs consisting of coexisting liquid-rich and vapor-rich inclusions, and the presence of bladed calcite and/or chalcedonic quartz. The primary fluid inclusions in quartz were found in clusters and have a feather-like texture resulted from their trapping on different quartz faces. Growth zones can also be defined by darker bands of chalcedonic quartz. These are features commonly observed in epithermal environments according to published data. Quartz contains coexisting V-rich and L-V fluid inclusions, some of which contain semi-prismatic solids, probably trapped during boiling. In quartz and calcite, the eutectic melting temperature (Te) was observed between –20 °C and –40 °C. Majority of fluid inclusions homogenize to liquid (Thliq), and comprise the bulk of the measurements. The homogenization temperature data for the fluid inclusions in quartz and calcite are 185–270 °C and 200–250 °C, respectively. All fluid inclusions homogenized into the liquid phase. The Tmice values for L-V fluid inclusions in quartz and calcite are between 0 °C and –2 °C (0 to 3.3 equiv. wt.% NaCl), but could not be observed in V-rich fluid inclusions. The salinities of the fluid inclusions in both minerals essentially cover the same range with very low salinity. However, the highest salinities were in quartz-hosted inclusions. The obtained data from the Surnak deposit are similar to those previously published but the data about boiling of fluids are new ones.

In conclusion, the fluid inclusion data from this study have similar characteristics: homogenization temperatures in quartz and calcite of 185–270 °C and 200–250 °C, respectively. The Tmice values for L-V fluid inclusions in quartz and calcite are between 0 °C and –2 °C (0 to 3.3 equiv wt.% NaCl) with the highest salinities in quartz-hosted fluid inclusions. There is strong evidence for boiling in the samples studied, which include FIAs consisting of coexisting liquid-rich and vapor-rich inclusions, and presence of bladed calcite and/or chalcedonic quartz.

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The Alluvial Gold from Olănești and Cheia Rivers, Southern Carpathians, Romania

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Native gold was discovered in the placer deposits of the Olănești and the Cheia rivers. There is no previous scientific reference on these alluvial gold occurrences in the Romanian literature to our knowledge. These rivers are flowing down from NW to SE through the Căpățânii Mountains, in the Southern Carpathians, and are tributaries of the Olt River, which is flowing towards south to the Danube. The bedrocks along the middle and lower courses of both rivers consist of marls and sandstones of Upper Cretaceous to Miocene age. However, the alluvial deposits contain abundant metamorphic rocks (quartzite, amphibolite), and limestones gravels.

The majority of the native gold grains, which may reach up to several millimeters in size were found at the boundary between the river deposits and the bedrock, together with cm-sized pyrite spheres. The largest gold grains are rounded to sub-rounded and have quartz inclusions, while the small-sized particles show different shapes from rounded to elongate with sharp edges and no quartz inclusions.

The source of the native gold is still unknown. However, the shear-zone related Cu-Au Valea lui Stan ore deposit (Udubașa and Hann, 1988) is located at approximately 15 km towards north. According to these authors, native gold mineralization is hosted by quartz lenses in Precambrian metamorphic rocks.

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Metallogenic Implications of the High-Precision U-Pb Zircon Geochronology of Igneous Rocks from the Rogozna Skarn-hosted Au-Zn-Pb-Cu Project

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Rogozna Mountain and its eponymous volcanic complex located in SW Serbia hosts multiple base metal deposits associated with variable rock types and structural expressions (*e.g.*, Janković, 1995; Heinrich and Neubauer, 2002; Borojević Šoštarić *et al*., 2011, 2013). The volcanic complex is part of the Serbian Cenozoic igneous province, which is composed of geochemically diverse igneous rocks and often shows evidence of magma hybridisation (Borojević-Šoštarić *et al*., 2012, and references therein). Unlike the majority of deposits at Rogozna Mt., which are dominated by base metal sulphides, the Rogozna project (composed of the Gradina, Medenovac, Copper Canyon and Šanac deposits) shows also Au-Cu mineralisation along with base metal sulphides (Budinov *et al*., 2015; Burkhard, 2017), due to its favourable first-order structural framework. Based on the isotope geochemistry, a single magmatic source was responsible for sulphide crystallisation associated with the Au-Cu mineralisation at Copper Canyon (*i.e*., Karavansalija) deposit (Budinov *et al*., 2015). Therefore, a detailed determination of igneous events and their temporal relationship remains crucial for understanding the formation of the Rogozna mineralised system and its multiple deposits.

High-precision CA-ID-TIMS U-Pb zircon geochronology of 6 representative samples revealed an earlier Au-Zn mineralisation system at the Medenovac deposit that occurred prior to 28.833 ± 0.154 Ma (constrained by clasts of mineralised skarn in igneous breccia), older than values previously published for mineralisation at Copper Canyon deposit (quartz-monzonitic porphyry PP; CA-ID-TIMS on Zr; 27.62 Ma; Hoerler *et al*, 2022). Based on the ubiquitous replacement of magnetite with hematite, this mineralisation at Medenovac is oxidised, unlike the other Rogozna deposits that are reduced (*e.g*., Gradina, Copper Canyon). Unmineralised trachyandesitic/trachybasaltic dykes emplaced at 25.384 ± 0.068 Ma represent the youngest igneous event at Rogozna Mt. Previous models of the formation of Rogozna mineralised system were likely flawed by inaccurate unit classification and incomplete sampling of intrusions associated with the deposits, resulting in unrealistically short-lived mineralisation event. Therefore, a reinterpreted temporal hierarchy of the Rogozna Mt. igneous suite is proposed based on new compositional and geochronological data, defining multiple Au-Cu mineralisation events. This work highlights the necessity of combining a robust suite of textural analyses, field relationships and high-precision geochronology to make accurate interpretations for deposit formation.

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New Data on Sakdrisi Au-Cu vein deposit (Georgia, Lesser Caucasus)

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Sakdrisi Au-Cu vein deposit is located on the southeastern part of small (app. 50 sq. km) Darbazi-Abulmulk caldera, representing part of the large Bolnisi volcano-tectonic depression. The deposit area is built up of Upper Cretaceous volcano-sedimentary sequence, intruded by bimodal (basalt-rhyolite) extrusions, covered by Plio-Pleistocene breccias and dolerites as well as by Holocene breccias. During mapping campaign in 2020–2021, two complexes have been recognized in the Upper Cretaceous sequence: the Lower (LVSC) and the Upper (UVSC) ones, separated by unconformity.

LVSC is built up of thick (over 200 m) sequence of layered ash tuffs and tuffites, intruded by dacite extrusions. Two suites are recognized in this complex: a suite of gray-green ash tuffs and tuffites, and a suite of white Fe-spotty tuffs. The upper parts of LVSC are affected by intense silicification and related economic Au-Cu mineralization.

UVSC is built up of 2 suites: sedimentary (mainly black breccia-conglomerates and clays interbedded by limestones, dolomites, and sandstones) and volcanic (mainly ignimbrites), intruded by acid (rhyolite-dacite) and basic (basalt) extrusions (sills, dykes, stocks). This complex lies discordantly on different stratigraphic levels of the LVSC.

Key problem in our structural model is the presence of basal sediments (mainly breccia-conglomerates) at the base of UVSC, marking significant erosional period separating two tectono-magmatic stages of the caldera evolution. During previous investigations, these sediments were disregarded, interpreted as fault breccias or their importance was not properly estimated. As a result, the boundary between ore-bearing quartzites (LVSC) and ignimbrites (UVSC) was interpreted as follows: 1) subvertical normal fault with uplifted SE block, comprising the ore-bearing quartzites and subsided practically barren (due to big fault amplitude) NW block, or 2) thrust along which the NW block (ignimbrites) was trusted over the SE block (quartzites).

New structural model is based on the stratigraphy, recognizing a basal sedimentary suite between quartzites and ignimbrites. Late magmatic rocks (dacites, basalts) are intruded in this suite, as well as along its boundary with ignimbrite suite. They did not destroy the normal stratigraphic sequence because usually are intruded along the bedding, like detachment related sills.

Following this model, a drilling project started in 2021 aiming discovery of ore mineralization on the periphery of the deposit area. Drillings proved an ore body rich in Au-Cu below UVSC. Currently, drilling continues in order to outline the ore body and possibly discover new ore bodies.

During previous investigations the ore mineralization was considered to be related to single-stage hydrothermal activity. Following the new geological data, two types of ore mineralization established in 4 stages, have been recognized (2 hydrothermal and 2 placers).

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New Pb isotopic data for Romanian ore deposits – A new step for paleopollution assessment and metal tracing in the Carpathian-Balkan region

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Lead isotopic data for Romanian ore deposits started to be available in 1997 but most of them were obtained for samples from only two areas, the Neogene epithermal ore deposits of the Baia Mare ore district, Eastern Carpathians, and the epithermal and porphyry ore deposits from the South Apuseni Mountains region (Marcoux *et al*., 2002; Baron *et al*., 2011; Chernyshev *et al*., 2014). Scarce data on other ore deposit types of older ages were however published by Cook and Chiaradia (1997), Marcoux *et al*. (2002) and Chernyshev *et al*. (2014).

We selected a larger spectrum of ore deposits types (*e.g*., magmatic, skarn, carbonate replacement, volcanogenic massive sulfide) with ages ranging from Cambrian to Neogene and representing the different known metallogenic provinces in Romania (*e.g*., Banat, Dobrogea, Poiana Ruscă Mountains). The preliminary results suggest that the Pb isotopic signature of the ore deposits changes depending on their age, but shows no relationship with their genetic type and metallogenic district/region.

The newly acquired Pb isotopic data will be useful in the future to assess the impact of pollution by ancient mining and metallurgy industry using the Pb-isotopic data acquired/published for peat-bog deposits and to trace the metal present in archaeological artifacts (copper, bronze, gold-silver) discovered in the Carpathian-Balkan region or elsewhere.

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New Exploration Data on Geology, Structure and Mineralization of Rozino Sediment-Hosted Low-sulphidation Epithermal Gold Deposit, Eastern Rhodopes, Bulgaria

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The Rozino Au deposit is located within the Tintyava Property, which lies within the municipalities of Ivaylovgrad and Krumovgrad in southeast Bulgaria, about 350 km by road east-southeast of the capital, Sofia. The deposit was discovered in the mid 1980's by the Asenovgrad exploration organization "Geo-engineering" by trenching and drilling, and the exploration had delineated two mineralised bodies with 3515 kg at 1.49 g/t Au (0.5 g/t cut-off grade) and 12190 kg at 0.54 g/t Au (0.2 g/t Au cut-off grade). Exploration by Hereward Ventures plc started in April 2001 and the first 35 diamond drilling holes, some of which were undertaken in joint venture with Asia Gold Corp, ("Asia Gold") showed intervals of much higher grades reaching up to 246 g/t Au over metric intervals. Further drilling has indicated that the Rozino deposit inferred resource comprises at least 12757 kg at 2.3 g/t Au.

Velocity Minerals Ltd. completed detail exploration campaign from 2017 to 2020 that included initial work in the Rozino area, and regional exploration within the Ivaylovgrad Paleogene Corridor. This work incorporated surface mapping, soil sampling, rock chip sampling, stream sediment samples, trenching and drilling. As a result of detail exploration and infill drilling at Rozino deposit in 2020, Velocity issued a new Mineral Resource estimation reported in accordance with NI 43–101 (Rozino Gold Project Preliminary Feasibility Study, 2020). The new estimate includes Indicated Mineral Resource of 16244 kg at 0.87 g/t Au (0.3 g/t Au cut-off grade) from which converted to Probable Reserve of 10433 kg at 1.22 g/t Au (0.5 g/t Au cut-off grade).

Geology of the Rozino area comprises a series of discrete Paleogene syn-tectonic pull-apart sedimentary basins within metamorphic basement. Rozino is a low sulphidation epithermal (LSE) gold deposit hosted within breccia and conglomerate of Paleogene sediments, as disseminations, replacements and vein-type mineralizations. Alteration is characterized by a quartz, carbonate, chlorite, adularia, and pyrite assemblage. The mineralogy consists mainly of pyrite with traces of base metals and rare arsenopyrite. Gold occurs at sulphide mineral boundaries and less commonly as very fine native gold grains or encapsulated inclusions. The dominant mineralization strike is northwest, parallel to the regional extensional fault regime, with local mineralization development controlled by the intersection of steep structures sub-parallel to the bounding extensional faults, and gently dipping bedding.

Geographic distribution, stratigraphic location and the ages dating of Rozino gold deposit (36.0–36.5 Ma) suggest for an intimate association of gold mineralization to the metamorphic core-complex formation, rather than to nearest magmatism (Marchev *et al*., 2003).

The purpose of this presentation is to present new exploration data on geology, structure and hydrothermal alteration of Rozino LSE gold deposit as a summary of the detail exploration activities done by Velocity Minerals. Updated conceptual genetic model of the mineralization is also proposed and potential new gold target areas are discussed as well.

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Relationship of sulfur isotope composition and common trace element content in pyrite and marcasite from the low-sulfidation Surnak gold deposit, SE Bulgaria

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This study presents new data on sulfur isotope composition and trace elements in pyrite and marcasite of the economic quartz-sulfide stage from the epithermal, low-sulfidation, late Eocene Surnak gold deposit to shed new light on likely reason for sulfur isotope fractionation and precipitation mechanism of pyrite and marcasite.

This study is based on five pyrite ± marcasite samples taken from drillhole cores (drilling of DPM Krumovgrad). Four samples are from the high-grade metamorphic basement and one is at the tectonically reworked contact between the sedimentary cover and metamorphic basement, and they are at levels –20, –15, –12, –8 and 0 m relative to the contact. The methods used were optical microscopy, scanning electron microscopy coupled with EDX analysis with standards; Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), and sulphur isotope analysis.

Pyrite is the main ore mineral in the samples, in places accompanied by marcasite, the latter being largely transformed into pyrite. The gangue minerals co-deposited with the FeS_2 polymorphs are quartz and adularia, all cross-cut by later carbonates. Pyrite and marcasite show great textural diversity of primary and recrystallized origin. In BSE images pyrite displays very often oscillatory and patchy zonality – alternation of light grey and dark grey bands/patches. SEM-EDX microanalysis showed presence only of As and Sb as minor elements in pyrite and marcasite. Arsenic is found in all the EDX microanalyses (totally 117 points in both light and dark grey pyrite/marcasite bands/patches) while Sb was detected only in 15% of analyses. Light grey bands/patches of pyrite/marcasite are characterized by increased contents of As (up to 5.95 wt.%) while in the dark grey areas As contents are up to around 3 wt% (*i.e.*, FeS_2 is arsenian). Sb is up to 0.69 wt%. LA-ICP-MS analyses (139 spots in total) revealed that Mn (43.41), Co (6.77), Ni (58.67), Cu (64.91), Zn (16.64), As (23925.40), Mo (20.32), Ag (194.80), Sb (2024.06), Au (8.3), Hg (80.36), Tl (638.74), and Pb (40.16) are common trace elements in the studied pyrite/marcasite grains (in brackets the respective average content in ppm is given). Gold is present as invisible in zonal As-rich pyrite (up to 180 ppm, LA-ICP-MS data) and as later electrum entering pyrite along cracks (optical microscopy and SEM-EDX). Values of $\delta^{34}S_{V\text{-}CDT}$ of Surnak's pyrite/marcasite range from –6.42‰ up to +1.73‰ for the studied levels, and are typical of low-sulfidation deposits. Nevertheless, the sulfur isotope composition records a significant variation whose most notable feature is its coupled behavior with the contents of Ni, Co, Au, Ag, and Pb. These elements show two peaks of increased contents: *a*) at –15 m and b) at –8 m relative to the aforementioned contact which coincide with $\delta^{34}S_{V\text{-}CDT}$ shifts from negative to positive values, *i.e*., a shift to heavier sulfur isotopic composition. In contrast, Mn, Sb, Hg, Tl, Zn, and Cu display a smooth increase from –20 m level to –12 m level and then a smooth decrease toward the contact. Arsenic has constantly high contents in terms of distance to the contact. The coupled behavior of $\delta^{34}S_{V\text{-}CDT}$ with the contents of Ni, Co, Au, Ag, and Pb reveals a common reason for the isotopic and trace element variations obtained. The well-defined association of vein adularia with pyrite/marcasite in the Surnak deposit is an indication for boiling of fluid, recently proved by fluid inclusion data from vein quartz. Likely two boiling horizons (levels of –15 m and –8 m) are recorded in both the $\delta^{34}S_{V\text{-}CDT}$ and trace element content trends. The other group of trace elements (Mn, As, Sb, Hg, Tl, Zn, and Cu) correlate with negative values of $\delta^{34}S_{V\text{-}CDT}$, and the respective drillhole core samples reflect intense fluid-rock interaction.

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LA-ICP-MS study of pyrite and chalcopyrite from quartz-polymetallic veins in Hurd Peninsula, Livingston Island, Antarctica

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This study adds new data on the chemistry of pyrite and chalcopyrite from quartz-polymetallic veins in Hurd Peninsula, in the area of Bulgarian Antarctic Base (BAB), Livingston Island. The ore veins, hosted by sandstones of Miers Bluff Formation were sampled during the Antarctic season 2019/2020. The main ore minerals are pyrite, chalcopyrite, galena, and sphalerite (Sabeva *et al*., 2020).

Trace element concentrations in pyrite and chalcopyrite were measured by LA-ICP-MS on polished sections at the Geological Institute (Bulgarian Academy of Sciences). A total of 39 analyses were performed on PerkinElmer ELAN DRC-e ICP-MS equipped with a New Wave UP193-FX excimer laser ablation system. NIST SRM 610 glass and MASS were used as external standards and Fe as internal standard, measured by electron microprobe (EPMA) at Eurotest Control Laboratory, Bulgaria.

Pyrite from the ore veins is deposited together with galena, sphalerite, and chalcopyrite. It occurs as subhedral to anhedral crystals in nests up to several mm in size. Pyrite is often porous and fractured. Gold inclusions up to 5 µm were established in pyrite. EPMA indicate that composition corresponds to native gold with 16.34 wt.% Ag and fineness 836, and electrum with 19.94–27.22 wt.% Ag and fineness 774–727 (Sabeva, 2022). Chalcopyrite occurs mainly as anhedral grains, forms nests and veinlets.

The LA-ICP-MS dataset shows variable concentrations of trace elements in pyrite. Structurally-bond in the lattice are As (from not detectable (bdl) to 28759 ppm, average 8719 ppm), Cu (from bdl to 30436 ppm, average 2419 ppm), Co (from bdl to 13690 ppm, average 806 ppm). Zn (from bdl to 6396 ppm, average 765 ppm) and Pb (from bdl to 3586 ppm, average 643 ppm) were also established and represented as micro-inclusions of sphalerite and galena. Pyrite contains Au from not detectable to 169 ppm (average 19 ppm) and Ag from not detectable to 33 ppm (average 9 ppm). These elements display irregular profiles with spikes, which suggest the presence of micro-inclusions of native gold and electrum. The elements with concentrations < 100 ppm are Se, Sb, Mn, and Ni.

The LA-ICP-MS analyses of chalcopyrite reveal the presence of Zn, Se, Ag, Mn, and rare Pb, Ni, Sn, Bi, Cd, In, Ga, and Sb. Zn (from 111 ppm to 531 ppm, average 324 ppm) and Se (from bdl to 570 ppm, average 237 ppm) are with the highest concentrations. Mn and Ag (up to 497 ppm, average 179 ppm) were detected. The irregular profiles of the depth spectra suggest they are probably inclusion-related. Au was established in one ablation spot with contents of 0.45 ppm and is represented as micro-inclusions.

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Vein stratigraphy in the Ada Tepe and Kupel low-sulfidation gold deposits, Bulgaria: Implications for ore-forming processes

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The sedimentary-rock hosted gold deposit of Ada Tepe with low-sulfidation characteristics is the most prominent from a number of deposits and occurrences located along the northern border of the Kesebir-Kardamos metamorphic dome complex in the Eastern Rhodopes, Bulgaria. Mineralization is often spatially associated to a low-angle extensional fault (Tokachka fault), separating a lower plate of metamorphic basement rocks from a hanging wall consisting dominantly of the presumably Eocene to Oligocene in age Shavar Formation, composed by coarse terrigenous rocks at the basis, deposited in half-graben basins. Main host for the gold mineralization is the sedimentary sequence. Two types of ore bodies share characteristics indicative of strong structural and lithological control: i) a tabular orebody located immediately above the low-angle fault, consisting of sub-horizontal veins in a highly damaged cataclasites within the fault zone, referred to as “the wall zone”; ii) vein ore bodies dominantly controlled by high-angle E–W and NE–SW-trending structures in the highly permeable sedimentary rocks. These sub-vertical veins intersect the wall zone and consist of a high-grade gold mineralization.

The Kupel North prospect is located about 1 km east of the Ada Tepe open pit. The mineralization lying approximately 200 m above the low-angle fault at higher levels of the sedimentary sequence, is hosted in finer-grained sandstone, siltstone and conglomerate units, and consists of a stockwork-like quartz-chalcedony veins controlled by NE-striking, high-angle SE-dipping fault structures.

Detailed vein stratigraphy on oriented cores from the two deposits allowed defining similarities and differences between the mineralization styles at Ada Tepe and Kupel. Combination of Qemscan (quantitative mineralogy), optical microscopy, textural analysis, optical cathodoluminescence (CL), portable XRF profiling, LA-ICP-MS analysis of hydrothermal minerals, and fluid inclusion studies on oriented samples was applied, as a new promising methodology with large potential in mineral exploration and comparative studies.

Despite the fact that sub-horizontal and sub-vertical veins share some common characteristics (*e.g.*, mineral composition), textural features are indicative of contrasting scenarios in terms of vein propagation and ore-forming processes. Sub-horizontal veins have very typical unidirectional (bottom-to-top) crystallization features, evidencing overpressure-induced hydrofracturing due to fluid flow focused along horizontal paths, probably favored by pre-existing mechanical anisotropies. These structures are cut by subvertical veins with typical banded “boiling” textures, bidirectional crystallization features and high gold grades (often over 100 g/t), attesting repeated fluid supply generating vein propagation in the hanging wall by a hydrothermal system with a cyclic fault valve behavior.

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Mineral alterations and gold assemblages in Krassen HS epithermal deposit, Panagyurishte ore region, Bulgaria

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The Krassen HS epithermal Cu-Au deposit is hosted in Krassen-Petelovo volcano-plutonic complex, located in a 80–100 m thick enargite-rich breccia zone trending 110–115° and dipping 50–65° to NE. Phyllic, propylitic and advanced argillic alterations are the most commonly observed in association with lens-like fault controlled ore bodies. Phyllic (quartz-sericite), propylitic (epidote-chlorite-albite) and advanced argillic (sericite-diaspore, quartz-pyrophyllite, quartz-kaolinite-dickite, quartz-topaz, quartz-alunite) host rock alterations are commonly observed around the ore bodies according to our XRD data. Drone supported and field mapping outlined clearly all hydrothermal alteration styles and structural domains.

The enargite-chalcopyrite-bornite mineralization is dominating at the western part of Krassen deposit. Massive pyrite ore, replaced by chalcopyrite along the contacts, and low-grade vein pyrite mineralization are commonly observed in the eastern part of the deposit. The ore-forming processes in Krassen deposit were developed in three mineralization stages: pyrite-quartz; copper-pyrite and anhydrite-barite (Bogdanov, 2017a). The early massive pyrite-quartz assemblage is overprinted by enargite-covellite, chalcopyrite-pyrite, bornite-tennantite and galena-sphalerite-chalcopyrite assemblages. All of them are overprinted by late quartz-pyrite, pyrite-marcasite and anhydrite-barite assemblages. Enargite is abundant in Krassen deposit and together with covellite is evidence for high sulfidation style of mineralization. Native silver has also been found in late anhydrite-barite stage.

According to LA-ICP-MS data in pyrite and chalcopyrite, the following trace elements: Bi (1.79–45.92 ppm), Ge (6.19–62.84 ppm), Ga (1–170 ppm), In (1–16 ppm), Te (1–57 ppm), As (10–200 ppm) and Se (18–511 ppm) were detected, in addition to "invisible" gold as nano-inclusions. These trace elements could be used as geochemical vectors toward gold enrichment for further prospecting and evaluation of the Krassen epithermal system.

Native gold and electrum are abundant in the enargite-pyrite and galena-sphalerite-chalcopyrite rich ores (Bogdanov, 2017b). The gold fineness varies between 88.2 wt% and 99.8 wt%. At the early pyrite-quartz stage the fineness range is between 93 wt% and 96.3 wt%. In the main copper-pyrite stage the gold fineness varies between 88 wt% and 98.4 wt%. In the late anhydrite-barite stage, gold has fineness from 99 wt% to 99.5 wt%. Commonly found trace elements in the native gold and electrum grains recorded by 23 EPMA are Ag (up to 11 wt %), Cu (~2.2 wt %), Te (~0.6 wt%), Bi (up to 0.9 wt%), As (~0.1 wt%), Sb (up to 0.4 wt %) and Hg (~0.6 wt%).

Nine gold grains were recovered from stream sediments in proximity to Krassen deposit. They are small in size (180–460 µm, avg. 320 µm) with discoidal, bladed, equant and rod-like shapes as well as low (rarely moderate) degree of roundness. Surficial SEM-EDS analysis of most gold grains shows very high fineness, from 86.8 wt% up to 100 wt%. Only two of the grains indicate the presence of Ag (up to 13.25 wt%) and Cu (up to 5.39 wt%). Our study is focused on the perspectivity for further gold exploration in Krassen deposit.

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Metallogenic Evolution of Bulgaria

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The present metallogenic study is based on paleotectonic analysis, distinguishing the rocks, tectonic structures and associated ore deposits and occurrences formed during different epochs and stages in the geotectonic evolution of Bulgaria. Data from more than 1200 ore deposits and occurrences were used. The ore deposits are systematized and characterized by determining their genetic types, relationships with the ore-generating and ore-hosting rock complexes and tectonic structures, the age, and the structural, mineralogical and morphological features of the ore bodies. The Neoproterozoic–Hercynian and Alpine geotectonic and metallogenic epochs and the respective tectonic-metallogenic stages, such as ocean, subduction, rifting, collision, *etc*., are distinguished in the metallogenic evolution of Bulgaria (Popov and Popov, 2022).

The Neoproterozoic–Hercynian Tectonic and Metallogenic Epoch in Bulgaria is marked by Ocean Spreading Stage (Neoproterozoic) with podiform chromite, copper-nickel, magnetite-ilmenite and metamorphic iron ore deposits and occurrences; Subduction and Magmatic-Arc Stage (Neoproterozoic–Cambrian) with mainly iron and copper-nickel mineralizations; Collisional Stage (Ordovician–Early Carboniferous) with skarn iron and hydrothermal lead-zinc, fluorite, copper, gold, iron, polymetallic, molybdenum and uranium ores and Post-Collisional Stage (Late Carboniferous–Permian) with copper, lead-zinc, gold, molybdenum, uranium and barite deposits and occurrences.

The evolution of the Alpine Tectonic and Metallogenic Epoch in Bulgaria is marked by Intracontinental Rifting Stage (Triassic) with SEDEX (?) iron ore deposits; Ocean Rifting Stage (Jurassic) with sedimentary iron deposits; Subduction and Early Collision Stage (Tithonian–Neocomian) with hydrothermal lead-zinc and barite deposits and weathering bauxite and iron-nickel occurrences; Intra-Collisional Rifting Stage (Late Cretaceous) with variety of porphyry copper (±Au, Mo), VMS copper-pyrite (±Au), iron (±Cu) skarn, copper and polymetallic (Pb-Zn-Cu) vein and carbonate replacement type, uranium, barite, etc. deposits; Late Collisional Stage (Maastrichtian–Lutetian) with pegmatites, iron skarn and hydrothermal predominantly tungsten, molybdenum, fluorite occurrences and uranium deposits and Post-Collisional Stage (Bartonian–Quaternary) with hydrothermal mainly lead-zinc and uranium, sedimentary manganese and exogenous uranium deposits.

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Mineral composition and technological properties of Kaolin-Quartz deposit ‘Esenitzite’ Northern Bulgaria

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The Esenitzite Kaolin-Quartz deposit is located in central north Bulgaria, at the Moesian platform. The deposit is part of the Vetovo–Senovo mineragenic region, which consists of the Vetovo, Esenizite and Zlaten Dol deposits. The kaolin-quartz raw material is hosted in paleo karst structures into limestones of the Lower Cretaceous Ruse Formation.

The length of the deposit is about 6 km and its width varies between 300 m and 1200 m. It is separated in 10 parts. The thickness of the kaolin-quartz raw material is up to 90 m, and the overburden layer is about 40 m in average. The production is made by open cast method. The composition of the raw material shows a vertical zonation according to its quality and content of kaolin and quartz sand.

The mineral composition of the raw material (determined by XRD) shows that the main minerals are quartz and kaolinite, with minor feldspars, muscovite, calcite, and dolomite. The main size fractions are from 0.5 mm to 0.05 mm, representing about 85 wt% of the raw material.

Kaolinite is the main mineral in the pelitic fraction – about 88%. It is characterized by low content of Fe_2O_3 and TiO_2 and high whiteness (after heating on 1350 °C), up to 92% (average 85% whiteness). Minor minerals in this fraction are illite, quartz and felspars. Quartz sands are white, with monomineralic composition, and traces of mica, feldspars and other accessory minerals.

Different kaolin and quartz size fractions were tested for manufacture of various trade products. They have suitable chemical and technological properties for different industrial applications as porcelain, electroporcelain, fine ceramics production, foundry, glass production etc. The raw material and main trade products fractions have undergone various laboratory and industrial test to determine their properties as chemical composition, whiteness (after heating on 1350 °C), refractoriness, etc.

Enrichment of rare earth elements in coastal black sands from Kavala district, Northern Greece

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The coastal area of the Kavala district, Northern Greece, is characterized by beach placers enriched in minerals containing rare earth elements (REE) (Stouraiti *et al*., 2020). Six black sand samples have been collected from different locations over a 40 km long distance that extends from the Strymonikos gulf to the Eleftheres bay, adjacent to the Kavala pluton. The heavy mineral fraction includes amphibole, epidote, hematite, goethite, mica, allanite, garnet, titanite, zircon, monazite, ilmenite, rutile, magnetite, chlorite and thorite. The purpose of the present work is to determine the mineralogy and to comprehend the mineral chemistry of the epidote mineral group regarding the substitution mechanisms and the REE, Th and U distribution in the pattern zones.

Based on SEM-EDS and XRD analysis, allanite-(Ce) is volumetrically the most important REE- carrier, present in all samples, in a variable percentage of 2–5 wt %. Epidotes (6–38 wt %) and monazite-(Ce), -(La) (up to 2 wt %) contribute to a lesser extent to the REE content, because of their low REE content and their low presence, respectively. The ΣREE content of allanite-(Ce) varies and reaches up to 23.24 wt%, with a dominance of Ce among the other REE (La, Nd, Eu, Y). Allanite-(Ce) transitions into ferriallanite-(Ce) due to the significant involvement of Fe^{3+} (>0.5 wt%) in the crystal chemistry (Gieré and Sorensen, 2004). The ΣREE+Y content in all analyzed allanites from Kavala varies between 0.505 and 0.830 apfu. The average chemical formula of the allanite-(Ce) from Kavala is: $(REE_{0.597}Ca_{1.360}Th_{0.047}U_{0.002})(Al_{1.732}Fe^{2+}{}_{0.443}Fe^{3+}{}_{0.620}Mn_{0.052}Mg_{0.154})(Si_{2.962}Al_{0.038}O_{12})(OH)$, where $REE_{0.597}$ represents the sum of the atoms of individual lanthanides and yttrium, e.g., $La_{0.184}$, $Ce_{0.331}$, $Nd_{0.070}$, $Eu_{0.007}$ and $Y_{0.005}$. Thorium content reaches 0.081 apfu, while U is typically present in lower concentrations, up to 0.021 apfu, when it is present.

The high-resolution backscattered electron (BSE) images and several points of microanalysis within a single allanite-(Ce) crystal demonstrate the presence of darker and lighter grey domains that correspond to variations in REE, Th and U. These patterns indicate the REE decrease and the transition of allanite-(Ce) to REE-rich epidote (>0.5 REE^{3+} apfu) and finally to epidote (<0.1 REE^{3+} apfu) in single grains. In the normal zoning textures, the magmatic allanite-(Ce) occurs as a core that progressively lapses into epidote in the rim, while the patchy internal textures, with irregular limits are possibly generated by hydrothermal fluids (Gieré and Sorensen, 2004). These modifications follow the exchange mechanism $(Ca+(Fe^{3+}, Al))_{-1}$ $(LREE,Y,Th,U+(Fe^{2+},Mg,Mn))_{+1}$ to compensate for the charge imbalance in the substitution mechanism.

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The stibnite vein-type mineralization in Rizana, Northern Greece

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The stibnite vein-type mineralization of Rizana belongs to the metallogenic region of Kilkis, Northern Greece. The main host rock is the gneiss of the Vertiskos unit in the Serbo-Macedonian massif. Two magmatic bodies occur in the broader area of Rizana: the Xylopolis granite of Mesozoic age, and the Rizana volcanics, *i.e.*, rhyolite, dacite and rhyodacite of Cenozoic age. The mineralization spreads over an area of 10 km in length and 2–4 km in width, and has a potential for future exploitation. In the years 1930–1943, mining operations produced 10.000 t of ore containing 30–40 wt.% Sb and minor quantities of W. The estimated reserves are over 0.1 Mt with 30 wt.% Sb.

The mineralization forms disseminations, veinlets, and massive ore in quartz veins, which extend over 100 m in length and 10 m in width. It is tectonically controlled by normal faults, and demonstrates brittle deformation with extensive breccias. The breccias are mineralized and contain clasts of quartz and gneiss, cemented with massive stibnite. Quartz and minor barite are the gangue minerals. Hydrothermal alteration, dominated by silicification, sericitization and chloritization, has affected the gneiss in the vicinity of the veins, while supergene oxidation is evident.

Stibnite is the dominant ore mineral, but pyrite, sphalerite, chalcopyrite, arsenopyrite, and berthierite ($FeSb_2S_4$) also occur in traces. Wolframite and native antimony, arsenic and gold, have been also reported in earlier studies (Dimou, 2006). Valentinite (Sb_2O_3) and Fe-hydroxides are the main products of the supergene oxidation. ICP-MS analyses of selected ore samples showed a relative enrichment in As (up to 1282 ppm), Cu (up to 495 ppm), W (up to 331 ppm), Li (up to 54 ppm), Ga (up to 21 ppm) and Tl (up to 14 ppm). Au (up to 22 ppb) and Ag (up to 160 ppb) are found in traces.

The study of the fluid inclusions in quartz of syn-mineralization stage, showed only one primary type, with liquid rich inclusions. They contain a vapor phase of 20–30% by volume, which homogenizes into the liquid phase. Based on the first melting temperatures (~ –22 °C), the only constituent of the fluid is NaCl. Microthermometric results showed low to moderate salinities (6.6–8.8 wt.% equiv. NaCl) and relatively low homogenization temperatures (217–254 °C, with a maximum at 220 °C).

These conditions indicate an epithermal hydrothermal system, formed by mixing of magmatic fluids with meteoric water, at hydrostatic pressures from 23 bar to 40 bar and a depth of up to 400 meters. The magmatic origin of the fluids is also confirmed by the presence of wolframite and the elevated concentration of W. The adjacent Cenozoic volcanics of Rizana were probably the sources of the magmatic fluids and the shear zones enabled the ascending of magmas and the circulation of hydrothermal fluids.

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Geochemistry and laser ablation mineral chemistry of pyrite and sphalerite from the epithermal veins overprinting the porphyry type mineralization at Aspra Chomata, Kassandra mining district, Northern Greece

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The epithermal vein mineralization at Aspra Chomata (Kassandra mining district, NE Chalkidiki) is related to the porphyritic phase of the Stratoni granodiorite, which intruded the footwall of the Stratoni fault during Oligocene. Magma emplacement in upper crustal levels led to the development of the porphyritic phase, which is associated with distinct hydrothermal alterations. The potassic alteration is associated with pyrite + chalcopyrite, while the overprinting chloritic-sericitic and sericitic alterations are related to pyrite. In the late sericitic alteration, pyrite is hosted in D-type veins. The assemblage pyrite + sphalerite + boulangerite ± arsenopyrite ± galena ± chalcopyrite ± tennantite is associated with a late overprinting epithermal event and is hosted in sheeted base metal sulfide veins. Bleaching and kaolinization of the granodiorite porphyry are ascribed to the epithermal stage.

The analyzed bulk samples from the epithermal veins are enriched in precious, critical and rare metals and metalloids: Sb (<0.40 wt %), Cd (<1180 ppm), Ag (<610 ppm), Hg (<32 ppm) and Au (<3.1 ppm), compared to the analyzed samples from the potassic and sericitic alterations of the granodiorite porphyry. In the epithermal vein mineralization, pyrite and sphalerite were first deposited. Pyrite crystallization continued resulting in overgrowths on sphalerite and in the development of oscillatory zoning. Minor euhedral arsenopyrite is found as inclusions in pyrite, while galena, chalcopyrite and tennantite appear in pyrite interstices. Boulangerite occurs as replacements in pyrite and sphalerite, as well as between quartz grains associated to the syn-mineralization stage.

Based on LA-ICP-MS analysis, pyrite from the epithermal veins incorporates base (As, Cu, Pb, Zn), precious and critical (Ag, Au, Co, In, Sb, Ti) metals and metalloids as stoichiometric substitutions or as solid solutions in specific growth zones. Pyrite exhibits oscillatory zoning and incorporates significant contents of As, which are correlated with Au and Ag. Gold may be related to nanometer-sized inclusions found in pyrite. The uncorrelated contents of As and Pb, and of Sb and Zn indicate the random incorporation of these elements as solid solutions in specific growth zones enriched in As. Pyrite, contains nano-scale inclusions of boulangerite.

Sphalerite includes Mn (<7253 ppm), Cd (<1933 ppm), Cu (<809 ppm), Sn (<128 ppm), Ag (<52 ppm), as well as traces Ga, Ge, Hg, In, Nb and W, which are hosted as solid solutions. The absence of Co and the In depletion, coupled with the Ga and Ge contents indicate that sphalerite was formed under low temperatures (Cook *et al.*, 2009). Hg and W were precipitated in sphalerite rather than in co-crystallizing pyrite. Sb contents in sphalerite may be related to nano-scale inclusions of boulangerite. In addition, chalcopyrite is interpreted to be incorporated in sphalerite. Despite the restricted presence of the epithermal veins at Aspra Chomata, in the broader area there are several veins of this style (*e.g.* Vina, Zepko).

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Geology, mineralogy and geochemistry of the metamorphic rock- and quartz-hosted polymetallic vein mineralization at Kolchiko, Serbo-Macedonian Massif, Northern Greece

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The Kolchiko metamorphic rock- and quartz-hosted polymetallic vein mineralization is located in the Kilkis ore district in the Serbo-Macedonian Massif, Northern Greece. Mineralization styles include polymetallic massive and quartz veins, quartz-pyrite veins, as well as disseminations and aggregates occurring in thin shears in mica-schist. Northwest trends characterize all the vein sets, which were formed following the tectono-metamorphic evolution of the Serbo-Macedonian Massif. The formation of the polymetallic massive veins was associated with ductile to brittle deformation and slightly preceded or was contemporaneous to the Eocene to early Oligocene retrograde greenschist facies metamorphism. Under these metamorphic conditions doleritic intrusions and milky quartz-chlorite veins were also emplaced at Kolchiko. The polymetallic quartz veins and the quartz-pyrite veins were developed under the subsequent brittle deformation. Their formation is most probably related to the development of the late Oligocene to early Miocene dextral strike-slip fault zone along the western edge of the Serbo-Macedonian Massif.

The early polymetallic massive veins contain arsenopyrite + pyrite + chalcopyrite + galena + pyrrhotite ± galenobismuthinite ± native bismuth ± native gold ± titanite ± ilmenite ± rutile ± uraninite. They are subdivided into arsenopyrite- and pyrite-dominated veins. The subsequent polymetallic quartz veins include pyrite + chalcopyrite + arsenopyrite + galena + sphalerite + pyrrhotite ± native bismuth ± hessite ± tellurobismuthite, while the quartz-pyrite veins accommodate pyrite ± chalcopyrite. Quartz is the gangue mineral in these mineralized veins. Disseminations and aggregates of pyrite occur in restricted hydrothermal halos, where alteration assemblage includes sericite, quartz and chlorite. The arsenopyrite geothermometry and the occurrence of galenobismuthinite and native bismuth in the polymetallic massive veins suggest formation temperatures varying between 240 °C and 444 °C. Oxidation related to supergene processes resulted in the formation of goethite, scorodite and covellite in the polymetallic massive veins, as well as hematite, anglesite and bismite in the polymetallic quartz veins. In the polymetallic massive veins arsenopyrite and pyrite exhibit porphyroblasts and 120° dihedral angles due to annealing related to the overprint of metamorphism, and cataclastic textures ascribed to brittle deformation. Open filling textures and crack and seal processes are ascribed to the formation of the polymetallic quartz veins and to the quartz-pyrite veins, respectively.

The bulk geochemical analysis of the polymetallic massive veins revealed that they are enriched in Au, Ce, La, U and W, relatively to the polymetallic quartz veins, which include higher contents of Ag, Bi, Cd, Co, Ga, In and Te, as well as of Gd, Nd, Se, Sm and Th. Arsenic (<37.09 wt.%) and Au (<9.2 ppm) are significantly incorporated in the polymetallic massive veins. The quartz-pyrite veins are more depleted in trace elements compared to the other vein sets. They show minor enrichment in Au, Bi, Sb and Te.

The metamorphic rock- and quartz-hosted polymetallic vein mineralization at Kolchiko belongs to a distinct group of mineralization occurring along the western border of the Serbo-Macedonian Massif in Northern Greece. This group comprises veins hosted in metamorphic rocks (*e.g.* at Laodikino and Drakontio) ascribed to shearing and to dextral strike-slip fault zones. These vein sets could be considered as promising exploration targets for precious (Ag, Au) and critical metals (Bi, Cd, Co, In, Sb, Se, Te, W).

Session GT11

Energy resources (hydrocarbon, geothermal)

Conveners:

Miloš Markič, Nikola Botoucharov

The thermal maturity of the organic matter in sedimentary rocks in the area of East Herzegovina (Bosnia and Herzegovina)

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East Herzegovina area belongs to the External Dinarides of Bosnia and Herzegovina and is part of a Carbonate platform. The thermal maturity of the organic matter of the Triassic, Jurassic, Cretaceous, Paleogene, and Neogene sequence was studied, using much more samples than in the previous study (Aleksić *et al.*, 2021). Thermal maturity determination was performed using organo-petrographic analyses, including vitrinite reflectance, as well as T_{max} parameter from the Rock-Eval pyrolysis. The Rock-Eval 6 apparatus was used to analyze cca. 100 surface samples. Total of 23 samples were selected for a detailed microscopic analysis and for the vitrinite reflectance measurements. The samples are mainly gray to dark-gray laminated limestone and marl with a high content of kerogen, some free hydrocarbons (bitumen) and coal particles. The petrographic composition is characterized by carbonate and clay minerals with significant content of pyrite, vitrinite, inertinite, lamalginite, bituminite and especially granulated solid bitumen in the cracks.

The HI-T_{max} plot from the Rock-Eval pyrolysis shows that Triassic and Jurassic sedimentary rocks contain kerogen type II and II/III, with T_{max} values from 404 °C to 460 °C. The analyzed Cretaceous samples mainly contain kerogen type I, with low amount of kerogen type II, and have extremely low T_{max} values – from 397 °C to 414 °C. The Paleogene rocks contain kerogen type III, with T_{max} values from 410 °C to 438 °C, while the analyzed Neogene (coal) sample also contain kerogen type III and T_{max} of 411 °C.

The results of vitrinite reflectance, which is a more reliable method for determining the thermal maturity, show that the analyzed Triassic sediments are in the catagenetic stage, with the vitrinite reflectance from 0.58% to 0.78% Rr. The Jurassic samples with vitrinite reflectance values from 0.58% to 0.65% Rr also imply early mature stage, as well as the analyzed Cretaceous sediments, whose values are somewhat lower – from 0.53% to 0.54% Rr. The Paleogene and Neogene samples are characterized by a reflectance of 0.38% and 0.34% Rr, respectively.

It was interesting that most of the obtained vitrinite reflectance results are not in good correlation with too low T_{max} values. That is probably the consequence of specific kerogen type, but also of the bitumen alteration at surface conditions. It is concluded that altered bitumen does not distill at usual temperature anymore during pyrolysis (300 °C; peak S1), but at much higher temperatures – thus making significant overlap of S1 and S2 peaks (S2 peaks widening). That leads to the anomalous decrease of the T_{max} values, especially in the Cretaceous samples, and also to certain „increase" of generative potential (S2) and hydrogen index (HI).

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Theoretical and applied principles of forecasting, prospecting and exploration of hydrocarbons within onshore and offshore areas of Ukraine by innovative geological-structural-thermo-atmospheric-hydrochemical research approach

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According to the geological-structural-thermo-atmo-geochemical methodology and the hydro-biogenic-mantle concept the regularities of space-time functioning of fluid-conducting hydrocarbon systems are substantiated. Fluid-dynamic models and criteria for forecasting and optimization of prospecting and exploration of oil and gas deposits of Ukraine gave been developed. The modern structural plan of the sedimentary complex is composed mainly of fragments superimposed on the Eastern European paleocraton by a system of paleorifts of the Cretaceous-Cenozoic age and boundary depressions. According to the systematic analysis of geological, stratigraphic, litho-facies, morphostructural, tectonic, geodynamic, thermometric, geophysical (in particular 3D seismic) data, the geological structure and regularities of geochemical composition of hydrocarbons have been defined.

In the oil- and gas-bearing provinces of Ukraine, according to stratigraphic, formational, sedimentological, geodynamic and morphostructural criteria, the productive horizons of Meso-Cenozoic sediments are defined. They are associated with the industrial and non-industrial deposits of gas, gas condensate and oil. The predictive value of the regularities of spatio-temporal timing of breaks, unconformity is substantiated, with which hydrocarbon stratigraphic traps are connected. An important prognostic factor is the fans of paleorivers. They impact on the stratigraphic structure of lithostratons both onshore and offshore. These morphostructural elements reproduce the conditions of sedimentation and regularities of modern tectonic, geodynamic, morphologic structure and criteria for substantiation of perspective areas of oil and gas accumulation associated with unconventional traps: clinoforms, olistostromes, erosions forms and paleodelta of the Black Sea. Their relationship with the oil and gas basins with the giant hydrocarbon deposits of the Crimean, Caucasus and Caspian regions is described.

The issue of the fuel and hydrogen energy is being developed. According to the multi-vector system approach to theoretical and applied problems of the cycle of matter in nature, where hydrogen is an energy and genetic component of lithosphere processes, forecasting and search system technology and criteria for distribution of hydrocarbon accumulations and hydrodynamic phenomena are substantiated. Areas of hydrogen and helium concentrations are mapped within the perspective licensed oil and gas structures. These areas with high concentrations of hydrogen and helium are of undoubted exploratory interest of geological research as phenomena of energy source and geoecological forecasts. The location of oil and gas provinces serves as a search prerogative in the placement of renewable biogenic sources of hydrocarbons as initial products of organic compounds and biochemical processes confined to river systems, deltas, estuaries, canyons. The anomalous zones of hydrocarbon degassing have been mapped for the purpose of detailed forecasting and prospecting for industrial hydrogen accumulations.

Software and specially developed programme complexes protected by the State Patents of Ukraine and Certificates have been used for the effective implementation of the direct search technology within onshore and offshore areas of Ukraine.

The research technology has been implemented (success rate over 90%) at 165 fields during forecasting and exploration works, both onshore and offshore in the Black and Azov Seas, and within the sites of the Eastern, Western, Southern oil and gas regions of Ukraine, impact structures, and coal fields. In order to increase the energy potential of Ukraine recommendations for drilling of more than 100 oil and gas fields have been prepared.

Lower–Middle Jurassic source rocks in North Bulgaria (south central and western parts) – review from the basin and Rock Eval analyses

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The territory of North Bulgaria includes two major tectonic units – Balkanides (the segment of the East-European Alpine orogen) and its foreland – Moesian Platform. The study area is located in the South Moesian platform margin (SMPM), central and western parts of the Forebalkan and their neighboring border zones. The SMPM is the most subsided part or southern slope of the Moesian platform between the Alpine thrust front of Balkanides and South Moesian fault.

The enriched in organic matter intervals of Lower–Middle Jurassic sequence (total thickness up to 1.5 km) are considered as fair to very good source rocks for the discovered oil fields in North Bulgaria. The present study is a continuation of the last decade's efforts of scientists to evaluate the hydrocarbon potential of this section through different geochemical methods. Therefore, the 32 well-core and outcrop samples of the Bachiishte Fm. (J_1 Hett–Sin), Bukorovtsi Mb. of the Ozirovo Fm. (J_{1-2} Plb–Aal) and Stefanets Mb. of the Etropole Fm. (J_2 Aal–Baj), consisting mainly of shales, siltstones and marls, are investigated by basin analysis and Rock-Eval pyrolysis.

Mesozoic geodynamic evolution of the region is dominated by extensions and failed rifting (P_2–T_1, T_3, J_1, and K2), interrupted and followed by compressional phases (T_3, K_2, Eoc_2). Increased tectonic subsidence is observed during rifting cycles and north-vergent advancing of Alpine thrust-fold belt. Basin analysis clearly demonstrates that post-rift stages are favorable for sedimentation of relatively deep-water source rocks in the study area. Jurassic sedimentation began in the Hettangian–Sinemurian with thin very shallow-water clastic deposits of the Bachiishte Fm. Then Pliensbachian–Early Aalenian sedimentation of the Ozirovo Fm. reflects mainly shallow marine conditions. The observed increase of clay content in the carbonates of Bukorovtsi Fm. argues for some deepening of the depositional environment. The Etropole Formation is heterogeneous, but the lower part with the Stefanets Mb. is dominated by shales showing that the basin evolution reached its deepest-water pelagic development in uppermost Aalenian–lower Bajocian stages.

The obtained total organic carbon (TOC) contents are in the range of 0.14–3.31 wt.%. The highest values are registered for the shales of the Stefanets Mb. and the Bachiishte Fm., as for the latter this might be due to the presence of thin coal seams. Total inorganic carbon (TIC) is recorded in low amounts in most samples (<1 wt.%) except for the samples of the Bukorovtsi Mb. and a few from the Bachiishte Fm. and the Stefanets Mb. Total sulfur (TS) contents are high (>2 wt.%) for the sediments deposited under marine conditions and very low (<0.3 wt.%) especially for the outcrop samples, because the sulfur might have been lost during weathering. The values of S_1 and S_2 are between 0.01 and 3.49 (mg HC/g rock). T_{max} varies from 418 °C to 610 °C and PI is <0.4. HI argues for kerogen type III and II/III. It is low for the rocks in the postmature stage. The fair to very good quantity, low quality, as well as the high level of thermal maturity of the organic matter, assume remaining gas-prone generation potential of investigated source rocks.

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Gas generation potential of the organic matter on the example of the sedimentary layer of the Ukrainian Carpathians (Western oil and gas region)

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In order to establish the kerogen gas generation potential, on the example of sedimentary layer of the Ukrainian Carpathians from the Western oil and gas region of Ukraine, a method of modeling the composition of geochemical systems were applied. This method is based on the determination of equilibrium temperatures, depths and methane generation of kerogen on the ratio of butane isomers to the amount of methane. The range of values of the i-C_4/n-C_4 coefficient in the experiment and the simulation results coincide with high accuracy and are between 0.4 and 3.2, while in the experiment this range is 0.3–3.4.

Based on the results of comparison of experiments and calculations, we conclude trends similarity and a tendency for the i-C_4/n-C_4 coefficient to increase with increasing methane yield. In addition, this coefficient shows a monotonic dependence on the equilibrium temperature.

The ratio of butane isomers established the equilibrium temperature of formation of the gas/kerogen system in the deposits, assuming correctly that the kerogen is in contact with the gas. Equilibrium formation temperatures for two heat fluxes – 75 and 100 mW/m^2 were calculated.

The distribution of equilibrium temperatures of gas formation of hydrocarbon fields in the Western oil and gas region shows certain patterns. First of all, areas with high values of equilibrium temperatures (400–600 °C) are clearly distinguished. These areas are concentrated in Boryslav-Pokutsky oil and gas district, but on the other hand the gas fields of Bilche-Volytsky oil and gas district are characterized by significantly lower values. The two areas with the highest values of equilibrium temperature with sufficient accuracy represent the location of the intersections between regional faults – Sambir-Nadvirnyansky with Tyachiv-Nadvirnyansky in the area of Nadvirna and Sudovo-Vyshnyansky with Sambir-Nadvirnyansky.

Determination of the amount of methane V_{CH4} (l or dm^3) released from a unit mass (kg) of kerogen was carried out according to the formula:

$$V_{CH4} = V_m\,(Ae^{0.5/B} + C)\,({}^{nCH4}/\textstyle\sum n_i);$$

where V_m is the molar volume of an ideal gas (22.4 dm^3/mol), A and C are dimensionless coefficients equal to 0.1594 and 0.0494, respectively, B is the dimensionless ratio of volume fractions of isobutane to n-butane, n_{CH4} is the volume fraction of methane in gas and $\sum n_i$ is the sum of molar fractions of all components of the gas mixture for which the measurement was performed. The above formula gives reliable results only in the butane isomer ratio range of 0.3 to 3.5.

The research established that kerogen, which was the source material of hydrocarbons of Boryslav-Pokutsky oil and gas region, has practically exhausted its gas generation potential. The center of the areas of maximum catagenetic dehydrogenation of kerogen are the Hvizdetske and Pasichnyanske oil fields, as well as the Pivdenno-Hvizdetske oil and gas condensate field, which are genetically and geographically related. Another center of kerogen depletion is located in the area with the center near the North-Dolynske oil and gas condensate and Dolyna and Vyhodsko-Vytvytske oil fields.

Lithofacial and hydrogeological features of the Upper Jurassic sediments of the Ukrainian Precarpathians in terms of oil and gas potential

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In Ukrainian Precarpathians, the Upper Jurassic sediments form a single carbonate reefal complex. It is represented by lateral series of reefal facies: fore-reef, reef and back-reef sediments of the Oxfordian, Kimmeridgian and Tithonian–Berriasian ages. There are also lagoon-evaporite sediments of early Kimmeridgian age. The displacements of the facial belts depend on the eustatic changes and tectonic processes. The surface is eroded, karstified, and is mainly covered by Miocene anhydrites, which are favorable as a seal in the hydrocarbon traps.

The reefal formations are characterized by a standard distribution of facies. Lithology and organic composition, structural and textural features and secondary changes that determine the reservoir properties of carbonate rocks depend on facial variety.

Hydrogeochemical composition of formation waters of the Upper Jurassic complex are determined by geochemical conditions in sedimentary basin, duration and intensity of ancient infiltration stages of paleohydrogeological development.

The main factors of hydrocarbon fields' formation are the peculiarities of carbonate sedimentation, as well as their subsequent geological history under the influence of geodynamic processes. The establishment of sedimentation and diagenesis conditions, lithofacial composition, structure of these formations, hydrodynamic and hydrogeochemical conditions are a reliable basis for the efficiency of the geological prospecting. As a result of the studies conducted, the connections between lithofacies distribution and hydrogeochemical peculiarities of the Upper Jurassic carbonate complex of the Ukrainian Precarpathians are determined. The sedimentary-hydrogeochemical model of the northwestern part of the Upper Jurassic carbonate complex in Precarpathians demonstrates the impact of the lithology, sedimentation conditions and post-sedimentation processes on the hydrogeochemical peculiarities of the formation waters.

The general hydrogeochemical background is formed by sedimentogenic thalasogenic waters and characterized mainly by high salinity waters (Cl-Ca-Na and Cl-Na types), occasionally magnesium chloride Cl-Mg-Na with different degrees of metamorphism. The coefficient of sulfation (rSO_4x100/rCl) is from 0.01 to 3.3.

The comprehensive interpretation of lithofacial and hydrogeochemical data allow to ground distinguishing hydrogeochemical zonality related to facies and corresponding lithological peculiarities. The eroded surface of the Upper Jurassic rocks and areas of partial erosion and distribution of lagoon-continental sediments are characterized by formation waters of low salinity of different genetic types, mainly calcium chloride (Cl-Ca), and less often sodium hydrocarbonate (Hyd-Ca-Na).

Regional hydraulic vectors are directed both from the Western and Eastern European platforms in the direction of Carpathian Foredeep Inner zone (infiltration system energy) and from the side of subtrust of Inner zone in the direction of platforms (elisional system energy). Reef structures are located in the zone of hydraulic equilibrium of infiltration and elisional water drive systems, which created favorable fluid dynamic background for sufficient hydrodynamic protection and localization here of the hydrocarbon fields.

The local hydraulic vectors caused by the formation pressure growth in the direction of transverse tectonic faults and a clear connection between the local reef structures with areas of piezominima have been established. Fluid discharge areas characterized by local piezominima at the background of regional hydro pressure fields are perspective for oil and gas.

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Oil and gas in the Mura-Zala Basin (Pannonian Basin System, North-East Slovenia)

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The most prospective geological area for oil and gas in Slovenia is the Neogene Mura-Zala Basin situated in the SW part of the Pannonian Basin System. Within the Mura-Zala Basin, Middle-to-Upper Miocene strata of the Petišovci area have the most known potential for oil and gas resources and reserves. Oil and gas were discovered in this area in 1942 – as an extension of the already known Lovászi field in the neighbouring Hungary. Also in Croatia, there were known oil and gas fields at Selnica and Peklenica, having been exploited already since the mid of 19th century.

Oil- and gas-bearing reservoirs of the Petišovci area (7×2 km wide) are divided into two bed-sets, the shallow and the deep one. Both bed-sets consist of alternating 10–40 m thick impermeable marls and porous oil- and gas-bearing sandstones of low porosity – below 15%, decreasing with a depth to ca. 7 % only. The Petišovci hydrocarbons are therefore characterized as the tight ones. Shallow oil and gas reservoirs occur in 4 main horizons in a depth interval from 1000 to 1800 m. They were exploited in the 1950s (mostly oil) and 1960s (mostly gas). Nowadays, they are depleted – offering a possibility for *e.g.*, storage of imported natural gas or of CO_2. The deep reservoirs start at a depth of 2200 m and are developed as ~17 tight gas-bearing (“A-Q”) layers down to a depth of 3550 m (deepest wells), maybe even more. The deepest well was Mg-6 (3858 m) drilled in 1985 being also the only one reaching the pre-Tertiary carbonate basement.

The Petišovci gas is composed of 85–90% methane. Its sulphur content is below 0.05%. Based on recent carbon isotopic investigations, it is clearly thermogenic gas. Density of oil varies between 800 and 825 kg/m^3.

The whole set of the Petišovci reservoirs is a typical antiform setting formed by lifting between the Donat and Ljutomer reverse faults. It is interpreted that hydrocarbons were generated in an originally synform setting (to reach the oil and gas maturity windows), which was later lifted – lifting had lasted still in the Pontian times as known from the coal measures antiform structure in the uppermost Mura Formation. This lifting with accompanying fissure system enabled migration of hydrocarbons upwards into porous sandstone reservoirs in which the hydrocarbons were trapped by impermeable marl layers.

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Reservoir Characterization of the Gas Condensate Field F03-FB, Netherlands

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Reservoir characterization is a key element of an economic plan to develop a potential field in a safe and cost-effective environment. Of great necessity are studies aiming to create static models and test their validity using production data; however these are time and money consuming.

This study uses an open access dataset to interpret the main reservoir, the Lower Graben Formation, within F03-FB field in the North Sea, to create a static model using porosity-permeability data from wells and seismic attributes to populate the model, and to analyze the production history records to assess production decline. The associated reservoir is Upper Jurassic sandstone interbedded with mudstones. Based on detailed sedimentology on cores (information gathered from the post-wells studies) and log interpretation, the reservoir facies are interpreted as distributary channels and crevasse splay deposits with porosity up to 24% and horizontal permeability in a range of 10–500 mD. The crest of the structure is at 3047 m TVDSS (True Vertical Depth Sub Sea) and the net reservoir thickness is 100 m. Field size is approximately 10 km^2.

Although discovered in 1974, production started in 2004. Analysis of the production data indicated a life expectancy of 10 years. Production of field F03-FB stopped in 2021, which means that the reservoir was producing above expectations. The field was depleted via 10 wells.

Acknowledgements. The study is part of the MSc thesis using data provided by the Dutch Ministry of Economic Affairs under the Article 123 of the Mining Act. Seismic dataset, well reports and logs are available on the website: www.nlog.nl.

Fluid and rock properties characterization using seismic reconnaissance attributes in Bulgarian Black Sea shelf

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In Bulgarian Black Sea shelf some gas fields are discovered in the sediments with Palaeocene–Maastrichtian Age. In this study, the Amplitude Vs Offset analysis is carried out and Extended Elastic Impedance is used to predict fluids and lithology properties. Thus, in these special cases, amplitude vs. offset (or reflection angle) can significantly de-risk the existing Palaeocene prospects and focusing on the Miocene–Oligocene section where some 5 prospects have been identified. By examining variations in amplitude with angle (or offset), we may be able to unravel lithology and fluid effects at the top of a reservoir. This approach allows a better distinction between seismic anomaly caused by lithology and those caused by fluid content (hydrocarbon). Then seismic modelling is used to determine what sort of seismic response in terms of AVO to expect at the depth of interest in the study area. There are basically five classes or types of AVO responses, and in the study area Class 1 and Class 2 are defined in the Miocene/Oligocene prospects. Brine filled reservoirs and Conglomerates have a Class 1 AVO response whilst Gas filled reservoirs show Class 2 AVO responses. EEI has capability to estimate elastic parameters such as S-wave impedance, Vp/Vs ratio, bulk modulus, shear modulus, Poisson`s ratio and so on. In current study simultaneous inversion testing is done and looking at all the wells together, Poisson’s ration is the most promising fluid and lithology indicator showing good separation between water and gas responses although there is some overlap. A projection about a EEI38deg through brine points gives a useful separation of brine, 10% gas and 90% gas reservoirs. However, the amplitude of the resulting projection is still low, which may make it difficult to resolve fluid variation once seismic noise has been added.

Session GT12

Hydrogeology

Conveners:

Aleksey Benderev, Peter Gerginov, Zoran Stevanović

Use of multivariate statistical analysis for the identification of the hydrochemical processes in the Tirana – Fushe Kuqe alluvial aquifer, north-western Albania

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The Tirana–Fushe Kuqe alluvial aquifer extends from Tirana at SE to the Mat River at NW, covering an area of over 300 km^2 in central-western Albania, and represents an important basin for drinking water supply of about 1/3 of the country population. In this study, 71 groundwater samples were collected over the Tirana-Fushe Kuqe alluvial aquifer which were analyzed for 11 parameters (pH, K^+, Na^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, TH and TDS). Both geochemical conventional (Piper and Chadha diagrams) methods of groundwater classification and multivariate statistical (principal components analysis – PCA and hierarchical cluster analysis - HCA) methods were applied to the dataset to evidence geochemical processes controlling groundwater geochemistry evaluation through the aquifer. The conventional geochemical methods revealed four (G1–G4) hydrochemical groups where the dominant group is G2 whose samples are from unconfined to semiconfined recharge zone and the majority of them have Ca–Mg–HCO_3 groundwater. Group G3 includes samples from the confined coastal aquifer having Na–Cl groundwater. Group G1 includes three groundwater samples of Ca–Mg–SO_4 from the central part of the aquifer, while group G4, whose samples are spatially located between G3 and G2 zones, has Na–HCO_3 groundwater. The first four components of the PCA account for 85.35% of the total variance. Component PC1 is characterized by very high positive loadings of TH, Ca^{2+}, and Mg^{2+} suggesting the importance of dissolution of carbonate rocks in the aquifer recharge zone. Component PC2 is characterized by very high positive loadings in Na^+, K^+, and Cl^- and moderate to high loadings of TDS revealing the involvement of seawater intrusion and diffusion from clay layers. Because of their characteristic loadings, the first two components are defined as the "hardness" and "salinity", respectively. The HCA produced four geochemically distinct clusters, C1–C4. Samples of cluster C1 are from the coastal confined aquifer and their groundwater belongs to the Na–Cl type. Samples from cluster C2 are mostly located in the south and east recharge areas and the majority of them have Ca–Mg–HCO_3 groundwater, while samples from cluster C3, which are located in the northeastern recharge zone, have Mg–Ca–HCO_3 groundwater. Finally, cluster C4 includes two groundwater subgroups having Na–Cl–HCO_3 and Na–Mg–Cl–HCO_3 groundwater in the vicinity of cluster C1 and Na–HCO_3–Cl and Na–Mg–HCO_3–Cl groundwater next to cluster C2 and C3.

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Hydrogeology development in some core CBGA countries – a centenary overview

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Many applied geological disciplines experienced significant development in the hundred years that passed since the founding of the Carpathian-Balkan Geological Association (CBGA). This article focuses on hydrogeology and the achievements of “core” countries of the Carpathian-Balkan region, *i.e*., the countries of origin of four famous founders of the CBGA (former Czechoslovakia, Poland, Romania and former Yugoslavia), as well as Bulgaria as the host of the CBGA congress. When the CBGA was founded (in 1922), hydrogeology was still a young discipline with just a few decades of development behind under its belt. Although the first information about groundwater, and mineral waters in particular, can be found in the works of experts in medicine, chemistry and physics as early as at the beginning of the 16th century, most CB countries view the appearance of certain milestone books on groundwater as the actual birth of hydrogeology. Such books were written by relevant authors just few decades prior to the founding of the CBGA, *i.e*. 45 years in Czechia, 27 years in Romania and 25 years in Serbia. In its early stages, hydrogeology mainly belonged to the “classical” geological schools, *i.e*., groups of natural sciences. But over time, and due to its multidisciplinary and practical character, certain branches that studied the origin, distribution and utilisation of groundwater become oriented toward technical and engineering sciences as well. Still, this dual character of hydrogeology did not limit its further expansion or successful results achieved by groundwater experts in various fields. Hydrogeologists from the national Geological Surveys, but also from universities’ research groups and specialised companies, created hydrogeological maps of different scales and designed and prepared technical documentation for various engineering solutions in water supply, irrigation, mine dewatering, capture and use of mineral waters and geothermal energy. The work of hydrogeologists from the CB region in third countries (Africa, Asia and South America) was highly intensive, enabling the construction and completion of many engineering projects, including large dams and water infrastructure projects. To conclude, although we were born and raised in different political and cultural environments, we can find many similarities in the countries of central and South-East Europe related to the successful development of hydrogeology, as one of the main applied geological disciplines.

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Influence of geological substrate on runoff formation, a case study: small river catchments in southeastern Serbia of similar size and with comparable pluviographic regimes

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We are witnessing climate change globally and regionally, as well as on a local level. As a result of the expected climate change impact on Southeast Europe, first there is a redistribution of precipitation within the year (frequent extreme events) and then an increase in temperature, which already has a significant effect on evapotranspiration and runoff formed in a particular catchment area. In addition to climatic factors, the geological structure (*i.e.*, the hydrogeological characteristics of the catchment area itself) is of great importance in the formation of runoff. Catchment areas of similar size and under the influence of comparable pluviographic regimes were chosen to define the effect of the catchment's geological substrate on the formation of runoff. Two pilot areas in southeastern Serbia were selected, the first relating to the Vlasina River and the Lužnica, its largest tributary, and the second the Toplodolska and Dojkinacka rivers.

In 1955, in the village of Svodje, the Hydrometeorological Service of Serbia established water level and flow gauging stations on the Lužnica, about 1 km upstream from the mouth of the Vlasina, and on the Vlasina, just before the mouth of the Luznica River. These stations have been in service since their inception. Common to the two gauging stations is that they have relatively the same length of observation time-series and their catchments are almost of the same size (the Luznica at Svodje 318 km^2 and the Vlasina at Svodje 350 km^2). They are neighboring catchments, and their pluviographic regimes are similar.

Monitoring of the Dojkinacka River runoff is conducted at Visocka Rzana, where the gauging station is located only 250 m upstream from that river's junction with the Visocica. Observations began in 1981 and continued with almost no interruption to the present day. At the Topli Do gauging station, which monitors runoff from the catchment of the Toplodolska River, water level observations and flow measurements have been performed since 1990, albeit with frequent interruptions. The catchments are of similar size (hydrological areas about 135 km^2) and they are also under the influence of a similar pluviographic regimes (adjacent catchments).

The following analyses were undertaken to define the effect of the geological substrate of the catchments on the formation of runoff. The hydrographs of adjacent catchments were compared and showed that in mostly karst catchments the peaks were lower and lagged behind flood wave peaks in mostly non-karst catchments. Autocorrelation analyses indicated that largely karst catchments had longer memories than non-karst catchments. The base flow index of the catchments with karst was much higher than of those without karst. Finally, water balance equation calculations revealed that the runoff coefficient of non-karst catchments was considerably higher than of those that featured carbonate sedimentary rocks.

On the temperature regime of karst springs in Bulgaria – status and problems

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In most of the observed karst springs in Bulgaria, groundwater temperature has been systematically determined over the years. Until now, this information has not been the subject of research; it allows drawing a conclusion about the formation and movement of groundwater, especially in the karst environment. The relatively regular measurement of spring temperatures started in 1959. The present study aims to summarize and evaluate the quality of data from water temperature measurements and proceed with their processing. The information on more than 140 karst springs was reviewed. It was found that the temperatures of the groundwater vary within different limits according to the type of the karst and altitude of their watersheds, the conditions of recharge, and the hydrodynamic zone they drained. With the lowest temperature in the range of 4–9 °C are springs whose drainage watersheds are located in the highest part of the mountain with a significant snow recharge of the groundwater (Yazo and Kyoshka). They are situated on the base of the Pirin Mountain like Kleptuza (Velingrad) and Mugla springs in the Rhodopes. With a relatively elevated temperature – around and above 20 °C are ascending springs whose waters come out from deep (Devnia springs), the springs near the villages of Musomishta, Dolni Rakovets, Kuklen, and Opitsvet. The springs with temperatures between 8 °C and 15 °C are predominant. The average values of the water temperature for certain periods are compared, as well as with the air temperature. Different amplitude of change in the temperature of the springs was also established. With a relatively constant temperature (amplitude up to 2 °C) are the springs draining the saturated zone of the karst massif with significant volumes of water – the springs near Krachimir, Opitsvet, Stoyanovo, Trivoditsi, or springs along faults from deep – the Devnia springs. With the widest range of temperature changes (over 8 °C), springs in which the “fast flow” is essential, such as the springs near Stoyanovo, near the town of Montana, Hotnitsa and others. Preliminary statistical treatments have been made for springs with continuous data series.

Several springs with different temperature regimes are selected in which the dynamics of temperature change for the period 2019–2020 were traced and compared to air temperatures. Springs recharged by rivers that drained the saturated zone (Pali Lula Village) with a temperature range of 9.2 °C to 15.8 °C were selected, a spring that drains a karst basin with the movement of water along a channel-gallery network, in the unsaturated zone with a range of 7.2–14.3 °C (Lakatnik station), a spring that drains a karst basin with the movement of water along a canal-gallery network recharged by rivers that completely lost their flow (Iskrets Village) with a range of 7.9–3.8 °C, a spring that drains water from a saturated zone with a fissure-karst character (Drugan Village) with a range of 10–14.0 °C, the spring near Trivoditsi Village is ascending, overflowing with a large saturated zone with a range of 16–17.4 °C, as well as the springs which are fully recharged by snowmelt Yazo and Kyoshka near the town of Razlog with a range of 7–10.1 °C and 5–10.3 °C. The established regularities help to clarify the factors determining the changes in the groundwater temperature and the role of the different nature of karstification in the catchment areas of the springs and the nature of their recharge.

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Karst aquifers importance and utilization – a comparative study of westernmost and southernmost parts of the Carpathian Arch

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Unconfined karst has large extensions in the elongated and "snakelike" structure of the Carpathians, especially in its marginal parts, *i.e*., Slovakia in the northwest and Serbia in the southeast. Karst aquifers of the Carpathians do not cover a large territory in either country and have an approximately equal distribution in both, of about 3,000 km^2, which corresponds to 7% and 5% of the entire territories of Slovakia and Serbia, respectively (Kullman, 1990; Stevanović and Filipović, 1994). In the Slovakian karst, the main carbonate structures are Malá and Velká Fatra, Nizke Tatry Mts., Male Karpaty, Slovensky Kras and Slovensky Raj, while in eastern Serbia the largest karst mountains are Kučaj-Beljanica, Rtanj, Svrljiške Mts., Ozren, Devica and Tupižnica. Although not of large extension, karst groundwater is one of the main sources of potable water at the national level (for about 20% of the population in Serbia, nearly 54% in Slovakia) and a very important one at the local level. Larger cities in central and eastern Serbia that utilise karst waters for drinking purposes are: Niš, with some 250,000 inhabitants, Paraćin, Bor, Pirot with more than 50,000, as well as several others with populations of 20,000 or more (*e.g*., Ćuprija, Knjaževac). The largest consumer of karst waters in Slovakia is Banská Bystrica, a city with about 80,000 inhabitants, but in the central part of the country, nearly each bigger city is supplied by karst groundwater. In both these countries, several successful engineering projects have been completed in the last fifty years to stabilise the variable regime of karst springs' discharge and ensure regular water supply. A group of wells and a horizontal gallery were drilled near Slovakian karst springs Jergaly and Biele vody, enabling over-pumping during the critical drought period of the year (Kullman, 1984, 1990). Similarly, several successful karst aquifer regulation projects have been completed in Serbia to support the supply of the cities of Niš, Bor and Knjaževac with potable water (Stevanović, 2009). Documented karst aquifer resources are similar in the Carpathian karsts of Slovakia and Serbia, amounting to some 12.5 m^3/s of the dynamic (replenishable) reserves (19.7 m^3/s in Slovakia). Besides the use of fresh karst groundwater for drinking, the use of karst mineral waters for medical and recreational purposes also has a long tradition in both countries (*e.g.* Pieštany, Bojnice, Turcianske Teplice, Trencianske Teplice, Rajecke Teplice spas, Niška Banja, Soko Banja). Thermal waters in deep, confined karst systems are also an important potential resource for geothermal energy utilisation and substitution of fossil fuels. However, the main difference in the development of karst aquifers in the two countries is their monitoring. While Slovakia systematically observes hundreds of karst springs (Malik *et al*., 2021), the situation in Serbia is far from satisfactory: with the exception of captured karst springs, which are the responsibility of the Waterworks, only a few karst springs' continual discharge has been recorded for more than one decade.

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Geothermal water field “Rupite”, Bulgaria – additional research

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Geothermal water field “Rupite” is one of the most interesting in Bulgaria, both due to its high temperature of 75 °C and specific chemical composition compared to neighboring thermal fields and due to the high content of CO_2 – over 90 mg/l. The waters are carbonated, with a slightly acidic reaction (pH = 6.7–6.8), hydrocarbonate, sodium, fluoride and silicon with mineralization from 1.9–2 g/l to 2.5 g/l, most often 2.0–2.2 g/l. The content of fluorine is 4.3–6.9 mg/l and H_2SiO_3 is 66–97 mg/l. It was formed in “Tertiary” dacites and trachydacites embedded in pre-Paleozoic metamorphites. Initially its water came out naturally in the bed of the Struma River, but later thermal waters were revealed by 3 boreholes (Petrov, 1960, Harkovska *et al*., 2010). Currently two of them are being exploited, with depths 177 m and 244 m, and the exploitation resources of the deposit amount to 25 L/s. The purpose of the present study is to supplement the information on the quantities and qualities of thermal waters by conducting new studies. The forms of presence of the elements in the groundwater and the probability of dissolution of the minerals that make up the aquatic environment are determined. Express geophysical surveys were conducted using the SP method, which outlines the areas of movement of thermal waters to the surface. The problems related to the deposition of a substance when water comes to the surface are also discussed – mainly carbonate and iron-containing minerals. The final outcome helps to clarify the geological-hydrogeological and geochemical features of the thermal waters of the “Rupite” geothermal field.

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Hydrogeological conditions of gas fields formation in the Bilche-Volytsia zone of the Carpathian Foredeep (Ukraine)

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In the Carpathian oil and gas province, the vast majority of gas fields have been discovered within the Bilche-Volytsia oil and gas-bearing zone (OGBZ) of the Carpathian Foredeep. Hydrogeological studies in the search for hydrocarbon deposits in the Carpathian Foredeep have been led for more than than 50 years. The authors investigated the history of paleohydrogeological development of the district, performed their own calculations, and indicated promising areas for the search for gas deposits. The conclusions are made taking into account the analysis of modern hydrochemical, hydrobaric, and gas-hydrochemical characteristics of sedimentary strata of the Bilche-Volytsia OGBZ.

It is established that the paleohydrogeological development of the territory of the Bilche-Volytsia OGBZ was marked by the intensive washout of sedimentary strata (potential reservoirs) during the Paleozoic, Mesozoic, and Early Cenozoic. Powerful dynamics, deep penetration, and enrichment of water with sulfates would make it impossible to maintain the existing hydrocarbon accumulations. The most favorable time interval for the formation and preservation of hydrocarbon deposits in the Bilche-Volytsia OGBZ of the Carpathian Foredeep is the elision stage in the Early Miocene hydrogeological development history, which began 22 million years ago and continues up to these days.

The groundwater origin within the northwestern part of the Bilche-Volytsia OGBZ in the early Miocene is associated with the prolonged sedimentation in the sea basin. Relict thalassogenic sedimentogenic waters of the Badenian and Sarmatian ages are preserved here. The reason for this was a rather closed hydrodynamic situation of these strata and the low intensity of infiltration water exchange.

In our opinion, the formation of hydrocarbon deposits of the Bilche-Volytsia OGBZ of the Carpathian Foredeep took place as follows. During the Sarmatian period, a powerful stratum of the Upper Molasse deposits formation of the Bilche-Volytsia OGBZ was influenced by the dynamo-elision from the Carpathians and the process of immersion of the Eastern European plate. Such geotectonic processes cause elastic-pulsation migration of deep fluids through the permeable zones of disjunctive faults areas.

The primary accumulation of hydrocarbons took place in the lithological, structural, and tectonic traps adjacent to the faults, with the displacement shift of the reservoir waters available in them. In the process of migration through the compacted zone of the structural layers the gravitational differentiation of hydrocarbon mixtures into oil, gas condensate, and gas components occurred. Given the potential for penetration into the upper aquifer complexes, it was possible for hydrocarbon gases to dissolve in formation waters with their subsequent migration in the water-dissolved state at short distances and degassing in elevated structures with reduced formation pressures (piezominimums).

Much of the gases have dissolved in the formation waters, where it stays now, without producing of free accumulations. The reduction of reservoir pressures in the process of gas field development contributed to the flow of free gases from the lower floors to the upper, as well as the possibility of degassing of water-dissolved gases and the output of additional resources.

Opposite movements of infiltragenic waters from the Eastern European plate and dynamo-elision waters from the Carpathians promoted the existence of a squeezed hydrodynamically balanced system, which is characterized by favorable conditions for the formation and preservation of hydrocarbon deposits.

G. Bonchev's paper "Contribution to the springs in Bulgaria", 1937 and its significance for hydrogeology in Bulgaria

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In 1937 one of the first summarizing works of the famous Bulgarian geologist Georgi Bonchev "*Contribution to the springs in Bulgaria*" related to groundwater in the country was published. In his field research the author has visited and described about 60 natural springs or groups of springs with temperatures from 20 °C to over 75 °C, attached to different tectonic zones, over 40 lukewarm and cold springs with mineralized waters and about 290 karst and other cold springs. Data for discharge, temperature and chemical composition are given for some of them. A comparison of the springs visited by G. Bonchev with more up-to-date information based on detailed hydrogeological mappings shows that the number of new water sources is not so large. The presented general picture of the places of the spring, the discharge and qualities of the waters from the natural springs before 1937 allows to make comparisons for the occurred changes due to natural and anthropogenic factors. The most complete information is presented about the natural thermal springs and groups of springs, where significant changes have occurred since 1950 due to drilling in the areas around them. As a result, the discharge of the thermal waters in these areas have increased from 1.5 to over 10 times, which has allowed the construction of modern balneological and spa resorts (Velingrad, Hissar, Strelcha, Sliven, Sandanski and others). Extraction of water from boreholes from greater depths also leads to higher temperatures compared to natural springs. For example, the hottest water discovered by drilling in Bulgaria is at Sapareva Banya – 98 °C with a flow rate of about 14 l/s, at a temperature in natural springs before 1937 from 42 °C to 86 °C and a total flow rate of only 1.7 l/s. Similar cases are found in a number of other deposits of thermal waters (*e.g.*, Beden, Varvara, Velingrad, Pavel Banya). For some thermal water deposits there is an initial increase of their discharge and a gradual decrease over time, but still higher than natural discharge (Guliya Banya and others). Some of the lukewarm and cold springs with mineral waters have also been the subject of additional research and drilling for mineral water (Voneshta Voda, Stefan Karadzhovo). Georgi Bonchev's information about the cold karst and other springs is relatively small, as only for a small part of them there are single measurements of their discharge. It is of interest for future research to establish whether all the sources registered by G. Bonchev still exist.

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Large extent of karstic formations but lack of large karstic springs. Tectonic structure explains the paradox

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Carbonate rocks cover 35% of the area in Greece, and, consequently, karstic aquifers are a crucial, as much as vulnerable, water resource. Recharge areas have to be mapped in detail in order to construct reliable source and resource protection zones.

In the western part of the Parnon Mountain (Peloponnese), the Mesozoic–"Tertiary" limestones and dolomites of the Tripolis Unit cover hundreds of square kilometers. The tectonostratigraphic structure of the area includes an aquitard/aquiclude system of schists and quartzites at the base of this carbonate series (Phyllites–Quartzites Unit), which should create a particularly extensive hanging karstic system of aquifers, with a large capacity.

However, major outcrops of karst formations are not drained through significant outlets, although surface mapping shows they are relatively isolated from other aquifers. Estimates show that, from a total of almost 60 million m^3 of yearly infiltration for a total area of 137.6 km^2 that correspond to the largest isolated outcrop of Tripolis' carbonates, significant karst springs discharge from 10 to 20% at most (between 6 and 12 million m^3).

Field research, in combination with the construction of the tectonic contour map of the contact of the Tripolis carbonate series with the underlying geotectonic Units, showed the following:

i) The tectonic contact of the nappe of Tripolis Unit carbonates is an extensional detachment fault characterized by gently dips in various directions, having many times the form of a turtle shell. In general, however, the dip of the contact is to the west, where its absolute altitude becomes lower towards Evrotas river basin, but large springs are not always present at the lower extremes of the nappe. Folding and faulting resulted in the development of a fragmented network of underground water divides, which (with exceptions) prevent the creation of large, continuous underground drainage axes. Even in these cases, however, discharge is not proportional to the extent of the karstic field.

ii) The thickness of the carbonate nappe is mostly very small in the area compared to that in other outcrops in Peloponnese. Usually, it is less than 250–300 m but in many areas it is less than 100 m, but even less than 50 m. To understand this observation, the thickness of the carbonates nappe of the Tripolis Unit on the eastern Parnon is often greater than 800 m and their stratigraphic thickness is more than 2,500 m.

iii) The contact with the underlying schists in many areas is a high-angle fault.

The combination of the above observations creates a peculiar state of underground circulation, where the groundwater flow into the limestones of Tripolis Unit is simultaneously diffuse and fast, while there are zones where groundwater can escape quickly to a great depth. In a large part of the area, the thickness of the underlying schists is very small (a few meters) or is completely absent, resulting in the direct communication of the limestones of Tripolis Unit with the carbonates of the deepest Plattenkalk Unit and the relative groundwater losses to the depth. This interaction is also reinforced by high-angle faults that cross the entire tectonostratigraphic column of the study area. Towards the south, Tripolis formations dip under postalpine sediments and communicate laterally with downthrown tectonic blocks, creating deep confined aquifers in both carbonate and postalpine sediments.

The tectonic deformation of the alpine formations is very well expressed in recent landforms, indicating that it is relatively recent and not yet eliminated by the exogenous morphogenetic forces. By extension, the effect of active tectonics on the hydrogeological conditions of this region is obvious.

The above reveals that detailed knowledge of the geological structure can explain the location and potential of the karstic springs and lead to correct findings regarding the water resources management plans and the extent of protection zones of the karstic springs.

Session GT13–14

Geohazards, engineering geology and urban geology

Conveners:

Alexandros Chatzipetros, Nikolay Dobrev, Plamen Ivanov,
Vesna Ristić Vakanjac, Georgi Dimov

Landslide movement study and land cover changes in the Balchik area on the northern Black Sea coast of Bulgaria

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The Black Sea coast of Bulgaria north of Varna is severely affected by landslides (Northern landslide zone; Berov *et al*., 2013; Evstatiev and Evlogiev, 2013; Nankin and Ivanov, 2019). The region is characterized by plateau relief (the southern part of the Dobrudzha plateau) and sedimentary rocks of Paleogene and Neogene age, whose layers are slightly inclined to almost horizontal (3–5° to the east).

The studied area is located in the northern part of the Bulgarian Black Sea coast, between Albena resort and the town of Kavarna (Balchik Landslide Area). This area is covered by old and recent landslides. In the Balchik Landslide Area, there are several active and potential landslides. Landslides of lateral-spread mechanism are typical for the Balchik landslide area. Along the shores of the Bulgarian Black Sea coast, they are one of the most spectacular geological hazard processes and phenomena. The aragonite sediments of the Topola Formation and their specific properties are essential for the occurrence of landslides in this area. The main sliding often takes place in contact with the Evxinograd Formation.

Advanced geospatial technology proves to be the basic component of recent environmental monitoring and mapping. This study aims to assess landslide development and urban land cover changes in the Balchik area on the Northern Bulgarian Black Sea Coast based on an integration of GIS and remote sensing. A land cover geodatabase for urban changes was created using satellite and orthophoto images. It was used to assess and map the land cover spatial structure and to reveal urban change patterns for the period 2000–2020. Remote sensing and GIS were used to deliver reliable quantitative information on change patterns and development of the urban areas for a 20-year period. An analysis of the results of the field research has been carried out related to the dynamics of landslide processes in the Balchik landslide area. Sections with development of active landslides along the northern Black Sea coast of Bulgaria have been identified. The research provides new knowledge and can ensure scientific support for informed decision-making on the sustainable development of coastal zones.

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Tectonic regime of the Vlachogianni fault in the epicentral area of the March 2021 earthquake sequence in Northern Thessaly (central Greece)

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The earthquakes that occurred in Northern Thessaly (central Greece) on 3–4 March 2021 highlighted significant details of its neotectonic regime. Two main shocks of Mw6.3 and Mw6.0 occurred on an unmapped low-angle NW-trending and NE-dipping normal fault, triggering other faults in the area. The villages within the epicentral area were seriously damaged and several primary and secondary surface effects were recorded.

After the mainshock doublet, a series of unmapped structures was identified within the epicentral area. We focus on a partially mapped normal fault SE of Vlachogianni Village, the Vlachogianni fault (VF), which was triggered during the earthquake sequence. This fault is interpreted as the northwestern extension of the known Larisa Fault. Together with its antithetic Mesochori fault (MF), they form a small graben valley crossed by the Titarissios River and filled with Neogene–Quaternary deposits. These overlie unconformably the Pelagonian Nappe consisting of Triassic–Jurassic recrystallized carbonates and alternations of Paleozoic gneisses and schists.

The bedrock formations show evidence of a series of Alpine deformational phases, while the post-Alpine deformation consists of two distinct extensional phases, one during the Pliocene–Early Pleistocene and the active one since the Middle Pleistocene. The former phase formed the NW–SE trending normal faults in the epicentral area, including the Vlachogianni fault. The second stage is associated with the E–W trending major normal faults of the area. Both of those extensional phases are interpreted as a result of the slab roll back and post-orogenic collapse.

During the post-earthquake field survey, we studied the broader area of the Vlachogianni fault, particularly the previously unmapped central part. The fault forms a linear scarp and separates the folded bedrock gneisses of the footwall from the fluvial deposits of the hangingwall. Its general azimuth is ~130° dipping ~75° towards NE. The morphology of the area was also modeled by performing a targeted UAV survey. The morphological signature of the footwall is strikingly different from the hanging wall, since the former shows systematic deep incision, indicating active uplift, while the latter is characterized by an almost flat terrain. Furthermore, there are strong indications of drainage deflection along the inferred fault trace, which however does not have a continuous and pronounced expression. Based on structural, geological, morphological data, as well as surface earthquake effects, we propose that this newly identified fault should be considered a separate segment of the Larisa fault zone, which was triggered during the recent earthquake sequence. The lack of significant active deformation features, such as deformed Quaternary sediments or prominent fault surfaces, indicate that it is a lower activity segment and possibly older than the Larisa one.

Tsunamigenic seismic sources in the seas adjacent to the Balkan Peninsula

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This study evaluates the individual seismic sources in the aquatory of the Balkan Peninsula with the ability to generate tsunami waves. The Adriatic, the Ionian, the Aegean, the Marmara and the Black seas have been investigated. The seismicity and strong offshore earthquakes are selected from open access catalogues and published papers. The European Database of Seismogenic Faults (EDSF) is used to define the main tectonic features in the seas adjacent to the Balkan Peninsula. The tsunamigenic seismic zones described by Dimova and Raykova (2016) are supplemented with focal mechanisms associated with past or recent earthquakes. Tsunamigenic seismic sources are grouped depending on focal mechanism over the fault plane. For each zone, we constructed a set of fault geometries according to the scaling laws for finite-source and empirical relationships among the moment magnitude, surface rupture length, surface rupture width and surface displacement proposed by Mai and Beroza (2000) and Wells and Coppersmith (1994), respectively. The results from this study are compiled into an archive and used as initial conditions for the simulations of tsunami generation and propagation.

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Landslide risk for the territory of Bulgaria by administrative districts

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An assessment of the landslide risk (R_{ls}) for the territory of Bulgaria by administrative districts has been made by combining the vulnerability (V) and landslide hazard (H_{ls}) maps.

Landslides are a significant part of geological hazards and are widespread throughout the country (Ivanov *et al*., 2017). To assess the landslide risk for the territory of Bulgaria, it is necessary to take into account not only all landslides for a particular region, but also its vulnerability (Ivanov and Berov, 2017; Frantzova, 2021), and thus to assess the level of landslide risk for this region, $R_{ls} = f(V, H_{ls})$. Landslide risk is determined by a selected risk matrix, using the obtained values of vulnerability and landslide hazard. Assessing the vulnerability of a region to geological hazards is a key component in risk assessment. It includes the exposure of infrastructure, industrial facilities and production capacity, residential buildings, regional GDP per capita and the potential for human disability (defined by population density in the district) and others. The information on these indicators, as well as the coping capacity, is combined to create a map showing the overall vulnerability of each administrative district. In the present study, indicators of population density, GDP, length of the road and railway networks and number of residential buildings were used to assess vulnerability.

The landslide hazard in each administrative district is determined by the intensity of landslide processes in the district, depending on the level of their activity and the affected area. The normalized (distributed) hazard of landslides for an administrative region is given depending on the area of the given administrative region. Landslides are categorized as active, potential and stabilized. The results express the weighted average hazard. Landslide hazard is rated from 1 to 5, where 1 means no landslide hazard and 5 means that landslide hazard has a very high intensity (very high hazard). The high degree of landslide hazard in turn leads to possible economic losses, social and environmental consequences (landslide risk). The intensity (level) of landslide vulnerability, hazard and risk is assessed as very low, low, medium, high and very high, and is shown on the relevant maps.

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Field experiment of cement-modified loess

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In Bulgaria, a soil improvement technique widely applied in foundation works in collapsible loess ground is the construction of a compacted and stabilized layer with local soil from the excavation, mixed with Portland cement. Commonly the role of that cement-modified layer is to replace a part of the collapsible ground, to increase the bearing capacity of the soil base and/or to be an engineering barrier against migration of harmful substances in the geoenvironment.

A multi-barrier near-surface short-lived low and intermediate level radioactive waste repository is under construction in Bulgaria. A cement-modified soil layer (indicated as loess-cement cushion) beneath the disposal cells is going to be built by in-situ compacted mixture of local loess and Portland cement. The cement-modified layer is not a continuation of the foundation, but it is a part of the soil base and performs two main functions: to be an engineering barrier against eventual migration of radionuclides in the geoenvironment and to increase the bearing capacity respectively to restrict deferential settlement of the soil base.

Based on the results from particular classification and physico-mechanical tests of a set of loess-cement mixtures, the optimum cement content of the loess-cement layer beneath the repository disposal cells was defined to be 5% (by the dry weight of soil) of Portland cement type CEM I 42.5 N – SR 5 (Karastanev *et al.*, 2016). Laboratory measurements of the geotechnical parameters showed that the selected loess-cement mixture prepared at optimum water content W_{opt} and standard (maximum) dry density ρ_{ds} after proper curing possesses strength and deformation characteristics which completely meet the design stress-strain requirements to the soil-cement cushion beneath the repository foundation (Tchakalova and Karastanev, 2017).

The present paper describes a field experiment aiming to verify the strength and deformation characteristics of the selected optimum loess-cement mixture by implementation of in-situ cement-modified loess ground. After 28-day curing at in-situ conditions the loess-cement did not exhibit any fissuring or other disturbances. The allowable bearing capacity q_a of the cement-modified loess ground exceeded 900 kN/m^2 and it possessed the following strength and deformation characteristics: deformation (plate) modulus E_{PLT} = 500 MPa; coefficient of sub-grade reaction k_s = 2158 MPa/m and unconfined compressive strength q_u = 2.00 MPa.

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Inventory of landslides in the Gorce National Park and its vicinity

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The Gorce Mountains are located in the polish Outer Carpathians and formed of Magura Nappe flysh deposits. The Gorce National Park protects most of the Gorce Mountains territory.

Landslides, as often emphasized in the literature on this topic, are a common element of the relief of the Outer Carpathians slopes (*e.g*., Margielewski *et al*., 2008; Łajczak *et al*. 2014). The formation of landslides is conditioned, among other things, by the geological structure of the terrain. The fact that the Outer Carpathians are built of flysh formations, which are cut by numerous fault zones, facilitates land masses movement. This phenomenon is underlined by the fact that 95% of all landslides occurring in the territory of Poland are located in the Carpathian Mountains (Poprawa and Rączkowski, 2003). Most of the extensive landslides are associated with wet interglacial and Holocene periods. Fragments of these landslides during times of more abundant precipitation may be renewed, but also new structures can be created (Poprawa and Rączkowski, 2003).

At the beginning of the 21st century as a result of the occurrence of long-lasting torrential rains during summer periods, landslide movements intensified, which at the same time caused damage to infrastructure and buildings. Therefore, the government administration began to inventory landslides within the SOPO (system of antilandslide protection) database. However, the areas of national parks were excluded from this work. Therefore, the presented studies are supplementary to this database, as a considerable research area is located within the Gorce National Park.

The research work is carried out by means of traditional geological mapping supported by analyses based on high-resolution DEMs derived from airborne laser scanning. The elevation model is characterized by a pixel resolution of 1$^{\times}$1m.

In the Gorce Mountains we encounter rotational, translational, and complex landslides as well as run-offs. In some places, rock falls occur. The above-mentioned types of landslide may occur in rock formations, weathered rock formations, or rock and weathered rock formations. Complex landslides are the most common type that occurs in the Gorce Mountains. About 300 landslides ranging in size from several acres to several tens of hectares were identified in the study area. The largest landslide, which has an area of more than 4 km^2, is located on the southern slopes of the Kudłoń Mount. However, most of the time the size of the identified landslides does not exceed 0.05 km^2. Only 20 of the described objects cover an area larger than 0.2 km^2. Landslides in the study area are unevenly distributed and cover approximately 10% of the area. In total, they cover about 22 km^2, which is comparable to the values recorded in different parts of the Carpathians by other researchers.

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Session GT15

Cultural heritage

Conveners:

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Geoheritage in the Neogene Gutâi Volcanic Zone (Eastern Carpathians, Romania) – state of the art

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The Neogene Gutâi Volcanic Zone (GVZ) in the Eastern Carpathians (Romania) is well known for its long lasting (ca. 8 Ma) and complex volcanism, as well as the associated, century mined, precious and polymetallic hydrothermal ore deposits. The region has a huge but insufficiently valued geoheritage potential. Based on the new "8Gs" concept (Brocx and Semeniuk, 2019) we are reviewing the current status of the geoheritage in the volcanic area.

The geoheritage of GVZ includes numerous sites of geoheritage significance, some of which have been declared protected areas: three nature monuments (IUCN category III), two natural protected areas (IUCN category IV) and a scientific reserve (IUCN category IV). Four European NATURA 2000 network sites, including some of the above mentioned geosites have been also designed in the GVZ. Numerous other geological and geomorphical sites which satisfy the criteria for being recognized as geoheritage sites are in the region: *Laleaua Albă*/White Tulip andesite and dacite composite dykes with large gabbroic enclaves and sanidine macrocrysts (up to 5 cm) in the dacites, unique in the Eastern Carpathian volcanic range; *Piatra Roşie*/Red Stone Hill in the Dăneşti-Cetăţele composite dome with *in situ* and resedimented hyaloclastites with erosion caves in its high escarpment; the impressive andesite columns and the amazing erosional landform (*e.g*., Igniş „Sphinx") from Igniş volcano; the Mine Hill with interesting ore minerals outcropping in an abandoned quarry and many very old galleries (e.g., Borcut adit dug in the XVIIIth century). Many other geoheritage sites, which are going to be assesed in order to get the designation of protected areas, occur in GVZ.

Regarding the geoconservation, urgent measures are required for the protection and conservation of some geosites (*e.g*., the Chiuzbaia fossiliferous scientific reserve, which represents *type locality* for many Upper Miocene flora). Geomanagement requires to establish or improve the management plans by the institutions managing the protected geosites, both for protection (e.g., the IUCN III category – protected area *Lacul Albastru*/Blue Lake from Mine Hill, unique in Europe) and for visitors risk assessment (*e.g*., the Rooster's Crest in Gutâi andesitic extrusive dome, the IUCN IV category - protected area, which is a traditional place for rock climbing). Numerous scientific field trips of important international conference (IAVCEI, IMA, UNESCO IGCP356 Project) took place in GVZ, including some geoheritage sites. Field trips for the students in geoscience are organized each year in GVZ, as important part of the geoeducational process. Despite its high potential (many geoheritage sites are located in the European NATURA 2000 network sites and in the vicinity of some UNESCO/World Heritage Sites – cultural heritage), the geotourism in GVZ only sporadically benefits from institutional arrangement (responsible supervision, brochure, maps and geological informations disseminated to the visitors).

Concluding, it is necessary to enhance the involvement of the local authorities and institutions in geomanagement, geoconservation and geotourism of the GVZ. Therefore, sustained efforts are needed in the future to value its high geoheritage potential.

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Phase and thermal analysis of Roman ceramic materials

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Ceramic materials refer to bricks, tiles, pottery, and wall plasters made of clay and water. Three stages of the ceramic-making process, in the beginning, were carried out - clay paste preparation, forming and shaping into an object, and air drying of the final product. Later, the fourth stage appeared - firing. Ceramic was defined as the first composite material manufactured and developed by humans. Its production was simple, low cost, and continuous during many archeological epochs. Additionally, it is resistant to weathering. Thus, ceramic is the most abundant archaeological artifact, making it significant for archaeology (Goffer, 2007).

The archaeological ceramic research includes a classification by macroscopic description. A transition from observation to empirical investigations is needed to obtain additional information on ceramic materials. By the application of natural sciences knowledge and the use of analytical techniques, the transition could be achieved. Such interdisciplinary study of ceramic allows for determining phase composition, used raw clay, and firing temperature in the kiln (Peacock, 1970). The first studies of phase composition were petrographic by thin sections, published by Shepard in 1936. Later, powder X-ray diffraction was applied (Neff, 1993). Now, for the determination of phase composition most often, a suitable set of analytical methods is defined - powder X-ray diffraction, Fourier transform infrared spectroscopy, and thermal analysis (simultaneous TG-DSC) (Palanivel and Rajesh Kumar, 2009; El Ouahabi *et al*., 2015).

This work aims to investigate the phase composition and determine a firing temperature and possible type of raw clay used for ceramic production in the Roman archaeological site Dimitrievo (Bulgaria). The site was defined as Emporion Pizos (Boyanov, 2014). The Roman brick, tile, pottery sherds, and clay wall plaster samples were investigated by the mentioned set of methods. The obtained results will help specify economic and cultural aspects of Roman society living in the Dimitrievo Emporion Pizos.

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A cultural institution as a geotourism attraction: Baia Mare Mineralogical Museum (Romania)

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The County Museum of Mineralogy "Victor Gorduza" Baia Mare (MusMin) is one of the largest geological museums in Romania, and one of the most important regional mineralogical museums in Europe; its uniqueness is due to the fact that almost the entire collection of specimens comes from the well-known Baia Mare mining region (NW Romania). The impressive collection of the MusMin (over 20,800 pieces) consists of minerals from all the main ore deposits, rock-types from the region and representative fossils (*e.g.*, Chiuzbaia Upper Miocene fossil flora, with some species described for the first time world-wide). The mineral collection, representing the most significant part of the MusMin heritage, includes nine minerals described for the first time in the world in the Baia Mare mining region (andorite, semseyite, dietrichite, szmikite, felsöbányte, klebersbergite, fizélyite, füloppite and rhodocrosite) and many other spectacular minerals, such as: acicular to prismatic crystals of stibnite, different coloured of tabular barite, black and white calcite spheres, large and perfectly transparent gypsum, reddish prismatic realgar, perfect shapes of vivianite and many minerals with zoomorph shapes.

Representative pieces of the mineral collection were presented in a large number of temporary exhibitions organized in different cities in Romania and in more than 40 exhibitions held in numerous localities of several European countries (Austria, France, Hungary, Germany, Belgium, The Netherlands, Monaco and Moldova Republic).

By its collection and the representative graphic materials (*e.g.*, 3D large diagram representing the 1:50 000 scale geology of the NW Romanian territory), MusMin became a key-site of knowledge, research and education in the region. The main ore deposits from which the minerals originated are presented in a special section of the museum, with representative geological maps and cross-sections, rock and ore samples. Another special section displays the minerals based on the classification criteria and specific properties offering great opportunities for learning to students in Geosciences and general public. MusMin developed an important educational activity in the last years, organizing guided tours for students, workshops for those interested in mineralogy and a wide range of educational projects (*e.g.*, "Geodiversity in Maramureș" Summer School, Earth Sciences Week, "The minerals from our life" and "Mineralogy for all" competitions for students).

Articles on the minerals from the MusMin collection have been published in prestigious journals (Minerals, European Journal of Mineralogy, Acta Mineralogica-Petrographica, Studia Universitatis Babes-Bolyai, Geologia series) as result of the scientific collaboration between the specialists of the museum and those of several universities and research institutes.

MusMin is the most visited cultural institution from the northwestern part of Romania, not only by geology specialists (*e.g.*, IMA 2010 Field trip participants) but also public visitors from Romania and abroad. The assessment of the MusMin as an ex-situ geoheritage site, using the semi-quantitative method of Brilha (2016), reflects the high scientific (380/400), educational (390/400) and touristic (380/400) attraction of the museum, that can play a key role in the development of the geotourism in the region.

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Aerial photogrammetry at the Argamum archaeological site

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Dobrogea is a region in the eastern part of Romania that is rich in cultural heritage, mainly of Greek and Roman origins. The archaeological objectives, found in Dobrogea, are mostly represented by ancient settlements (forts, fortresses, towns, and cities) and can either be located on land, and accessible, or submerged and inaccessible. The Argamum fortress is one of the most important Roman settlements and can be found in the central part of the Dobrogea region, on the bank of the Razelm Lake. This settlement is considered to be the oldest fort in Romania and was founded by Greek settlers who came from Asia Minor in the 6^{th} century B.C. Most of its surviving buildings and edifices are of the late Roman-Byzantine era and are composed of at least 2 gates, defensive walls, several streets and household structures, and at least 2 early Christian basilicas.

At the Argamum archaeological site, the more exposed and defined area of 4.62 hectares, was surveyed by using an unmanned aerial vehicle (UAV) system through which a great deal of information can be obtained just by viewing the subject, or area of interest, from certain distances and angles that are impossible to reach from the ground level. The generated photogrammetric products, such as orthomosaics, digital elevation models (DEMs), digital terrain models (DTMs), contours maps, 3D meshes, and textured 3D meshes, have improved the visibility and access to areas that previously could not be identified without working in an intrusive way. Also, the detailed models obtained from the processing of photogrammetric data will guide the archaeologists in future excavations by determining the most adequate areas for archaeological excavation. Photogrammetry can be either a standalone technique or combined with other geophysical survey methods (*e.g*. GPR and magnetic surveys), as complementary techniques.

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Geoconservation problems of the protected karst phenomena in Bulgaria

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The karst terrains are an essential element of the geodiversity of the Bulgarian lands and cover 22.7% of the country‘s territory. Their high scientific, cognitive and aesthetic value is a significant part of the objects of the Bulgarian geological heritage.

The karst phenomena have been used since the emergence of the humans. Some of these uses are of considerable cultural significance. Of the impressive number of uses of karst forms by man, in Bulgaria, the following groups are covered: (1) Water supply: The waters of about 40 Bulgarian caves and numerous karst springs are captured and water supply a significant number of settlements. More than 320 dams and other types of hydraulic constructions are directly or indirectly connected to karstified carbonate rocks; (2) Quarries for limestone and marble: Some quarries threaten karst forms; (3) Different aspects of scientific research: Relatively few Bulgarian scientists are currently studying karst; (4) Tourism and recreation in various forms: Twelve Bulgarian caves are being developed for mass tourist visits as electrified show caves. Several other caves are with guided tours with local cavers; (5) Food industry: Some underground karst landforms in Bulgaria are used for food production and aging; (6) Religious purposes: A considerable number of karst forms are known in Bulgaria - sanctuaries related to religious cults, doctrines and beliefs from antiquity to the present day; (7) Military goal: In this aspect, the enormous entrance chamber of the Devetaki Cave and the entrance parts of Emen Cave (North Bulgaria) were used as fuel depots of the Bulgarian Army during the Cold War time; (8) Medicine: It is well known the experiment of 1974 and 1975 for the treatment of bronchial asthma in Magura Cave.

These uses result in a remarkable range of negative impacts – degradation of the physical structure of the karst landforms, alternation of the karst hydrology and microclimate.

This paper deals with some problems connected to their protection, conservation and management. These problems are separated in theoretical and practical parts.

Geochemical characterization and provenance of obsidian artifacts from the middle Neolithic site of “Episkopi”, Ioannina region, NW Greece.

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“Episkopi” is a middle Neolithic site some 14 km south of the city of Ioannina in Epirus, NW Greece. The site lies on a low hill in the southern part of the Ioannina basin, in an area of seasonal polje. Rescue excavations between 2007 and 2010 revealed the use of the area in the Neolithic, Hellenistic and Roman times. On the top of the hill, severely disturbed by a roman cemetery, the remains of an extended Neolithic settlement were investigated. The remains include 11 pits of various sizes, which are attributed to subterranean dwellings. Radiocarbon dating places the habitation in the Middle Neolithic. A substantial number of chert artifacts were recovered, along with a total of 11 obsidian artifacts, a unique so far occurrence in Epirus. The obsidian sample group includes one pressure flaked bladelet core, flakes and bladelets.

The raw materials for the obsidian from various prehistoric sites in Greece originate mainly from Milos Island. In only one case, obsidian was reported from the Carpathians, and in two cases from Çiftlik of Cappadocia (Turkey). The geological outcrops in Milos occur in two sites, at Adamas or “Nychia” and Demenegaki, and the obsidian from there is the most suitable for the manufacture of tools. Other outcrops around Aegean are found in the islands of Antiparos and Gyali of Nisyros, and only few artifacts dating to the Bronze Age, were manufactured from this obsidian.

Three representative obsidian artifacts from the “Episkopi” Neolithic site were selected for geochemical analysis by non-destructive X-ray Fluorescence (XRF). They have a similar chemical composition with a high content of SiO_2 (76.30 wt% to 76.97 wt%). Also, Al_2O_3 ranges from 12.38 wt% to 13.29 wt%, Na_2O from 3.81 wt% to 3.98 wt% and K_2O from 2.96 wt% to 3.11 wt%. Fe_2O_3 (1.23 wt% to 1.89 wt%) and CaO (1.18 wt% to 1.53 wt%) are found in small concentrations, while MnO, MgO and TiO_2 are in traces (<1 wt%). In the diagram $Na_2O + K_2O$ versus SiO_2, the three artifacts are projected in the field of rhyolites, and based on their black color and their convergent fragmentation, it is confirmed that their raw material is certainly obsidian.

These analyses were compared with the published geochemical compositions of obsidian from the Aegean (Milos, Antiparos, Gyali), Italy (Palmarola, Lipari, Pantelleria), Sardinia, Cappadocia (Turkey), and Central Europe (Carpathians, Slovakia), and confirmed that the obsidian used for the artifacts from “Episkopi” comes from “Nychia” site of Adamantas, Milos Island. Obsidian from Milos has been found in prehistoric excavations throughout the Aegean and mainland of Greece: from Thrace, Macedonia and Thessaly, to Peloponnese and Kefalonia island in the Ionian Sea, but also in Neolithic settlements of Asia Minor, such as Aphrodisias and Beycesultan. This shows that the obsidian mining and transportation industry played an important role during the Prehistoric period around Aegean (Milić, 2014). The present study confirms that the “Episkopi” Neolithic site is of twofold importance: it adds fresh data to the poor Neolithic record of Epirus and documents the presence of Melian obsidian in the region of Ioannina for the first time.

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Mineral kingdom in the Earth and Man National Museum Sofia, Bulgaria

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The Giant crystals collection is emblematic for the Earth and Man National Museum. With samples mainly from Brazil and Bulgaria it is one of the two large collections of giant crystals in the world.

Yet, if only one word has to be used to describe the Earth and Man National Museum, it will be mineralogical, and from the very beginning the museum was intended to have a much broader profile – that of intensive, ecological use of mineral raw materials and the continuity of scientific knowledge.

The Earth and Man National Museum is a museum of the mineral kingdom, presented in 7 permanent exhibitions: Giant Crystals, Minerals of the Earth, Minerals of Bulgaria, Mineral Resources of the Earth, Mineral Resources of Bulgaria, Materials, Gemstones and decorative stones. It is a relatively young museum, but it has the biggest systematic collection of Bulgarian minerals and the biggest systematic collection of minerals in the South Eastern Europe. A number of author's samples – holotypes and cotypes of minerals from all over the world are deposited in the museum.

The Bulgarian deposits have been systematized by regions, aiming to preserve the entire mineral association of a deposit *ex situ* in accordance with the ideas of Sofia Initiative for Mineral Diversity Preservation. There are complete collections from large deposits such as Kremikovtsi, Madan, Ardino pegmatite field, as well as from individual mineral localities – Nova Mahala, Davidkovo, Brusevtsi, etc. There are two large collections of the preserved mineral diversity of Rila and Vitosha and a unique collection of Bulgarian agates.

Minerals, ores and rocks lay in the foundation of modern technological civilization. That's why in the museum there are two divisions, which show the modern approach to efficient and sustainable usage of mineral raw materials - Mineral resources of the Earth and Mineral resources of Bulgaria. Emphasis is placed on their exhaustibility and non-renewability, hence the need for waste recovery. We have displayed various raw materials that were considered to be waste before the discovery of an economically effective technology for their processing.

Of course, there is a large Gemstones and Decorative Stones collection with over 1,000 specimens of traditional, rare and exotic gemstones and some synthetic gemstones.

The Materials exhibition is really special. Metals, glass, ceramics, composites, monocrystals produced from mineral raw materials are part of the samples demonstrating the progress of technologies as a result of the accumulated Human knowledge.

Since the creation of the museum in 1986, the collections have been committed to ensure the continuity and development of scientific knowledge. The museum has a separate Scientific collections division, where the collections (mineral samples, scientific publications, photos and manuscripts) of well-known Bulgarian scientists are kept, and over 8000 units are stored in a scientific-auxiliary division, the purpose of which is to provide material for further research, which is especially relevant, given the fact that nowadays the life of a mineral deposit rarely exceeds several tens of years.

New petrography data of golden Engobe pottery from Site “Orlovo”, Eastern Rhodope, South Bulgaria

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Pottery with a golden engobe from the archaeological site “Orlovo”, Eastern Rhodope Haskovsko municipality has been studied. These types of pottery from the Middle Byzantine period, are characteristic of settlements from the XI–XII century period in Thrace.

The site is located in the Eastern Rhodopes, Haskovo region, between the villages of Mandra and Orlovo. The petrographic and mineralogical studies carried out complement those obtained by archaeological data from the site and provide new information on the texture, structure, source of the raw materials, and the technology of production of the pottery. Through complex research methods (optical, XRD, and SEM-EDX) the pottery with golden engobe has been divided into three groups. Each of these groups has been characterized – by mineral and rock inclusions, texture, the chemical composition of the used white mica, and technology conditions of manufacturing as the temperature of firing and the way of laying the engobe to the surface. These groups are compared to the published separated technology groups by Koleva (2018).

According to obtained petrographic characteristics and technological features of production, the two groups from the separated pottery suggest a local source of the raw material. The results by SEM-EDX analyzer on the white mica used for the production of the golden engobe from these two groups confirmed the local source, also. The golden engobe was achieved by applying clay with big in sizes flakes of white mica laid on the surface of the vessel after its initial drying and before firing. This type of engobe is unevenly applied, quite finely on the surface of the vessels, without separating into a separate layer and it is absent in places. The observed third group of pottery is totally different in texture, mineral composition, and manufacturing technology we suppose its import genesis. The golden engobe in this group is a result of applying to a denser outer layer of very fine-washed clay enriched by fine-flaked muscovite on the outer part of the vessels, before its firing.

The present archaeometric study gives new information about pottery with golden engobe from Thrace, bearing in mind that published results of this type of research are still limited.

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Professor Vladimir K. Petković (1873–1935) – one of the founders of the Carpathian-Balkan Geological Association

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Vladimir Petković – professor of natural sciences at the St. Sava Theological Seminary, professor of geology and rector of the Belgrade University, member of the Serbian Royal Academy (SRA), founder of the Geological State Institute, editor of the journal *Annales Géologique de la Péninsule Balkanique* and longtime associate of the Natural History Museum in Belgrade (Maran Stevanović 2021). He was born on June 19, 1873 in Boljevac, eastern Serbia. He graduated from the Department of Natural Sciences and Mathematics at the Faculty of Philosophy of the Great School in 1896 and continued his studies with the Austrian geologist, Professor Eduard Suess in Vienna. After succeeding the professorial examination (1901), he was elected assistant geologist at the Faculty of Philosophy of the Great School in March 1905, six months before the formal founding of the University of Belgrade. At the Belgrade University, he began systematic geological field research in eastern Serbia, studying the tectonic, morphological and paleontological structure of the wider area of Zaječar, Boljevac and Knjaževac. He received his doctorate in 1908 on the topic „Tupižnica and its foothills“ and became not only the first doctor at the University of Belgrade but also the founder of the regional geology in Serbia. He specialized in paleontology and stratigraphy of Cretaceous in Paris and Grenoble, applying the acquired knowledge in identifying the fossilized remains of the Lower and Upper Cretaceous fauna, collected in eastern and central Serbia. The Balkan Wars and the First World War he spent as a conscript on the battlefields, and in the short periods of the armistice he performed the duty of organizing schools in the liberated territories. From 1918 to 1920 he was the Head of the Ministry of Education in Corfu (Greece). He was elected corresponding member of the SRA in 1921, and a full member in 1930 with the introductory speech „On the tectonic structure of eastern Serbia“. During the International Geological Congress held in Brussels in 1922, Petković together with colleagues from Czechoslovakia, Poland and Romania, initiated the founding of the Carpathian Geological Association, which later grew into the Carpathian-Balkan Geological Association (1958). He was elected dean of the University's Geological Survey for three terms; in the period 1930–1933, he was the rector of the University of Belgrade. According to many researchers, Vladimir Petković was the greatest expert on the geology of eastern Serbia as well as of the Cretaceous sediments in Serbia. He has published more than 70 scientific papers, mainly in regional geology. Among the most important are: „Tupižnica and its foothills“ (1908), „Gault formations in Serbia“ (1913), „On the Barremian age of the Greben/Djerdap Gorge“ (1921), „On the tectonic structure of eastern Serbia“ (1930), „On the geological composition and tectonic position of the southeastern part of the Timok Basin“ (1931) and posthumously, „Geology of eastern Serbia“ (1935). His long illness, difficult financial situation and years of intensive work influenced his early death; he passed away in Belgrade on March 20, 1935.

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3D model of Mlynky Cave, Ukraine

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The caves are one of the most mystical environments on the Earth. The first habitation for mankind were the caves. In recent years, significant progress has been made in 3D surveying of geological outcrops, including caves.

The main purpose of this research is to create a 3D model of Mlynky Cave. Such models are useful for geologists, speleologists, archaeologists, biologists. The created model makes it possible to study faults, cracks, sedimentological features, etc.

Depending on the objects, different techniques are used. For some use photogrammetry, for others - laser scanning. The studies of the outcrops are often performed by the two methods mentioned above to compare the accuracy and effectiveness of the research. The situation for caves is a bit more complicated. With the experience of scanning the cave, we have expanded the range of research opportunities. It is necessary to scan not only inner part of caves but also the outer part, because it can carry important information, as the cave can be a part of a specific geological complex. It would be good to link to the international coordinate system and the conventional UTM projection.

The object of our research is the Mlynky Cave, located in the West of Ukraine in the Ternopil region. It is a geological natural monument of national importance. The cave is formed in Badenian gypsums, and the total length of the famous labyrinths reaches 40 km.

Global Navigation Satellite System (GNSS) used geodetic benchmarks and photogrammetric markers. This was done by a satellite signal receiver and Real Time Kinematic (RTK) method from the network of base stations of Geoterrace of Lviv Polytechnic.

Photogrammetric studies were performed in the Valley of the Mlynka River using a Phantom 4 (UAV). The inner part of the cave was investigated using laser scanning technology.

The Leica Cyclone 3DR combined three point clouds: one from the photogrammetric method (outside the cave) and 2 from laser scanning (inside the cave). The result is a digital 3D model in a single coordinate system and conventional UTM 35 projection.

The use of laser scanning technologies and digital photogrammetry allowed us to obtain a 3D model of the Mlynky Cave. This model can be used for further research: detection of new underground chambers, faults, cracks and volumes estimation.

Non-invasive investigations at Măgura Călanului Dacian limestone quarry. Technical challenges in a geosite with heritage value

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An extraordinary geosite with complex heritage value, the limestone quarry from Măgura Călanului, was operational since the reign of Burebista until the Roman conquest (105–106 AD). The Dacian fortresses for which the use of this stone has been demonstrated are Sarmizegetusa Regia, Costești-Cetățuie, Costești-Blidaru, Piatra Roșie, Fețele Albe and Bănița (Mârza, 1995). The main categories of constructions in which the limestone had been used are: walls, towers, civil constructions, public buildings, pavements, roads, stairs, decorative pieces, temple components, drainage channels, cisterns (Pețan, 2018).

Although known as ancient source of stone and registered as Archaeological Site of Călan-Măgura Călanului, the quarry area has never been systematically studied or declared historical monument. To confirm its global heritage value, the geological research of the quarry was integrated in a larger project. In addition to previous research conducted by an independent multidisciplinary team, topographic positioning and geophysical measurements (Geo-electrometry, Georadar) were performed in order to establish the geometry of the historical quarry.

The quarry consists of two semi-circular exploitation areas, totalling up to 800 m in length parallel to the edge of the hill and at least 600 m wide. The size of the quarry and the traces preserved within the landscape prove its complexity (Cetean and Pețan, 2019), as well as the succesive stages of exploitations, from N to S, and from W to E.

Nine vertical Electric Sounding profiles were made, totalling 990 m in the quarry area and 756 m on the waste dumps. Difficulties encountered due to the perimeter morphology and land cover by stone fragments, soil and vegetation required successive returns and correlations, to increase the accuracy and to validate the results of the data acquired. Valuable information has been obtained in outlining the limits of the eastern and western areas of the quarry and the central part left unexploited between them. At this stage of the research, it is considered to be also the only useful method of in-depth investigation of waste rock dumps, even if the non-uniformity of the components and the residual moisture of the clay filling sometimes lead to errors in data acquisition.

Where the topography of the terrain allowed, 545 m of Ground Penetration Radar (GPR) profiles were made, to determine whether the method is applicable and provides interpretable and reproducible data. Seven GPR profiles were made within the quarry limits and 4 as reference measurements in an unexploited area. The radar charts revealed lithological sequences and clear signal differentiations between layers. However, it has also been highlighted that in high vegetation area, in saturated soil and in the proximity of a tower relay there could be induced aberrant signals or those of the geological substrate could be shielded.

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Session GT16

Education in geology and public awareness

Conveners:

Stanislav Stoykov, Goran Tasev, Michael Sandy

Remnants of Soviet-Era In-Situ Leaching Uranium Mining infrastructure in the Thracian Basin, Momino, near Rakovski, Plovdiv District (Bulgaria) – a preliminary investigation; preservation potential and educational value

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In-Situ Leaching (ISL) Uranium mining was developed in Cenozoic sedimentary basins of Bulgaria during the second-half of the twentieth century. The mining was shrouded in secrecy during the Soviet Era and consequently records of aspects of the mining operations may be difficult to access – if they exist.

This is a preliminary report on a former ISL mining area on the Upper Thracian Plain located between Momino Selo and Rakovski (Plovdiv District, Bulgaria). The remnants of ISL mining have been identified using the computer programme Google Earth, Soviet Military Topographic Maps of Bulgaria at 1: 50 000 scale, discussions with local residents, and site investigations including mapping, Geiger Counter observations, and the use of a drone (Unmanned Aerial Vehicle [UAV]).

Three sites can be identified, two where infrastructure associated with mining can be seen, the third being an administrative center. Remnant structures include ground-level outlines and the remains of demolished and abandoned concrete structures, buildings, basins and concrete foundations and bases that mark the former location of equipment and storage tanks that held chemicals. Machinery and storage structures (e.g., holding tanks) were removed soon after the cessation of ISL mining activity. The well-field areas have been returned to agriculture, the pipelines removed during decommissioning; well heads were removed and concrete poured to seal the wells. The state of other ISL sites in Bulgaria has not been assessed in this study.

Defunct concrete separating basins still exist at two of the sites. The final process at Momino Selo was the mixing of the mined uranium with resin beads and then transport to Buhovo, 15 km SE of Sofia. Processing into yellowcake occurred at Buhovo, then additional transport to the Soviet Union for nuclear weapons. Uranium mining also provided nuclear fuel for Bulgaria's electricity-generating nuclear power reactors at Kozloduy Nuclear Power Plant, the first reactor commissioned in 1974.

It is just about 30 years now since the last ISL uranium mines were active. Although remaining derelict ISL uranium mining sites are typically considered eyesores and of no value, these surviving remnants are monuments to the Cold War and its appetite for building nuclear arsenals. As such, perhaps such sites should not be ignored and left to rot and crumble, but recognized as sites with historical, scientific, technological, industrial, political, military and economic significance – and of educational value for future generations of Bulgarians. Conservation of at least one ISL site would provide a physical record of a significant aspect of Bulgaria's geoheritage.

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Central European Exchange Program for University Studies (CEEPUS) is a unique educational entity comprising 15 countries, which promotes students' and teachers' mobility as primary activities (https://www.ceepus.info/content/about). The network CIII-RS-0038: „Earth-Science Studies in Central and South-Eastern Europe" (EURO Geo-Sci) is continuously prolonged from its foundation 24 years ago. It is one of the oldest (from 1999) and the largest (18 universities from 10 countries: Albania, Austria, Croatia, Czech Republic, Hungary, Poland, Romania, Serbia /network coordinator/, Slovakia and Slovenia). The participating countries encompass a unique geological Alpine-Dinaride-Carpathian-Balkan area, sharing similar research problems and having common interest in the application of the acquired geological knowledge (Šarić and Ionescu, 2018). EURO Geo-Sci (https://ceepus.rgf.bg.ac.rs/) is dedicated to development of science-driven education in both fundamental and applied geological disciplines. The network follows modern trends in higher education primarily via: i) modifying the actual curriculums by introducing new courses given by visiting professors, ii) increasing the study outcomes through students' outgoing mobility and iii) reinforcing educational infrastructure of the participating units (Šarić, 2022). The network involves an extensive knowledge transfer in a wide spectrum of geodisciplines, such as geo-materials (minerals, rocks, fossils, coal, oil and gas) and products of their technological treatments, regional geology, engineering geology, hydrogeology and geophysics, which ensures that students are trained to continue either with academic careers or to work in industry. It is clear that EURO Geo-Sci network is designed to respond to current and future societal needs in a best way. Students who are today trained through the network are tomorrows' geologists who will participate in finding and exploit new resources, solving problems of air, water and soil pollution, taking care of other issues of environmental protection and global warming, developing of green technologies, saving drinking waters and working on various geo-hazards, such as landslides, floods and earthquakes, as well as preservation of natural and cultural heritage. This is a primary motivation for all coordinators within EURO Geo-Sci to continue their work and promote the network in the best way – emphasizing the great significance of the geological education for serving the society.

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Session GT17

Agrogeology, environmental geochemistry, resilience

Conveners:

Arjan Beqiraj, Mateja Gosar, Stefan Shilev

Characterization of serpentine soils from the eastern and south Rhodope Mountains (Bulgaria)

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Serpentine soils are widespread in the Balkan region. They are also found in Bulgaria, most of them in the Eastern and Central Rhodopes. Serpentine soils originate from serpentine rocks, which are usually shallow, and have specific physical and chemical properties, such as low nutrient status, cation imbalance, low Ca/Mg ratio, moisture stress, soil instability, high surface temperature and high metal contents such as Ni, Co and Cr.

The aim of this work is to characterize serpentine soils in Bulgaria and to examine the biogeochemistry of pedogenic Ni in serpentine soil and its relation to Ni available forms.

Soils were collected from serpentine soils of the Eastern and Southern Rhodopes (Bulgaria). Standard soil parameters (C, N, pH, CEC, etc.) were used to characterize serpentine soils. Ni fractions of different operational defined extractability (aqua regia, DTPA, $Sr(NO_3)_2$) were determined. The ratio between amorphous Fe-oxides and well-crystallized Fe-oxides was also determined, as it is a relative indicator of the degree of soil development and the intensity of weathering. Pearson correlation matrix was calculated for all soil physico-chemical parameters and elemental concentrations in soils.

The chemical composition of serpentine soils from the Eastern and Southern Rhodopes is similar to serpentine soils from the Balkan Peninsula, and is characterized by high contents of Ni (1270–2281 mg/kg), Cr (32.7–1877 mg/kg), Mg (38,676–236,569 mg/kg), and extremely low Ca/Mg ratio (0.02–0.04). The soils had a neutral to slightly alkaline reaction (pH 6.4 to 7.6) and a medium to high organic matter content. The textures vary from sandy, sandy loam to heavy sandy loamy. Of the primary minerals, those of the serpentine group (antigorite and lizardite), the talc group (willemseite), the amphibole group (riebeckite), the feldspar group (albite and anorthite) and quartz are mainly present in the soil samples. The secondary minerals present in the samples include calcite and dolomite, and also representatives of the clay minerals, clinochlore and montmorillonite. The contents of free iron oxides (Fed), amorphous iron oxides (Feo), well-crystallized iron oxides (Feo) (Fed-Feo) and activity index showed significant differences ($p<0.05$) among soils from different locations. Ni is associated with both well-crystallized and amorphous Fe oxides. In the soils from Dobromirtsi, Parvenets and Golyamo Kamenyane, Ni bound to Fe oxides was evenly distributed between the well-crystallized and amorphous phases; in the soils from Kardzhali, Chernichevo and Dyulitsa, more than half of the Ni bound to Fe oxides was bound to or occluded in amorphous Fe oxides, while in the soils from Kazak it was bound to well-crystallized Fe oxides. Nickel availability in soils is controlled by soil weathering and mineral-bearing phases. Ni was adsorbed onto amorphous Fe-oxides and was also exchangeable in secondary minerals. High availability of Ni in soils was confirmed by DTPA extractions. However, it varied significantly among different locations, being higher in soils where Ni-bearing amorphous Fe-oxides were abundant and total organic matter was higher. Therefore, pedogenesis, weathering intensity and Fe-geochemistry have a major influence on Ni availability.

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Geochemical study of biomarkers in coal-fired TPP combustion wastes, Bulgaria: Bobov Dol TPP

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The National Energy and Climate Plan 2021–2030 previews reduction of the energy portion from coal-fired thermoelectric power plants (TPPs). However, their shutting down will not automatically solve the problems of combustion waste management. Presently, in their majority, TPP wastes are considered as potential environmental pollutants. Some studies have pointed out that they could be used as a feedstock for value-added materials. Fly ash (FAs) minerals and toxic metals in TPP combustion wastes are well documented, while the organic components are somewhat neglected. It is explained by the low amount of organic matter and necessity of multi-step analytical protocol. The successful analysis requires sophisticated equipment for identification and quantification of compounds in trace amounts and interdisciplinary knowledge. The studies in the field quickly augment, a fact assigned to the obligation to respect the EU regulation norms.

A suite of studies was set up to obtain geochemical proxies from FA biomarkers (Kostova *et al*., 2020; Apostolova *et al*., 2021), focusing on polycyclic aromatic hydrocarbons (PAHs). The aim of the present investigation includes: (*i*) a comprehensive analysis of the main coal biomarkers (*i.e.*, *n*-alkanes, isoprenoids, di- and triterpenoids, hopanes, PAHs) in the Bobov Dol TPP feed coal blend and FAs from the three electrostatic precipitator (ESP) rows; and (*ii*) the assessment of potential pollutants in the FA extractable portion, mainly PAHs.

Feed coal blend and FAs from the Bobov dol TPP were selected for the study. Extractable organic matter compositions (EOM) were determined according to the protocol developed for biomarker investigations on Bulgarian coals of different rank. Briefly, EOM was obtained by Dionex ASE 200 extraction with dichloromethane. Asphaltenes were precipitated and maltenes were fractionated by medium-pressure liquid chromatography (MPLC). *n*-Alkanes and aromatic compounds were analyzed by gas chromatography-mass spectrometry (GC-MS). Compounds were quantified relative to that of internal standards.

The data received pointed out that, in combustion wastes, many biomarkers are still capable of identification. Biomarker assemblages were dominated by diterpenoids: 16α(H)-Phyllocladane (maximal at the neutrals) and for the aromatics – Simonellite. PAH distributions according to the United States Environmental Protection Agency (USEPA) were featureless, *i.e.*, Phenantrene and Perylene were detected. PAH amounts in FAs were lower, as in the ESP rows only Phenantrene was registered in appreciable amount of 0.28 μg/g TOC (~2 μg/kg FA).

Generally, in FAs from coal combustion in TPPs, low amounts of PAHs were determined. As there is still not a regulation for PAHs in FAs, their amounts were compared to soils. The total PAHs are <150 μg/kg soil, fixed by the Bulgarian legislation (Regulation No. 3, 2008). However, PAHs harmful effects for the environment must be estimated in combination with data for other toxic substances.

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The environmental impact of closed mining waste deposits in Slovenia

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Mining waste deposits (MWDs) can be a source of pollution with potentially toxic elements (PTE) as well as a useful secondary source of raw materials. The results of more than 10 years of research on the impact of closed and abandoned MWDs of metal mines on the environment in Slovenia will be presented (Gosar *et al*., 2020; Miler *et al*., 2022, and references therein).

PTE contents in mining waste, bottom stream sediment and water were determined to define environmental burden according to regulation values. Influence of mining waste to sediment pollution was estimated with the use of the Geoacumulation index. Furthermore, mineral phases in both solid materials were determined with the use of SEM/EDS (scanning electron microscopy coupled with energy dispersive spectrometer). The results show that, in the area of the closed Pb-Zn mine Mežica, investigated MWDs are important source of PTEs in stream sediments and PTEs mostly occur as fine-grained sediments. MWDs generally have the greatest impact on sediments in streams close to them. Because fine-grained material containing PSE is also transported over long distances, in some places high levels of PSE are also found in the sediments of major watercourses far from MWDs causing regional pollution (Miler *et al*., 2022). Main ore minerals are to some extent soluble in stream water. However, measured PHE leaching potential of MWDs is negligible. PHE levels in stream waters are low.

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Naturally occurring radioactive materials and risk assessment in the Lișava uranium mining sector, Banat Mountains, Romania

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The Lișava uranium mining sector is situated ~5 km to the south from Ciudanovița, in the Banat Mountains at the western margin of the South Carpathians, part of the Alpine orogenic belt. Uranium is hosted by the Ciudanovița Permian series completely developed in the eastern part of the Natra-Girliste anticline, where five cyclothems have been identified: Ciudanovița, Conglomerate Mesorhythm, Natra, Lișava, and Dobrei Rhythm. Each cyclothem is 20–200 m thick and begins with a basal conglomerate, ending with a fine-grained facies, predominantly siltstone. The uranium mineralization occurs in three horizons, each consisting of three or four cycles of gray to grayish-green cross-bedded microconglomerate/gritstone, sandstone, and bituminous siltstone of alluvial and lacustrine-alluvial origin. Intercalated barren horizons comprise well-sorted conglomerate and sandstone derived mainly from volcanic rocks. The mines from the Lișava sector were exploited underground between 1953 and 1986 (Dahlkamp, 2016).

The aim of this work is to assess the current levels of natural radionuclides ^{232}Th, ^{238}U and ^{40}K in soil and waste rock samples in the Lișava uranium mining area. Also, this study evaluates the radiological risk as a result of uranium mining activities.

The specific activity of ^{238}U, ^{232}Th and ^{40}K in 15 soil samples was determined by low background gamma-ray spectroscopy, using an n-type high purity germanium detector (relative efficiency of 27%, resolution of 1.80 at ^{60}Co 1.33 MeV and peak/Compton ratio of 56:1) connected with an MCA (ORTEC). The radiological risk was estimated as radium equivalent activity (Raeq.), absorbed dose rate (DR), annual effective dose equivalent (AEDE), annual gonadal dose equivalent (AGDE), external and internal hazard indices (Hex and Hin) and gamma representative level index (RLI). The mineral contents of selected waste rock samples (conglomerate and sandstone) were examined, using a Hitachi TM 3030 Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-Ray Spectrum (EDX).

For soil samples, the results show average values of 197.21 Bq/kg for ^{238}U, 16.21 Bq/kg for ^{232}Th and 543.21 Bq/kg for ^{40}K. ^{238}U activity is distinctly higher than ^{232}Th and ^{40}K. These values reflect geological settings and influences of human activities such as mining practices and tipping of radiological waste. The high levels of uranium in soils are found in samples collected from the vicinity of the radiological waste dump.

The mineralogical study of waste-rocks reveals that brannerite, pitchblende and uraniferous anthraxolite are the most important uranium-bearing minerals. Uranium minerals occur in sandstone as dispersed inclusions in solid bitumen and coal matter. Associated ore minerals include minor amounts of polymetallic sulphides (chalcopyrite, galena, pyrite, and sphalerite) that commonly associate with bitumen.

The world average absorbed gamma dose rate (84 nGy/h) recommended by UNSCEAR is exceeded in the area of waste-rock dump (241 nGy/h). All calculated values of the radiological hazard parameters show a similar trend.

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Eutrophic water conditions of Lake Belsh (Albania): preliminary results

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This research considers the eutrophication status of Lake Belsh, which is one of dozens karst lakes spread over the Belsh evaporitic dome in Central Albania. This lake, located in the center of Belsh Town, represents an important tourist destination, which is also an object of civil and agricultural pollution. This research gives the preliminary results of a study performed in July 2010, July–September 2021 and June 2022, where the water quality of the lake is presented by means of DO, BOD_5, NO_2^-, NO_3^-, NH_4^+, PO_4^{3-} and chlorine values.

The pH is slightly alkaline (8.03–8.53) while electric conductivity increased from 238.34 ± 2.05 µS/cm (July 2010) up to 314.76 ± 3.53 µS/cm (June 2022), probably due to continuous evaporation. NO_3^- shows a significant decline, from 6.35±2.84 mg/l (July 2010) to 1.98 ± 0.26 mg/l (June 2022), while NO_2^- and NH_4^+, occurring in low (0.07 mg/l and 0.17 mg/l) content, do not show any clear variation. PO_4^{3-} content is more stable (0.42 ± 0.25–0.57 ± 0.32 mg/l), whereas chlorine indicates a decline from 0.75 ± 0.15 mg/l (July 2021) to 0.27 ± 0.04 mg/l (June 2022).

In particular, the eutrophic conditions of the lake water are mainly characterized by the dissolved oxygen (DO) content measured in July 2010, July 2021, September 2021 and June 2022, showing values of 5.64 ± 0.19 mg/l, 3.47 ± 0.96 mg/l, 1.28 ± 0.03 mg/l, and 8.50 ± 0.20 mg/l, respectively. The decreasing tendency in DO content from July 2010 to July 2021 is probably conditioned by the cumulative effect of the temperature along with the increased O_2 amount consumed by respiration of a more abundant getting live organism. The immediate decline of DO content from July to September 2021 was due to both prolonged high temperatures during that time period that fostered the release of DO from the lake water into the atmosphere and the lack of precipitation, which is the main source of water recharge of the lake, and, consequently, of the O_2 introduction in the lake water. The concentration of DO is found to be high during the day because of the high radiation intensity, which stimulates the process of photosynthesis of the chlorophyll aquatic vegetation generating the DO in the water. The higher concentration of DO in June 2022 is related to heavy spring rains followed by sporadic precipitation at the beginning of July and with low rates of evaporation, as well.

The above DO contents measured in June 2022, July 2010, July 2021 and September 2021 characterize the trophic state of the lake water as oligotrophic (8.50 mg/l), mesotrophic (5.64 mg/l), eutrophic (3.47 mg/l) and dystrophic (1.28 mg/l), respectively. The dystrophic state of the lake water, which is considered a state of anoxia of the living world, has been confirmed by the death of fish (carp) that is reported by fishermen and also photographed during our fieldwork.

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Mineralogy and geochemistry of edible salts and their solid residues from the Greek market

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The consumption of salt is widespread in everyday life. Thus, the geochemical characterization of edible sea and rock salts are of great importance. In this study, eight edible salt samples, including rock and sea salts from the Greek retail market, were analyzed for their geochemical composition. The salt samples include the Mediterranean Sea salt (WS1), the Fleur de Sel from the Mediterranean Sea (WS2), the Hawaiian black salt (BS1), the Himalayan black salt (BS2), the Himalayan pink salt (PS1), the Hawaiian red salt (RS1), the Persian blue salt (BLS1) and the Alpine salt (BRS1). The primary classification criterion was the macroscopic color of the salts, which led to the discrimination of the white (WS1, WS2), black (BS1, BS2), pink (PS1), red (RS1), blue (BLS1) and pale brown (BRS1) groups. The insoluble impurities of three solid residue samples (PS1s, BS1s, RS1s) were also examined. Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) and X-ray diffractometry (XRD) were applied for mineral characterization. X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) were performed for major and trace elemental analysis on the salt samples and their solid residues, respectively. Correlations between elements were established by using ioGAS and IBM SPSS software.

As indicated by the XRD analyses, halite is the main mineral in all the samples. This is in accordance with the Na (33.1–38.8%) and Cl (59.7–61.5%) contents derived from the XRF analysis. Traces of sylvite were detected in sample BLS1, which also includes 5.7% K. The rest of the samples apart from RS1, contain minor amount of K (0.03–0.5%). Impurities of S (0.05–0.62%), Ca (0.07–0.56%) and Fe (0.01–0.23%) were detected in all the samples. Silica (0.02–0.1%) was found in four samples (WS1, PS1, RS1 and BRS1), Mg (0.02–0.05%) in four (WS1, BS1, PS1, BRS1), Sr (0.01–0.05%) in four (BS1, PS1, BLS1 and BRS1) and Al in two samples (RS1 and BRS1). The highest positive Pearson correlation coefficients ($p<0.05$; values>0.970) are defined by the elemental pairs Ca-Si and K-Si.

The residue samples consist of gypsum, Fe-oxides and silicate minerals, as revealed from the SEM-EDS analysis. The ICP-MS analyses showed that samples RS1s and BS2s contain Fe (<0.08%) and Mg (<0.21%), while K (<0.6%) was detected in samples BS2s and PS1s. Cerium (<0.3 mg/kg), Ge (<0.24 mg/kg), Mo (<0.21 mg/kg), Rb (<2.9 mg/kg) and Sr (<39.2 mg/kg) are found in all the residue samples. Sample BS2s incorporates the widest variability in trace elements including Ag (0.03 mg/kg), Ba (11 mg/kg), Co (0.2 mg/kg), Cr (2 mg/kg), Cs (0.14 mg/kg), Cu (13.2 mg/kg), Ni (0.8 mg/kg), P (142 mg/kg), Pb (1 mg/kg), Re (0.015 mg/kg), Sn (0.2 mg/kg), V (2 mg/kg) and Zn (8 mg/kg). Significant positive Pearson correlation coefficients ($p<0.05$; values>0.997) for the trace elements of the residue samples are defined by the elemental pairs Rb-K, Ce-Ca and Sr-Ge.

High-energy milling application as an ecological approach for increasing chemical reactivity of sedimentary phosphorites

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Applying mechanical tribo- and thermo-chemical methods for remodeling phosphate raw materials has a range of priorities over traditional conventional technologies. Conventional technologies for preparation of phosphorous fertilizers cause environmental pollution and even climate changes. This raises the problem of using rational and non-traditional methods for processing of poor raw phosphate materials. Recently, high-energy milling (HEM) activation finds growing application in treatment of sedimentary phosphorite ores of low total P_2O_5 ($P_2O_5^{tot}$) content and high content of admixtures (Elliot, 1994; Chaikina, 2002). The impact of mechanical forces over the samples is mostly related to an increase in the quantity of assimilable form of P_2O_5 ($P_2O_5^{ass}$) for the plants.

In this work are investigated untreated and HEM activated (for 5–240 min) natural phosphorites from Tunisia, Syria and Estonia, using chemical analysis, specific surface area (SSA), powder X-ray diffraction (XRD) and Fourier Transformed Infrared (FTIR) measurements. The HEM activation was carried out in a planetary mill with Cr-Ni milling bodies of diameter 20 mm.

The results from chemical analysis are presented. The exponential growth constants display the most rapid increase in the $P_2O_5^{ass}$ % with increasing HEM activation time for the samples from Bulgaria and Estonia, which contain greatest amount of SiO_2. The sample from Estonia contains larger quantity of SiO_2 and lower $P_2O_5^{tot}$.

The obtained results reveal that, after HEM activation, the richest in quartz sample E shows: (*i*) most rapid increase in $P_2O_5^{ass}$; (*ii*) shift of the maximal values of SSA to the longer milling time; (*iii*) formation of new isomorphic forms of carbonate-hydroxyl apatite in the presence of quartz. The results from the chemical, spectroscopic, and powder XRD methods give evidence for the formation of a mixture of fluorine apatite, hydroxyl carbonate apatite, and hydroxyl carbonate fluorine apatite taking place during the activation period.

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The impact of cement replacement materials in phase formation in mortars

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One of the main approaches to reducing the environmental impacts of the construction industry is the use of mineral additives reducing quantity of cement used in mortars and concretes for construction. Solid industrial wastes, including construction and demolition wastes, are traditionally used in conventional cement-based composites. Their application is limited by the application of compositions, requirements of desirable properties of fresh and hardened mortar/concrete, as well as the required durability and corrosion resistance to known exposure. White decorative mortars and concretes have restrictions on white color of the binder and mineral additive, good workability, and a dense structure that does not have significant destructive processes at various atmospheric impacts (Hamad, 1995; Ling and Poon, 2011).

The object of this research are different cement composites with high content of inert mineral fillers (marble and quartz sand) and low water-cement ratio, obtained after hydration of White Portland cement. The aim of the work is to investigate the phase formation and to measure the density, compressive strength and porosity of the cement composites, where the research is made after 28 and 120 days of water curing. The phase compositions (new formed phases as well as formation of C-S-H gels) are defined using X-Ray powder diffraction, Infra-Red Spectroscopy measurements and scanning electron microscopy. The experimental data show that the cement composites with higher water content exhibit a variety of new-formed phases, such as hydration products of C-S-H type. The use of marble as addition leads to the creation of carbo-sulpho-aluminates. Testing of samples with high content of inert mineral fillers showed that their structure is denser. Prolonged hardening of cement systems in the conditions of constant access of water increases the compressive strength by 17.9%.

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Influence of dust events on mineral matter input to ombrotrophic bog

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Mineral matter is deposited on peatlands as both dry and wet atmospheric deposition and represents about 1% of the total peat mass in ombrotrophic peatlands. Periods of increased atmospheric deposition, such as dust events, could be one of the most important factors contributing to the total amount of mineral matter in peatlands.

Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) was used to characterize the mineral matter deposited on Šijec bog (Pokljuka plateau, Slovenia). We collected solid atmospheric deposition from snow, rainwater, and using passive samplers. Samples were collected at average atmospheric conditions and after two dust events. Size, morphology, and chemical composition of individual particles were determined.

We classify analyzed particles into the following main groups: quartz, aluminosilicates, carbonates, organic matter and Fe-oxyhydroxide. Proportions of these groups vary between samples and between sample types, though aluminosilicates and quartz predominate in all samples. Samples affected by dust events are richer in solid particles. This is well observed in passive deposition samples. Carbonates and organic particles represent smaller fractions and are probably of local origin. Iron-oxyhydroxides make up a smaller, but significant part of particles and are, according to their shape and chemical composition, of both geogenic and anthropogenic origin.

Particles deposited during the March 2020 dust event originated from Central Asia (Tositti *et al*., 2021), whereas particles from the February 2021 dust event originated from North Africa (Francis *et al*., 2022). The difference in origin is reflected in the properties and composition of the particles.

Although local origin may be of greater influence for certain particle groups (carbonates and organic matter), particles transported over long distances represent an important fraction of annual atmospheric deposition.

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Session GT18

Open Session

Conveners:

Lubomir Metodiev, Rositsa Ivanova

An in-depth study of blast induced flitch movement

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Blast movement monitoring based on physical measurements is one of the leading ways to establish a good understanding of the nature of blast movement, as well as the locations of post-blast ore zones. This paper serves as a continuation of a previous study of the nature of blast induced rock movement in benches with a relatively low height (5 m). Following the example of previous works on the topic, established key factors were utilized in this analysis in order to obtain a better understanding of how blast movement differs for both flitches in bench blasting. The use of statistical hypotheses was utilized in this study as a method of determining whether the distributions of different spatial parameters used to describe 3D movement vectors differ on both flitches in a statistically significant manner. Furthermore, correlations were established between the movement parameters between both flitches. Last but not least, a ternary plot analysis is introduced in this paper for obtaining a better understanding of how blast movement and kinetic energy are distributed throughout blasting, based on numerous observations of the three spatial components of the movement vector in different shots.

Lithofacies of the Trypali Unit at the Samaria Gorge (western Crete, Greece)

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The Trypali Unit (W Crete) is a succession of (meta)carbonate rocks (*e.g*., dolostones, dolomitic limestones, carbonate breccias, marbles), showing various degrees of recrystallization (Creutzburg and Seidel, 1975). Both the main lithologies and the fossil contents (algae, corals, and gastropods) suggest that it was formed in a shallow depositional environment. According to the earliest investigations, this unit grades with a normal transition into the metaclastics of the "Phyllite-Quartzite series", and as also documented in various sites from the Central South Crete. On the contrary, Krahl *et al.* (1983) suggested that it is in tectonic contact with the underlying formations of the Plattenkalk Group. These rocks were conditionally assigned to the Rhaetian–Lower Jurassic and considered as a separate different tectonic unit. Krahl *et al*. (1983) provided biostratigraphic data for the "Phyllites series", and, based on numerous conodonts and ostracods, assigned it to the Upper Carboniferous–Lower Triassic. In addition, these authors considered that the Trypali Unit may possibly be a part of the Upper Triassic–Lower Jurassic carbonate sequence of the "Phyllites series", as it forms the reverse of an isoclinal fold, but also shows lithofacies distinction from the rocks of the Plattenkalk Group. Following Manoutsoglou and Steiakakis (2012), who considered that the intense karstification of the Trypali Unit affects the huge hydrogeological system of western Crete, and that clear tectonic relations between the Trypali Unit and the Plattenkalk Group are observed in the northern part of the Samaria Gorge, we conduct lithofacies and geochemical studies of the (meta)carbonate rocks of the Trypali Unit at the northern region of Samaria Gorge. Our studies aim to answer two key questions: what is the extent of the dolostones and dolomitic limestones within the sequence and whether the geochemical features of the rocks of the Trypali Unit significantly affect the water chemistry of the springs of the Samaria Gorge? In particular, the dolostone-limestone percentage ratio affects the dissolution of Ca and Mg ions, and therefore, the dissolution rate of the strongly tectonized metacarbonate rocks, located at the tectonic contacts between the Trypali Unit and the Plattenkalk Group, in parts at the south of the Samaria Gorge area. Consequently, the water quality of various aquifers, developed in these two tectonic units, are affected by this dissolution. The XRD and geochemical analyses results of 120 different rock samples, obtained from the Trypali Unit, extending north of the Samaria Gorge, highlight the minor to negligible dolostone occurrences into this unit.

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Small-sized Pliocene (Dacian) trovants from Bistriţa (Mehedinţi, Romania)

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The sands from the upper part of the Lower Dacian (Getian) in the area of Bistriţa locality (Mehedinţi, Romania) contain scattered small-sized "sandstone concretions", called trovants. In this area, the Lower Dacian deposits are mostly sandy, unlike the Upper Dacian (Parscovian) deposits which include a coal facies with lignite seams. Within the Dacian Basin, this stage (Dacian) corresponds stratigraphically to the lower part of the Pliocene. The Pliocene (Dacian) sands with trovants are developed in the border area of the Getic Depression, in the western part of the Dacian Basin, near the village of Bistriţa (Mehedinți, Oltenia). They contain small trovants that can reach up to about 5 mm in diameter. Generally, these mostly spherical-shaped trovants, have diameters of a few centimetres but can reach up to about 10–15 cm in diameter. These Dacian sands with small trovants have a cross-stratification, they are white-grey, but also include yellow-brown or reddish levels rich in iron oxides. At a certain level, the trovants are quite frequent, but they are individually disseminated in the mass of the sands in which they are located. Unlike the trovants of other ages known from different formations in Romania or around the world, sometimes they have small or very small sizes that can place them among the smallest trovants that exist worldwide. Trovants of other ages (from the Upper Cretaceous to the Pleistocene) are known from many distinct places in Romania, but their size is usually much larger. Often, however, along with trovants with meters-sized diameters, there are also trovants of smaller dimensions, but their diameters are decimeters-sized and rarely centimetres-sized. A good example are the Meotian trovants from Costeşti (Oltenia). The best-known trovants with ordinary dimensions in the Carpathian area are those from the Sarmatian (Volhynian) sandy deposits, which are very common, especially in the Transylvanian Basin. Slightly smaller trovants (diameters up to 10 cm) are known from Pontian (Upper Miocene) deposits near the Cohani locality (NW Transylvania). Among the larger trovants in Romania are the Eocene and Oligocene trovants from the Carpathian and sub-Carpathian areas. Sometimes they can reach meters-sized diameters. Large or very large trovants are known from around the world, as well as smaller trovants with centimetre-sized diameters, such as those reported by Jurand Wojewoda from Early Cretaceous deposits in Saudi Arabia (so-called „bubbles sandstone" in Biyadh Formation). If we take into account the possible palaeodynamic (palaeoseismic) origin of the trovants (Ţicleanu et al., 2008), we can admit that the presence of the small-sized trovants disseminated in the Dacian sands from Bistriţa is mainly conditioned by the presence of numerous drops of calcium acid carbonate randomly arranged, which were present in the mass of those sandy sediments, before the dynamic (seismic) shock that led most probably to the formation of the trovants.

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The role and importance of economic geology of Serbia in current market and strategic conditions

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Modern complex, changing and turbulent working conditions and functioning of the mineral economy and mineral sector of Serbia determine the special importance, place and role of economic geology, as a special scientific, professional and practical geological discipline, in classical, neoclassical and modern terms. The classic role of economic geology in the basic part is unchanged and it consists of finding, defining and providing the necessary mineral reserves in ore deposits, from the domains of metallic, non-metallic and energy minerals, necessary for the standard functioning of a number of industries dependent on mineral resources. The neoclassical role actualizes the operational and economic importance of economic geology in the conditions of additionally changed mineral market, crisis conditions related to the COVID19 pandemic period, as well as the topicality of the mineral sector due to military-operational-war events between Russia and Ukraine. The modern role of economic geology includes providing the needs of modern communication, computer and transport technologies, important for further communication and information improvement of means of transport and development of military-strategic-missile systems of the new generation.

In considering the current role of economic geology in Serbia, special attention should be paid to the changed circumstances of its functioning, which are related to the influence of four dominant factors, namely: (a) transitional conditions of economic activities within which mineral resources are used; (b) application of the concept of sustainable development in geological exploration, exploitation and market valorisation of mineral resources; (c) a pronounced ecological trend that accompanies the conditions of geological and economic work in Serbia; and (d) the operation of a large number of foreign companies with exploration or exploitation rights to mineral resources in Serbia.

In the full consideration of the current position of economic geology in Serbia, four important functional roles can be singled out, namely: (a) production; (b) economic; (c) ecological; and (d) strategic role. The production role includes providing the necessary quality and quantity of mineral raw materials for mineral production. At the moment, the exploitation of the necessary quantities of coal for the needs of electricity production is especially problematic, which is why there is a focus on imports, despite the availability of sufficient mineral reserves. The economic role is important from the point of view of creating significant production value and increasing the share of the mineral sector in the GDP of Serbia. With certain new mineral raw materials, such as the potential valorization of lithium and boron, new development perspectives are opening up, aimed at a higher level of mineral processing related primarily to lithium batteries in the communications industry, IT industry and the automotive industry. The ecological role is linked to the growing ecological trend, which was accompanied by recent mass environmental protests, with the aim of preserving the environment. The analysis of geo-ecological factors indicates the possibility of economically and ecologically sustainable exploitation of mineral raw materials, with the application of modern technologies with the prevention of water, soil and air pollution as key environmental media. The strategic role concerns the main strategic directions of the development of the mineral sector in accordance with the long-term plans of economic and social development in which mineral raw materials have a significant share. The connection between strategic management and economic geology in geological exploration and providing conditions for sustainable exploitation of numerous metallic, non-metallic and energy mineral raw materials for the needs of many economic branches is especially important. By fulfilling these four important roles, economic geology makes a very significant contribution to the successful functioning of the mineral sector and the mineral economy of the country in the upcoming period of economic development.

Economic evaluation of mineral reserves of Serbia in the function of successful market valorization of the results of geological exploration of mineral resources

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Modern conditions of market operations of the mineral sector and mineral economy require special improvement of the economic approach in defining the profitability of geological exploration of mineral resources. Quality mineral projects in accordance with the principles of project management and with the appropriate structure, type and scope of exploration work are an important prerequisite for the success of geological exploration. At the next step, it is necessary to carry out quality exploration work in compliance with the quality standards as well as appropriate procedures. The obtained results of exploration work, as well as laboratory tests require professional-expert geological-economic analysis and interpretation. Depending on the obtained results, two types of evaluation are prepared, namely: (a) natural evaluation expressed in natural indicators, at the first level of analysis; and (b) economic evaluation expressed in value indicators, at the second level of analysis.

The natural evaluation is the starting point for a demonstration of: (a) practical evaluation of the potential of the study area for metallic, non-metallic or energy minerals; (b) a review of the completeness of the exploration process; and (c) the natural expression of the mineral resources found. Among the elements of natural evaluation, quantitatively defined mineral resources, their spatial dimensions, spatial position, degree of concentration and quality and are especially important. However, the natural evaluation is not the final evaluation of the success of the geological exploration of mineral raw materials, but requires mandatory preparation of the economic evaluation, as well. There is a semi-direct relation between natural and economic evaluation, where a positive natural evaluation is a precondition for a positive economic evaluation, but not a guarantee of its positivity.

Economic evaluation is an obligatory part of geological-economic activity after the completion of geological exploration. It is precisely this that represents the practical application of the principle of staged economic evaluation, which obliges to provide economic evaluation at the end of each stage of geological exploration, which in its most complete form includes; (a) regional metallogenetic exploration; (b) prospective exploration; (c) previous exploration; and (d) detailed exploration. This obligation is in direct function of the economic viability of the mineral project of the subject exploration. Cost-effectiveness is defined on the basis of the analysis of the appropriate set of factors and the set of indicators of the economic evaluation of the results of the mineral project. The following factors are among the key factors that represent the starting analytical basis of economic evaluation: (a) metallogenetic (mineragenetic); (b) geological; (c) technical-exploitation (mining); (d) technological; (e) market; (f) regional; (g) socio-political-economic-strategic; (h) geoecological; and (i) legislative factors. In the final part of the complete geological-economic analysis, the expression of the subject factors is performed through three sets of indicators, namely: (a) a set of neutral ones (in a narrower and broader sense); (b) a set of values ones; and (c) a set of synthetic indicators. For each mineral project, the analysis of factors and the expression of a set of indicators are performed, so that the final economic evaluation can be defined. The primary economic result is the economic evaluation, which represents the difference between the market value of the result of geological exploration and the amount of costs of realization of the mineral project in question. The secondary result is obtaining expert geological-economic arguments for continuing geological exploration in the case of a positive economic evaluation or suspending further exploration in the case of a negative economic evaluation. In this way, economic evaluation directly appears as a very important geological-economic tool in making project, business and financial decisions based on appropriate geological exploration in the country's mineral sector and is the basis for economically justified market valorization of found mineral reserves.

Factor analysis of the geochemical associations in Sedefche epithermal ore deposit, Bulgaria

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The geochemical associations and spatial distribution of chemical elements in the Sedefche deposit are studied in this paper. The epithermal low sulphidation epithermal Au-Ag Sedefche deposit is in most eastern part of the Zvezdel-Pcheloyad ore field, Momchilgrad depression (Georgiev, 2012). Factor analysis was applied to determine the geochemical associations composed of groups of elements with similar spatial distribution. A total of 28 elements were included for the statistical data processing (Au, Ag, Pb, Zn, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, S, Sb, Sr, Ti, Tl, V). Some of the analysed elements which are not typical of the ore-forming processes or their contents are below the detection limit of the analysis are excluded from further statistical processing. The methodology to determine geochemical associations by factor analysis (Popov, 2002, 2016) is applied to evaluate the spatial correlation of the elements and the 3D modelling of the factor loadings. The results of the factor analysis reveal the total variation is decomposed on 7 factor axes. Thus, the obtained geochemical associations of elements with similar spatial distribution presented by each factor are as follows:

Factor 1: ([Mn, Be, Co, Zn, Fe] Al, Ni, Tl).
Factor 2: ([Ag, Pb, Sb, Au] Cu, As, Cd).
Factor 3: ([Hg, Tl, Mo, As] S, Au, K, Sb).
Factor 4: (Al, V, K, S, P)-([Ca, Mg]).
Factor 5: ([Ni, Cr] Ti)-(Ba).
Factor 6: ([Na, Ti] V, K, Ba)-(S).
Factor 7: ([Sr, P] V, Al).

Based on the factor analysis, the scores for each sample in the given factor can be calculated (Popov, 2002, 2016). This approach allows to perform further 3D modelling concerning that the factor scores represent the spatial relationship between elements. The first factor considers the behaviour of the group of elements Mn, Be, Co, Zn and Fe. The lower weights of Al, Ni and Tl mark their tendency to connect to this group. This factor follows the spatial distribution of the main ore zone. The second factor represents the distribution of the main ore elements in the Sedefche epithermal deposit, joined in association of Ag, Pb, Au and Sb, as well as As, Cd, and Cu with lower loadings. This factor follows the spatial distribution of all ore zones. The association with core of Hg, Tl, Mo and As, which have a high correlation with each other, is described by the third factor is. Elements Au, K, S and Sb also join here with lower weights. The development of this group of elements also falls within the limits of the main ore body, as their distribution is much more fragmented than factor 2.

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Special session SS1

Studies of ophiolites and mafic igneous rocks and their mineralizations: examples from Southern Europe and beyond

Conveners:

Ivan Savov, Nikolay Bonev

U-Pb zircon age constraints on a metaophiolite peridotite body from the high-grade metamorphic basement of the eastern Rhodope Massif, Bulgaria

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Metamorphosed ultramafic bodies commonly occur within the high-grade metamorphic basement of the Rhodope Massif (RM), and they have been considered as fragments of dismembered Precambrian ophiolite association (Kozhoukharova, 1984). The crystallization age of the ultramafic bodies is unknown, for which the only temporal constraints come from U-Pb zircon dating of eclogites that often rim these bodies. In the eastern RM, within the core of the Byala Reka dome, amphibolitized eclogite at Chernichevo peridotite body yielded an age of 381 Ma (Peytcheva *et al*., 2018) and other eclogite within the Kazak peridotite body yielded an age of 298 Ma (Bonev *et al*., 2019). Here, we report new U-Pb LA-ICP-MS zircon age constraints for the Zhalti Chal peridotite body in the Byala Reka dome.

The Zhalti Chal body consists of dunite (Bazylev *et al*., 1999), which is cross-cut by gabbroic dykes considered of metasomatic origin (Kozhoukharova, 1999). Field observations confirmed cross-cutting relationships of the dykes with the serpentinized dunite, and their NW-SE strike that parallels the elongation of the dunite body. The dykes consist of medium- to coarse-grained gabbro, which is transformed into massive and banded amphibolite. Amphibole and plagioclase are the main mineral constituents, followed by epidote and Fe-Ti oxides. Accessory minerals include titanite, rutile and zircon.

Two metagabbroic dykes have been dated, in which the zircons show a homogeneous pattern and oscillatory zonation consistent with magmatic origin. Zircons yielded concordia ages at 247.8 ± 2.3 Ma and at 244.7 ± 3.1 Ma for the first and second dyke, respectively, which are interpreted to date the gabbro crystallization.

The cross-cutting relationships and crystallization ages of the gabbroic dykes give an upper age limit for the crystallization of the Zhalti Chal dunite. Even the gabbroic dykes have emplaced in the late stage of the magmatic evolution of the dunite, and are affected by ocean-floor hydrothermal metamorphism, they provide a unique evidence for the late Paleozoic age of the Zhalti Chal ultramafic body in the eastern RM. Thus, the new age constraints for the RM metaophiolite ultramafic bodies connect them as remnants of the Paleotethyan oceanic lithosphere.

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Structure and volatile content of ultramafic magmas

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We employ atomistic calculations to model the structure of ultramafic magmas, with pyrolitic composition. This system is the approximant of the Bulk Silicate Earth (McDonough and Sun, 1995) and the global magma ocean that dominated the first stages of Archaen.

We monitor the atomic coordination, the interatomic bonding, and the chemical speciation in the melts as a function or pressure and temperature. We find that the ultramafic magmas are dominated by SiO_4 tetrahedra at low temperatures and pressure. As the pressure increases the building blocks of the melt acquire higher coordination. The melt is constituted of a framework of polymerized SiO_4 tetrahedra; the cations freely float between these units.

Then we monitor the behavior of a series of volatiles, like H_2O, CO, and CO_2, in the temperature and density ranges characteristic to large magma bodies. We compute the chemical speciation and the solubility of these volatiles in the magmas, and follow, at the atomic level, the process of bubble formation, which lies at the base of volcanic eruptions.

In the melt, in low concentrations, the water molecules are split and form hydroxyl groups, usually attached to the silica tetrahedra. They decrease the polymerization of the melt, and as such, render it less viscous. The carbonated oxides form free molecules, which are attached to Fe only at very high pressures, equivalent to more than 1000 km depths in the mantle. At these conditions, the carbon fraction forms oxocarbon species in the upper parts of the magma ocean. In the deeper parts, carbon formed complex polymerized species, involving both Fe and Si (Solomatova and Caracas, 2019).

Close to the surface, we find that carbon is massively released in the first outgassing stage, mostly as CO_2. The first CO_2 bubbles can form as deep as 40 km. Water is degassed only at a later stage, close to the surface, when the pressure and the temperature dropped significantly. The relative proportion of released CO_2 vs CO increases with increasing oxidation state, decreasing density, and decreasing temperature (Solomatova and Caracas, 2021).

Thus, our simulations offer a remarkable atomistic view in the mechanisms of magma outgassing and reactions with atmospheric gases. Our results can have extensive implications not only in understanding the chemistry of the atmosphere from the early Earth, but also in understanding magma emplacement and evolution, and volcano degassing and eruptions today.

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LA-ICP-MS U-Pb zircon age of amphibolite protoliths associated with the metaophiolites near the villages of Dobromirtsi and Bubino, east Rhodopes, Bulgaria

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The eastern part of the Rhodope Massif exposes mafic and large ultramafic metaophiolite bodies, whose origin and age are not clear enough to reconstruct past tectonic environments. The Variegated Complex in east Rhodopes hosts such associations characterized by a high-grade metamorphic overprint (Haydoutov *et al*., 2003), but the available protolith ages cover a huge time span. The present study focuses on two orthoamphibolite bodies, one found in association with the ultramafic massif near Dobromirtsi Village and the other belonging to the group of the Avren ophiolites near Bubino Village that previously were reported to relate to Precambrian protoliths.

The Dobromirtsi Ultramafic Massif is a lens-like ultramafic body that associates with amphibolites on its northernmost edge. The available Os model ages on chromites of ultramafic rocks showed large distribution of peaks within 2.6–0.13 Ga as well as Hf model age of 2.77 Ga and U-Pb age of 2253 ± 90 Ma obtained on xenocrystic zircons (José María González-Jiménez *et al*., 2015). In this study, 45 zircons from Dobromirtsi amphibolite yielded concordant clusters of xenocrysts in the range of 502–182 Ma and youngest Concordia age at 160.1 ± 1.8 Ma, corresponding to the protolith age of the amphibolite.

The metagabbro located south of Bubino Village builds up an elongated body, alternating with biotite and two-mica gneisses and marbles. Its chemistry displays of a boninite-like signature indicative of a subduction setting (Haydoutov *et al*., 2003) and the available U-Pb zircon age points to 572 ± 5 Ma (Carrigan *et al*., 2003). In this study, 36 analyses on zircons from the metagabbro revealed a wide range of inheritance within 678–173 Ma and the youngest autocrystic population of 22 zircons clustering at 166.8 ± 0.96 Ma thus providing the crystallization age of metagabbroic protolith.

The abundance of xenocrystic within the zircon populations found in the Dobromirtsi and Bubino amphibolites testifies for incorporation of a crustal material into the magmatic protoliths. The only plausible explanation involves magmatism related to an island arc environment. Therefore, the oceanic lithosphere mantle fragments from the Dobromirtsi and Avren ophiolites must date older than Middle Jurassic and connected with the Neotethyan seafloor spreading between Africa and Eurasia after the break-up of Pangea.

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Insights from the eclogite-facies Raspas Complex (Ecuador) into subduction of oceanic lithosphere at the South American convergent margin

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The Raspas Complex in Ecuador represents the only occurrence of eclogite-facies rocks of oceanic origin along the Andean convergent margin. It is a high-pressure (HP) ophiolite sequence that comprises metamorphosed mafic oceanic crust, sediments and mantle peridotites.

The geochemical characteristics of the metamorphosed oceanic crust are variable. Eclogites are similar to typical mid-ocean ridge basalt (MORB), whereas blueschists show a seamount-like geochemistry. The metasediments have compositions similar to bulk continental crust, reflecting a continent-derived origin, like sediments accumulating into accretionary wedges on the slopes of active continental margins today. Peak pressure-temperature conditions of ~550–600 °C at 1.8–2.0 GPa were reached contemporaneously for blueschists, eclogites and metasediments at ~130 Ma, suggesting that the different units were subducted as a coherent section of oceanic lithosphere (John *et al*., 2010). The MORB-type eclogites record Sr-Nd-O isotopic evidence for low-temperature alteration on the seafloor, whereas a fluid-induced, subduction-related metasomatic overprint of eclogites is only locally observed (Halama *et al*., 2011).

The mantle section of the Raspas meta-ophiolite serves as analogue for serpentinised oceanic mantle and hydrothermal processes on and near the seafloor. The peridotites exhibit REE patterns like depleted MORB mantle, but locally strongly serpentinised peridotites have positive Eu anomalies and elevated initial $^{87}Sr/^{86}Sr$ isotopic ratios, pointing to hydrothermal alteration of the peridotite precursor. Mafic dykes in the peridotites with HP metamorphic mineral assemblages originated as olivine gabbros and troctolites based on their major element geochemistry and positive Eu anomalies resembling those in gabbroic and troctolitic rocks of the Mid-Atlantic Ridge (Halama *et al*., 2013).

The close spatial association and the similar peak PT conditions indicate that the rocks of the Raspas Complex were subducted together in the down-going slab. The evidence for the subduction and exhumation of seamounts agrees well with the common observation of 2–3 km high seamounts on oceanic plates that migrate towards continents, which can remain intact despite prolonged subduction (van Huene, 2008).

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Brief overview on the Neoproterozoic Ophiolite association in the Rhodope Massif

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The Ophiolite association in the Rhodope Massif (OAR) is an ancient Precambrian metamorphosed ophiolite formation built on continental gneiss sole. Its genesis is related to a Neoproterozoic supra-subduction zone (SSZ) during ocean closure. OAR is a part of the stratigraphic sequence of the Precambrian metamorphic complex in the Rhodope Massif, which consists of two rock groups: the lower – Prarhodopian and the upper – Rhodopian group. The ophiolites occupy the lower stratigraphic levels (the Lukovitsa Variegated Formation) of the Rhodopian Group and mark the boundary between the groups.

The Ophiolite association is composed of: *a*) serpentinites; *b*) amphibolites – metamorphosed volcanic rocks and tuffs; and *c*) metagabbros and metagabbro-diabases.

The serpentinite bodies are placed concordantly between the lower layers of the Lukovitsa Formation, often directly on the gneiss sole of the Prarhodopian Group and are covered or included by amphibolites, schists and marbles. They are composed of lysardite, chrysotile and antigorite, rare relics of olivine, pyroxene and chromite. Mineralization of native copper, gold, pyrrhotite, pentlandite, laurite, sulfur-arsenide and elements of platinum group: Os, Ir, Ru, Rh, Pt, Pd have been established in some serpentinite bodies.

Amphibolites, as layers (thickness of 0.5 m to 15–20 m), alternate with amphibole-biotite schists, quartzites, carbonate schists and marbles. They are composed of amphibole (tschermakite-hastingsite) and plagioclase (andesine to bytownite), with variable amounts of quartz, biotite, garnet, epidote, pyroxene, titanite, rutile, magnetite, ilmenite. Amphibolites generally correspond to low K, high-Mg tholeiite basalts, locally enriched in Ti and Fe, and to a lesser extent to basaltic and peridotite komatiites.

The metagabbros form isolated small bodies. Rare dykes of massive amphibolites cut biotite and leptite gneisses of the Prarhodopian Group as well as the serpentinites.

The ophiolites are affected by three types of metamorphic changes: regional metamorphism, eclogitization and metasomatism. Products of regional metamorphism are amphibolites and talc-chlorite-actinolite schists. Eclogitization has taken place in shear (seismotectonic) zones of friction, where thin layers, lenses and stripes of eclogites and garnet lherzolites are formed *in situ*. Inclusions of microdiamonds in garnet document HP/UHP conditions within seismotectonic zones. The influence of metasomatism and pegmatite-aplite veins on basic and ultrabasic ophiolites produces hybrid rocks such as metasomatic gabbroids and corona gabbro-norites.

The formation of the Rhodope ophiolite association had taken place in three stages: a. *static* – serpentinization of the oceanic ultrabasic plate; b. *dynamic* – ocean closure, plate subduction and obduction of serpentinite fragments, scraped from the hydrated coat of the sliding ultrabasic plate; c. *constructive* – autochthonous subintrusive magmatism and SSZ-type volcanism, covering the serpentinite bodies. This determines heterogeneous nature of OAR formation.

The oldest ages by U-Pb on zircons from the chromitites indicate Paleoproterozoic era 2257 and 1952 Ma of the oceanic plate from which the serpentinite fragments have been torn off and 610–566 Ma for metamorphic basic rocks. The Neoproterozoic dates coincide with the time of ocean closure, preceding the amalgamation of the Gondwana supercontinent.

The Balkan-Carpathian Ophiolite REVISITED: Insights from new petrology, geochemistry and age results.

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The Balkan Carpathian Ophiolite (BCO) consists of four separate massifs that outcrop in Romania, Serbia and Bulgaria. After the pioneering works of Prof. Ivan Haydoutov (1933–2019) and his collaborators, the BCO was correctly interpreted as a well-preserved slice of mid-oceanic ridge (MOR), containing serpentinized peridotites, troctolites and gabbro cumulates, as well as ~1km thick sheeted dyke section and associated pillow and massive basalt lava flows and their umber (high Fe+Mn) sediment cover. Over the last two decades we have examined and sampled >100 outcrops of the little studied lower parts of the BCO succession in Bulgaria (Tcherni Vrah Massif) and Serbia (Deli Jovan and Zaglavak Massifs). We have also re-sampled the entire sheeted dyke and extrusive basalt (MgO>6 wt%; TiO_2>1 wt%) sections of the Tcherni Vrah Massif. Our new results largely confirm previous studies and reveal further evidence for genetic relationships between all of the ultramafic-to-mafic successions of the BCO. All BCO samples are metamorphosed to only low grade (greenschist facies) and although often deformed during exhumation and Alpine folding or intersected by Variscan intrusions, are highly suitable for petrological and geochemical studies. Here we report *in-situ* mineral chemistry (EPMA/LA-ICP-MS) dataset for fresh CPx grains from the pillow basalt and the sheeted dyke sections of BCO. The CPx grains are diopside/augite with Na^+ of ~0.025 wt% and Mg# >0.8. Importantly they all show LREE-depleted CI-normalized patterns that are identical to CPx grains from MOR settings. Trace element modelling and generally high Zr, Nd and Ti contents of the CPx crystals reveal low degrees (~5%) of partial melting of non-fertile (abyssal) mantle source. We also report spinel chemistry of peridotites and troctolites from BCO that display Cr# of 0.4–0.6 and Mg# of 0.3 to 0.6. Their Al_2O_3 ~25 wt% is straddling the boundary between SSZ-type and MOR-type (abyssal) peridotite sources that appear to have suffered low (~15 %) fractional (non-batch) melting regime. We also found fresh olivines from dunites and troctolites from the Deli Jovan Massif and those reveal Fo contents of 84 to 88 and low NiO of ~0.2 wt%, characteristic for MOR-like mantle source unmodified by subduction. The mineral chemistry results are in good agreement with the WR dataset for the extrusives, showing high Ti/V (20 to 50), as well as high Y (>20ppm) and high Cr (100–400 ppm), all resembling modern MORBs. In addition, the MOR setting is also supported by the trace element dataset that reveals Hf/Lu ~5, as well as generally flat CI-normalized REE patterns, low Th/Yb (<0.15) and low Nb/Y (<1). Finally, we report new Late Devonian (range is 357–383 Ma) ages [in situ LA-ICP-MS U-Pb dating of zircons (n=14)] for two microgabbro/diabase dyke samples from the vicinity of Gorni Lom Village in the Tcherni Vrah Massif. These ages agree well with ages reported for the other parts of the BCO. The age corrected isotope ratios of $^{86}Sr/^{87}Sr$ (all ~0.7034; n=16) and $^{143}Nd/^{144}Nd$ (all ~0.5129; n=8) for the basalts and sheeted dykes from BCO provide strong support for lack of significant contribution from any subduction component to the BCO mantle source. We shall discuss the exact geodynamic and paleogeographic position of the BCO in the context of other regional findings, as well as the new Devonian ages and our own paleomagnetic results.

Thermal history of the lower crust of the central part of the Siberian craton

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Garnet granulite xenoliths from kimberlites from the Archean Anabar province in Siberia underwent multi-stage metamorphic transformations at various pressure and temperature conditions, reaching at some point a temperature of ~900 °C. At present, the temperature at the Moho beneath kimberlite fields is in the range of 380–580 °C, according to Cherepanova and Artemieva (2015). Therefore, to understand when present-day conditions have been attained and to compare the geological history of the upper and lower crust we need to know their thermal histories.

We have compiled available age and thermobarometric data for lower crustal xenoliths from Devonian kimberlites in Siberia: the Alakit, Daldyn and Muna fields near northwestern boundary of the Markha Terrane, and the Nakyn field in the central part of the terrane. Relic magmatic cores of zircon grains have Archean ages: 2.7–3.2 Ga. The granulite-facies association (Grt+Cpx+Pl+Rt±Ilm) was formed at 750–50 °C and 1.0–1.4 GPa in dry conditions. Its age is 1.87–1.85 Ga for xenoliths from the Daldyn field as follows from the age of metamorphic zircon equilibrated with garnet and ≥1.88 Ga for xenoliths from the Nakyn field. The appearance of titanite replacing rutile, pargasite, scapolite, and the growth of new Ca-rich garnet requires a fluid influx. These minerals were formed at 600–650 °C, 0.9–1.0 GPa. The results of titanite dating show that this event occurred at 1.85 Ga. Rutiles from these samples have discordant ages with the upper intersection with the Concordia at 1.48 Ga that can be related to a slow cooling in the lower crust or another thermal pulse. Our data show that granulite-facies associations exist metastably in the lower crust and that fluid flux events can drive the associations to re-equilibration in conditions approaching those in stable lower crust beneath Precambrian terranes.

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Special session SS2

Large Cenozoic explosive eruptions in the Carpatho-Balkan Region and their influence on climate and ecosystems

Conveners:

Réka Lukács, Peter Marchev

Revealing the age of the detrital component and the potential sources of Miocene distal large pyroclastic eruptions recorded in Maritsa East lignite basin, Bulgaria

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The age of the detrital component of a sedimentary basin is crucial for recognizing the potential source of the supplying provinces. The careful study of coal bearing successions gives opportunity to find unusual (“exotic”) rocks, known as tonsteins that preserve evidence for large distal pyroclastic eruptions. They are represented as thin but widespread marker beds of clay-altered layers of volcanic ash, dominated by kaolinite with remnants of volcanogenic minerals like quartz, feldspars, biotite, zircon, etc., which can be precisely dated using radiogenic methods.

We studied the U-Pb age (using LA-ICP-MS) of the detrital zircons from the Miocene succession of Maritsa East lignite basin, part of Trace basin and report a new finding of thin kaolinized pyroclastic beds (tonstein) in the coal bearing succession. The aim of the research is to reveal the age of the detrital component, which give clues for the sources and the oldest age of deposition and to date the tonsteins in order to recognize the potential sources of the large explosive eruptions.

The age of the tonstein dated during the present study is 14.31 ± 0.30 Ma, which correlates with the age of the deposition of the organic matter that led to the formation of the productive middle lignite seam in Maritsa East basin. The revealing of the potential source of the large pyroclastic eruption that formed the distal pyroclastic layers is an intriguing problem. The closest by age volcanic activity in Bulgaria is the trachydacite cryptodome of Kozhuh volcano, dated at ≈ 12 Ma, but along with the age difference there are also no signs for large explosive eruptions related to it. Analysing the volcanic events in Greece and Turkey there were no large explosive eruptions at this concrete age. Nevertheless, in the area of Afyon-Eskişehir (Turkey), there are large Miocene ignimbrite deposits that could be still considered as a probable source area. One of the most possible sources of the pyroclastic material can be related to the Bükkalja Volcanic Field (NE Pannonian Basin, Hungary), where successive ignimbrite sheets are dated in the interval 18.2–14.4 Ma. One of the last large pyroclastic eruptions, represented by the ignimbrite of “Harsány”, is precisely dated using zircon U-Pb CA-ID-TIMS at 14.361 ± 0.016 Ma. Distal pyroclastics are correlated with this eruption in Romania (Dej tuff) and also as thin beds in Miocene successions in Western Europe. Other possibility for the volcanic source is the Gutai ignimbrite (in Romania), which is also considered as the proximal part of the Dej tuff, dated around 14.4–15 Ma.

The studied detrital zircon populations of the two samples from the Miocene succession show resemblance. Most of the detrital age clusters correspond to the local basement in the area of the basin. Several detrital age clusters were distinguished: 35 Ma; 49 Ma; 240–277 Ma; 290–315 Ma (most abundant); 400 Ma; 430–443 Ma; 603–612 Ma, 756–768 Ma and 1780 Ma. The most abundant age cluster 290–315 Ma shows that the predominant sources are the Early Permian-Late Carboniferous intrusions in the area.

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The role of the 33.4 Ma Duzhdovnitsa supereruption in the formation of the giant Mn concentration in the Paratethys: inferences from the Obrochishte and Binkilic Mn deposits

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The Early Oligocene (Rupelian) was the period of the formation of the giant manganese Phanerozoic Mn concentration in the Paratethys which includes Obrochishte (Bulgaria), Chiatura (Georgia), Nikopol (Ukraine) and Binkilic deposits (NW Turkey), as well as the small deposits in Hungary and Slovakia. The deposits contain reserves of ~ 600×10^6 metric tons of Mn, which makes the region the second largest accumulation of Mn in the world.

The deposits have attracted the attention of geoscientists because of the vast covered territory; similarity in age, facies relationships and lithological, mineral, and chemical compositions of the mineralized beds and their host. All deposits have formed in very shallow anoxic near shore or lagoon sea environments of the Oligocene Paratethys sea. Their origin and source of metals are a matter of long-standing debate. Despite the convincing evidence for the existence of the volcanogenic material (ash) and products of its alteration (zeolites, glauconite, opal, rarely chalcedony, diatomite, spongilite, rarely glass shards), the most favor a sedimentary–diagenetic origin.

We present for the first time high-precision sanidine $^{40}Ar/^{39}Ar$ and zircon U-Pb LA-ICP/MS ages for the Varna (Obrochishte) (Bulgaria) and Binkilic (Turkey) Mn deposits that establish synchrony of the deposits with the 33.38 Ma Eastern Rhodopes Duzhdovnitsa eruption from the Rhodope Massif, Bulgaria. The volcanic ash of the Duzhdovnitsa eruptions covered vast areas in the Central and Eastern Europe and were categorized as supereruptions. The age identity of the eruption and Mn deposits is further confirmed by the similarity of their crystal clast compositions. Such large eruptions expel enormous amount of ash and gases (H_2O, CO_2, S, Cl and F), their acids (H_2SO_4, HCl and HF) and aerosols that caused significant impacts on stratospheric chemistry leading to regional or global scale climatic and biotic changes.

To reconcile the deposition of the Mn deposits and Duzhdovnitsa supereruptions, we propose a new conceptual model. The large amount of solid particles (ash and dust), gases and aerosols with absorbed soluble fluoride, chloride, and sulfate metals released from the supereruption come into contact with the surface of the sea water. The absorbed acid salts dissolved instantaneously and released high amounts of Mn, Fe, Si and P, whereas dissolution of volcanic gases (H_2S, Cl, F) created anoxic-euxinic conditions which is a prerequisite for deposition of the Mn. Critical for the formation of the deposits is the concentration of the dissolved metals which depends on the volume of the water. It explains why the Mn deposits formed only in the shallow sea and lagoon basins but not in the open deep sea, although ash of the eruption formed tick tuff layers in the deeper sea. In these shallow basins, reaction of the Mn^{2+} and Ca^{2+} with the volcanic and sea CO_2 lead to formation of Mn-Ca and pure Ca carbonate minerals.

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Distal distribution of the Badenian Demjén Ignimbrite eruption unit in Hungary

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The largest Miocene explosive eruptions of silicic magmas in Europe are known from the Carpathian-Pannonian Region (CPR), which produced a huge amount of silica-rich pyroclastics between 18.1–11.5 Ma. Eruption centres are supposed to lie in the northern part of the Great Hungarian Plain covered by younger sediments. Pyroclastics are widespread in the Bükkalja Volcanic Field and in the Mátra Mts. as thick ignimbrite series, but in many sedimentary basins of the CPR their distal counterparts can be found as thin tuff/tuffite layers. In this work we examine the distribution of the pyroclastics of the Demjén Ignimbrite (DI) eruption unit, one of the most significant eruptions at 14.88 ± 0.014 Ma (zircon U-Pb age), with sharply different petrographical and chemical composition from other eruption units (eg. dacitic compositon, HREE depletion). We performed new LA-ICP-MS zircon U-Pb dating, whole rock ICP-AES, MS and glass LA-ICP-MS and EPMA geochemical investigations on various distal occurrences, and compared these with the proximal DI occurrences.

Between the Mátra Mts. and the area of Budapest, 10–40 m thick dacitic pumiceous pyroclastic flow deposits (lapilli tuffs) occur. Budafok and Fót occurrences provided ages of 14.9 ± 0.2 Ma, which suggest these units belong to the DI. In the area of Herend (Bakony Mts.) and in the Mecsek Mts, ~250 and ~300 km far from the Mátra Foreland, the supposed eruption centre, various successions of Badenian sedimentary basins contain thin, mostly 0.1–3 m thick tuff/tuffite intercalations. The lowest tuffite layer of Herend gave age of 14.9 ± 0.2 Ma, while the ones of Komló-Mecsekjánosi, Abaliget, Hetvehely and Hidas (Mecsek Mts.) provided ages between 15.1 and 14.8 (±0.2) Ma. Whole rock and glass chemistry data of these rocks are very similar to the published compositions of the DI proximal deposits.

The tuff layer of Kisbeszterce (Mecsek Mts.) gave a slightly older age (15.3 ± 0.2 Ma) and its chemistry slightly differs from the DI. However, it correlates well with samples from Požega Mts. (Croatia) in age and trace element composition, which was related to the Kuchyna Tuff of Slovakia.

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Traces of mantle explosive events in sediments of the Eastern Carpathians

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In the course of previous research, the assemblages of exotic highly reduced mineral particles were discovered in the kimberlites of the Ukrainian Shield and kimberlites of the Arkhangelsk and Yakutia diamondiferous provinces (Yatsenko, 2016). The term high-reduced mantle mineral association (HRMMA) has been proposed to describe these mineral particles. The HRMMA particle suite includes silicate spherules with native iron inclusions; spherules composed of iron oxides with a native iron core; particles of native metals (Fe, Cu, Pb, Sn, Zn) and their intermetallic alloys; Ti-corundum with trapped highly reduced phases, that are made of tistarite (Ti_2O_3), osbornite (TiN), khamrabaevite (TiC), intermetallic alloys (Fe, Fe-Si, Si-Ti-Fe). The study showed that the formation of HRMMA is not associated with the initial sources of kimberlite magma, but probably comes from deeper individual sources during the explosive breakthrough of gas-melt streams.

Various combinations of HRMMA components similar to those from kimberlites were encountered in different stratigraphic horizons of the Eastern Carpathians (Yatsenko *et al*., 2013) including Cretaceous deposits (Skyba Zone), Paleogene sediments (Krosno Zone) and Neogene sediments (Boryslav-Pokuttia Zone). Earlier, Hungarian researchers described two varieties of spherules from the Cretaceous sediments of the Carpathian Basin (Berczi *et al*., 1999). The study showed that the Carpathian HRMMA particles are pyroclastic material, not epiclastic (redeposited). Consequently, gas explosions occurred simultaneously with the formation of host rocks. HRMMA transportation to the surface was carried out by specific gas-explosive processes, which have never been witnessed. The characteristic features of this type of magmatic activity are: its catastrophic character with a sudden release of large amounts of gas with dispersed melt droplets; the inferred high temperature (more than 2000°C) of the erupted material; a large depth of melt sources; the repeated character of explosions; the lack of a connection with the stages of magmatic activity in the Carpathian region. We tend to believe that the vents of mantle explosions were located within the Carpathian and adjacent regions. However, it should be taken into account that the distribution of pyroclastic material could have a global character. Morgan *et al*. (2004) have demonstrated that deep explosions can produce microspherules, ejecting and transporting gas and large volumes of mantle material into super-stratospheric trajectories, with planetary dispersion of pyroclastic matter. Such catastrophic phenomena called “Verneshot” events could cause mass extinction events.

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Marine nannoplankton response to the Rhodope early Oligocene supereruptions: a case study from the St. Sozon and St. Irini sections, Limnos Island, Greece

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The Eocene-Oligocene transition (EOT, ~34–33 Ma) is characterized as a period of global cooling, disruption of marine ecosystems and the onset of Antarctic glaciation. However, the driving mechanisms of the cooling are still widely debated. Despite the convincing evidence for intensive volcanic activity during that period, the effect of the volcanism on the climate changes remains poorly understood. Herein, we present the variations in the marine nannoplankton on Limnos Island (Greece) as a result of two early Oligocene supereruptions (Dazhdovnitsa – 33.4 Ma; and Borovitsa – 33.8 Ma) from the Rhodope Massive, SE Bulgaria. Currently, Limnos Island is situated about 200 km south of the Borovitsa supervolcano, which is the assumed source of the eruptions. We studied quantitative and qualitative changes in the calcareous nannoplankton assemblages across three tuff beds from the supereruptions, included in a 1000-m-thick deep-water rhythmic turbidite sedimentary succession. The tuffs were studied in two sections: Cape St. Sozon and Cape St. Irini, located in the SE part of the island. The three tuff beds were precisely dated at 33.38 ± 0.37 Ma, 33.31 ± 0.61 Ma and 32.87 ± 0.51 Ma, respectively, thus correlating perfectly with the timing of the Dazhdovnitsa and Borovitsa supereruptions. The succession encompasses the Eocene-Oligocene boundary, defined by the first common occurrence of the species *Clausicoccus subdistichus* – an event recorded 4 m below the base of the first tuff bed in the St. Sozon section.

The Cape St. Sozon section (39º48′24.1″N; 25º21′48.5″E) has a measured thickness of 325 m. The total number of examined samples is 78. Nannofossils were taxonomically and quantitatively assessed by logging at least 300 fields of view of each smear slide. Our biostratigraphic results show that nannofossil zones CNE20, CNE21 and CNO1 are present.

The Cape St. Irini section (39º47′14.1″N; 25º21′14.5″E) represents a stratigraphic continuation of the St. Sozon section, with an overall thickness of >500 m. The total number of examined samples is 21. Nannofossil zones CNO1 and CNO2 have been documented.

The quantitative analysis of nannofossil distribution shows some fluctuations in the absolute abundances and species diversity below, within and above the tuff layers. Prior to the eruptions, the nannofossil assemblages are dominated by warm-water oligotrophic taxa, such as rosette-like discoasters (*D. saipanensis* and *D. barbadiensis* in CNE20), *Reticulofenestra*, *Cyclicargolithus*, *Helicosphaera* (in CNE21). The tuff layers are completely devoid of nannofossils. Above the eruptions, the nannofloras display reduced total abundances, gradual depletion of species diversity and increased relative occurrences of the genus *Clausicoccus* (*C. subdistichus*, *C. fenestratus*).

We opine that the products of these supereruptions (pyroclastic flows, ash and gases) triggered significant environmental perturbations on a large area, including present-day Limnos Island, and caused substantial decrease in nannoplankton production.

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Proximal and distal deposits of Miocene large explosive volcanic eruptions of Si-rich magmas in the Carpathian-Pannonian Region: a summary of the latest results based on zircon U-Pb age and geochemical data

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The formation and evolution of the Pannonian Basin as part of the Mediterranean region was accompanied by eruptions of compositionally diverse magmas during the Neogene to Quaternary. The long-lasting magmatic activity started with the most voluminous silicic eruptions in Europe for the last 20 Myr, resulting in more than 4000 km^3 of tephra during a period of major lithospheric extension. The chronology of the largest eruptions has been determined in the Bükkalja Volcanic Field, the Mt. Kalnik area and the Tokaj Mts. using high-quality zircon U-Pb dating suggesting eruptive phases between 18.1 Ma and 14.4 Ma (5 separated eruption events) and between 13.1 Ma and 11.5 Ma (4 separated eruption events), respectively. Volcanic glass, zircon and bulk rock chemical data show distinct features yielding specific geochemical fingerprints. They indicate the development of different silicic magma types, thus, these fingerprints help to correlate the eruption products even with scattered distal occurrences over large distances. We compare and correlate the distal volcanoclastic beds occurring in Hungary, Czech Republic, Austria, Croatia and Romania with the proximal deposits. Based on the notable isochronous radiometric ages within uncertainty as well as the zircon and glass trace element signatures we could define the largest eruptions, which might possibly reach even the supervolcanic size, such as at 18.2 Ma, 17.3 Ma, 14.9 Ma, 14.4 Ma and 13.2 Ma. Integrated zircon geochronology and trace element geochemistry are a powerful correlation tool even in case of severely altered deposits. Volcanic ash deposited over 1000 km away from the eruption centers and occasionally accumulated by local redeposition in subaqueous environment. These pyroclastic units serve as key-horizons in the lithostratigraphy of the Carpathian-Pannonian Region and the surrounding areas as well as in Paratethys stratigraphy.

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Perspectives on the Early Miocene silicic volcanism of the Carpathian-Pannonian Region

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The Carpathian-Pannonian Region (CPR) hosted some of the largest silicic volcanic eruptions in Europe during the Early and Middle Miocene contemporaneously with the major lithospheric thinning of the rift Pannonian Basin, which was recorded as an ignimbrite flare-up event from ~18.1 Ma to ~14.4 Ma. In order to gain in-depth perspectives on the eruption chronology, tephrostratigraphy, and petrogenesis at the onset of CPR silicic volcanism, we applied a multi-proxy approach on the Lower Miocene rhyolitic ignimbrites and volcaniclastic deposits ranging from the northern CPR to the Dinaride Lake System. High-precision zircon geochronology indicates there were two discrete pulses of volcanic activity at ~18.1 Ma and ~17.3 Ma. Based on combined tephrostratigraphic signatures, we propose that large 18.1 Ma Kalnik and 17.3 Ma Eger eruption events produced far-traveled, massive rhyolitic ignimbrites, which were deposited across northern and southwestern regions of the CPR. Due to easterly winds which carried volcanic ash hundreds of kilometers to the southwest, Eger eruption products also reached distal intra-montane Dinaridic lacustrine basins. Both events therefore capture important marker horizons in basin stratigraphy. Integrated zircon and bulk glass Nd-Hf isotope compositions have a positive correlation, defining a regional mantle array. A systematic isotopic change was recorded, moving from more crustal signatures in older eruptive events towards more juvenile compositions through time. This implies variations in the interaction between metasomatized lithospheric mantle-derived magmas and various crustal melts with time.

It is likely that CPR eruptions also contributed significant protolith material for subsequent Dinaridic karst bauxites in the region. By combining our new volcanic data set with high-precision zircon petrochronology from these bauxites, it is possible to refine models of transport of weathered material and provide a glimpse into CPR magmatic evolution during Early Miocene lithospheric thinning. Finally, these geochronology data from the bauxites help constrain broader Miocene environmental processes by constraining the timing of bauxitization in paleo mid-latitude Europe, providing continental paleoclimate data, and provide significant insight into the Miocene Climatic Optimum.

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Correlation of the tuffs from Eastern Thracian Basin, Turkey with the Oligocene Rhodope Massif supereruptions

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Thracian basin in NW Turkey is a large Middle Eocene–Early Miocene sedimentary depocenter with thicknesses of over 10 km. Numerous tuff layers alternating with the sediments have been described in surface outcrops and drill holes. However, precise geochronology and thorough mineralogical characterization are very limited which hinders their correlation with ash falls and ignimbrites in the nearby Rhodope Massif.

During the Upper Eocene to Lower Oligocene, the Rhodope Massif was the locus of intensive continental-arc volcanism and plutonism in an extensional environment with silicic volcanism comprising a significant part of the volcanic activity. Four voluminous silicic eruptions, which produced ignimbrites and co-ignimbrite ash, erupted within a ~4 Ma (34.3–31.8) flare-up period in the massif. The ashfalls covered large areas in the Central and SE Europe which can be correlated within and between sedimentary basins and to proximal deposits at source volcanoes. Two of these eruptions, designated as First and Second acid volcanism (FAV and SAV) or Dazhdovnitsa and Borovitsa supereruptions, respectively, likely originated from the Borovitsa supervolcano, forming a large 34×15 km caldera. These eruptions have been used as valuable stratigraphic markers in Bulgaria for over 60 years.

We sampled tuff layers from two sedimentary sections in Kıyıköy and Kızılcaali from eastern and central part of the Thrace basin in order to attempt to correlate them with the Dazhdovnitsa and Borovitsa supereruptions. Correlations have been established by applying precise geochronology in conjunction with glass and mineral chemistry.

The results from the zircon U-Pb ages (33.9 ± 0.4 and 33.2 ± 0.9 Ma) from the closely spaced lowermost two tuff layers from Kıyıköy and the lowermost tuff layer from Kızılcaali in the Thrace basin coincide with the $^{40}Ar/^{39}Ar$ age (33.3–33.4) ages of the Dazhdovnitsa supereruption. The second tuff from Kızılcaali 32.3 ± 0.7 Ma, coincides with the zircon U/Pb age (32.8 Ma) of the Borovitsa eruption. The age correlations are supported by the mineralogical studies. The tuff layers are composed of fresh glass shards and crystaloclasts of plagioclase, biotite, Fe-Ti oxides ± sanidine ± amphibole ± quartz and accessories – apatite, zircon ± titanite. Microprobe and LA-ICP-MS studies of the crystaloclasts show similar compositions to crystaloclasts of either Dazhdovnitsa or Borovitsa supereruptions. The glass shards and melt inclusion glasses show small variations, recording chemical heterogeneity present in the silicic magma chambers.

The identification of Dazhdovnitsa and Borovitsa supereruptions in the Turkish Thrace basin extends its known dispersal area. Along with other known tuff localities in the Central and SE Europe they demonstrate that these eruptions are the largest eruptions currently known from the Early Oligocene in Europe. As such, they can be valuable markers in establishing Oligocene chronology for paleontological and paleoclimatic studies.

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Late Miocene Si-rich pyroclastites in the Tokaj Mts and in the covered Nyírség area: New Zircon U-Pb Age and Geochemical Data

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In the north-eastern part of the Carpathian-Pannonian region large volume of silicic magma erupted in the extensional setting during early to late Miocene time (~18–11 Ma). The youngest rhyolitic pyroclastites with larger areal distribution and stratigraphic significance (up to 500 m thickness) were formed in the second half of the synrift phase (Tokaj-Slanec Mts., East Slovakian Basin, Beregovo area, Oaş Mts.). These are commonly associated with large volume of andesite, dacite, rhyolite volcanic edifices (lava dome fields and composite volcanoes) accompanied by significant hydrothermal alteration and ore mineralization. The total thickness of the volcanic successions is estimated to exceed the 2000 m (3000 m in Nyírség) according to borehole and geophysical data. The significant eruptions of Si-rich explosive volcanic material were contemporaneous with the andesitic-rhyolite volcanism around 15–10 million years ago (based on former K-Ar ages). In our work, we investigated the rhyolitic pyroclastites of the Tokaj Mts. from a zircon U-Pb geochronological, geochemical, petrological and stratigraphic perspective. This region provides the most complete stratigraphic profile of these youngest pyroclastites. Based on zircon dating, we can distinguish 4 major eruption events in the interval between 13.2±0.2 and 11.5 ± 0.2 Ma, representing three of the revised lithostratigraphic units: Sátoraljaújhely Rhyolite Lapilli Tuff (13.2 ± 0.2 Ma), Szerencs Rhyolite Lapilli Tuff (12.6 ± 0.2 Ma and 12.0 ± 0.2 Ma) Ma and Vizsoly Rhyolite Lapilli Tuff (11.5 ± 0.3 Ma) Formation. The exploratory boreholes drilled all three units in Nyírség and Tiszántúl areas (50–350 m thickness) but currently only K-Ar data are available for correlation. The general SiO_2 content ranges from 72–77 m%, they are peraluminous in nature. Less silicic, rhyodacitic material occurs only within the Sátoraljaújhely Formation (also drilled in Nyírség). The variability in major element compositions is usually connected to secondary effects on the rocks (compaction, mineralization). Based on zircon geochemistry the units slightly differ in Eu-anomaly, Ti, Hf and Yb/Dy, while whole rock and volcanic glass chemistry show more pronounced differences in Sr, Eu, Zr, Hf, Ba concentrations. The intercalating sedimentary rocks help to clarify the paleo-environment of the late Badenian and Sarmatian stages, confirming the transition from shallow marine to terrestrial environment (Central Paratethys NN 5-7 biozone) during the volcanism. The reviewed biostratigraphic markers represent the marine, reduced salinity lagoon and limnic environments.

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Special session SS3

Geologica Rhodopica – updated

Conveners:

Jan Pleuger, Kalin Naydenov, Neven Georgiev

The Middle Allochthon and possible solutions for its modes of appearance within the Rhodope Metamorphic Complex

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The Rhodope Metamorphic Complex (RMC) is interpreted as a Late Alpine nappe edifice consisting of four allochthons, namely Lower, Middle, Upper and Uppermost. The units that comprise each of the allochthons share common paleogeographical, tectono-metamorphic and age "DNA". The Middle Allochthon (MA) consists of orthogneisses and amphibolites with dominantly Late Jurassic protolith ages (~155 Ma) that associate with a variegated section of metasediments. The amphibolites and metabasites were interpreted as ophiolites of the Vardar Zone and Neotethys Suture within the RMC. The MA can be divided in two larger-scale groups of units – migmatized and non-migmatized. The age of migmatization is dated between 70 Ma and 60 Ma. Both the migmatized and non-migmatized units are intruded by synkinematic granitoids between 56 Ma and 50 Ma and again between 43 Ma and 40 Ma. The MA was cut by Oligocene post-kinematic plutons and dykes.

Problematic for the allochthon remain: (1) the particular relationships between the migmatized and non-migmatized units in different parts of the MA; and (2) the absence of the MA in some parts of the RMC.

The relationships between the migmatized and non-migmatized sections vary considerably in the western and central parts of the complex, whereas, to the east, such a distinguishing is rather difficult. In the western parts, a sequence of repeated non-migmatized and migmatized units forms a duplex, which shows an inverted metamorphic zonation, and thus a compressional and rather not significantly disturbed by the later extensional tectonics structure. In the Central Rhodopes, the migmatized section occupies the lower and the non-migmatized upper structural levels of the allochthon. The boundaries between the two types of units here represent extensional low-angle shear zones that eliminated a large volume of the section creating a ~200–250 °C gap.

While the units of the MA are well presented in the Western and Central Rhodopes, their existence in the eastern parts of the RMC is still questionable. However, amphibolites with ~155 Ma protolith ages that host ~50 Ma metapegmatites were interpreted as parts of the MA, sandwiched between units of the Lower and the Upper allochthons in the easternmost part of the RMC.

In summary, we can suggest a possible tectonic scenario where the western parts of the RMC underwent a lesser amount of Late Eocene extensional shearing, and thus relic compressional structures were preserved. In the central part, the extension was more advanced, so the initial compressional fabrics were largely obliterated and a part of the sequence was excised, although the units of the MA still constitute significant part of the complex. In the areas east of the Kesebir-Kardamos Dome, due to the intensive Late Eocene extensional shearing, the proven MA units represent different in size bodies (boudins), and thus reducing the thickness of the entire nappe pile in that area. The Late Eocene extension and related thickness reduction of the MA can explain the large differences in the crust thickness beneath the Rhodopes, decreasing considerably from west to east.

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Angular unconformity constraining the stratigraphic relationships of gold mineralization host units in the Surnak prospect, Eastern Rhodopes, Bulgaria

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In the Eastern Rhodopes of Bulgaria, several mining prospects in the area of the low-sulphidation sedimentary-hosted epithermal gold deposit Ada Tepe are a subject of intense industry interest, but questions regarding the stratigraphic relationships of the host units and factors controlling gold mineralization are yet to be answered. Exploration activities have so far been focused on the pre-mineralization sedimentary Shavar Formation in the immediate hanging wall of a regional detachment fault controlling gold mineralization in the region. The marl-limestone unit overlying the Shavar Formation and the conglomerate-sandstone unit in the basin is widely considered to post-date ore-forming hydrothermal activities. New field evidence from a 1:5000 geological mapping campaign complemented by core-logging data brings that commonly held belief into question. An angular unconformity separating the marl- and organogenic reef limestone-dominated base of the marl-limestone unit from the thin-bedded wavy limestone-dominated upper portion marks the transition from syn- to post-mineralization units of the sedimentary basin.

A structurally controlled ridge zone of intense hydrothermal silica alteration and carbonate-replacement textures to the east of the Surnak prospect provides key evidence for hydrothermal fluid activities at the base of the marl-limestone unit. Elevated gold assays from rock sampling of silica-altered marl and organogenic reef limestone suggest that deposition of the base of the marl-limestone unit pre-dates gold mineralization in the Surnak region. Those observations are supported by a drillhole interval of intersected silica-altered marl with anomalous Au content to the north of the silica-ridge zone.

In this work, it is suggested that an angular unconformity separates pre- from post-mineralization units of the sedimentary basin, thus constraining the stratigraphic relationship of units hosting gold mineralization in the immediate vicinity of the Surnak prospect and representing a marker for future exploration activities in the sedimentary sequence.

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Structural and thermochronological constraints on the late Alpine evolution of the northern Rila Mountains (Rhodope Metamorphic Complex, Bulgaria)

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The Rhodope Metamorphic Complex is exposed in several mountain ranges in southern Bulgaria and northern Greece, including the Rhodope, Rila, Pirin, Vrontous and Pangaion mountains. Numerous studies on the massif during the previous thirty years have revealed complex Alpine evolution that includes continental collision, partial subduction and syn-metamorphic nappe stacking followed by syn- to post-compressional extension (*e.g*., Burg, 2012). Generally, the geology of the Rhodope Mountains has attracted far more attention than some other parts of the complex, *e.g*., the Pirin and Rila mountains in southern Bulgaria. One of the probable reasons is that the Pirin and Rila mountains are the highest and least accessible parts of the Rhodope Metamorphic Complex, culminating at 2925 m in the Rila Mountains.

Unlike the Central and Southern Rhodope metamorphic complexes, rocks from the lowermost tectonic unit of the complex are not exhumed in the Rila Mountains (Gorinova *et al*., 2019). Furthermore, the rocks exposed in the Rila Mountains do not provide evidence for any syn-extensional migmatization and most probably escaped the Alpine high-pressure events that are characteristic of most other metamorphic complexes (Gorinova *et al*., 2019).

We present new $^{40}Ar/^{39}Ar$ and fission-track data that have been combined with detailed structural studies to investigate the tectonothermal evolution of the northern Rila Mountains. Late Early Cretaceous (~101 ± 0.1 Ma) cooling of the Variscan high-grade metamorphic basement through 440–400 °C was caused by either erosion of the emplacing thrust sheet or post-compressional denudation. A pulse of increased extensional cooling during the Eocene (39–35 Ma) was related to exhumation along the North Rhodopean Extensional System. The extensional system became inactive in the early Oligocene and was sealed by transgressive terrigenous deposits. Exhumation of the rocks in the northern part of the Rila Mountains below 110 ± 10 °C during the Middle–Late Miocene was associated with displacement along a system of normal faults and the formation of extensional sedimentary basins.

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The Middle Allochthon of the Rhodopean Complex and its geochronological "DNA" code

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With this work-in-progress, we would like to contribute to the geoscience community by developing and presenting a geochronology database of the Rhodope Metamorphic Complex. Each stage in the evolution of the different major units (allochthons) in the tectonic edifice of the Rhodopes has left a unique mark in the geological records. Analyzing the available publications, we started reconstructing the geochronological signature ("DNA") of the units. To demonstrate this database, we present here summarized age data for the Middle Allochthone (MA), which comprises variegated metamorphic units of continental and oceanic origin including voluminous Jurassic arc products.

In order to decrypt the DNA code of the MA, we used ~400 unique records. Very little is known about the metasedimentary units, but the story could start with the Middle–Late Triassic maximum sedimentation age of one segment of the MA. Almost all magmatic protolith ages of predominantly orthogneisses and minor metagabbro samples fell within the interval 145–160 Ma with a very pronounced maximum at ca. 152 Ma. Only two out of 50 records show protolith ages at ~250 Ma.

Reading the metamorphic record is more challenging as the samples are from different structural levels, even though within the same allochthone. The story revealed an early HT-metamorphism at 68 Ma in the western section of the MA, with one sample (interestingly, further west) extending the event to 82 Ma. A lower-temperature overprint has a broad peak centered at 46 Ma, although a good marker – the syntectonic veins/pegmatites/dykes – cluster at 51 Ma. The later tectonic evolution is emphasized by the crystallization age at 43–40 Ma of synkinematic granitoids. Some units reveal yet another, even younger, metamorphic event at ~35 Ma, which we consider a local phenomenon related to a strong strain partitioning and deformation localization during late tectonic stages. This age corresponds to cooling ages from other sections of the MA, which are the next integral part of the geochronology-DNA. An Oligocene post-kinematic magmatic event is also well depicted.

All units in the MA contribute to the formation of an interference pattern creating age-peaks, which correspond to contemporaneous events that occurred under the same general tectonic setting. This chain of events with their particularities is what we refer to as the "DNA" of the allochthone. There are outliers that carry information as valuable as the rest of the results. In some cases, they would push to reevaluation and reinterpretation of the facts in large domains, and hence would allow for significant improvement of the tectonic model. In other cases, the outliers indicate that there are still missing, or not yet fully understood, pieces of the jigsaw puzzle of the orogen. Harnessing the database, such outliers could be picked-up in a matter of seconds among more than 600 records covering 50 years of research and a whole orogen.

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The Strandja Massif – a Late Jurassic orogen

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The Strandja Massif forms a northwest-trending mountain belt of metamorphic rocks, about 280 km long and 40 km wide, along the southwestern margin of the Black Sea in Turkish Thrace and Bulgaria. It is strikingly different from the Rhodope Massif in the west in that the Strandja Massif does not show any significant Cenozoic orogenic activity. The contact between the metamorphic rocks of the Strandja Massif and those of the Rhodope Massif in the west is covered by Eocene–Oligocene sedimentary rocks, with the poorly defined Maritza Fault forming the boundary.

In the southeastern part of the Strandja Massif near Istanbul, the oldest rocks are late Neoproterozoic metagranites, which are overlain by a Paleozoic low-grade sedimentary sequence. In the northwestern part close to the Turkey-Bulgaria border, there are high-grade metamorphic rocks, including gneisses and amphibolites with Late Carboniferous metagranites. Close to the Carboniferous-Permian boundary, the Strandja Massif underwent a late Variscan metamorphism and deformation. Subsequently, it was intruded by voluminous Permian granites. The late Variscan basement, including the Permian granites, is unconformably overlain by a Triassic to Jurassic continental to shallow-marine sequence. During the latest Jurassic, the whole Strandja Massif underwent a second phase of deformation and greenschist-facies metamorphism. The deformation was north-vergent, with the Permian metagranites emplaced northward over the Mesozoic metasediments. The metamorphic rocks of the Strandja Massif are unconformably overlain by early Late Cretaceous (Cenomanian) marine sandy limestones, which provide a younger age for the deformation and metamorphism. During the Cenozoic, the Strandja Massif formed a broad ride between the Black Sea and the Thrace Basin, and was not involved in any orogenic activity.

Geology of the Byala Reka-Kechros Dome in the Eastern Rhodopes

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We integrate results of own field work and published geological maps into a newly compiled map of the Eastern Rhodopes. We group the tectonic units into four nappe complexes where the Lower Complex is interpreted to be derived from the Adriatic continent (including Pelagonia), the Middle Complex from the Vardar branch of the Neotethys, and the Upper Complex from the European margin. The structurally highest position is occupied by the Circum-Rhodope Belt.

The Lower Complex is represented by orthogneisses of the Byala Reka-Kechros and Kesebir-Kardamos domes. The Byala Reka-Kechros orthogneisses are overlain by a lithologically variable unit consisting of paragneiss, metapelite, orthogneiss, amphibolite, a few lenses of retrogressed eclogite, and marble. The latter occurs mostly in higher parts and along the top of the unit. This Byala Reka Variegated Unit may be either the original host rocks, into which the granitic protoliths of the Byala Reka-Kechros intruded, or a nappe that was thrust over the Byala Reka-Kechros orthogneisses. If the latter is true, the Byala Reka Variegated Unit may belong to either the Lower or the Middle Complex. The next higher unit, separated from the Byala Reka orthogneiss and Variegated units by the Eocene top-to-the-SSW Byala Reka low-angle normal fault, is the Luda Reka Unit, for which we obtained LA-ICP-MS U-Pb zircon protolith ages of 163.5 ± 2.6 Ma and 154.2 ± 1.0 Ma. Together with trace element patterns resembling those of MORB and lower oceanic crustal cumulates, these ages indicate that the Luda Reka unit represents former oceanic crust of the Vardar Ocean, and thus the Middle Complex. The Upper Complex is represented by the Krumovitsa-Kimi Unit that, in turn, locally underlies the Mandritsa-Makri Unit. This unit is traditionally included in the Circum-Rhodope Belt, which is partly based on the notion that it underwent only low-grade (greenschist-facies) metamorphism. We found peak temperatures of c. 530 °C and minimum peak pressures of c. 1.4 GPa by Raman spectroscopy of organic matter and of quartz inclusions in garnet, respectively, for the Mandritsa-Makri Unit. These data indicate that the metamorphic peak of the Mandritsa Unit was related to subduction, by contrast to the overlying Maglenik-Melia Unit that shows only anchizonal metamorphism. Considering that the contact between these two units is the top-to-the-NW Mandritsa low-angle normal fault of Eocene age, we interpret the Mandritsa-Makri Unit to be part of the Upper Complex and the Maglenik-Melia Unit to be the only unit representing the Circum-Rhodope Belt proper.

Modeling of the crustal and uppermost mantle structure in the Bulgarian Rhodopes

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The Rhodopes are a metamorphic complex that is part of the Alpine orogen. The geologic and tectonic evolution of the region is still highly discussed. In order to contribute to our understanding of the geodynamic evolution of the Rhodopes, we modeled the deep subsurface structure specifying the physical properties of the crust, lithospheric mantle and asthenosphere.

We obtained the lithosphere-asthenosphere structure of the Bulgarian Rhodopes as a west–east profile down to a depth of 350 km. The Bulgarian Rhodopes are covered by six cells, each with an area of 0.5°×0.5° and, for each cell, we collected lithological data for the uppermost 5 km of the structure (thicknesses for different lithologies, densities, shear and compressional wave velocities). These data are generalized into cellular lithostratigraphic columns. With this information and surface-wave dispersion data, a non-linear inversion procedure was used to obtain multiple solutions for each cell, using the lithological data and seismic surface-wave data with a period range of 5–150 s, following Raykova *et al*. (2015). The structures below the uppermost 5 km were parameterized, varying the thicknesses and the shear-wave velocities V_S. For each of the six cells, several models were obtained that fit the data within the error range. Additional geological and geophysical information was used to select a representative model for each cell in order to construct the west–east profile section of the Bulgarian Rhodopes.

We obtained that the crustal thickness decreases from 45 km in the Western Rhodopes to 34 km in the Eastern Rhodopes and the lithosphere thickness varies between ca. 55 km and 80 km; the V_S in the range 4.4–4.7 km/s for the lithosphere and between 4.2 km/s and 4.4 km/s for the asthenosphere.

We attribute the thin lithosphere to asthenospheric upwelling caused by fast rollback of the Hellenic slab from below the Rhodopes to its present-day position since the Eocene. This is in accordance with the maximum-allochthony hypothesis that assumes that the Neotethys suture is close to the northeastern margin of the Rhodopes and continued underthrusting of Adria-derived tectonic units below the Rhodopes until the middle Eocene (Froitzheim *et al*., 2014). Generally shallower depths of the lithosphere-asthenosphere boundary in the Eastern Rhodopes probably result from greater amounts of rollback in the east than in the west.

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A new structural model for the Surnak prospect, SE Bulgaria: exploring the potential for listric fault-related epithermal gold mineralization

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The Surnak prospect is located 5 km SW from Krumovgrad, Bulgaria, and is a part of the Eastern Rhodope gold mineralized district formed at the Eocene-Oligocene transition. It is characterized as an epithermal style gold-silver mineralization with quartz, illite and smectite as the dominating alteration minerals in the mineralized zones. Petrographic and EMPA studies suggest that the ore paragenesis consists of arsenian pyrite, gold, electrum, rare arsenopyrite, galena, sphalerite, chalcopyrite, marcasite, tetrahedrite and acanthite. The sulphide mineralization is closely related to a major N–S-striking sub-vertical normal fault.

The metamorphic basement in the explored area is represented by the NW flank of the NE-trending Kesebir-Kardamos dome and consists of amphibolite, gneiss, marble and calc-schist. The Tokachka detachment zone, which is a major structure in the region, separates the basement into upper, amphibolite-dominated, and lower, gneiss-dominated, units. The sedimentary rock sequence overlying the basement consists of Paleocene continental clastic rocks (Krumovgrad group), followed by two Eocene units: a pre- to syn-mineral coal-bearing-sandstone unit and a post-mineral marly-limestone unit.

During the period of 2019–2021, Dundee Precious Metals Krumovgrad completed a systematic diamond drilling and surface exploration at Surnak, which resulted in an extensive lithologic, structural and geochemical dataset that has been integrated and interpreted in Leapfrog Geo 3D model. Below, we aim to provide the key stratigraphic and structural aspects of this new model and define the main ore controlling factors.

The following structural elements have been identified and interpreted in the explored area:

1. N–S-striking and steeply dipping to the east transfer fault structures that involved syn-tectonic thickening of the sediments towards the east (Ludetina Graben) and provide the first-order control on the distribution of the highly mineralized syn-tectonic phreatic breccias;

2. Multiple N- to NE-dipping low-angle listric faults have been localized in the strongly deformed amphibolite unit, at the basement-sedimentary rock contact and within the sedimentary unit. These listric fault zones are marked by cataclastic tectonic breccias zones and are associated to strong argillic and silica alteration and Au-Ag mineralization;

3. Steep post-mineral NNW-striking graben faults and E–W-striking normal faults further complicate the area and contribute to the preservation and exhumation of Au-Ag mineralization.

This structural architecture identifies the N–S-striking subvertical structures as the key fluid pathways, which feed the deposition sites from deep fluid sources. The presence of the syn-detachment deformation provides conditions to form a good host for mineralization in the form of the cataclastic deformed upper metamorphic unit and basement-sedimentary contact. These factors provide potential for lateral and vertical continuity of Au-Ag mineralization outside of the existing resource contours.

Special session SS4–5

Pre-Alpine basement evolution between the Alps and Iran: significance for Western Tethys evolution

Conveners:

Franz Neubauer, Ianko Gerdjikov, Yongjiang Liu

Pre-Alpine tectonic evolution of the Eastern Alps: From Prototethys to Paleotethys

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In all reconstructions published during the last two decades, the Austroalpine and the correlative Southalpine basement units of the Eastern Alps were considered to represent a uniform continental block that split off from the northern Gondwana margin during Early Paleozoic times and collided with microcontinental blocks during the Variscan orogeny in the early Late Carboniferous. Afterwards, these units formed finally the outboard part of the European Variscides adjacent to the Paleotethys Ocean. The combined Austroalpine/Southalpine basement extends to the Western Carpathians, contains Ediacaran and Early Paleozoic ophiolites and magmatic arcs and Devonian passive margin successions and represents a key region for resolving the Late Neoproterozoic to Late Paleozoic tectonic evolution of the basement in the Alpine-Mediterranean Mountain belts. The Austroalpine and Southalpine basement contains well-known fossil-rich Ordovician and Silurian rift and mainly Devonian passive margin successions summarized as the Noric and Carnic domains, which were juxtaposed to amphibolite-grade metamorphic complexes during Early Carboniferous plate collision. In the metamorphic units the following main stages of tectonic evolution are: Two distinct Ediacaran to Cambrian arc systems were recognized, correlating with subduction of the Prototethys (Ran) Ocean. The continental Wechsel Arc stopped its activity during Late Cambrian times, whereas the Silvretta-Gleinalpe Arc was reactivated at the Devonian/Carboniferous boundary during subduction of the Devonian Balkan-Carpathian Ocean. The Prototethyan oceanic crust is preserved in the ophiolitic Upper Neoproterozoic to Middle Ordovician Speik Complex, that was obducted onto the Silvretta-Gleinalpe Arc during Late Ordovician to Early Silurian times. On the other hand, the Noric domain was initially part of the northern Gondwana margin and includes a virtually continuous sedimentary section ranging from the Early Ordovician to earliest Pennsylvanian. It started with an Early to Late Ordovician rift succession with mafic and acidic volcanic rocks related to rifting of parts of the Noric domain from the northern Gondwana margin forming an oceanic basin (Rheic Ocean of previous interpretations) in between and back-arc rifting is the likely setting. In both Noric and Carnic domains, Silurian strata were deposited during a tectonically quiet period followed by onset of a second rifting period during Late Silurian times, which resulted in deposition of thick Devonian carbonates heralding the opening of the Balkan-Carpathian Ocean and separation of the Paleo-Adria microcontinent from Gondwana. Late Devonian–Carboniferous plate convergence led to subduction of this oceanic rift followed by subduction of the Paleo-Adria margin underneath the accreted Variscan convergence belt, collision and Late Carboniferous intramontane molasse deposition. However, new data argues that a third ophiolitic belt, the Plankogel ophiolitic mélange, which formed as part of the Paleotethys Ocean during the Devonian and was reactivated as trench during initial consumption of the Paleotethys Ocean during late Permian–Triassic times. In this preliminary model, Mid-Late Triassic plutonic and volcanic rocks of the Southern Alps are considered to represent the magmatic arc associated with the Paleotethys subduction. (For more details of data and models, see Neubauer et al., 2022, Pre-Alpine tectonic evolution of the Eastern Alps: From Prototethys to Paleotethys. Earth-Science Reviews 226, 103923).

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Tectonic history of Proto- and Paleo-Tethys Oceans in the Eastern Alps: Evidence from the Schladming Complex

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The pre-Mesozoic basement of the Austroalpine mega-unit of the Eastern Alps suffered Variscan and Alpine polymetamorphism and magmatism and records important tectonic information since the late Neoproterozoic. The Schladming Complex is an important component of the Austroalpine mega-unit, which can reveal the tectonic history and relationships of tectonic units formed closely related with Proto- and Paleo-Tethys Oceans.

We analyzed the whole-rocks geochemistry, zircon U-Pb ages and zircon Hf isotopy of numerous amphibolites and (meta-)granites from the Schladming Complex. The whole-rock geochemical data show that these rocks generally are depleted in Nb, Ta, Ti and, less reliable, enriched in LILEs (*e.g.*, K, Rb, Ba) and show subduction-related features. These features proved the evidence of a “magmatic arc root” proposed by the Neubauer and Frisch (1993).

According to the zircon U-Pb dating results, the inherited zircons of Schladming Complex show similar age peaks with Cadomian basement units, implying that the Schladming basement split off from the northern margin of Gondwana. The ages allow distinction of magmatism and metamorphism of the Schladming Complex into three phases: (1) Early Cambrian to Middle Ordovician (540–480 Ma); (2) Middle Devonian to Carboniferous (380–320 Ma) and (3) Late Permian to Middle Triassic (270–240 Ma). The Early Cambrian to Middle Ordovician magmatism was related to the subduction of the Prototethys Ocean and separated the Schladming basement from the northern margin of Gondwana by formation of a back-arc basin. The Middle Devonian to Carboniferous magmatism and metamorphism reflects the Variscan orogeny in the Eastern Alps resulting from of subduction of Balkan-Carpathian Ocean or of a branch of either the Paleotethys or Rheic Ocean. However, the final assignment to a specific ocean still needs more evidence. The Permian-Triassic A-type granite reflect Permian to Middle Triassic A-type granites associated with back-arc extension in the Schladming Complex, which is related to the subduction of the Paleotethys Ocean and opening of Meliata oceanic back-arc basin (Huang *et al*., 2022).

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Subduction initiation in the west Proto-Tethys Ocean record by the ophiolitic Speik Complex of the Eastern Alps

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Supra-subduction zone (SSZ) ophiolites form in forearc settings, *e.g*., the Izu–Bonin–Mariana (IBM) in-situ forearc and show conversions from normal mid-ocean ridge basalt (N-MORB) to boninitic affinities, which are widely interpreted as rules for the evolving chemical geodynamics of subduction initiation magmatism (Ishizuka *et al.*, 2018). Here, we report newly documented forearc rocks, generated during subduction initiation of the Speik Complex in the Eastern Alps, which is part of the Middle Austroalpine basement unit. Lithologically, the Speik Complex consists of variably serpentinized ultramafic rocks, plagioclase amphibolites, garnet-amphibolites, locally exposed eclogites, granitic gneisses and some metasedimentary rocks (Neubauer *et al*., 2022). New zircon U-Pb dating results show that the garnet-amphibolites, plagiogranitic gneisses and plagioclase amphibolites were formed during latest Cambrian (496 ± 5 Ma–489 ± 6 Ma), latest Cambrian (491 ± 2 Ma) and Early Ordovician (476 ± 3 Ma–472 ± 4 Ma), respectively. The amphibolites have geochemical characteristics similar to those of IBM forearc basalts, with nearly flat REE patterns and positive ε_{Hf}(t) values (2.5–14.9), and show enrichment in Rb, Ba, and Sr and slight depletion in Nb, Ta, and Zr, suggesting an origin by decompression melting of a depleted mantle source. The granitic gneisses have low K_2O contents (0.56–0.59 wt%), low K_2O/Na_2O ratios (0.14–0.15), $(La/Yb)_N$ ratios (1.54–1.60) and $(Gd/Yb)_N$ ratios (0.93–0.98), flat REE distribution patterns and positive ε_{Hf}(t) values (4.7–8.0), indicating that their protoliths are typical oceanic plagiogranites. The plagioclase amphibolites are similar to those of typical boninites with low rare earth element and high field-strength element contents, and show depletion of Nb, Ta, Zr and Hf. These geochemical features and the depleted ε_{Hf}(t) values (6.1–8.7) suggest that the protoliths of plagioclase amphibolites were generated later during residual, highly depleted mantle fluxing by the subducting plate. Because the subduction of the Proto-Tethys Ocean, the Wechsel arc was detached from the northern margin of the Gondwana and a backarc basin was formed during the late Ediacaran. The backarc basin continued to expand thus forming the Speik Ocean. An intra-oceanic subduction initiated in the Speik Ocean and formed the ophiolitic Speik Complex during the late Cambrian–Early Ordovician.

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Protolith and metamorphic ages of eclogites from the Eastern Alps: The Permian to Cretaceous Wilson cycle of the Austroalpine mega-unit

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The Austroalpine mega-unit contains the type locality for eclogites (Haüy, 1822) but their protolith ages are largely unknown except that of the Permian Bärofen metagabbroic eclogite, for which three Sm-Nd ages between 275 ± 18 and 275 ± 18 Ma have been reported (Thöni and Jagoutz, 1992; Miller and Thöni, 1997). Therefore, we studied the abundant non-gabbroic eclogites from the Saualpe-Koralpe and Sieggraben Complexes, which are considered to represent a previously coherent subducted and then exhumed fragment of a continental rift, which led to the formation of the late Middle Triassic Meliata oceanic basin. A combined zircon U-Pb and Hf isotopic study, whole rock geochemistry of two complexes revealed a protolith age of 242.3 ± 2.6 Ma (Middle Triassic) in the Sieggraben Complex, and 283 ± 5 Ma, 255 ± 3 Ma (early and late Permian), 251 ± 3 Ma, and 241 ± 3 Ma (Early to Middle Triassic) in the Saualpe-Koralpe Complex. Magmatic zircons from the Sieggraben eclogites have $^{176}Hf/^{177}Hf$ ratios of 0.283067–0.283174, εHf(t) values of +15.7 to +19.4, and that from Saualpe-Koralpe eclogites have $^{176}Hf/^{177}Hf$ ratios of εHf(t) 0.282935–0.283090, εHf(t) values of +10 to +17.4 showing their juvenile mantle source rather than significant crustal assimilation. In both complexes N-MORB geochemical characteristics are established. Associated ultramafic rocks of the Sieggraben eclogites as part of oceanic or Permian subcontinental mantle lithosphere suggest a depleted mantle source and a deep subduction environment. Two zircon grains of the Sieggraben eclogites with low Th/U ratios yield ages of 113 ± 2 Ma and 86 ± 4 Ma and represent the approximate age of eclogite metamorphism during Cretaceous. A trondhjemite dike cutting the eclogite gives a crystallization age of 82.19 ± 0.4 Ma and was formed by partial melting of likely eclogite during decompression. The host metasedimentary rocks of the Sieggraben and Saualpe-Koralpe Complexes are interpreted as old continental crust close to the margin of the Meliata basin, which were affected by Permian migmatitic metamorphism. Metamorphic zircons of one eclogite from the Saualpe-Koralpe Complex give an age of 87–93 Ma (peak at 91 ± 1.2 Ma). The results of this study combined with previous results are used to present a new model for the tectonic evolution of the distal Austroalpine unit associated with the Meliata Ocean in the Wilson cycle: the Austroalpine Sieggraben and Saualpe-Koralpe Complexes represent a location on the distal thinned continental margin during Permian to Middle Triassic rifting. The mafic rocks are associated with numerous Permian and potentially Triassic acidic pegmatites, whereas the structurally separated thick Triassic sedimentary cover successions lack any magmatism, likely excluding the present-day eclogite-bearing units as Triassic basement of the sedimentary cover successions.

The now eclogite-bearing piece of continental crust adjacent to the Meliata oceanic lithosphere subducted during Early Cretaceous times to mantle depth. The subducted continental crust was then exhumed incorporating even ultramafic mantle rocks. During exhumation and decompression of mafic rocks, partial melting took place forming the trondhjemite dike in Late Cretaceous times.

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Permian–Triassic metagabbros in the Raabalpen basement of the eastern Lower Austroalpine Unit: U-Pb zircon dating and palaeogeodynamic implications

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The Lower Austroalpine Raabalpen Complex of the Eastern Alps comprises mainly a purely clastic metasedimentary succession of micaschists, migmatitic paragneisses and retrogressed quartz phyllites and phyllonites. The Strallegg Gneiss is a migmatitic, locally alumosilicate-bearing biotite-rich paragneiss with a wide range of migmatite textures mixed with leucosomes. The migmatites host the widespread "Grobgneis", a mid-Permian coarse-grained porphyric metagranite (Yuan *et al.*, 2020), Undated metagabbros and amphibolites occur as decameter thick lenses within paragneisses and along margins of the "Grobgneis". To further understand the palaeogeodynamic setting of the magmatism, we carried out detailed geochronological and geochemical investigations on these mafic rocks.

LA-ICP-MS zircon U-Pb dating of four samples provides the first reliable evidence for the mid-Permian (264.8 ± 1.4 Ma, 265.4 ± 1.4 Ma) and early Triassic (251.9 ± 1.1 Ma, 251.4 ± 1.2 Ma) mafic magmatism of the Raabalpen Complex. Cathodoluminescence images of zircons display clear oscillatory zoning, and Th/U ratios are between 0.3 and 1.2 documenting magmatic formation. Permian–Triassic magmatic bodies and volcanics are widespread not only in the Alps but also in Western Carpathians (*e.g.*, Villaseñor *et al.*, 2021; Huang *et al*., 2022 and references therein) and other Southeast European Mediterranean Mountain belts (Molli *et al.*, 2020) but the Permian–Triassic geodynamic setting of the Alpine-Carpathian Orogen remains controversial and is crucial for palinspastic reconstructions of the Pangea breakup.

Mafic magmatic bodies and granites in the Lower Austroalpine Unit were almost emplaced during Permian to Triassic times. We contend that mafic and acid magmatic rock groups belong to a bimodal association, tentatively interpreted as a continental rift attributed to the Paleotethys subduction associated with a back-arc stretching (Huang *et al.*, 2022). The metagabbros and amphibolites in the Raabalpen basement are characterized by a continental arc. Considering the Permian–Triassic Pangea breakup, we argue that the Permian–Triassic rifting is modified by the Paleotethys subduction.

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Lower Paleozoic low-grade metamorphic units from the Central Balkan Zone, Bulgaria: tectonic relationships, framework and geodynamic significance

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The Central Balkan Zone, best exposed within the Stara Planina Mountains chain in Bulgaria and Northeast Serbia, is part of the Alpine Balkan orogen. Pre-Permian low-grade metamorphic rocks build a large portion of the basement of this zone. Metamorphosed during the Variscan orogeny, they were later involved in the Alpine compressional tectonics. Yet, the Alpine overprint is mostly localized along discrete shear zones and therefore the pre-Permian tectonic configuration is largely preserved. For the western part of the Central Balkan Zone, a key stratigraphic benchmark is the paleontologically well-dated Middle–Late Ordovician Grohoten Formation. This formation is stratigraphically overlaying the low-grade metamorphic rocks affiliated to the Diabase-Phyllitoid Complex (DPC) and other meta-sedimentary formations. Upward, above the Grohoten Formation, the section continuous with Late Ordovician to Devonian sediments, including late Hirnantian glaciomarine deposits, clearly indicating Gondwanan affinity of the Lower Paleozoic sequences in the Central Balkan Zone.

We propose a new framework for the Lower Paleozoic low-grade volcanic and sedimentary rocks from the Central Balkan Zone, applying a critical analysis of the existing data combined with new geochronological data and detailed field observations. In the areas of Murgash, Bilo, Etropole and Zlatitsa mountains, we are distinguishing three low-grade metamorphic units: Korduna, Zvezdets and Bilo. The Korduna Unit, located between the high-grade metamorphic basement of the Sredna Gora Zone to the south and the Zvezdets Unit to the north, represents a strongly sheared mélange-like complex. An inverted metamorphic gradient from a mid-greenschist in the uppermost levels to low-greenschist in the lowermost domains observed in this unit is related to the crustal-scale top-to-the-N shearing along the Variscan Stargel-Boluvanya Tectonic Zone. We assume an Early Ordovician–early Silurian maximum age of the sediments of the Korduna Unit suggested by the younger xenocrystic zircon population of 474–441 Ma from a syn-metamorphic quartz vein. We consider these xenocrystic zircons as representing a detrital input in the host sediments later trapped in the metamorphic vein. These data are consistent with the early Silurian U-Pb zircon age of 443.0 ± 1.5 Ma reported for a diabase from the upper structural level of the Korduna Unit. The underlaying Zvezdets Unit represents a very low-grade greenschist succession of phyllites exposed in Murgash and Etropole mountains. There are not any paleontological and geochronological data reported from this unit and a Cambrian–Ordovician age is assumed, due to the fact that it is covered by the Middle–Late Ordovician Grohoten Formation. The lower contact of the Zvezdets Unit with the underlaying Bilo Unit is gradual, marked by a downward increase of the metamorphic grade. The Bilo Unit, representing a mélange of low-grade metasediments and mafic rocks, is very similar to the DPC (s.s.), exposed along the Iskar River Gorge. Most probably, both represent Cambrian–Lower Ordovician mélange complexes formed in an accretionary prism along the southern, Gondwanan margin. The confirmation of the normal stratigraphic position of the Grohoten Formation over Zvezdets and Bilo Units supports the idea of their Gondwanan provenance.

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Reconstructing the Adria platform at the Permo-Triassic boundary: a Bahama Bank model

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The end of the Permian marks the greatest mass extinction in the geological record, and many recent studies are exponentially increasing knowledge of the Permian/Triassic boundary interval in an attempt to determine the causes of the mass extinction. This concentration of research lets us use the boundary as a timeline, along which we can relate both vertical and lateral facies changes to possible causes. The Permo–Triassic sections of the western Paleotethys, lie on the Adria block, which forms parts of the Apennines, Dinarides and eastern Alps and was highly deformed by enormous lateral displacements between structural units during the closing of the Paleotethys and the opening and closing of the Neotethys oceans. Tectonically restoring the bank gives the original Permo-Triassic facies distributions, which show shallow-deeper ramp variations on the generally uniform bank analogous to those of the Quaternary Bahama bank.

Hf isotopic constraints for the Austroalpine basement evolution of the Eastern Alps: review and new data

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The Alps, as part of the Alpine-Mediterranean Mountain chain, are one of the classical localities for orogenic studies, where the Mesozoic–Cenozoic tectonic evolution is well known. However, the pre-Alpine basement remains poorly known because of the lack of sufficient age data, complex polyphase deformation and polymetamorphism. New data from the mainly amphibolite-facies pre-Alpine basement of the Austroalpine mega-unit indicate its heterogeneous composition by continental units, island arcs, ophiolites, subduction mélanges, accretionary wedges, and seamounts affected by different metamorphic grades. We present new results of LA-ICP-MS U-Pb zircon dating and MC-ICP-MS Lu-Hf isotopic tracing of zircons from three key areas of the Austroalpine basement, including the: i) the Wechsel Gneiss and Waldbach Complexes, and the Wechsel Phyllite Unit, (ii) Saualpe-Koralpe-Pohorje, and (iii) Schladming areas. We determine the Wechsel Gneiss Complex to be a continental magmatic arc formed during 500–560 Ma proximal to a continental block with a ‘memory’ of late Archean to early Proterozoic continental crust. Hf model ages of 2.1 Ga to 2.2 Ga and 2.5 Ga to 2.8 Ga that indicate a close relationship to the northern Gondwana, with depleted mantle Hf model ages as old as 3.5 Ga. The Wechsel Phyllite Unit structurally overlying the Wechsel Gneiss Complex has partly different sources, including juvenile crust formed at ~530 Ma. In contrast, the Waldbach Complex constantly added new crustal material during the 490–470 Ma period and bears considerably positive εHf(t) values with young, depleted mantle model ages of 700 to 500 Ma. The Waldbach Complex is, therefore, interpreted to be part of a magmatic arc formed during closure of the Prototethys and metamorphosed during Variscan orogenic events at ~350–330 Ma. The Schladming-Seckau and Wechsel Complexes represent a Cambro–Ordovician magmatic arc system formed by Prototethys subduction processes with the associated upper Neoproterozoic to Lower Ordovician ophiolitic Speik Complex having formed in its back-arc basin or as Prototethyan lithosphere. The Plankogel Complex and structurally overlying mica-schist and amphibolite units represent accreted ocean, ocean island, and continent-derived materials, interpreted to be an accretionary complex formed during the Permo-Triassic closure of Paleotethys. Many granites with Permian ages (*e.g.*, the porphyric Grobgneiss and other granite gneisses, and associated pegmatites) were likely formed in an extensional environment culminating with the opening of the Middle–Late Triassic Meliata oceanic rift. These granites are formed by partial remelting of a crust with mainly middle Proterozoic Hf model ages. Taken all these data together, we find that the Austroalpine basement is heterogeneously composed and includes complexes of different ages, different tectonic evolutionary histories and different remolten sources representing different locations before the final accretion. The composite of the pre-Alpine complexes in the Austroalpine mega-unit is likely assembled not earlier than late Permian or Early Triassic. Tectonically, the Hf composition in Eastern Alps produce a fanning isotopic array, the lowest εHf values increase from –38 at ~550 Ma to –10 at 200 Ma, and the highest εHf values increase from +5 to values of the contemporary depleted mantle (~+16) over the same time interval, indicate an external orogenic system.

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Early–Middle Palaeozoic metasediments and metagabbros in the Western Balkan and Fore-Balkan Units (NW Bulgaria): U-Pb zircon dating, palynological age and palaeogeodynamic implications

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The Balkan-Carpathian Ophiolite (BCO) consists of Tisovitsa-Iuti (Romania), Zaglavak and Deli Jovan (Serbia) and Tcherni Vrah (Bulgaria) ophiolitic massifs. Recent geochronological data for the BCO determined the time of its formation at Early–Middle Devonian (380–406 Ma, *cf*. Plissart *et al*., 2017, and references therein). Previously published U-Pb data of a Cadomian age of the BCO have been assumed as a result of dating of a xenocrystic component (Kiselinov *et al*., 2017).

Numerous published Early–Middle Devonian absolute ages of the BCO require a new re-evaluation of the concept of the lithostratigraphy, ages, and the importance of the Palaeozoic low-grade metamorphics. A new hypothesis concerning the Neoproterozoic to Early Devonian evolution of the West Balkan in Bulgaria (BCO, Berkovitsa Group and Dalgi Del Group) is launched herein. The Vlasina Series and Inovo Formation in the eastern Serbia are correlated with the Berkovitsa and Dalgi Del groups, respectively. New and previous palynological data of a Silurian–Devonian age of the Dabravka Formation in Bulgaria and the Inovo Formation are discussed.

The Vlasina Series have yielded the lower Cambrian achaeochyatid *Aldanocyathus anabarensis* from marbles clasts. The marbles of the Zdravchenitsa Formation (Berkovitsa Group) might be of Early Cambrian age as well. The Pilatovo Gabbro (Berkovitsa Group) is dated at 493 Ma (Carrigan *et al*., 2003; *i.e*., Cambrian/Ordovician boundary). Thus, the Berkovitsa Group is supposed herein to correspond to the Cambrian and Ordovician. The Inovo Formation has been defined as Silurian–Devonian in age on the basis of palynological data (Ercegovac *et al*., 2011). The present re-study of the Inovo Formation has confirmed this age determination since finely granulate and spinate trilete spores have been identified. Lithological correlation indicates that the Dalgi Del Formation might be of the same age. In the Dabravka Formation, numerous land plant tissue fragments have been found, suggesting that its formation is not older than Early Devonian. The Tcherni Vrah Gabbro was dated using the U-Pb method at 391 Ma, *i.e*., Emsian/Eifelian (Kiselinov *et al*., 2017). This confirms the hypothesis (Plissart *et al*., 2017) of an Early Devonian opening of the Rheic Ocean and incorporation of the pre-Alpine Upper Danubian and West Balkan basement units in the southern Variscan Galatia suture.

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Provenance and detrital zircon study of the Tatric Unit basement (Western Carpathians, Slovakia)

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The Western Carpathians crystalline basement (WCCB) recorded common indications of the Cadomian/Avalonian precursors. The pre-Mesozoic crystalline rocks of the Tatric Unit were studied with respect to its lithological, structural, metamorphic and age characteristics. The obtained data proved that these rocks are made of two different rock complexes – the older *Lower Étage* (Cambrian to Silurian) showing a high-grade metamorphic evolution, and the *Upper Étage* (Upper Silurian to Devonian) presenting low-grade metamorphism and a younger stage of development.

The *Lower Étage* is composed of a leptynite-amphibolite complex (LAC) with remnants of retrogressed eclogites and metaultramafites, tonalitic gneisses, sheared Cambrian-Ordovician felsic magmatites – now orthogneisses and these metaigneous rocks are intercalated with metamorphosed psammites/pelites (gneisses) with rare carbonate (calc-silicates) lenses, and scarce black schists. The metamorphic conditions of this complex are usually characterized by 650–800 MPa and 600–780 °C, sometimes with characteristic widespread migmatization/granitization, whereas P-T reached up to 1.2–2.5 GPa and 700–750 °C in the HP eclogite remnants.

The *Upper Étage* is late Silurian – Devonian in age, and typically comprises volcano-sedimentary sequences composed of metagreywackes, phyllites, metabasites (epidote-actinolite amphibolites), black shales, lenses of calc-silicates, Fe + Pb–Zn Lahn-Dill mineralizations, and scarce apatite-rich rocks. Their low-grade metamorphism reached greenschist facies only (below 350 MPa and 650 °C), and weak intrusive migmatitic zones are merely observed. Mutual relationship of the Lower and Upper structural étages is commonly in normal position in respect of the Variscan tectonics, albeit overturned stacking is documented as well. Noteworthy, the LAC metabasic rocks of the Lower Étage have low positive εNd values and high Nd model ages what indicate its origin from the recycled SCLM, whereas the Upper Étage mafic (gabbroic) members show an affinity to juvenile mantle products with high positive εNd values and low Nd model ages, identical to their U–Pb zircon magmatic ages. Most of the Lower Étage rocks show high-grade metamorphism and have their origins in the Rheic Ocean. However, all rocks of the Upper Étage recorded only low-grade metamorphism, and, because these never experienced high-grade overprint, it is evident that the Upper Étage volcanic-sedimentary rocks were not significantly subducted and were deposited in a different realm like was the Rheno-Hercynian basin.

Representative U-Th-Pb detrital zircon data from metamorphosed siliciclastics of the Tatric Unit WCCB indicate a general dominance of Neoproterozoic – mainly Ediacaran source rocks. The latter are interpreted to have been located at the Cadomian arc. Combined with less frequent Archean and Paleoproterozoic zircon populations a common Gondwanan provenance is proposed. However, some samples contain Mesoproterozoic detrital zircons populations that are typical for the Avalonian microcontinent. The studied metamorphic rocks are interpreted to originate from the Rheic Ocean and also partly from the Rheno-Hercynian basin. Indeed, significant differences in the metamorphic evolution of both metamorphic rock assemblages suggest their recent juxtaposition and or their thrusting during the Late Devonian to Carboniferous (Visean) Variscan subduction/collision processes. The Variscan amalgamation of the Western Carpathians basement was a consequence of subduction of the Rheic Ocean under Galatian Superterrane, and final collision with the marginal Rheno-Hercynian zone.

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A large Permian plutonic system crosscutting different Austroalpine basement units: implications for Permian and Cretaceous tectonics of Eastern Alps

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In some high-grade metamorphic basement units of the Austroalpine mega-unit, temperature-dominated Permian metamorphism is well established as well as the formation of numerous small pegmatites and rare metagabbro bodies. As no sourcing pluton was found up to now, these pegmatites were recently considered to have formed as a result anatectic metamorphism (Knoll *et al.*, 2018). Based on new U-Pb zircon dating results, we show, for the first time, that a large Permian granitic plutonic system occurs in the footwall units of the pegmatites, which could be considered as the host magma body for pegmatite intrusions. In ascending order of basement units, studied granitic orthogneisses include the foliated Humpelgraben granite-gneiss in the upper part of the Gleinalm "Core" Complex with a $^{206}Pb/^{238}U$ average age of 271.0 ± 2.2 Ma. The sheet-like Gleinalm augengneiss stretches over 55 km and forms the structurally highest lithology of the Gleinalm "Core" Complex. The westernmost sample from the Gleinalm augengneiss yields a $^{206}Pb/^{238}U$ average age of 272.5 ± 5.0 Ma, whereas the ages of two samples further east are significantly younger (260.8 ± 2.0 Ma, 261.5 ± 2.2 Ma). The Gmeinalm augengneiss has its origin in the Gleinalm augengneiss and crosscuts the ophiolitic Speik Complex and reaches the base of the overlying Rappolt-Almhaus Complex (Neubauer, 1989). It yields a weigthed mean $^{206}Pb/^{238}U$ age of 256.9 ± 2.2 Ma, which is similar to previously reported ages from pegmatites within the Rappolt-Almhaus Complex in the structurally upward extension of this body but also with pegmatite ages in the overlying eclogite-bearing Koriden Complex as well as in the southern part of the overlying Plankogel Complex (Knoll *et al.*, 2018; Neubauer *et al.*, 2022). Together, the new data reveals the existence of a still well-preserved, although structurally disrupted, Permian plutonic system, which was considered as part of three major Early Alpine (Cretaceous) nappes. As the northern margin of the Gleinalm "Core" Complex is covered by low-grade metamorphic Permian–Triassic strata, the Gleinalm Permian plutonic system is independent from the similar-aged Permian Grobgneiss of the Raabalpen Complex with its cover, which include Permian volcanics. The results also indicate much more Permian magmatism in the Austroalpine mega-unit of Alps as envisaged before. The new results also imply the need of a new tectonostratigraphy and a new model for the Cretaceous subduction and exhumation.

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Special session SS6

Magma fertility vectors and hydrothermal alteration footprints related to mineralization systems of the Carpathian-Balkan area

Conveners:

Albrecht von Quadt, István Márton, Vladica Cvetković

Detrital zircon chrono-chemistry of mineralized Cretaceous and Tertiary magmatic complexes in the Balkans

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Porphyry copper deposits are a relatively common phenomenon in syn- and post-subduction arc magmatic belts. Most of the tools we use to identify these mineral deposits is based on the recognition of gangue minerals in hydrothermal alteration has a systematic spatial relationship to ore: we map the silicate minerals with our eyes and with spectral tools; we map the distribution of pathfinder trace elements and chargeability associated with hydrothermal pyrite, and we map the addition or destruction of magnetite with magnetometry. Most of these properties are common to all porphyry-style alteration zones, regardless of size and grade, and regardless of whether these are barren, contain only Au, or only Cu at economic concentrations. Explorers have therefore long sought proxies for the quality of porphyry prospects; tools to help us recognize which prospects may become mines before too much time and money are spent.

The Balkan domain of the Western Tethyan is an excellent natural laboratory for testing tools of this nature as it hosts two mineralized arc-magmatic cycles that include a range of porphyry- and associated magmatic hydrothermal deposits. The Late Cretaceous Timok-Srednogorie arc includes world class porphyry and epithermal Cu-Au deposits early in its history, and evolves over ~20 m.y. to epithermal, Au-only styles, and eventually barren magmatism. The post-collisional Eocene to Miocene Lece-Halkidiki-Menderes arc also hosts Cu deposits that formed during its earlier history, and likewise evolved to Au, and Au-Pb-Zn metallogeny. In both belts, the transition from Cu-rich to Au-rich or barren magmatism is associated with a tectonic shift from compression to extension. However, existing magma fertility tools such as "Loucksian" whole rock chemical proxies for magma hydration or high-pressure evolution suggest almost all the magmatic products of the early and late stages of both belts to be fertile.

In this study, the zircon chemical and chronological record of these magmatic events was investigated to determine if zircon could discriminant the metallogenic styles and/or quality. To better approximate a representative sample of all magmatism in an area, as well as to mimic real exploration programs, we applied LA-ICP MS zircon geochronology and trace element chemistry to detrital zircons in modern alluvium downstream of the volcano-plutonic complexes associated with major mineral districts. The initial results of the ongoing study are promising. We observe:

- The Cretaceous arc in the Srednogorie Zone is marked by a complex basement that includes Archean, Paleoproterozoic and Neoproterozoic history, whereas the younger belt appears to recycle an entirely Paleozoic basement;
- Cu-rich districts are associated with zircon chrono-chemical proxies that suggest hydrous magma compositions and protracted fractionation that included amphibole and/or titanite;
- Au-rich districts are associated with zircon proxies that suggest hydrous magma compositions but short-lived or amphibole-free fractionation, perhaps implying low degree melting of an enriched source; and:
- Barren districts are marked by zircon proxies that suggest less hydrous magmatism, or incomplete fractionation, and/or strongly radiogenic crustal sources.

On the basis of these results we suggest that this approach may permit more confident regional evaluation of porphyry metal potential than conventional petrology and whole rock chemistry.

Correlation between alterations and Cu-Au mineralization within first phase andesite in the Čukaru Peki deposit

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Čukaru Peki deposit represents a hydrothermal Cu-Au system in the Bor metallogenic zone (Tethyan Eurasian Metallogenic Belt). Its lower part is represented by porphyry and stockwork-impregnation mineralization, whereas in the upper part high-sulfidation type with massive sulfide Cu-Au mineralization is developed. Host rocks are andesites of the first volcanic phase (V1A) that is further distinguished, according to the texture (size and amount of phenocrysts), degree of mineralization and the depths, into three sub-phases: V1A1, V1A2 and V1A3 (Bosić *et al*., 2022). This paper discusses the correlation between mineralization and alteration within these sub-groups.

V1A1 is represented by hypocrystalline porphyritic plagioclase-hornblende andesites with aphanitic groundmass that may indicate surface emplacement. Plagioclase phenocrysts are pervasively altered into sericite, calcite, albite, illite, ±alunite, ±kaolinite and anhydrite/gypsum, whereas hornblende is altered to chlorite and opaque phase. The matrix consists of quartz, adularia, sericite, anhydrite, ±neobiotite. V1A1 contains two types of mineralization: porphyry Cu mineralization with impregnations of pyrite-chalcopyrite-bornite±magnetite/hematite (>1500 m depth), and a transitional (from 1500 m to 800 m depth) with pyrite, covellite, enargite, chalcopyrite and bornite as main phases, digenite, chalcocite and molybdenite as minor, and sphalerite and galena as rare constituents. Bornite and chalcopyrite are deposited in a separate, probably earlier succession with respect to covellite and enargite. Samples displaying chloritization and sericitization contain only porphyry type mineralization, whereas those with alunite and kaolinite are associated to the epithermal and porphyry type mineralization.

V1A2 is represented by shallow intrusive plagioclase-hornblende-biotite andesite. The rocks are holocrystalline porphyritic with plagioclase, hornblende and biotite phenocrysts settled in a holocrystalline matrix of the same composition. Hydrothermal minerals are quartz, illite sericite, chlorite, neobiotite, magnetite, anhydrite, adularia, calcite, albite and sulfides. Alteration is determined as weak to strong sericitization, moderate to intensive chloritization and potassic with albite, adularia, anhydrite, neobiotite. These rocks contain impregnations and quartz veins with chalcopyrite-bornite±molybdenite±magnetite assemblage. The samples with sericite/potassic alteration are probably cogenetic and associated with bornite and chalcopyrite grains around which covellite and digenite occur later. Samples with typical potassic alteration host chalcopyrite, bornite and magnetite.

V1A3 is represented with coarse plagioclase-hornblende andesites with phenocrysts rich porphyritic texture. They are characterized by advanced argillic or ‘secondary quartzite’ alterations with quartz, kaolinite, alunite, dickite, sericite, ±diaspore, ±corundum, ±andalusite. This association most probably indicates advanced argillic alteration formed at moderate temperatures (200–300 °C). These rocks carry massive sulfide mineralization where the main Cu minerals are covellite and enargite, and subordinate colusite, digenite and luzonite. Covellite, pyrite and enargite were deposited simultaneously or in a very short period.

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The geochronological comparison of three major porphyry systems in Timok magmatic complex: Bor, Veliki Krivelj and Čukaru Peki

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The Bor deposit is a world-class porphyry-high sulfidation system located in eastern Serbia. It has been mined since the very beginnings of the 20th century. Veliki Krivelj is a porphyry type Cu-Au deposit, currently mined by open-pit, located around 4 km north of Bor mine. Čukaru Peki is a recently discovered porphyry and high-sulfidation type Cu-Au deposit located 5 km south of Bor mine. All these mineral deposits are genetically associated with the first magmatic phase of the Timok magmatic complex.

Most of the performed U-Pb measurements of zircons from Bor (using LA-ICP-MS method) imply that the age of this system is around 86–84 Ma (von Quadt *et al*., 2002; Kolb *et al*., 2013). The recently obtained ages of the zircons from the Bor deposit (Klimentyeva, 2022) yield ages of mineralization between 84.5 ± 1.27 Ma and 83.25 ± 1.25 Ma.

Kolb (2011) have conducted U-Pb dating of zircons from Veliki Krivelj deposit and concluded that the mineralization age is in range from 86.12 ± 0.29 Ma to 84.4Ma ± 0.86 Ma.

The zircons from Čukaru Peki have concordia ages of 86.2 ± 2.6 Ma (mineralized diorites) and 84.95 ± 1.8 Ma (late non-mineralized dykes, Velojić, 2021).

All the presented data implies that the main mineralization stage in this magmatic complex occurred in the period of 87 Ma to 83 Ma, which is quite similar to the ages proposed by von Quadt *et al*. (2002). The obtained zircon ages of Čukaru Peki and Veliki Krivelj are very similar (between 86.2 Ma and 84.5 Ma), whereas the recently obtained U-Pb ages of Bor imply very similar ages (84.5 ± 1.27 Ma–83.25 ± 1.25 Ma). The measured ages overlap if maximum values of analytical uncertainties are considered.

The occurrence of two or more relatively adjacent porphyry systems with similar ages is common in other porphyry systems worldwide, such as Chuquicamata district (Chile) and Yanacocha district in Peru (Sillitoe, 2010). One explanation for age discrepancies of intrusions in porphyry districts, given by Sillitoe (2010) is that porphyry clusters reflect the intermittent activities of underlying magma chambers and their replenishments.

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LA-ICP-MS trace element study of alunite from Pesovets epithermal system, Central Srednogorie, Bulgaria

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The Pesovets epithermal system is located in Panagyurishte ore region, part of the Late Cretaceous Apuseni-Banat-Timok-Srednogorie magmatic and metallogenic belt, defined by intensive magmatic and volcanic activity and formation of many porphyry and epithermal deposits. Hydrothermal alterations of advanced argillic (AAA), propylitic-argillic and propylitic type had affected andesite to latite volcanic and pyroclastic rocks. AAA consists of alunitic rocks in the central parts, kaolinitic rocks in some places and diaspore-pyrophyllite (+ zunyite) rocks in the deeper parts. Alunitic rocks form well-developed zone about 0.5 km^2. Alunite is small-grained at the top of the system while coarse-grained tabular alunites dominate at depth.

SEM-EDS study shows that alunite is K-Na- to Na-type in composition with Na/K ratio from 1/1.5 to 4/1. It always contains limited amounts of Ca, Sr, Ba, REE up to 0.2 apfu, associated with higher contents of P. Rarely mixed phases between alunite and other APS minerals are distinguished. Other APS minerals are svanbergite-woodhouseite solid solutions with Ca/Sr ratio from 1/1 to 2/1. On BSE images alunite crystals often show chemical zoning due to P, Ca, Sr, Ba, REE, as well as K and Na variations.

LA-ICP-MS study of alunite confirms the mixed K-Na alunite in Pesovets with a slight increase of sodium content in alunite towards the top of the system. Trace elements that were permanently detected in alunite and have high concentrations are Sr, Ba, Sn, V, Pb, Ga, La and Ce. The highest content of Sn, V, Ga, Pb, La and Ce are measured in the samples from the top of the Pesovets system. Sr, P, Ti and La/Pb ratio do not show any trend, while Ba and Sr/Pb ratio increase in depth.

Strontium, Ba, Pb, La and Ce are incorporated in D position substituting for K and Na. This substitution is charge-balanced by incorporation of phosphate anion PO_4^{3-} that leads to the formation of solid solutions of alunite with svanbergite, woodhouseite, hinsdalite and florencite. It is worthy to note the presence of V, Ga and Sn in alunite, most probably incorporated in G position substituting for aluminum (Bayliss *et al*., 2010). Incorporation of V and Ga is explained by their similar ion radii. According the authors incorporation of Sn in G position is also possible but such cases are very rare.

The observed decrease of Pb content and increase of Sr/Pb ratio in depth towards the presumed intrusive center are in agreement with the findings of Chang *et al.* (2011) and suggest that the chemical properties of alunite could be used as vectors. In alunites from Pesovets an increase of Sn, V, Ga, Pb, La, Ce towards the upper parts of the system is registered, most pronounced for Sn (from 86.6 to 1700 ppm). These elements have higher content (together with Sr and Ba) in the whole rock alunite samples from the upper part of the system. Most probably the accumulation of these elements in alunite from the upper part of the system is a result of the fluid evolution. Our results indicate that V, Ga and Sn content in alunite has a potential to be used as a vector to the intrusive center of the system but it requires further research.

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Application of decision trees and random forests to zircon geochemistry

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Machine learning has been gaining acceptance as an industry-wide used tool for analyzing whole rock and mineral chemistry data during the last decade (*e.g*., Ahmed *et al*., 2020, Dmitrijeva *et al*., 2022), with the range of applications from classifying rock types and alteration styles to vectoring during mineralization prospecting.

We have obtained geochemical data for zircons from Bor and Čukaru Peki and performed a benchmark comparison to weakly-mineralized younger intrusion of Valja Strž and the barren Ridanj-Krepoljin zone based on data from earlier studies (Kolb, 2011). Logistic regression, Random Forest Classifier, K neighbors Classifier and Decision tree algorithms were used for classifying rock types and degree of mineralization. Overall, it is possible to predict rock types from zircon geochemistry with an average precision of over 80%; this level of precision was achieved by all the algorithms.

The results provide the following insights into the magmatic development of these systems. Eu anomaly vs Hf shows that andesites at Bor are distinctly higher in Hf and plot above 0.3 in terms of Eu anomaly, while approximately half of Valja Strž zircon data are characterized by lower Eu anomaly. This could reflect that Bor andesites were evolving towards suppressed plagioclase crystallization under higher oxygen fugacity conditions. Higher Hf content of older host rock volcanics at Bor can imply that the host rock andesites were emplaced before the replenishment of the magma chamber and represent evolved melts before mixing; alternatively, deep Borska Reka porphyries might represent a totally unrelated magmatic event. Generally speaking, most of the zircons from this study, as well as from the larger dataset from the Timok area (Kolb, 2011), plot above 0.3 in terms of Eu anomaly. The comparison of Bor, Čukaru Peki and Veliki Krivelj samples to weakly-mineralized Valja Strž and barren Ridanj-Krepoljin suggests that the cut-off value for magmas that can produce deposits with significant Cu endowment would be around 0.6 in terms of Eu anomaly in the Timok area.

Based on Th/U vs Yb/Gd ratios, we suggest that magma mixing was an important mechanism for Čukaru Peki, while Bor followed the normal fractionation trend to a greater degree.

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From porphyry copper to distal epithermal mineralization in the Elatsite-Chelopech ore field (Bulgaria): Insights from trace element signatures of sulfide minerals

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The Srednogorie Zone is part of the Late Cretaceous Apuseni-Banat-Timok-Srednogorie Magmatic and Metallogenic Belt of the Alpine-Balkan-Carpathian-Dinaride Orogenic System. The Srednogorie zone hosts several important porphyry Cu-Au-(Mo) and epithermal Cu-Au deposits (*e.g.*, Elatsite, Assarel and Chelopech). Elatsite-Chelopech ore field, located in the northern part of the Panagyurishte district (Central Srednogorie) comprises several spatially associated porphyry copper and epithermal gold deposits and occurrences. Most of them are genetically associated to the Late Cretaceous magmatism, only Svishti Plaz is considered possibly linked to the Carboniferous magmatism in the region. The ore field is an excellent area for studying the alteration and mineralization features of porphyry copper, base metal and gold-base metal mineralization associated to a porphyry system by deciphering the trace element signatures of hydrothermal sulfides and their changes from the porphyry to closely spatially associated base-metal prospects in the epithermal environment. Hence, the main aim of our study is to determine the trace element composition of sulfides and to test whether their geochemistry can be used as a reliable exploration tool for distinction of porphyry copper, base metal (mainly Pb-Zn), and gold-base metal mineralization in the region. To achieve this goal, we focused on some exploration prospects and mineral occurrences around the Elatsite porphyry Cu-Au (-PGE) deposit in the northern sector of the ore field. Samples from the three types of mineralization were analyzed using LA-ICP-MS technique to determine trace element content in different sulfide minerals.

The LA-ICP-MS data reveal similar trace element composition of pyrite from the three porphyry centers, as well as pyrite from the base meal and gold-base metal veins. Analyzed pyrite crystals from the porphyry Cu deposit/prospects have low As and Au contents and relatively high Se content. Typical features of pyrite from the porphyry mineralization are the high Co and Ni and low Ag, Cu, Pb and Sb contents. Measured chalcopyrite crystals from these deposits have also high Se content and are depleted in Au and Ag.

Pyrite samples from base metals and gold-base metal veins show higher As, Au, Cu, Pb and Sb and lower Se content than those from the porphyry copper mineralization. The Au content is highly variable (from few ppm up to 100 ppm) and shows positive correlation with the As content. Similarly, there is a positive correlation between Ag and Au in zoned freibergite from base-metal veins. Pyrite is often in association with arsenopyrite that has also elevated Au content (up to 160 ppm). Two elements that behave differently in pyrite from base metal and gold-base metal veins and allow to distinguish among them are Co and Ni. In pyrite from the base metal deposits, these elements have similar contents to the pyrite from the porphyry copper deposits. On the other hand, pyrite from the gold-base metal veins shows lower Co and Ni contents. Sphalerite from the gold-base metal veins has lower Co and higher In content compared to sphalerite from the base metal veins.

The specific geochemical characteristics of sulfide minerals from the different types of mineralization in the studied ore field can be used as an exploration tool in the region.

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Revised geology model and exploration targeting vectors at the Chelopech high-sulphidation style Au–Cu deposit, Bulgaria

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The Chelopech Au-Cu ore deposit is located 70 kilometers east of Sofia, within the Panagyurishte metallogenic district. The deposit, having a considerable mining history since 1954, is operated as an underground mine by Dundee Precious Metals Inc., with an annual production rate of 177,000 ounces of gold and 35 million pounds of copper. Effective as of 31st March 2022, the Mine has a Proven and Probable Mineral Reserve of 19.3 Mt at 0.80% Cu, 2.72 g/t Au and 7.6 g/t Ag and has a remaining Mineral Resource (exclusive of Mineral Reserves) of 13.8 Mt (M+I) at an average grade of 0.89% Cu, 2.84 g/t Au and 10.6 g/t Ag.

The Chelopech hydrothermal system is part of a large Late Cretaceous magmatic complex which extends at least over an area of 5×4 km and hosts various types of mineralization, including 1) the economically most important high-sulfidation (HS) style Au-Cu mineralization in the Chelopech mine, West Shaft, Sharlo Dere and the Krasta prospects, 2) a porphyry Cu-Mo-Au stockwork mineralization in the Petrovden prospect, and 3) distal Au-rich base metal sulfide veins in the Vozdol and Wedge prospects.

The Chelopech magmatic complex relates to an inherited and reactivated regional Variscan basement relay structure which causes pre-, syn- and post-mineral Gosau-type subbasin formation with characteristic rapid facies changes, post-mineral thrusting and subsequent normal faulting. Recent exploration works resulted in an upgraded geology model, which integrates the Chelopech deposit into a larger zoned magmatic-hydrothermal system related to a multi-phase 91.9±0.2 Ma old intrusive complex, where transition between the deeper porphyry-type and the shallower high-sulphidation type environments is continuous. At deeper levels, the HS-style mineralization is constrained by WNW- and ENE-striking steep structural feeders and highly permeable sub-vertical phreatomagmatic breccia contacts. At shallower levels, the mineralization controls are represented by sub-horizontal hydromagmatic injections and surge flow deposits, syn-sedimentary exhalative sulphides precipitation and subsequently reworked mineralized clasts in debris avalanche and debris flow deposits. The contact between intra-mineral intrusion of dioritic magma and unconsolidated wet sediments produced a high variety of peperitic, mingling and fluidized features, which further complicates and obscures the primary mineralization geometries.

The HS-style mineralization is represented by transition from shallow intrusive related epithermal environment to seafloor hosted hydrothermal vent system and is characterized by sulphide- and sulphosalt-rich replacement zones associated with a well-zoned advanced argillic alteration (AAA) footprint. The inner core of AAA is represented by vuggy silica and APS minerals (alunite-svanbergite-woodhousite) surrounded by a competent dickite-silica-APS alteration assemblage which host the Cu-Au-As-Ag-Te bearing assemblages. The outer zones are represented by lower crystallinity kaolinite and illite alteration and marked by relative enrichment of Pb-Zn-Mn-Tl-Ag-Au. The deep part of the AAA is characterized by muscovite, pyrophyllite and diaspore alteration, which usually marks the lower limit of economic copper grades and the relative enrichment of Au-Sb-Bi-Te-W. The upper part of the system is characterized by rapid change in alteration environment due to seawater interaction and is characterized by sulphide precipitation as colloform bands, with kaolinite, barite and anhydrite alteration.

By using an integrated approach that includes the use of above described and revised geological model, alteration and metal zoning patterns, new HS-style Au-Cu near-mine targets were outlined, which are located 1–2 km NE, SE and SW from the Mine and extend below the post-mineral Chelopech thrust system. This presentation provides insights on the ore controlling vectors at these target areas with implications on the overall conceptual model of the Chelopech hydrothermal system.

Pb-S isotope geochemical signature of porphyry and base-metal vein deposits in the region of Elatsite Cu-Au porphyry deposit

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The Apuseni-Banat-Timok-Srednogorie (ABTS) Late Cretaceous magmatic arc in the Carpathian-Balkan orogen formed on the European margin during a northward subduction and subsequently closure of the Neotethys Ocean. Extensive calc-alkaline magmatism and associated ore deposits, mainly porphyry Cu-Au-(Mo) and epithermal Au were formed and are referred to as a magmatic and metallogenic ABTS belt. The Elatsite-Chelopech ore field is situated in the northern part of the Central Srednogorie (called Panagyurishte district) of this belt. It comprises numerous spatially associated porphyry copper and epithermal gold deposits and prospects. Their formation is clearly related to the Late Cretaceous magmatism, except one of them, the Svishti Plaz that is considered possibly linked to the Carboniferous granite magmatism in the region.

In present study we focus on exploration prospects and mineral occurrences around the Elatsite porphyry Cu-Au (-PGE) deposit in the northern sector of the ore field. It is an excellent area for studying the link of magmatic and hydrothermal events and metal sources in porphyry ore systems including porphyry Cu (i), base metal (ii) and gold-base metal (iii) mineralizations. By deciphering the isotope (Pb-S) element signatures of hydrothermal sulfides and their changes from porphyry to closely spatially associated base-metal prospects in the epithermal environment, we also may be able to check whether these mineralizations could be part of a single zonal porphyry system of Late Cretaceous age, or some of them (*e.g*. Svishti Plaz) represent distinct Late Carboniferous system. To achieve this goal, we applied bulk-sample and in-situ sulfur and ID-TIMS Pb isotope analyses on sulfide minerals of all three deposit types.

The sulfur isotope analyzes in sulfides from the porphyry copper and base metal vein deposits and occurrences reveal $\delta^{34}S$ between –2.5‰ and +1‰, whereas pyrite and chalcopyrite samples of Negarshtitsa West exhibit more positive values for $\delta^{34}S$ of +2.5 to +2.8, and +3.5‰, respectively. The above presented data are similar to the most typical values of $\delta^{34}S$ in sulphides from porphyry-copper deposits worldwide, which suggest that fluids of magmatic origin were responsible for the formation of the sulphides of these deposits. A trend of increasing $\delta^{34}S$ values of +3.5 to +10.6 is observed in the sulfide samples from the distal gold-base metal veins. Although showing lighter isotope sulfur compositions, the $\delta^{34}S$ values infer an igneous source.

The variations in the isotopic composition of lead in the sulfides clearly separate 2 groups of deposits. The first group (1) of porphyry-copper deposits and the polymetallic vein deposits is characterized by more evolved $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios, but with lower $^{207}Pb/^{204}Pb$ ratios. These data indicate a possible Late Cretaceous model age. The μ ($^{238}U/^{204}Pb$) values between 9.75 and 10.0 suggest an input of Pb from the continental crust. The second group of deposits (2) is represented by Au-polymetallic veins (Shipkite/Svishti Plaz). They reveal lower $^{206}Pb/^{204}Pb$ but higher $^{207}Pb/^{204}Pb$ (15.67–15.76) and suggest a lead contribution from old continental crust. The two groups are well distinguished also using the ratios $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ of the analyzed sulfide minerals.

The distinct isotope characteristics of the Au-base metal veins require further studies and the application of reliable isotope dating techniques (*e.g*., Re-Os dating of arsenopyrite) to definitely assign the Au-polymetallic veins Shipkite/Svishti Plaz to a distal part of a Late Cretaceous porphyry system, or to a distinct Carboniferous magmatic-hydrothermal system.

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Trace-element signatures and U-Pb geochronology of magmatic and hydrothermal titanites from Petrovitsa Pb-Zn deposit, Madan region, Central Rhodopes

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The current study presents new geochronological and geochemical data for the region of Petrovitsa Pb-Zn deposit (Madan ore district), located in the Central Rhodopes, South Bulgaria. It is based on in-situ U-Pb dating of titanites from pegmatites and skarnified and mineralized marbles within the mine. The study aims to provide new insights on the pegmatite formation and their relation to the hydrothermal system in the region. Pioneer investigation of the timing and compositional variation of pegmatite samples from the Pb-Zn mines in the Central Rhodopes are reported.

Titanite is one of the most abundant accessory minerals in the pegmatites and skarns within Madan ore district. Commonly, it is associated with feldspars, epidote, pyroxene, chlorite and hematite in both lithological types. The size of the grains highly varies from 5 μm to 600 μm. The combination of optical microscopy with SEM-WDS, EPMA and LA-ICP-MS methods revealed compositional and age variations of the studied titanites that define two main groups: (i) early formed magmatic, and (ii) later hydrothermal titanites. Titanites of the first group show typical magmatic characteristics with mean Th/U ratio values of 1.91, Lu/Hf average ratio of 0.59, and Dy/Yb ratio of 2.03. The chondrite normalized rare-earth element (REE) patterns show that the light REE prevail over the heavy REE. The total average amount of REE is 6548 ppm. In contrary, the hydrothermal titanites have a Th/U mean ratio of 0.22 as well as Lu/Hf and Dy/Yb average ratios of 1.20 and 1.50, respectively. The heavy REE contents are slightly higher than those of the light REE whereas the average sum of REE is 3388 ppm, which is almost two times lower than in the magmatic titanites. The negative Eu anomaly is the only common geochemical characteristic between both titanite types.

The LA-ICP-MS U-Pb dating shows a well-defined age distinction of magmatic and hydrothermal titanites. The calculated U-Pb weighted average age for the magmatic titanites is 48.9 ± 2.3 Ma, while the pegmatite-hosted hydrothermal titanites are dated at 39.2 ± 1.5 Ma. The hydrothermal titanites within the skarns yield a weighted average age of 37.7 ± 1.3 Ma. The data shows a pegmatite emplacement in the Middle Allochtone of the Rhodope Metamorphic complex during the early Eocene. Later on, hydrothermal fluids percolated within the rocks and younger titanites with different signature precipitated.

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Zircon petrochronological patterns of Au-rich porphyry and epithermal deposits in the Golden Quadrilateral (Apuseni Mts., Romania)

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Most of the world's gold and copper are sourced from magmatic-hydrothermal deposits. Their occurrence is controlled, among others, by the regional and local tectonics, as well as chemical and thermal evolution of their underlying magmatic systems (*e.g.* Hedenquist and Lowenstern, 1994). In this study, we apply zircon petrochronology to explore the interplay of these factors on the example of the Golden Quadrilateral (GQ) in the Apuseni Mts (Romania), where calc-alkaline magmatism produced punctuated porphyry and epithermal mineralization spread over a 7 Ma-long period (*e.g.*, Rosu *et al*., 2004).

LA-ICP-MS geochronology resolved three ore-related magmatic phases in the GQ, between ~13.2–12.1 Ma, ~11.5–10.7 Ma and ~8.2–7.3 Ma. Complementary high-precision geochronology demonstrates that individual ore-forming magmatic systems evolved over short time-scales—211 kyr at Colnic, 142 kyr at Rovina, 96 kyr at Certej, and 37 kyr at Ciresata – implying even shorter duration of respective mineralization events.

Commonly used fertility indicators for porphyry copper systems such as zircon Eu/Eu* and oxygen fugacity (reported as DFMQ), vary substantially between different deposits and show no systematic pattern with respect to the mineralizing events. Ti-in-zircon crystallization temperatures potentially suggest that some ore-forming magmatic systems in the GQ experienced late-stage heating whereas others cooled steadily. Hf isotopic composition of zircons from the ore-related units varies regionally in a narrow range between predominantly crustal and juvenile values, fingerprinting an isotopically heterogeneous mantle source and/or a locally variable degree of assimilation of basement rocks. Building on the available paleomagnetic data for the GQ, the new U-Pb magmatic ages support the previously proposed hypothesis that the ore-forming magmas in the GQ evolved in a dynamic tectonic environment dominated by significant (up to 70°) crustal block rotation (Panaiotu, 1999; Rosu *et al.*, 2004).

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Link between magmatic and hydrothermal processes: a case study on Ca-garnets from SW Bulgaria

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The geological evolution of southern Bulgaria is strongly marked by Late Cretaceous subduction-related and Cenozoic collisional to post-collisional magmatism. Late Cretaceous events are characterized mainly by volcanic-subvolcanic activity in the northern and central parts of the Srednogorie zone and plutonic granitoid intrusions in its southern parts and in the Rila-Rhodope and Sakar-Strandzha units. Cenozoic granitoids are wide outcropped in the western parts of the Rila-Rhodope unit (Dabovski and Zagorchev, 2009), *e.g.*, in Pirin, Rila and West Rhodope Mts. (SW Bulgaria), with various magmatic-hydrothermal processes, including pegmatite and skarn formation and ore deposition. In the present study, we report new in-situ LA-ICP-MS U-Pb analysis on Ca-garnets, to clarify the temporal relationships between magmatic and hydrothermal processes and to improve the existing geological knowledge on fertile processes of the region; mineralogical data on these skarn occurrences are associated with the Cenozoic tectono-magmatic processes.

The composition of the studied garnets defines them as members of the grossular-andradite (grandite) solid solution with a predominant grossular compound. Skarn garnets occurring in the vicinity of the Rila-West Rhodope Batholith (RWRB) and yielded an U-Pb garnet ages of 63.8 Ma (Belia Uley), 63.1 Ma (Sedefeni Ezera), both from NW of Rila; ages of 53.6 Ma (close to Eleshnitsa Village, western contact of the RWRB) and 43 Ma (eastern contact of the RWRB, close to Velingrad town) pointing to younger events. The grossular-diopside skarn assemblage associated with the Central Pirin pluton reveals Paleogene (32.3 Ma, Oligocene) grandite U-Pb age, similar to the andradite-epidote occurrences (30.2 Ma) at Teshovo granite.

Mineral, geochemical and age data are summarized to the following geological statement:

1) Formation of grossular garnets is mainly associated with the intrusion of granitoid plutons (RWRB and Central Pirin), partly localized at their periphery and to dyke occurrences in the surrounding host rocks. The grossular skarn zones are generally wide (reaching tens of meters) and often associate with wollastonite and diopside;

2) Garnets of andraditic composition are closely related to pegmatite dykes and associated with epidote, forming thin skarn zones (*e.g.*, eastern contacts of RWRB and Teshovo pluton related to shear zones).

3) The acquired garnet ages outlined four Paleogene tectono-magmatic events including garnet-rich skarn formation and activities around 63 – 53 – 43 – 32 Ma in the region of Rila-West Rhodopes and Pirin Mts. The group of Palaeocene ages might be the continuation of the Late Cretaceous ~67 Ma skarn formation (*e.g.*, in the Babyak base metal-Au deposit; Stavrev *et al.*, 2020).

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New insights into planetary processes at high temporal resolution using U-Pb zircon geochronology

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Significant developments in high precision U-Pb geochronology by CA-ID-TIMS (chemical abrasion, isotope dilution, thermal ionization mass spectrometry) now allow us to obtain $^{206}Pb/^{238}U$ dates with precisions as low as ±0.02% from a single zircon crystal. Given this precision, it is possible to resolve processes as little as 50,000 years apart in the Mesozoic, if they are recorded by zircon crystallization. This high temporal resolution gives us the ability to address scientific questions that were previously inaccessible due to lower analytical precision. One important caveat is that a thorough control on all analytical parameters is required to reliably quantify measurement accuracy and repeatability. It is also crucial to understand the internal complexities of analyzed zircon crystals, as multiple growth events or other open system behavior can impact any age calculated from bulk dissolution ID-TIMS data. The aim of this contribution is to (i) address fundamental issues that need to be controlled and mastered to obtain precise and accurate U-Pb ages, and (ii) show examples where this achievement has led to a new understanding of planetary-scale geological processes.

What is the best possible precision we can achieve, and how can we obtain full control on laboratory induced analytical variation so that we can identify real variation in the age of geological materials? CA-ID-TIMS analyses of zircon from an igneous sample often show a range of ages, but before we can use these data to estimate the duration of protracted zircon growth, we need to be able to subtract any component of analytical scatter from the data (Schaltegger *et al*., 2021). Analytical scatter is best assessed by repeated analysis of a synthetic U-Pb EARTHTIME solution that has a concordant age of ~100 Ma. Repeated measurements of this solution allow us to determine the repeatability of the isotope-dilution and mass spectrometry parts of the analytical workflow. Long-term measurement series of this synthetic solution are preferred over analyses of natural zircon crystals, since natural samples yield excess scatter due to heterogeneity within crystals from the same sample, and therefore are not suitable for resolving small quantities of analytical variation.

U-Pb geochronology at the highest precision can be essential for distinguishing concordant from discordant analyses: Igneous zircon may yield complicated spectra including both concordant and normally discordant dates, but the ability to determine concordance is based upon analytical precision (*e.g.*, Gaynor *et al*., 2022a). Reducing the amount of laboratory lead (lead blank) added to the samples during sample processing to below 0.2 picograms is also crucial for generating highly precise and accurate U-Pb ages through very high radiogenic/common lead ratios in analysis. Therefore, high precision, low-blank analyses are able to resolve multiple distinct zircon growth episodes within the same zircon population. Using a hypothetical two-component mixture model, in combination with published data sets, we can demonstrate that lower-precision ID-TIMS U-Pb analyses may not be able to resolve mixtures of age components and therefore data generated by low-radiogenic/common Pb ID-TIMS measurements and other lower precision techniques may be misinterpreted.

An area where high precision CA-ID-TIMS U-Pb ages have revolutionized our understanding of geological processes is in the emplacement of Large Igneous Provinces (LIPs). LIPs consist mostly of mafic extrusive rocks (flood basalts) and intrusive rocks (sills and dykes) which rarely crystallize U-bearing minerals, and are therefore difficult to date accurately and precisely. In some cases, igneous zircon may be found in paleosols and silicic ashfall deposits interbedded with basalt flows (*e.g.*, Kasbohm *et al*., 2018, Schoene *et al*., 2019), or in residual, interstitial melt pockets that formed after fractional crystallization of mafic minerals in coarse-grained dolerite intrusions (*e.g*., Davies *et al*., 2017; Greber *et al*., 2020; Zeh et al., 2015). High-precision U-Pb ages from dykes and sills of the Karoo Large Igneous Province (K-LIP) indicate that the mafic melts were extensively contaminated at the emplacement level by assimilation of sedimentary material. This assimilation locally saturated the melts in zircon, allowing us to perform high precision U-Pb geochronology on these difficult to date rocks (Gaynor *et al*., 2022b). Contamination by crustal material can also be traced through analysis of O and Hf isotopes combined with U-Pb ages of individual zircon crystals (Davies *et al*., 2021; Gaynor *et al*., 2022b). High-precision ages allow us to show that LIP magmatic activity may be pulsed, for example the K-LIP melts show a pulsed age distribution which may be correlated with biodiversity drops and C-cycle disturbances in the Pliensbachian–Toarcian transition (Lower Jurassic).

High precision U-Pb ages from both LIPs and ashes in sedimentary sections can also be used to link the degassing of magmatic and thermogenic SO_2 and CO_2 from LIPs to the response of the C-cycle recorded in marine carbonates. The massive volcanism of the Siberian Large Igneous province (S-LIP) caused destabilization of the global climate system and extreme reduction of marine biodiversity, known as the Permian-Triassic Boundary mass extinction. High-precision zircon U-Pb geochronology of volcanic ashes in marine platform slope sequences from southern China allow us to establish a precise age-depth model for the post-extinction biotic recovery, as well as for the duration and the timing of the subsequent C-cycle disturbance in the Lower Triassic (Widmann et al., in review). Subsequent, repeated icehouse-greenhouse cycles can be correlated to cyclic C-isotope fluctuations, unrelated to volcanic activity of the S-LIP in the Early Triassic. These results provide a basis for speculations about the possible origin of C-cycle disruption in the Early Triassic, and allow us to compare modeled S-LIP derived gas injection rates with present-day anthropogenic CO_2 injection rates.

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New $^{40}Ar/^{39}Ar$ evidence for Paleogene magmatic-hydrothermal activity in the Western Rhodopes, Bulgaria

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The Rhodope Massif is one of the main Alpine tectono-metamorphic, magmatic and metallogenic units in Bulgaria and Greece. The magmatic activity in the Rhodopes generates magmatic-hydrothermal systems of various sizes that formed numerous deposits and ore occurrences. The most significant include Pb–Zn–Ag (central Rhodopes), Au–Ag to Au-polymetallic (eastern Rhodopes), and W–Mo±Au-polymetallic mineralizations (western Rhodopes). We present new $^{40}Ar/^{39}Ar$ ages for the hydrothermal processes associated with the Babyak Mo-Ag-Au-W-Bi-base metal deposit. The study aims to introduce additional age constraints on the temporal and spatial relationships between mineralized ore zones and the hosting lithologies. In Babyak, the latter are represented by the granitoids of the Rila-West Rhodopes batholith (RWRB) – a complex pluton that intruded the metamorphic pile-nappes of the Rhodope zone. Medium- to coarse-grained and rarer porphyritic biotite to amphibole-biotite bearing granites and related veins of weakly differentiated to undifferentiated pegmatites (±aplites) intrude the metamorphics of a variegated Jurassic lithotectonic unit comprising gneisses, marbles, schists, calc-schists, amphibolites, and metabasic bodies.

Our new results are based on $^{40}Ar/^{39}Ar$ geochronology of white micas formed due to moderate to strong hydrothermal alteration in pegmatites from two different parts of the deposit. In the ore zones, white micas associate mainly with molybdenite and pyrite. One of the samples contains larger muscovite aggregates and associate with quartz, pyrite and molybdenite forming 1–2 cm wide greisen-like veins. Such hydrothermal alteration is relatively widespread in Babyk deposit and forms up to a few cm wide veins or larger irregular, and spot-like zones. The model plateau age of the muscovite is 50.026 ± 0.044 Ma. Another sample of fine-grained pale green sericite is from a zone of pervasive phyllic alteration in quartz-sulfide stockwork. The latter is characteristic for the deposit and outlines the central silicified parts of the alteration zones. The model plateau age of the sericite is defined at 38.424 ± 0.027 Ma.

Summarizing the age data for the region of the Babyak deposit, we can distinguish several Cretaceous-Paleogene events in the evolution of the RWRB and the associated magmatic-hydrothermal systems. Our earlier U-Pb zircon dating of the hosting granites in the region of the deposit gives evidence for a Late Cretaceous granitoid magmatism defined at 71.12 ± 0.72 Ma. This magmatism produced small-scale garnet-bearing exoskarn mineralizations at the contact with the marbles/calc-schists. Skarn grossular-andradite garnets are dated at 68.55 ± 0.74 Ma and interpreted to result from alteration during retrograde hydrothermal overprinting. Our new Re-Os age data of molybdenite from Babyak deposit mark the next fertile early Eocene magmatic-hydrothermal episode at ~53 Ma. The similar $^{40}Ar/^{39}Ar$ age for muscovite (~50 Ma) from the greisen-like hydrothermal alteration suggests a potential link with the same event. It also coincides with the age of the RWRB granites (51.74 ± 0.63 Ma) and their pegmatites that outcrop south of the Babyak-Grashevo shear zone. Consequently, there is evidence for extensive early-middle Eocene magmatism in the western parts of the Rhodope Massif and related base metal mineralization. In contrast, the $^{40}Ar/^{39}Ar$ age of sericite (~38.5 Ma) from the main quartz-sericite-pyrite alteration style in the Babyak deposit may reflect either younger (late Eocene-Oligocene?) magmatic-hydrothermal system as a source of some metal components, or could reflect partial resetting of the $^{40}Ar/^{39}Ar$ isotope system during the 42–39 Ma magmatism and subsequent exhumation (37–33 Ma). Further geochronologic and geochemical studies on alteration and ore minerals could contribute to better understanding of the multistage magmatic-hydrothermal activity in Babyak area.

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Special session SS7, SS9

Critical raw materials: mineralogy and geochemistry of new and unconventional mineral resources

Conveners:

Atanas Hikov, Jan Cempírek, Panagiotis Voudouris,
Rossitsa Vassileva, Marko Holma

Chemical composition of epidote-group minerals in pegmatites from the Petrovitsa Pb-Zn deposit, Bulgaria: evidence for REE redistribution between allanite and epidote during fluid-mineral interaction

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The geochemical behavior of trace and rare earth elements (REE) in members of the epidote-group minerals from the Madan ore district studied. Allanite and epidotes were formed at different stages of magmatic and hydrothermal activity in hydrothermally altered pegmatites at the 820 mine level in the Petrovitsa Pb-Zn deposit.

Feldspars and quartz are the major constituents of the pegmatites, where plagioclases predominate over K-feldspar. Main accessory phases are allanite, zircon, apatite and abundant titanite. Characteristic hydrothermal overprint of epidote, adularia, clinochlore, leucoxene, carbonates, hematite and quartz on pegmatites is essential.

Based on petrographic observations, mineral relationships and chemical properties two epidote generations were recognized: an early epidote (Ep1) and late one (Ep2). According to the chemical composition both epidotes types are defined as members of the clinozoisite-epidote solid solution, predominantly Fe^{3+}-rich clinozoisite. Enhanced aluminum content is characteristic for grain cores of Ep1, while in the periphery Fe increases. Epidote end members with Fe_2O_3 compounds of 16.32–17.99 wt% or 1–1.1 *apfu* are established in the later Ep2 generation. Ep1 is characterized by an increased Mn content, compared to the Ep2, and even in low amounts (up to 0.16 *apfu*) it is sufficient to act as chromophore and gives a pink coloring, despite the Fe presence. Both epidote generations have moderate concentration of REE, although Ep2 demonstrates relatively higher REE incorporation (averaging up to 12.94 ppm vs 8.41 ppm for Ep1). Increased REE contents (reaching 735.7 ppm) were established only in grains proximal to previously formed allanite, coincidental with the REE depletion in the latter.

Allanite is determined as Ce member (4.94–8.59 wt% Ce_2O_3) with high incorporation of La_2O_3 (2.6–4.15 wt%), Nd_2O_3 (1.3–3.34 wt%), ThO_2 (1.17–3.68 wt%), UO_2 (up to 0.19 wt%), Y_2O_3 (up to 0.89 wt%) and Cr_2O_3 (0.18–0.8 wt%). Its geochemistry indicates REE+ACT (Th, U) contents within the range of 0.31–0.59 *apfu* and together with the increased Al, Si and Ca suggest hydrothermal alteration of the mineral.

It is assumed that the influx of later fluids percolated through and extracted REE from allanite and/or titanite and reprecipitated them in late epidotes. This is evidenced by some increased REE contents in epidotes from both generations, formed in close proximity to allanite or titanite, and/or overgrowing them. The processes of leaching and migration of REE during fluid-mineral interaction results in chemical changes of the minerals and correspond to the allanite/epidote transformation as Poitrasson (2002) proposed. The REE enrichment of the epidote grown close to allanite does not record evidence of prolonged transport of the REE.

Allanite and epidotes could be a potential source for strategic elements due to their considerable REE concentrations and abundance in the pegmatites from the area of the Petrovitsa deposit.

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Geochemical characteristics and U/Pb geochronology of pegmatites from the Govedarnika Pb-Zn deposit, Central Rhodopes, Bulgaria

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The current study presents a pilot U/Pb dating on titanite and geochemical features of pegmatite-hosted minerals from the Govedarnika Pb-Zn deposit, situated in the Laki district, South Bulgaria. The geological setting of the region comprises two operating Pb-Zn(±Ag) deposits, which are related to four NNE-trending ore-bearing faults cutting the high grade Rhodopean metamorphic complex. Polymetallic vein mineralization is typical for the Djourkovo deposit, while metasomatic replacement in marbles led to the formation of large skarn-ore bodies and economic sphalerite-galena mineralization (Vassileva *et al.*, 2020) in Govedarnika. Furthermore, poorly studied pegmatite bodies, emplaced in the host metamorphics might be a potential source for strategic elements.

Pegmatite samples were studied by optical and EDS scanning-electron microscopy. U-Pb isotope characteristics and trace-element compositions were defined by LA-ICP-MS using MKED1 and Temora standards for age determination and NIST 610 for compositional characteristics. Correction for common lead (Andersen, 2002) was applied before titanite age calculation.

The studied pegmatites are composed mainly of K-feldspar, plagioclase and quartz. Intense hydrothermal alteration produced a specific secondary mineralization of chlorite, hematite, epidote, and carbonate. It was synchronous with the orre forming processes and affected both pegmatites and host metamorphic rocks. Pegmatite accessories of allanite, titanite, apatite and scarce zircon act as concentrators of incompatible elements such as Y, Nb, Ga, Ge and REE in pegmatite. Large amounts of Y (~3000 ppm), Ce (up to 40607 ppm), La (12945–18926 ppm) and Nd (11665–14378) incorporation are typical for the studied allanite crystals with a significant dominance of LREE over HREE. The overall sum of REE in allanite ranges within 71115–83788 ppm, whereas in apatite reaches 4119 ppm.

The analyzed titanites yielded a lower intercept age of 39.9 ± 2.3 Ma. The obtained mean concentrations of trace elements are: V (~180 ppm), Y (~225 pm), Nb (~2262 ppm) and Sn (~180 ppm). The average sum of REE in titanites from Govedarnika is very low (310 ppm), LREE slightly prevail over HREE. Moreover, relatively high Nb/Ta (25.96) and La/Gd (1.62), low Th/U (0.12) and Dy/Yb(<2.00) ratios, along with low HFSE contents and positive Eu anomaly suggest metamorphic influence or most probably hydrothermal origin of the studied titanite crystals (Liu *et al.*, 2022 and references therein). Such genetical suggestion is supported also by the fact that most of the titanite crystals (presumably with pegmatite origin) are transformed to leucoxene, apart from some 'fresh' crystals closely associated with chlorite alteration after pegmatites.

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New data on the geochemical and mineralogical features of the main manganese- and iron-bearing ore occurrences in the Central Srednogorie Zone, Bulgaria

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The main goal of the present study is is to characterize the mineralogical and geochemical features of polymetallic (Mn- and Fe-bearing) nodules, lens- and layer-shaped bodies from different localities in the central part of the Late Cretaceous Srednogorie metallogenic zone, Bulgaria. The research is based on field studies, sampling and optical microscopy followed by a combination of analytical techniques: XRD, SEM-EDS, ICP-OES and LA-ICP-MS methods. They define pyrolusite as main ore mineral of the studied occurrences, whereas manganite, todorokite, bixbyite, sarkinite, hematite and hauerite are rarer. The most common gangue minerals are quartz, calcite and zeolites. Based on the MnO/SiO_2 ratio, the established minerals are divided into two groups: manganese (i) and silica-manganese (ii) phases, respectively. Their trace element composition is dominated by a high content of V, Zn, Mo, W, Co, Ni, Cu, As, Tl and Sr, whereas some of these elements belong to the group of the critical raw materials for high-tech products. The measured values for Y and rare earth elements (REEs) of the studied oxides and hydroxides are low compared with their concentrations in modern polymetallic nodules of the Pacific Ocean. Chondrite-normalized patterns indicate weak LREEs enrichment with respect to MREEs and HREEs, which are minor depleted. Common slight to strong negative Ce anomaly as well as various Sm and Eu anomalies are also observed. The proximity of the Late Cretaceous volcanic rocks to the Mn- and Fe-bearing ore mineralization and some structural and textural features of the studied minerals suggest a hydrothermal origin of the main Mn-Fe ore occurrences in the Panagyurishte area.

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Facies analyses of the Upper Cretaceous bauxites in the Jajce area, Bosnia and Herzegovina, in response to lithospheric bulges caused by compressional regime during the gradual closure of the Dinaridic part of the Tethys

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The bauxite-bearing area Jajce is located northwest of the town of Jajce in the central part of Bosnia and Herzegovina. The region was exploited for karst bauxite during nearly a half a century activity. Geology of the area and the bauxite genesis were discussed in a number of papers. Geophysical surveys were also applied. Particularly important bauxite districts include Crvene Stijene, Bešpelj, Poljane and Liskovica. Our research was focused in the Bešpelj district, mined in open-pits and undergrounded mining, and giving opportunities for a detailed sampling and rock observations. Geochemical and mineralogical research of bauxites were made on the core samples of three boreholes. In total, 13 bauxite samples were studied by wet chemistry, ICP-MS (trace elements and REE), XRD, micro-XRF, optical microscopy, and differential thermic analysis. The bauxite deposits originated during the terrestrial phase in the stratigraphic range from the upper Albian to the Coniacian–Maastrichtian. The Jajce area is a part of the northeastern margin of the Adriatic Carbonate Platform, which existed from the end of the Early Jurassic up to the end of the Cretaceous. At the end of the Early Cretaceous and the beginning of the Late Cretaceous, the carbonate platform, as a passive continental margin, underwent an intensive compressional tectonics and emersion as a result of platform bulging. Hot humid climate and subaerial conditions were beneficial for effective bauxitization. The emersion lasted from late Albian to the Coniacian–Maastrichtian, approximately for 20 Ma. Six types of bauxites are distinguished: lenticular, canyon-like, graben type, sinkhole type, canyon-like with a sinkhole at the bottom and tectonized ones (Pavičić *et al.*, 2018). The bauxite deposits are mainly composed of carbonate clastics and limestones of Late Cretaceous age, exceeding thickness of 1000 m. The boundary between the Upper Cretaceous and the Paleogene clastics is not accurately defined. Bauxite lithology and genesis is defined by paleo-relief type and position of the water table and erosion basis. Deeply dissected karst, filled by a bauxitic material with synchronous bauxitization prefers vadose facies. The genetical observation recognizes juvenile, mature and senile phases. The complete profile is topped by an iron crust (duricrust). Bauxite lithogenesis is defined by pelitomorphic facies (mudstones with colloform texture, formed in a water saturated zone). Ooid/pisoid facies in the middle of the ore body assumes a development from autochtonous to allochtonous setting.

Paleosoils attested with pedogenic formations, rhizopods and syneresis, point to a new transgression in the Late Cretaceous as a response to collisional tectonics. Flexural bulges, due to uplift of crustal segments, are typical of the orogenic foredeeps, in areas affected by an active thrusting, nappe stacking and tectonic loading. New beneficial subaerial bauxitization areas were formed and shifted toward the inner part of the Apulian carbonate platform (Adriatic-Dinaric), in post- Cretaceous times.

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New mineralogical data from the Jolotca deposit, Romania: mineral hosts for Nb, Y, intermediate and heavy REE

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The Jolotca metallogenetic sector underwent a manifold history due to shifting approaches regarding its status as a mineral occurrence, prospect, deposit or even mining site for various commodities. The vein mineralization is related to the Ditrău Alkaline Massif, recording a short Carnian to Norian magmatic to postmagmatic evolution (Klötzli *et al.*, 2022, and references therein), as supported also by U-Th-Pb_T monazite ages.

Ianovici (1938) gives the first account of pyrite and subordinate base metal sulfides mineralization in carbonate gangue, associated with zircon/*malacon*/*beccarite* (in fact probably monazite). Pantó (1950) reports contemporaneous mining (in 1942) for pyrite and deems the Pb-Zn mineralization not worth recovering. Yet, prospecting and exploration work extended for a few decades and abruptly terminated in 1999 resulted in reserve estimations for Mo-Zn-Pb-REE (Constantinescu and Anastasiu, 2017, and references therein).

The most abundant phases of interest are niobian rutile for Ti and Nb (Săbău, 2009; Hirtopanu *et al*., 2015), formed early in the crystallization sequence, and late-stage monazite + REE-flourocarbonates for light REE.

A mineralizing stage occurring during/after rutile corrosion and overgrowth by massive to idiomorphic ilmenite, consist of streaks and sprays of micron-sized, lath- to needle-shaped oxide grains, associated with chlorite and partly included in ilmenite. The grains mostly represent intergrowths (partly epitaxial) of several phases. The minerals present are fergusonite-(Y) enriched in Gd+Dy or Nd+Sm+Eu, Ti-bearing fersmite and Fe-Mn-columbite, vigezzite, nioboaeschynite-(Y), Ce- and Nd-dominant aeschynite/nioboaeschynite, and a metamict viggezzite-like phase containing high Th and silicon. The latter phase matches the mineral UM2001-09-O:CaNbREESiTiY described by Aurisicchio *et al*. (2001), appearing in similar complex assemblages and intergrowths, though Ta and U-enriched unlike in the Jolotca occurrence.

At Jolotca most of REE, represented by Ce and La, and bound in phosphate, carbonate and silicate phases of the mineralization. The here reported mineral assemblage concentrates in oxides REE heavier than Ce associated with late-stage Nb not hosted in rutile.

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Rare earth mineral association in pegmatites from the Kroushev Dol Pb-Zn deposit

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Incompatible elements, including Th, U and rare earth elements (REEs) are accumulated in the process of crustal formation and granitic magmatism. Due to their geochemical behavior and chemical properties, they are seldom incorporated into major rock-forming minerals. Instead, they preferably form minerals in the late stages of magma differentiation and most frequently occur in pegmatite bodies, being a potential source for critical elements. Large pegmatite injections are part of the host rocks in the Central Rhodopean Pb-Zn deposits in south Bulgaria. An ongoing study on the mineral and chemical composition of pegmatites disclosed in the underground mine of Kroushev Dol revealed the abundance and diversity of REE accessory minerals.

The mineral composition of selected pegmatite dyke on the 865 m.a.s.l. in the mine comprises K-feldspar, plagioclases and quartz. Intensive overprint by epidote-chlorite-carbonate hydrothermal alteration takes place along the pegmatite contact with marbles and metasomatic ore mineralization. Detailed petrographic study along a profile across the dyke revealed that accessories have zonal distribution. Areas proximal to the lithological contacts are characterized by large titanite crystals, while in the inner pegmatite zone allanite, apatite, zircon, monazite and thorite prevail. Most of the minerals generally form single idiomorphic crystals within the feldspar-quartz matrix, apart from the monazite and thorite grains. They are both observed within the allanite crystals, but monazite appears as large hypidiomorphic crystal relics, while thorite grains (below 10 µm) are attached to certain microfractures together with epidote developed as an alteration product after allanite. The REE-minerals often form aggregates and/or accumulations in the pegmatite.

EPMA shows that the monazite is monazite-(Ce) with average contents (in wt.%) of Ce_2O_3~30, La_2O_3~16, Nd_2O_3~9.4, ThO_2~4, Pr_2O_3~3, Sm_2O_3 and Gd_2O_3 ~1. Silica content (likely substitution of Si for P) is ~1 wt.% SiO_2. Allanite inhomogeneity is defined by the reverse correlation within (Ce+La)/Ca and Fe^{3+}/Al^{3+} ratios. The Ce_2O_3-content varies within the range 6.73–13.95, while La_2O_3 is between 4.17 and 6.63 wt. %. REE-incorporation in other minerals, although abundant (detected by LA-ICP-MS), takes place in trace amounts only.

Despite the coexistence of several REE-bearing minerals, their relationships and chemical composition suggest formation of monazite and zircon in the earlier stages of the pegmatite crystallization. The acid leaching of the host rocks (*e.g.* marbles) led to Ca-enriched fluid, which lowered significantly the monazite stability (as suggested by Sato *et al*., 2014). The released LREE (Ce, La) and P are incorporated in allanite and apatite, while Th contributes to formation of thorite. Redistribution of REE within close proximity of monazite defines the observed allanite inhomogeneity and its REE enrichment around the monazite grains. The later hydrothermal activity led to allanite partial replacement by epidote with increased Ce-content. The studied minerals concentrate large amounts of critical elements with potential importance.

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Application of X-ray elemental mapping on REE minerals: a case study of allanite, monazite, apatite and zircon

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Rare earth elements (REE) have become extremely important to our world of technology owing to their unique magnetic, phosphorescent, and catalytic properties. X-ray mapping or compositional imaging of elemental distributions is one of the major capabilities of electron beam microanalysis, providing direct information on elements of interest (Friel and Lyman, 2006). Using X-ray mapping with SEM-EDS, we outlined REE-concentrating minerals in pegmatite-hosted mineral associations from the Kroushev Dol Pb-Zn deposit. The studied pegmatite mineral assemblage includes K-feldspar, plagioclase and quartz with an overprinting epidote-chlorite-carbonates hydrothermal association. The accessory minerals in the analyzed samples are represented by zircon, monazite, apatite, titanite, allanite, and thorite (Vassileva *et al*., 2022).

Mineral associations and paragenesis were studied with an optical microscopy prior to scanning electron microscopy. Back scattered electron images (BEI) were collected with JEOL GSM 6390. Chemical compositions of minerals were determined at 20 kV and a beam current of 50 nA. Standards used for the EDS analysis were natural minerals (jadeite, quartz, wollastonite and apatite for Al, Si, P, Ca, respectively), pure metals were used for Fe, Th, and U, zirconia for Zr, LaB_6 for La, CeO_2 for Ce, NdF_3 for Nd, SmF_3 for Sm, and PrF_3 for Pr. A representative area with accumulation of monazite, apatite, zircon and allanite-(Ce) was selected for the X-ray elemental mapping.

Elemental mapping with SEM-EDS was applied on an allanite mineral aggregate of monazite, apatite and zircon grains included within, and overgrown by epidote rim. The mapped elements are Al, Fe, Ca, P, Mn, Ce, La, Nd, Pr, Sm, U, Y and Zr. The obtained results are applicable to the qualitative assessment of the specific elemental composition of phases containing REE as major or minor constituents. The method was successfully used to quickly and easily track the concentration or diffusion of certain (*e.g.* La, Ce) chemical elements in the mineral association (*e.g.* allanite-epidote). However, particular attention should be paid in cases of X-ray elemental peak overlapping (*e.g.*, Y vs. P observed in apatite) that could lead to a wrong interpretation.

Based on the acquired X-ray maps, the REE-bearing minerals and their chemical variation in the studied mineral assemblage were easily outlined.

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Critical metals in deep-sea polymetallic nodules from the Interoceanmetal exploration area in the Clarion-Clipperton Fractures Zone (CCZ), NE Pacific

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Deep-sea polymetallic nodules are considered as alternatives to depleting land resources of industrially important metals such as Cu, Ni, Co, Pb, Zn, Mo, Pt, and REE. Many of metals found in polymetallic nodules in variable amounts (Bi, Co, HREE, LREE, Li, PGE, Sr, Ti, W, V) are defined as critical raw materials. The Clarion-Clipperton Fractures Zone (CCZ) in the NE Pacific Ocean is considered to be the most prospective region for exploration and future nodule exploitation, with a conservative estimate of the dry tonnage of nodules of 21,100 million tonnes.

The geochemical characteristics of the polymetallic nodules from the Interoceanmetal (IOM) exploration area in the eastern part of the CCZ were studied. Box-core samples from six stations were collected at depth varying from 4,300 m to 4,500 m. Data on board processing of sampled stations showed that wet nodule abundance parameter ranges from 10.3 to 19.9, averaging 13.5 kg/m^2. The metalliferous nodules were observed on the top of and partly buried in seabed sediments. The sediments composition is dominated by light brown siliceous silty clay down to 45 cm with a semiliquid dark brown clay variety (7–12 cm) on the top, denoted as geochemically active layer (GAL). The GAL Eh is between +462 and +545 mV and decreases with depth while pH data vary in a short span (7.01–7.52). An amorphous phase (biogenic opal, authigenic Fe-Mn (hydro)oxides and clay minerals) predominates. The crystalline phases are illite, kaolinite, chlorite, quartz, andesine, halite, cristobalite and barite.

The studied polymetallic nodules vary between 1 and 10 cm in size. They are built of one or more "core" zones and concentric ore-bearing microlayers. The bulk nodule mineral composition consists of todorokite, quartz, muscovite and traces of vernadite, apatite and barite. Results of LA-ICP-MS analyses of bulk nodule samples show Mn content from 22.62 to 32.95 (mean 27.47) wt. %, Fe from 5.44 to 8.26 (mean 6.74) wt. % and the Mn/Fe ratio is 2.74–6.06. The concentrations of main other metals are (in wt.%): Co (0.16–0.30, mean 0.23), Ni (0.58–1.70, mean 1.29), Cu (1.07–1.50, mean 1.23), Zn (0.09–0.21, mean 0.16). Trace elements include (in ppm): Mo (430–867), Li (77–177), Sc (7.7–11.7), V (403–513), Ga (38–52), As (67–152.6), Sr (431–656), Zr (204–340), Pd (0.34–0.73), Cd (8.6–20.8), In (0.14–0.25), Sb (35–65), Ba (2640–4346), W (51–111), Tl (53–410), Pb (307–616), Bi (2.5–7.1). The ΣREE varies from 339.2 to 719.1 (mean 594.27 ppm), ΣREY is from 380.8 to 800.8 (mean 664.27 ppm) and ΣHREE is from 47.8 to 105.5 (mean 87.72 ppm). The PAAS-normalized REE patterns show enrichment of MREE and HREE and positive Ce and Eu and negative Y anomalies.

The *in-situ* LA-ICP-MS analyses show significant variations of element contents among nodule layers. The behavior of trace element depends mainly on distribution patterns of Mn (Tl, Ba, Cu, Cd, Sb, W) and Fe (P, As, Zr, Sn, Hf, Pb, Co, U, Y, Th, REE). Part of the PAAS-normalized REE patterns has negative, other part has positive Ce anomaly (Ce/Ce*=0.13–1.73). The variations in the Ce anomaly correlate with Mn/Fe ratios and changes of layer genetic type (diagenetic or hydrogenetic). The Ce anomaly variations are a result of changing oxic/suboxic environment, and also a useful indicator for the nodule growth mechanisms.

The studied polymetallic nodules from the eastern part of the CCZ are rich not only in Mn, Fe, Ni and Cu but also in REE and other critical metals which could be significant by-product in the future exploitation of nodules.

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REY in pore waters of sediments hosting Fe-Mn nodules in the Interoceanmetal exploration area in the Clarion-Clipperton Fracture Zone, NE Pacific

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The deep-sea sediments containing Fe-Mn nodules are soaked of pore waters considered an important source of REE. The studies on REE+Y (REY) in marine pore fluids have been limited by analytical challenges, and too few pore water data are available. In our study we focus on geochemistry of REY in pore waters from core-box sediments. The samples were collected from the 0–5, 10–15, 25–30, and 35–40 cm intervals from four stations of the eastern part of the block H_22 of Interoceanmetal (IOM) license area of the Clarion-Clipperton fracture Zone, NE Pacific. The pore water analysis is based on a modern, improved analytical technique (ICP-MS, Perkin-Elmer SCIEX Elan DRC-e) with a cross-flow nebulizer and a spectrometer optimized for simultaneous determination of macro- and microelements (RF, gas flow, lens voltage) using a quadrupole cell in a DRC (Dynamic Reaction Cell) mode. The improved analytical technique allowed us to define the whole suite of REY in depth profiles. Subsequently, the REY distributions were normalized on Post Archean Australian Sedimentary Rocks (PAAS) and conclusions made about the elements' anomalies and sourcing.

The ΣREY values in the pore water samples vary from 4.05 μg/L to 106.34 μg/L. The REE contents measured are at least one order of magnitude higher than in an oceanic water. We followed the natural variations of La and Lu (the lightest and heaviest REE), and Ce and Y in absolute concentrations in the depth profiles for four layers sampled from station 3607. Ce and Y are slightly enriched around the water-sediment interface, *i.e.*, in the shallow sediment layer, while La and Lu are enriched in the deeper layers.

PAAS-normalized REY of the pore waters display similar patterns, typically characterized by a pronounced negative Ce/Ce* together with a little MREE and HREE+Y enrichment over LREE. We obtained relatively "flat" REE patterns that are typical of shallow open ocean REE patterns of the Western Pacific (Deng *et al*., 2017), Northern Cascadia accretionary margin (Kim *et al*., 2012), and California margin (Haley *et al*., 2004). This pattern type represents REE released from the degradation of an organic matter according to Haley *et al*. (2004).

In conclusion, we assume that the decomposition and adsorption of organic matter and oxidation conditions are the main factors for the fractionation of REE in pore water. The reason for some scatter in our REY data might most likely to be linked to a bioturbation that has affected the sediment profiles.

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First occurrence of gasparite-(Ce), chernovite-(Y) and retzian-(Ce) in Greece: mineral chemistry and implications for REE enrichment in the Varnavas Mn-oxide ore

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This work describes the mineral chemistry and mode of occurrence of a complex REE arsenate-phosphate mineral association, namely gasparite-(Ce) $Ce(AsO_4)$, chernovite-(Y) $Y(AsO_4)$, retzian-(Ce), $Mn_2REE(OH)_4(AsO_4)$, as well as the phosphates, monazite-(Ce), $Ce(PO_4)$. The association is reported from the metamorphosed Mn-oxide mineralization within a Triassic volcaniclastic unit from Varnavas, NE Attica (Greece), part of the Attic-Cycladic Blueschist Unit. The REE minerals were investigated using electron probe microanalysis (WDS) and scanning electron microscopy.

The Varnavas Mn ores have lenticular or banded textures; the ore bodies, only a few meters wide, are enclosed in piemontite-schists similar to those described from the Alps in Switzerland, Italy, and Austria (Stouraiti *et al.*, 2022; Pagliaro *et al.*, 2022). Gasparite-(Ce) is a common mineral hosting REE in the ore; it occurs as minute isometric grains up to 15 μm in size associated with chernovite-(Y) and retzian-(Ce), enclosed in todorokite-pyrolusite-hollandite ore. The Mn-rich rocks are also profoundly enriched in arsenic reaching concentrations of 2000 ppm. The geochemical data of the previously mentioned phases demonstrate a P-As substitution between monazite-(Ce) and gasparite-(Ce), as well as for the pair xenotime-(Y) and chernovite-(Y) (Pagliaro *et al.*, 2022). The above suggest that both monazite-(Ce) and xenotime-(Y) reacted with As-bearing hydrothermal fluids that converted them to arsenates (Ondrejka *et al.*, 2007).

The presence of ardennite-(As) in rocks surrounding the Mn-ore indicates the deposition of As under strongly oxidizing conditions. Notably, all the studied REE-minerals display a pronounced positive Ce-anomaly in the normalized REE patterns, which is known to result from oxidation of Ce on Mn-oxides. The inclusions of the REE-arsenates in the Mn-ore and the existence of the monazite and xenotime in the adjacent Mn-rich host rock, may indicate a short fluid transport of leached REE from the REE-phosphate minerals and oxidative deposition in the local Mn-oxide accumulations.

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Preliminary data on contents of critical elements in lignite from the Maritsa East basin, Bulgaria

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To assess their potential for critical elements, we examined organogenic and sedimentary rocks from the Troyanovo 1 and Troyanovo North mines in the Maritsa East basin, the largest lignite basin in Bulgaria. The studied samples include three composite coal, three lithotypes (lyptain, xylain, and fusain), and one black clay parting. Mineral matter in composite coal samples, lithotypes and clay is represented by clay minerals (montmorillonite, kaolinite, illite), quartz, pyrite, and gypsum in various quantities. A total of 66 elements were measured in all samples. The measured concentrations were compared to worldwide values of brown coal and upper continental crust and coefficients of enrichment (K1 and K2, respectively) were established. Most of the studied critical elements (REY, platinum-group metals, Li, Si, Mg, Ge, Ga, Nb, Sb, In, Co, Be, W) have low concentrations (K1 and K2 <2). The contents of rare earth elements, yttrium, and scandium in the studied composite coal and lithotype samples is lower than concentration in world low-rank coal (65 ppm) and lower than in the studied black clay (145 ppm). The K1 and K2 coefficients of Pd and Pt, Te, Re, and Au are anomalously high. Most of the trace elements occur in minerals (sorbed in clay minerals, trace elements in pyrite, and as discrete phases). Some elements in low-ash samples (lithotypes) demonstrate affinity to organic matter: Te, Re, As, Mo, Ca, P, Au, Ba, Sr, Cd, etc. The lithotypes show enrichment in HREE (Gd-Lu) and Y in the following decreasing order: xylain > fusain ≫ liptain. The anomalously high contents of Te, Re, Pd, Pt, Au, Se, As, Mo and others require further investigation.

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Rare-element pegmatites of the Bohemian Massif, Czech Republic

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The crystalline units of the Bohemian Massif host a large number of granitic plutons as well as numerous granitic pegmatites. Renewed interest in industrial (feldspars) and critical minerals (*e.g.*, ores of Li, Ta, REE, Sc) starts a new interest in pegmatites, especially those rich in rare elements such as Li, Be, Rb, Cs, Nb, Ta, or Sn. From metallogenic point of view, rare-element pegmatites are found in all major crystalline units of the Bohemian Massif.

In the Moldanubian Zone, pegmatites are widespread. Pre-Variscan pegmatites are small, simply zoned, and not suitable for mining. Only the Přibyslavice orthogneiss represents a specific example of complex orthogneiss/metagranite/granite with granitic pegmatites, where Nb, Ta, Ti, Sn-oxide minerals occur. Similarly, anatectic pegmatites of Variscan age are very small, and not suitable for mining. On the other hand, Variscan pegmatites of rare-element class are abundant and exhibit high variability in shape, size, textures, degree of fractionation and mineralogy; they range from simply zoned dikes to highly fractionated bodies. Some of the geochemically rather primitive pegmatites were mined for ceramic feldspars (Dolní Bory, Písek). The more evolved complex (Li) pegmatites with Li-micas and Li-tourmalines > amblygonite-montebrasite > petalite, are more common. Two subtypes are typical of this region - lepidolite-subtype pegmatites (*e.g*., Rožná, Dobrá Voda, Jeclov) and elbaite-subtype pegmatites (*e.g*., Řečice, Pikárec); solely the pegmatite from Nová Ves shows features of the petalite subtype. Some mostly “stockscheider-type” marginal pegmatites (LCT family), locally with beryl, are related to the Eisgarn granite and highly evolved granites of the Moldanubian Batholith. Small intragranitic pegmatites of NYF family occur in the Třebíč and Milevsko plutons but they contain only low amounts of Y, REE-minerals.

Granitic pegmatites in the Bohemicum mostly belong to the muscovite-rare-element class and occur almost exclusively along the western border of the Bohemicum (the Poběžovice-Domažlice and Teplá districts). The pegmatites and associated granites have been mined for ceramic sources for ca. 120 years; rare primary spodumene shows their potential for Li-ores.

Pegmatites of the Saxothuringicum are closely related to highly evolved leucocratic granites and greisens (Cínovec, Krásno). Besides pegmatites of the beryl-columbite-phosphate subtype, rather specific types are present (Podlesí – F, P-rich layered granite to pegmatite; Vernéřov – montebrasite-Qtz-Kfs veins with Sn (±Cu, Zn, Mo)-mineralization transitional to hydrothermal veins). The LCT granitic pegmatites exhibit F > P >> B and Li > Be commonly with very high activity of volatiles.

In Lugicum**,** rather rare intragranitic pegmatites mostly of the NYF family occur in the Liberec Pluton and Žulová Batholith. Their textures and mineralogy are specific compared to other regions; their volume is too small for practical use.

Two distinct populations occur in the Silesicum: pre-Variscan muscovite pegmatites with tourmaline and Variscan beryl-columbite pegmatites. Both populations exhibit Be >> Li but the activity of volatiles is higher in in the muscovite pegmatites (B >> P, F) compared to the latter. They are texturally and mineralogically unique within the Bohemian Massif, but common beryl and oxide minerals make them potential source of Be and Nb.

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Large-area multi-element LIBS mapping – versatile tool for petrogenetic research of rare-element pegmatites

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Elemental mapping of light (Li, Be, B, F) and trace elements in large-area geological samples represents an analytical challenge. Increased interest in Li and rare-element deposits showed a need for reliable mapping of light elements. One of the possible solutions is a laser-induced breakdown spectroscopy (LIBS) combined with sophisticated data processing (Limbeck *et al*., 2021; Pořízka *et al*., 2018).

We studied four large-area (~8 × 8 cm) samples from two rare-element Be-rich granitic pegmatites with moderate contents of Li (Maršíkov, Czech Republic) and high contents of Li+B (Rau property, Yukon, Canada). Cross-sections from host rock to the pegmatite evolved center were used for direct multi-element mapping, supervised semi-automated machine-learning mineralogy, and tracing of post-magmatic metasomatic and hydrothermal processes.

We used the LIBS device (FireFly, Lightigo, Czech Republic) equipped with a DPSS pulsed laser (266 nm, 10 ns, 50 Hz, 7 mJ). Each laser pulse was delivered to a fresh spot (40 µm spot size) to ablate material and produce luminous plasma. In total, up to 1 000 000 spots were ablated with 80 µm step size. Characteristic radiation was collected and spectrally analyzed with a series of Czerny-Turner spectrometers covering spectral range from 190 nm to 700 nm. From the obtained hyperspectral cube, elemental images of individual elements of interest were produced (incl. Li and Be). Then we used advanced statistical algorithms to elucidate mutual relationship of individual elements and provide unsupervised clustering of similar spectral responses. This led to cluster images manifesting the distribution of individual matrices (*i.e.*, minerals).

The study demonstrates a very good applicability of LIBS for detection and mapping of major (Si, Al, Fe, Mg, Mn, Ca, Na), light elements (Li, Be, B, F), and trace elements (Ge, Ga, Cu, Zn, Ti, Sr, Ba) in pegmatites, discerning their specific geochemical signatures during magmatic, metasomatic, and hydrothermal stage of the rock evolution.

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Combining agile exploration methods with mineral chemistry for better geo-modeling of critical raw materials in the Assarel porphyry copper deposit

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Global demand for critical raw materials (CRMs) continues to grow rapidly, mobilizing Europe's domestic potential. Europe has a long tradition of mining and extractive activities of copper and base metals but is less successful in projects to source CRMs. A new Horizon Europe project called 'AGEMERA: Agile Exploration and Geo-modelling for European Critical Raw Materials' is going to contribute to the unlocking of Europe's CRM potential by conducting local state-of-the-art geological and geophysical surveys (*e.g.*, Holma and Arancibia, 2022) in 6 EU countries and 1 external country (Zambia). Mineral exploration targeting, sampling, modeling, and geophysical field trialing are planned in the project, whereas the exploration sites are chosen to ensure a variety of locations and mineral systems. One of the sites in AGEMERA is the Assarel porphyry Cu-Au deposit in Bulgaria.

The Assarel ore deposit is situated in Central Srednogorie (also called Panagyurishte district) which is part of the Late Cretaceous Apuseni–Banat–Timok–Srednogorie belt of calc-alkaline magmatism and Cu–Au mineralization. The Assarel Cu-Au porphyry deposit is challenging with the development of a secondary enrichment zone, extensive alteration zones with a significant argillic to advanced argillic alteration, and complicated structure, with pre-, syn- and post-ore normal faults. One of the latter (the Mialski fault) displaced the eastern part of the deposit and resulted in the exhumation of basement rocks with cross-cutting subvolcanic dikes, exposing these on the same level as the volcanics in the western part. The copper mineralization is hosted in Late Cretaceous (~90 Ma) calk-alkaline subvolcanic rocks and rare volcanic rocks of mainly intermediate composition, and in Carboniferous granites.

Our preliminary studies on the CRMs potential of the Assarel deposit reveal high concentrations of several CRM elements in some ore and alteration minerals. In the studied pyrite, Co contents are up to 1000–1630 ppm, whereas galena features Se concentrations of 2–3 wt%. Molybdenite is not evenly distributed and is the main carrier of Mo and Re but the content of the latter varies from 600 to 45790 ppm. From the alteration minerals, hydrothermal rutile concentrates trace elements like V (110–6700 ppm), Nb (2300–4600 ppm), Ta, W, and Sc; epidotes and APS (aluminium-phosphate-sulphate) minerals have elevated contents of REE, whereas hydrothermal chlorite (the Ti/Sr ratio) could potentially be used as an exploration fingerprinting tool. Recent studies by Cioacă *et al*. (2020) indicate the occurrence of Au-, Ag-, Bi-, Te-, and Se-bearing minerals as minute inclusions in pyrite and chalcopyrite from the main chalcopyrite-pyrite ore assemblages and in the upper epithermal and supergene alteration zones. Platinum-group elements are scarce and reported as rare Pd-bearing tellurides occurring in pyrite.

Additional structural studies and new data on the distribution of CRMs in ore and alteration minerals will be linked with innovative geophysical methods in the frame of AGEMERA and will result in improved deposit models and enhanced knowledge about CRMs fast and effective exploration techniques.

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Enrichment of critical metals in mafic rocks: the case of the Maronia Pluton, Northern Greece

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The geochemical behavior of critical metals in magmatic and hydrothermal systems is of paramount importance in economic geology. Specific metals namely the REE, U and Th are predominately associated with alkaline felsic igneous rocks. Therefore, the presence of REE-U-Th minerals in mafic rocks is of particular interest, regarding the physicochemical conditions of the enrichment.

The Maronia pluton is an Oligocene intrusion, emplaced within the Rhodope Core Complex, as a result of arc-magmatism during subduction of continental lithosphere after the closure of the Pindos Ocean (Schaarschmidt *et al*., 2021). The pluton comprises three distinct lithologies: *a*) the basic group of gabbro; *b*) the intermediate group of monzonite, quartz monzonite, monzogabbro and quartz monzogabbro; and *c*) the felsic group, comprising granite cut by aplitic dykes and porphyry-type mineralized porphyritic microgranite (Melfos *et al*., 2020; Schaarschmidt *et al*., 2021). Felsic magmas, including the porphyritic microgranite, were generated by fractional crystallization of mafic magmas (Schaarschmidt *et al*., 2021). The shoshonitic affinity of the Maronia pluton is considered to reflect hydrous melting of a phlogopite-bearing mantle that was enriched by 3–5% of slab-derived sediment melts (Schaarschmidt *et al*., 2021).

The REE are presented in remarkably constant concentrations throughout the compositional range of the pluton, which is in contrast with the variable compatibility of these metals in minerals of mafic and felsic rocks. Therefore, a geochemical and mineralogical study was conducted in the mafic rocks to determine a) the host minerals of these metals and b) the geological processes responsible for their formation. Whole-rock composition of the studied samples was determined through XRF and ICP-MS, while the identified REE-U-Th minerals were investigated by SEM-EDS.

Geochemically, the studied samples are classified as metaluminous monzogabbros/diorites, and are composed of plagioclase, K-feldspar, pyroxene, amphibole, minor quartz, and iron oxides (ilmenite, magnetite). Accessory minerals include apatite, epidote and zircon. In addition, REE-U-Th minerals such as allanite-(Ce), monazite-(Ce), perrierite-(Ce), uraninite-thorianite, thorite, and zirkelite, were identified. The studied samples show a weak hydrothermal alteration, including biotite, sericite, actinolite and chlorite. A preliminary petrographic investigation suggests that perrierite-(Ce) and monazite-(Ce) are tentative magmatic phases, whereas the U-Th minerals and allanite-(Ce) could be of both magmatic and late magmatic-hydrothermal origin.

It is possible that late magmatic-hydrothermal fluids, potentially derived also from the surrounding granites and associated porphyry-type mineralization, may have contributed to the relative enrichment of REE, U, and Th in the monzogabbros. Furthermore, a possible dissolution of main magmatic REE-U-Th phases, could have, locally, remobilized U and Th (Papoutsa and Pe-Piper, 2013), and resulted in the formation of uraninite-thorianite, thorite and zirkelite.

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Pegmatites in Romania: present state of knowledge and perspectives for critical raw materials

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The pegmatite occurrences in Romania are widespread in Variscan and younger medium-grade metamorphic basement complexes of the Carpathians. Extensive prospecting followed by small-scale mining for commodities like feldspar and mica resulted in a fairly good knowledge of their distribution and composition. General features are the lack of an apparent association with coeval granitic rocks, occurrence as swarms of small lenses scattered in the host schists and gneisses, a simple mineralogy (quartz-feldspar-mica, subordinate tourmaline, garnet, apatite), homogeneous or irregularly zoned internal structure (Hann, 1987; Mârza, 1985). These features are invoked in support of metamorphic segregation/anatexis as genetic mechanism (*Ibid*.), and the definition of a Carpathian pegmatitic province, geographically divided in several subprovinces/districts (Mârza, 1980).

Exceptions to one or more features of this general scheme include pegmatites associated to undeformed granites of uncertain age (possibly Mesozoic, Pană *et al*., 2002) in the Apuseni Mountains, as well as large pegmatite bodies, and most importantly, local to areal concentration of Li and Be, and scattered beryl, Li-minerals and/or niobotantalate occurrences, all of these in the pegmatites of the Variscan basement of the Alpine Getic Nappe in the South Carpathians.

In the case of Li and Be concentrations, structural constraints such as the post-Variscan basement remobilization due to extensional differential uplift triggering upward concentration of volatiles, or occurrence in particular Li-rich formations (staurolite-bearing micaschists) could provide clues for this exceptional behaviour and guidelines for further investigation.

Metamorphic mobilization and segregation without or with rare/subordinate pegmatite formation appears also likely to concentrate disseminated critical and strategic raw materials. Areal distribution and constant structural position of K-feldspar migmatites locally enriched in Zr, Nb-Ta, Y, REE, Sn and U-Th (*e.g.*, Hîrtopanu and Fairhurst, 2014) could indicate a K-metasomatism localized along a Variscan metamorphic thrust, emplacing juvenile metapelites over reworked pre-Variscan felsic rocks in the Lotru Metamorphic Suite (basement of the Alpine Getic Nappe, South Carpathians).

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Metallogeny of the Dinarides in the frame of the Wilson cycle

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The Dinaridic metallogenic province is a part of the Alpine–Himalayan orogenic system, developed as a result of opening and closure of the Neo-Tethys Ocean by convergence of the African and Eurasian plates. The northern boundary of the Dinarides is related to the northern African margin (Adria–Apulia). The Tisia mega-unit, a small continental block, positioned between the Dinarides and the Carpathians, is genetically related to the South Eurasian margin.

The geology of the Dinarides is constrained by the Alpine Wilson cycle. The major stages of the cycle are: (a) Permian early intra-continental rifting; (b) Triassic advanced rifting; (c) Jurassic oceanization; (d) Cretaceous subduction; (e) Paleogene collision; and (f) Neogene post-collision and extension followed by orogenic collapse. Each stage creates characteristic ore deposits related to the specific geological environments.

Stage (a) bears hydrothermal siderite-barite-polysulphide deposits, epigenetic sedimentary uranium deposits, red bed-type, sabkha-type copper and barite deposits and evaporites. Stage (b) favored SEDEX and hydrothermal iron-polysulphide-barite-mercury and MVT deposits. Stage (c) developed chromites, asbestos, talc and magnesite deposits. The spatial position of stage (d) remains poorly constrained.

The Southern Tisia unit might be a possible candidate for the Neo-Tethyan active continental margin with the Cretaceous subduction zone positioned beneath. Absence of voluminous subduction-related magmatism and mineral deposits, however, favors subduction within the Vardar zone (the easternmost Dinarides), adjoined to the Serbo-Macedonian ensialic terrain with its large porphyry-Cu deposits. Stage (e) was a prelude to the prolific phase (f) with its numerous hydrothermal Pb, Zn and Sb deposits that mostly occur in the western Vardar Zone.

The presentation deals with metallogenic characteristics of the Dinarides, based on recently-gained knowledge on the regional geology, petrology and genesis of mineral deposits. Establishment of the plate tectonic model several decades ago greatly contributed to an integrated interpretation of ore deposit genesis. In turn, basic research in the field of ore genesis generated new data that can be used to improve the plate tectonic model.

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Cosmic-ray based density-scanning of large geological objects in mineral exploration and mining

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Cosmic-ray geophysics is a subdiscipline of geophysics that multidisciplinary combines various geosciences with high-energy physics and relies on several types of instruments specifically designed for elementary particle detection. The cosmic-ray geophysical methods can be further divided into a couple of subfields, such as cosmogenic isotope geochronology and cosmic-ray muography. In the case of muography, the elementary particle of interest is the muon. Muons exploited in muography are generated in the upper atmosphere via a continuous process in which atmospheric molecules constantly interact with primary cosmic-ray particle radiation. Muons made this way are highly energetic and almost light-speed-fast (relativistic), due to which they have a high potential to penetrate geological matter far more than any other type of radiation, excluding neutrinos. Although most muons are stopped by the first few meters of terrestrial material, the more energetic muons can reach hundreds of meters in depth.

Muography applied to geology is an imaging technique of soil and rock densities. It harnesses the ever-present flux of muons to collect information on the distribution of density contrasts within the volume of interest. Imaging is made possible because muons advance in straight paths and lose energy (and hence speed) according to the average density of the material they pass through. When a single muon has lost its speed, it instantly breaks down into other particles. In brief, muon flux attenuation allows imaging of density variations in geological materials, just like X-ray imaging allows transillumination of the human body. The number of muons detected in any given direction reveals average densities in those directions. Muographic imaging is carried out radiographically or tomographically, *i.e.*, the produced images are either two-dimensional or three-dimensional, respectively.

Considering physical appearance, two detector types stand out: borehole probes and larger box-like "telescopes". The two disadvantages of muography are that (a) the detector(s) must be installed underground, and (b) collecting robust statistics is a relatively slow process (from days to months) due to the low flux of muons. However, as demonstrated by the steadily growing number of applications and publications (Holma *et al.*, 2022), the benefits of muography surpass its shortcomings. First, muography is a totally independent density-characterization method from those already existing (gravity, seismics, petrophysics). Second, muographic data is not hampered by magnetic or electric fields. Third, if need be, the image resolutions can be improved relatively easily by technical means, such as adding more observation points or measurement time.

Potential applications of muography in geoscience are numerous and span from surface to deep applications. These include, for example, volcanology, groundwater exploration, weathering studies, glaciology, sedimentology, speleology and structural geology. The current work focuses on mineral exploration and mining.

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Muography: imaging the interior of large scale objects with cosmic radiation

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Muography is short for cosmic muon imaging: an emerging field of applied sciences, where instrumentation developed for high energy physics (nuclear- and particle physics) is used as means to catch a glimpse of the interior of large objects. There is a broad range of potential applications (Tanaka and Oláh, 2018), including high profile results in volcanology (Tanaka *et al*, 2014) and archeology (Morishima *et al.*, 2017). Geosciences in general, and particularly fields, such as mining exploration or structural geology (Zhang *et al.*, 2020), can largely benefit from muography measurements. Cosmic muons penetrate up to a few kilometers of rock, and their number (directional flux) depends nearly exclusively on the integrated density (Oláh *et al.*, 2018). This way, an underground tracking detector can measure the mean density above the detector location, with an angular precision better than 1 degree. With a suitable measurement layout, the density distribution of the screened rocks can be estimated as a solution to a tomographic problem. Hence the geological structure can also be reconstructed, depending on how it is mapped into the density distribution space. Measurement time may be rather long, as much as weeks or months, depending on the configuration, which requires reliable and low maintenance instrumentation. The talk aims at introducing the state of the art in muography (Oláh *et al.*, 2022), and discussing the applicability of the method based on examples and results from the tracking systems developed at the Wigner Research Centre for Physics (Varga *et al.*, 2016). Muography is a highly multidisciplinary science field, bringing together particle physicists and geoscientists, exploiting a surprising possibility which Nature offers.

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Geological signatures of critical raw materials in Zambia: A case review of sediment-hosted Cu-(Co) deposits and critical raw minerals

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The geotectonic setting of the critical raw materials in Southern Africa involves the geological evolutions of cratons, mobile belts and basins that gave rise to mineralization in the region. Notable are Copperbelt type ores, which are stratiform to stratabound, sediment-hosted copper – cobalt (Cu-Co) deposits characterized by finely disseminated copper-(cobalt)-iron sulphides (predominantly chalcopyrite, cobaltiferous pyrite and bornite ± carrolite) in host rocks that may include quartzite (arkose), shale and dolomite deposited in a continental rift environment.

In the Zambia-Democratic Republic of Congo (DRC) Cu-(Co) metallogenic province, the orebodies either have stratiform morphologies with fairly long strike lengths (3 km to 57 km or more) in Zambia or as megabreccias (tectonic breccias) containing stratiform mineralization in Katanga (DRC). The widths of the mineralized sections typically are in the order of 4 to 35 m and the orebodies are commonly folded together with the host rocks in synclinal structures with NW-trends on either side of the Kafue anticline in what is termed the Lufilian Arc of a Neoproterozoic age. This is the main copper-cobalt target including the Domes Region in Zambia. Other areas include the Central Zambia iron oxide copper-gold deposits.

Other deposits of critical raw materials are the Luapula Province weathered basement hosted manganese mineralization and Central Zambia Carbonate hosted lead and lithium pegmatites targets. The stratigraphic positions of these orebodies are in the Roan Group of the Neoproterozoic Katanga Supergroup. These orebodies may contain Cu-Co; Cu only; uranium-(Ni-Cu-Co); and Pb-Zn-Cu. For example, on the Zambia Copperbelt, this covers an area of 125,825 km^2 in three types of orebodies: footwall arenites, ore-shales and arenites. The ore grades average 3 wt. % Cu and 0.18 wt. % Co in deposits where cobalt is recovered. Trace amounts of Au, Pt and Ag have been recovered from the copper slimes. Detailed geophysical signatures (magnetic, electro-magnetic and radiometric) of these prospective areas have been undertaken, but require careful interpretation.

On the Zambian side of the Copperbelt, it is estimated that 30 million tonnes of copper metal have been produced since mining began on a full scale in 1930. Such a large concentration of metals has prompted a number of genetic theories for the origin of the Cu and Co in a continental rift depositional environment. The genetic models include syndiagenetic, syngenetic, diagenetic, hydrothermal-epigenetic and hydrothermal-diagenetic variants. These models have tried to address the issues of source, transport and deposition of the metals as well as the later effects of deformation and metamorphism during the Pan-African Lufilian orogeny. The various genetic theories are reviewed taking into consideration the vast amount of knowledge gained from the seventy plus years of mining on the Copperbelt with a special focus on the geological and geochemical characteristics of the ores and typical host rocks as well as recent isotopic and age data.

The geological and isotopic data, including a craton-specific Pb isotope model for the Copperbelt, indicate derivation of metals from the upper crust over a long period of erosion of basement source rocks, which originally contained the metals in the form of protore porphyry-type deposits.

Critical metal/metalloid endowment in Cenozoic gold and silver deposits of Greece

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The Aegean area of Greece hosts several types of Cenozoic (Oligocene to Pleistocene) gold-silver-bearing deposits (*e.g.*, porphyry, high-, intermediate-, and low-sulfidation epithermal, granitoid- and metamorphic rock-hosted veins, skarns, carbonate-replacements), and is one of the most promising regions for future precious and critical metal exploitation in Europe (Arvanitidis and Constantinidis, 1989; Voudouris, 2006; Melfos and Voudouris, 2017; Voudouris *et al*., 2019). Porphyry- and epithermal-style deposits/prospects in Greece contribute a major part of the total gold-silver endowment of the country. They mainly occur in the Rhodope/Serbo-Macedonian and Attico-Cycladic massifs. Common features of the northeastern Greek porphyry deposits are their shallow depth of emplacement, low Cu content, Re enrichment, and multistage Au deposition. At Skouries there is Au and PGE enrichment in association with bornite, chalcopyrite and magnetite. High-intermediate sulfidation (HS-IS) epithermal Au-Ag-polymetallic deposits may overprint porphyry-style mineralization, where they are associated with lithocaps of advanced argillic alteration (*e.g*. Viper and St Demetrios at Sapes with 0.82 Moz Au, and Fakos/Limnos), or occur within volcanic rocks, without any obvious relationship to porphyry-style ores (*e.g*., Perama Hill with 1.94 Moz Au, Pefka, Mega-la Therma). No Au-rich porphyry-style mineralization has been discovered yet in the Attico-Cycladic area. However, Au- and/or Ag-rich veins with epithermal affinities crosscut metamorphic rocks at Lavrion, and several Cycladic islands (*e.g*., Syros, Antiparos). Milos Island on the active South Aegean Volcanic Arc (SAVA) contains shallow submarine IS epithermal Pb-Zn-Au-Ag-Te deposits.

Gold-silver-rich intrusion-related systems (other than “oxidized” porphyry- and HS-IS-type deposits), are characterized by a “reduced and low-sulfidation” ore mineralogy including arsenopyrite and pyrrhotite (±magnetite) with native gold that is deposited from CO_2-bearing fluids. These systems include intrusion- and metamorphic rock-hosted veins, skarn- and carbonate replacement deposits (CRD). World-class CRD occur at Olympias and Mavres Petres at Chalkidiki and Lavrion in Attica. Both Olympias and Lavrion contain significant gold in early pyrite-arsenopyrite ore (Voudouris *et al*., 2008; Baker, 2019), with Olympias containing 5.4 Moz Au. Gold-bearing Fe-Cu skarns occur at Kimmeria/Xanthi, Lavrion and Serifos Island in the Attico-Cycladic Massif (*e.g*., Korosidis *et al*., 2022). Gold-rich intrusion-hosted sheeted quartz veins, and veins crosscutting metamorphic rocks occur at Kavala and Pangaion, and in several locations of the Serbo-Macedonian massif, mainly at Stanos/Chalkidiki; with the later sharing some affinities to orogenic gold deposits (Voudouris *et al*., 2007; Melfos and Voudouris, 2017). Similar veins (some with epithermal affinities) in the Attico-Cycladic massif occur at Kallianos/Evia and Panormos/Tinos Island. Gold is present as invisible gold at the Olympias deposit; however it also occurs in native form in most of the other deposits, usually together with native Bi, Bi sulfosalts, Bi chalcogenides and/or Au-Ag tellurides.

The Cenozoic gold (and silver) deposits in Greece demonstrate enrichment in critical and energy critical metals/metalloids (Te, Se, Bi, Sb, In, Ga, Ge, Re, Pd and Pt) (Voudouris, 2006; Melfos and Voudouris, 2012; McFall *et al*., 2018). PGE enrichment is present at Skouries (up to 1 ppm Pd+Pt) and the porphyry deposits in the Rhodope Massif and Lesvos island (up to 70 ppb Pd). Rhenium is extremely enriched in the NE Greek porphyry deposits (up to 20 ppm Re in Pagoni Rachi), related to Re-rich molybdenite and rheniite. Tellurium (>1000 ppm) and Se (> 100) are mainly present in epithermal deposits (*e.g*., Pefka, Perama Hill, and Profitis Ilias/Milos island), but also in Cu-Au rich ores of the carbonate replacement/vein type deposit at Thermes/Xanthi. Bismuth (>2000 ppm) occurs in epithermal-style veins at Lavrion, Perama Hill, St Philippos and Pagoni Rachi, in skarn and carbonate replacement ores, and also in Skouries (up to 390 ppm; McFall *et al*., 2018). Bismuth is present either in its native form or as Bi sulfosalts/chalcogenides. Low-intermediate sulfidation stibnite-bearing epithermal veins at Kallintiri, Gerakario, Vathi in the Rhodope and Serbo-Macedonian massifs and the Aegean islands of Samos, Chios and Lesvos, are enriched in antinomy (>2000 ppm) and mercury (>100 ppm). The deposits containing the highest In-Ga-Ge content are of epithermal HS-IS style, with Pefka containing up to 675 ppm In (related to roquesite and In-bearing tennantite), and St Philippos up to 222 ppm In. Germanium (> 100 ppm) occurs at St Philippos and in silica sinters at Moudros, distal to the Fakos porphyry Cu-Au deposit. Gallium at St Philippos (up to 466 ppm) and Profitis Ilias/Milos (up to 74 ppm), is associated with sphalerite and/or wurtzite.

Although the process of magma generation in the Aegean region is still debated (*e.g*., subduction vs post-subduction, *e.g*., Schaarchmidt *et al*., 2021), factors which played a role in the precious and critical metal/metalloid endowment of the Aegean province include magma fertility in source regions, emplacement depth and oxidation state of the magma, and fluid evolution at the site of ore deposition. Arc magmatism may be responsible for the enrichment in Re and possibly of other fluid-mobile elements such as Te, Pb, As, Sb, Cu, Au, and PGE in the mantle wedge, probably due to fluids released from the subducted slab and associated sediments. Gold enrichment may also reflect the very shallow level of emplacement particularly for some Au-rich Miocene porphyry deposits, and/or local scale fluid evolution (Baker, 2019; Voudouris *et al*., 2019). Oxidized felsic magmas capable of generating Mo-Re-Au mineralization, possibly inherited a Sn-In signature due to some contamination in the crust, thus producing distal Pb-Zn-Cu-Sn-In polymetallic lodes. Accordingly, the Pb-Zn-Ag-Bi endowment in several deposits indicates a high crustal source component and crustal inheritance for these elements during metamorphic core complex formation (*i.e*., Menant *et al*., 2018).

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Special session SS8

Geodynamic, metallogenic and magmatic evolution of the Central Tethyan Belt (Anatolides–Caucasus–Iranian Belts)

Conveners:

İlkay Kusçu, Hadi Shafaii Moghadam, Robert Moritz

Episodic ore deposit genesis during protracted orogenic evolution: Lessons from the Anatolide–Lesser Caucasus–Iranian segment of the Central Tethyan metallogenic belt

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The Central Tethyan orogenic belt hosts a variety of porphyry-epithermal and volcanogenic massive sulfide (VMS) deposits, which have been formed episodically during the Arabia-Eurasia convergence and collision. This overview examines the long-lasting Mesozoic to Cenozoic evolution of this belt, extending from Turkey through the Lesser Caucasus to Iran. Jurassic to Early Cretaceous subduction along the southern Eurasian margin generated a continuous magmatic belt from Turkey to Iran. Then, throughout the Early Cretaceous to the end of the Eocene, the Anatolides and the Lesser Caucasus underwent a complex geological evolution with the amalgamation of microplates, various subduction stages and collisions. It resulted in episodic formation of porphyry-epithermal systems during the Jurassic–Early Cretaceous arc maturation, the waning stages of Late Cretaceous northern Neotethys subduction, and the onset of southern Neotethys subduction during the Eocene. Episodic VMS and associated epithermal ore formation accompanied nascent Jurassic arc magmatism in the southern Lesser Caucasus, and Late Cretaceous subduction reactivation and extensional tectonics in the Turkish Eastern Pontides and the northern part of the Lesser Caucasus in Georgia. By contrast, long-lasting Cretaceous to Eocene subduction along the Iranian margin remained sterile. It is only with the onset of major post-collisional Oligocene to Pliocene magmatism that significant porphyry-epithermal ore deposits were formed in the Iranian belts, which is also recorded in the Anatolides and the Lesser Caucasus.

Spatio-temporal associations between the magmatic-hydrothermal system and associated magmatism in the Turkish Tethyan collage

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Turkey, a collage of complex terranes in the Tethyan belt, has largely been shaped by interplay of several subduction and collision events related to the opening, final closure, and terminal suturing of the Tethys oceanic realms since the Permian. The collision between Eurasia and Afro-Arabia in Turkey along the Tethyan subduction zones generated voluminous calc-alkaline and alkaline magmatism, which reflects a transition from arc to post-collisional settings and the effects of collision and onset of crustal thickening and subsequent extension between ~110 Ma and 5.5 Ma. Collectively, this resulted in a fertile metallogenic environment with abundant porphyry Cu, orthomagmatic, volcanogenic massive sulfide, skarn, epithermal, and iron oxide Cu-Au deposits, clustering in narrow arc segments, and post- to late-orogenic transtensional and transpressional settings. Based on geological, geochemical, and $^{40}Ar/^{39}Ar$, U-Pb LA-ICP-MS geochronological data, four metallogenic episodes: 1) Late Cretacecous; 2) early–late Eocene; 3) late Oligocene–early Miocene; and 4) middle–late Miocene. These are defined in four geographically distinct regions: the Pontides in the north, the western Anatolian province in the west, central Anatolian Crystalline Complex, and the Southeastern Anatolian Orogenic Belt in the east central part of Turkey. The Early to Late Cretaceous–Paleocene tectonomagmatic evolution of Turkey is synchronous with the magmatic-hydrothermal systems, particularly for the Pontides and southeast Anatolian orogenic belt. The geochronological data indicate Late Cretaceous magmatic rocks in the Pontides were emplaced between ~131 Ma and 65 Ma, peaking at ~88–76 Ma, and are host to porphyry Cu-Mo, cogenetic skarn and epithermal Au systems. The available ages between 87 Ma and 70 Ma at the southeastern Anatolian orogenic belt point to a coupled but relatively younger subduction with the Pontides and magmatic event with peaking at ~86 Ma to 80 Ma. The magmatism at the latest Paleocene to early–late Eocene (58–35 Ma) is due to the exhumation of thickened crust and the onset of extension throughout the Pontides, Anatolides, and southeast Anatolian orogenic belt. This magmatism is accompanied by the continental to shallow-marine sedimentation within roughly E–W- to NNE- to NE-striking strike-slip to high-angle normal faults or “Tertiary” basins across Turkey. This magmatism is responsible for the generation of the alkaline porphyry Cu-Mo, iron oxide Cu-Au (IOCG), and epithermal systems in the eastern Pontides (58–38 Ma); in the western Anatolian province in the Tavşanlı porphyry belt (~49–47 Ma) and the Biga porphyry belt (40 Ma), and in the Southeastern Anatolian orogenic belt (~47 Ma to 43 Ma). Despite the Oligocene–Middle Miocene magmatism (30–18 Ma) and associated hydrothermal systems prevail at ~27 Ma to 25 Ma the western Anatolian province in the Biga, it is occasionally common in other parts of Turkey except for in the Southeastern Anatolian orogenic belt. This magmatism across Turkey fits well into extensive porphyry Cu, Cu-Mo, and Au systems, skarn Fe-Cu, Cu, IOCG systems, and epithermal Au-Ag, Pb-Au-Ag systems, particularly in western Anatolia, the Central Anatolian Volcanic Province, and the southeast Anatolian orogenic belt. Middle–late Miocene magmatism (~16–8 Ma) predominates within the Afyon-Konya porphyry belt in western Anatolia, and contains the youngest porphyry-related magmatic and hydrothermal systems (14–9 Ma).

Calc-alkalic porphyry Cu±Mo-Au and co-genetic skarn systems dominate all belts except the Afyon-Konya porphyry belt where alkalic porphyry Au-Cu systems are present. Upper Cretaceous rocks have typical arc magma compositions except the Central Anatolian Crystalline complex, whereas Eocene to Miocene collisional to post-collisional rocks have compositional characteristics of arc magmas that, over time, interacted with and were assimilated by ancient crust and evolved towards slightly higher Sr/Y and La/Yb trace element characteristics. The trace element compositions, along with rare earth element patterns, share characteristics typical of rocks associated with porphyry Cu-related magmas, reflecting the hydrous and oxidized nature of the magmas.

The magmatic rocks hosting these systems are characterized by a gradual increase in Sr/Y and La/Yb ratios and southward shifts of the magmatic locus with time, particularly in western Anatolia. This is accepted to be because of progressive crustal relaxation of thickened crust and extensional deformation as the arc/trench migrated and/or the subduction zone stepped southward.

A 2.0-Ga long history of the Gondwana-derived Eastern Pontides, NE Turkey, recorded by a Variscan granitoid

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The Eastern Pontides constitute an Alpine segment in NE Turkey. They are a Gondwana-derived terrane that was accreted to the Eurasian margin and subsequently reworked during successive orogenic events associated with the closure of the Paleotethys and Neotethys oceans. There is only little evidence for this long history, which has been preserved in the rock record within the Eastern Pontides. The oldest relics of the pre-Alpine evolution are Carboniferous granitoids (~309–323 Ma; this study and unpublished U-Pb zircon ages) that crop out within the central part of the Eastern Pontides as a belt parallel array of Variscan granitoid plutons. The Variscan Artvin granitoid is one of the best exposed and preserved examples. While its northwestern and southeastern margins are obliterated by normal faults that probably also facilitated its exhumation during successive thermal relaxation/orogenic collapses of the belt, it is bordered in the northeast and southwest by concordant Jurassic detrital sedimentary sequences of the Berta Formation.

The Artvin granitoid is composed of several Al-rich granitic phases crosscut by several generations of mafic magmas. In this study, we report new LA-ICP-MS U-Pb zircon ages for the different events of granitic rocks. The first event corresponds to a 324.4 ± 0.6 Ma leucogranite, the zircon cores of which yielded inherited ages as old as ~2.4 Ga. It was followed by a 323.7 ± 0.8 Ma leucogranite with abundant zircon inheritance as old as ~1.9 Ga that hosts xenoliths of partially molten micaschist and felsic intrusive rocks. The main volume of the Artvin granitoid consists of a 320.6 ± 0.6 Ma leucogranite crosscut by mafic dykes and sills, and by 315.4 ± 0.7 Ma micro-leucogranite dykes.

These geochronological data, along with the chemical composition of the granitic phases, indicate that the Artvin granitoid is a syn-tectonic pluton emplaced during the Variscan Orogeny. Along with its inherited zircon grains, it represents a perfect natural laboratory to investigate the pre-Variscan evolution of the Eastern Pontides. Ongoing work will collect Hf isotopic compositions and trace elements in zircon that will be combined with the available U-Pb dates. These data will allow us to reconstruct the evolution of a Gondwana crustal segment of the Eastern Pontides since the early Paleoproterozoic.

The Late Cretaceous Sakdrisi epithermal deposit, Bolnisi district (Lesser Caucasus, Georgia): Geology and ore deposit setting

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The Bolnisi district is a part of the Lesser Caucasus and is located at its northern extremity with respect to Armenia. To the west, this ore district continues into the Eastern Pontides, Turkey. This favorable geotectonic location of the Late Cretaceous Bolnisi ore district (which is also part of the Arvin–Bolnisi Belt) between the Lesser Caucasus and the Eastern Pontides is reflected by its geological diversity and mineral deposit distribution. The Late Cretaceous (~87–71 Ma) bimodal volcanism in this region resulted in mafic and felsic rock types, the latter being a major host of ore deposits and prospects, and being defined locally as the felsic Mashavera and Gasandami suites. A stratigraphic control was recognized on the distribution of Upper Cretaceous ore deposits and prospects in the Bolnisi district (Gugushvili, 2004). The presently producing late Turonian to early Santonian Madneuli deposit and the Tsiteli Sopeli, Kvemo Bolnisi, and David Gareji prospects from the eastern part of the district are hosted by the stratigraphically older volcanic and volcano-sedimentary rocks of the Mashavera suite. A second group of Campanian ore occurrences, including the currently producing Sakdrisi and Beqtakari deposits, also the Darbazi, Imedi, Beqtakari, Bnelikhevi and Samgreti prospects, in the western district, are hosted by volcanic and volcano-sedimentary rocks of a stratigraphically younger suite named the Gasandami suite.

Exploration in Sakdrisi is very active, where new ore zones were discovered with promising resources. The Sakdrisi deposit consists of a 2-km long cluster of five major ore zones, which are aligned along a NE-oriented fault zone. Two complexes have been recognized in this deposit, and belong to the Mashavera suite. They include a lower mineralized volcano-sedimentary complex (LVSC) and an upper barren volcano-sedimentary (UVSC) complex, which are separated by a NE oriented thrust (Golay *et al*., 2018). The lower mineralized complex is composed of the following lithological units: bedded sedimentary mudstone with tuff interlayers, pumice-bearing volcaniclastic rocks, slightly mineralized rhyolite and rhyolite tuff, and crosscutting explosive breccia, which is well expressed in the Sakdrisi 5 open pit. The upper non-mineralized complex consists of welded and non-welded ignimbrite, limestone lenses and crosscutting andesite-basaltic and rhyodacitic dykes. The mineralized zones are present in the LVSC at certain horizons, and consist mainly in quartz-sulfide and quartz veins, as it was discovered as a bonanza zone located just beneath the thrust zone at the Sakdrisi 4 open pit. Recent data from 400–600 m deep drill cores indicate enriched mineralized zones, which is a new discovery for this deposit.

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Magmatic and metallogenic evolution of the Late Cretaceous Beqtakari epithermal deposit, Bolnisi District, Lesser Caucasus, Georgia

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The Bolnisi District is one of the ore zones in the Lesser Caucasus, which was formed during Late Cretaceous magmatism, and is linked to the northeast-verging subduction of the Neothetys Ocean along the Eurasian margin. The Mashavera and Gasandami suites have been interpreted as the two main stratigraphic units that host different epithermal gold and base metal deposits within the Bolnisi District.

This study focuses on the Beqtakari Deposit (9.4 Mt at 2.93g/t Au, 33.23g/t Ag, 1.44% Zn, and 0.66% Pb) for a better understanding of the absolute age of magmatic and alteration events, the composition of the magmatic host rocks, and the three-dimensional distribution of the hydrothermal alteration zones.

The volcanic and volcaniclastic rocks in Beqtakari are characterized by mainly rhyolitic to rhyodacitic and subsidiary intermediate to mafic compositions, which have been attributed to the Gasandami suite. New uranium-lead dating indicates that the felsic host rocks were emplaced between 85.32 ± 0.19 Ma and 84.68 ± 0.18 Ma. Barren volcaniclastic rocks of the Upper Gasandami unit overlie the felsic host rocks of the Beqtakari Deposit, and have been dated at 84.44 ± 0.28 Ma. These new results enable us to estimate the duration of the mineralization event between 84.68 ± 0.18 Ma and 84.44 ± 0.28 Ma

The predominant alteration minerals include chlorite, epidote, sericite (K-illite-muscovite±phengite) and kaolinite group minerals (kaolinite-halloysite-nacrite). These alteration minerals are accompanied by carbonates (calcite-dolomite-ankerite). Barite and gypsum are also observed in the deposit area.

Polymetallic mineralization is hosted by silicified and brecciated rhyodacite (84.68 ± 0.18 Ma). It consists of quartz-barite±calcite veins with pyrite-sphalerite-galena-chalcopyrite and subsidiary late crosscutting tennantite-tetrahedrite minerals. Smithsonite is associated with the late-stage veins.

One first fluid inclusion assemblage in Beqtakari, Fia (I), is hosted by sphalerite and is interpreted as primary in origin. It yielded homogenization temperatures ranging between 268 °C and 229 °C (mean of 232 ± 18 °C) and salinities from 3.9 wt% to 3.1 wt% NaCl (mean of 3.6 ± 0.4 wt% NaCl). Another fluid inclusion assemblage also hosted by sphalerite, Fia $(I)_{\text{sub-type}}$, yielded slightly higher homogenization temperature ranging between 294 °C and 261 °C (mean of 271.8 ± 13.3 °C), and a similar range of salinities from 3.9 wt% to 3.4 wt% NaCl (mean of 3.6 ± 0.1 wt% NaCl).

The sulfur isotope compositions ($\delta^{34}S$ values) of sulfide minerals from Beqtakari exhibit a narrow range between –1.7‰ and +4.0‰ VCDT and suggest a deep/magmatic sulfur origin. The $\delta^{34}S$ values of gypsum and barite samples partly overlap with the sulfur isotope composition of Late Cretaceous seawater sulfate.

Petrogenesis of the alkaline igneous Tezhsar Complex and its Ti-rich garnets (Lesser Caucasus, Armenia)

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The convergence of the Arabian plate with Eurasia caused the formation of diverse magmatic rocks in the Lesser Caucasus, which is part of the Central Tethyan orogenic belt (Rezeau *et al*., 2017). In the South Armenian Block, a part of the Taurid-Anatolian microcontinent in the southwestern part of the Lesser Caucasus, K-rich magmatism caused by low-degree melting of subduction-modified, metasomatized subcontinental lithospheric mantle formed several plutons between 43.0 Ma and 28.1 Ma (Grosjean *et al*., 2022). One of these plutons, the Tezhsar Alkaline Complex, is a ring complex consisting of several concentric units of both volcanic and plutonic rocks, interpreted to represent the remnants of an elliptical palaeocaldera. The volcanic rocks are predominantly phonolites and tephrites, with some rare occurrences of pseudoleucite phonolite (Sokół *et al*., 2018). The plutonic rocks comprise syenites and nepheline syenites, in places occurring as coarse-grained pegmatitic varieties, that are occasionally garnet-bearing.

Igneous garnet in alkaline rocks is of specific interest due to its global scarcity, the compositional complexity and the controversial petrogenetic origin of garnet in these rocks. One contentious aspect is whether the garnets are a primary magmatic liquidus phase or whether they have a secondary, late-stage metasomatic origin due to reactions between earlier mafic minerals and late-stage fluids. Garnet chemistry can provide further insights into the intensive parameters required to stabilize garnet and possible effects of polybaric differentiation, magma-mixing and kinetic effects.

In the Tezhsar Alkaline Complex, garnet occurs in euhedral to subhedral clusters in pegmatitic nepheline syenite and more rarely as phenocrysts in syenites. The calcic garnets are brown in thin section and have a high Ti content (c. 2–4 wt.% TiO_2), which is typical for garnet in alkaline igneous rocks. In the syenite, garnet is often rich in mineral inclusions, whereas garnet in the pegmatitic nepheline syenite is devoid of inclusions and shows only limited and non-systematic mineral chemical variability. Textures and mineral chemistry will be explored systematically to evaluate the origin and petrogenetic significance of the garnets.

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The Taftan volcano-plutonic complex, southeast Iran: a fertile young continental arc in an active subduction setting in the Central Tethys

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The Makran magmatic arc is part of the Makran arc-trench system, and extends from southeast Iran to West Pakistan. The arc consists of the Taftan and Bazman volcanic complexes in Iran, the Chagai arc, and the young Koh-i-Sultan volcano in Pakistan, developed during the northward subduction of the Makran Sea oceanic lithosphere underneath Eurasia. Subduction started in the Late Cretaceous and continues today at a rate of ~2 cm per year (Burg, 2018).

The Taftan volcanic complex (TVC) consists of several volcanic centers. The youngest is known as the Taftan summit, 4050 m.a.s.l. The substrate rocks include the Eocene flysch-type sediments and a Late Cretaceous ophiolitic mélange complex. The TVC is dominated by medium- to high-K calc-alkaline andesitic to dacitic lava flows, pyroclastic rocks, and volcanic dome complexes. The limited geochronology data suggest that most volcanism in the TVC occurred in the late Miocene-Quaternary period (Richards *et al*., 2018).

Recent prospecting and exploration in the TVC have proven a major potential for high-sulfidation epithermal gold and porphyry systems (Richards *et al*., 2018; Alirezaei *et al*., 2022). The TVC provides an excellent opportunity to investigate the various processes and products in an active subduction setting.

Compared to other young continental arcs, the TVC rocks are relatively more silicic (average 64% SiO_2) and potassic (average 2.4% K_2O). The Sr/Y ratios range between 20 and 100 (average 45), implying an adakitic affinity for the rocks. These characteristics allow us to discuss the origin, evolution, and ore potential of the TVC. The fertility of the magmas in volcanic arc systems appears to be consistent with the maturity of the arcs, with metal endowment increasing with time (*e.g*., Sillitoe, 2005; Hosseini *et al*., 2017; Moritz *et al*., 2021).

Detailed geological mapping to document the TVC stratigraphy and sampling for various purposes, including whole-rock geochemistry, radiogenic isotope systematics, and geochronology, are in progress to investigate the source and evolution of the magmas and associated ore deposits with time.

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Special session SS10

Application and advances in geochronology and thermochronology

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Intermediate temperature (>150 °C) thermochronology using the U-Pb and $^{40}Ar/^{39}Ar$ methods

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Most geological processes alter the temperature of minerals, and hence a quantitative determination of that change can be used to study a wide range of phenomena. The recovery of time(t)-Temperature(T) paths from isotopic data exploits the thermally driven diffusive loss of isotopes that form by radioactive decay, leading to key assumptions that form the basis of thermochronological methods. Arguably the most important assumption is that thermally activated volume diffusion has been the dominant influence on the redistribution and loss of daughter isotopes from minerals. The second key assumption is that laboratory diffusion experiments at high temperatures replicate the physical mechanisms that occur with natural rates of cooling and heating over geological timescales. Two methods that have been used to generate continuous t(time)-T(temperature) paths at >150 °C are the U-Pb (titanite, apatite) and $^{40}Ar/^{39}Ar$ (muscovite, K-feldspar) techniques. Here we will discuss the validity of the key assumptions that are applied to these methods by highlighting specific case studies.

The U-Pb method has been used to reconstruct continuous thermal histories, and it has been shown that i) complex relationships between bulk grain date (ID-TIMS; Paul *et al*., 2018) and grain size, and ii) complex core-rim intra-grain dates (LA-ICPMS; Paul *et al*., 2019) can be accounted for by volume diffusion when intra-grain variations in U and Th concentrations are accounted for. Such experiments have yielded sensible t-T solutions between ~550–330 °C for Triassic leucosomes in Ecuador, using the Pb-in-apatite diffusion parameters of Cherniak *et al*. (1991), and thus evidence exists that t-T paths obtained from some apatites are accurate. However, relationships between Pb diffusivity, activation energy and apatite composition are unconstrained, and the high non-radiogenic Pb content of apatite hinders accuracy and precision.

The multi-diffusion domain model (MDD) was developed for the $^{40}Ar/^{39}Ar$ system to generate continuous t-T by experimenting on K-feldspars from the Chain of Ponds Pluton (USA), and the MDD model has been applied (using both K-feldspar and muscovite) by many authors to address various structural and tectonic questions (*e.g*., Metcalf *et al*., 2009). However, several recent studies have shown that thermally driven diffusive loss of Ar is not the dominant mechanism for Ar loss. Recent petrological studies of alkali feldspar extracted from the Chain of Ponds Pluton showed they experienced significant modification to adularia and sericite (Chafe *et al*., 2014), and thus that Ar redistribution was dominated by fluid interaction, rather than thermally driven diffusion. Similarly, an early study of gem-quality megacrystic K-feldspar from Itrongay, Madagascar, interpreted in-situ $^{40}Ar/^{39}Ar$ (core-rim) dates as a diffusion profile, which was in turn used to derived a continuous t-T path (Flude *et al*., 2014). However, a more recent and better spatially resolved in-situ $^{40}Ar/^{39}Ar$ study (Popov *et al*., 2020a) combined with cathodoluminescence of the megacrystic feldspars shows that they formed during at least 5 dissolution-precipitation events, and thus that the Ar isotope compositions are primarily a function of fluid interaction. Other studies of K-feldspar from the Klokken syenite that compared K/Ca and $^{40}Ar/^{39}Ar$ dates have also shown the importance of accounting for fluid-catalysed Ar loss prior to extracting t-T information (Harrison *et al*., 2010).

The validity of t-T paths obtained from difusion modelling of Ar is also challenged by an expanding database of experimental evidence that shows that laboratory step-heating can induce structural and textural changes, and thus extreme caution must be made when extrapolating laboratory derived rate loss constants to the geological past. For example, step-heating results in the development of interconnected cracks, which form due to spatially uneven thermal expansion because of regions with varied chemical composition and state of Si-Al order (*e.g*., Popov *et al*., 2020b).

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Detrital rutile geochemistry, U-Pb Ages and origin of the Jurassic sandstones in the Western Sakarya Zone

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Sandstones of the Jurassic Bayırköy Formation are exposed in the western Sakarya Zone. LA-ICP-MS rutile U-Pb and trace element analyses were performed in order to reveal the origin and source rock lithology of the detrital rutiles. Detrital rutile grains are dark brown-colored and rounded-subrounded showing the sedimentary origin. Detrital rutiles have the size of 100–240 µm. Some of them include quartz and ilmenite inclusions. Cr contents of detrital rutiles are ranging between 18 µg/g and 5996 µg/g. However, Nb concentrations have wide range and vary from 35 µg/g to 9687 µg/g. High Fe contents (>1000 µg/g) show that the detrital rutiles are of metamorphic-origin. Source area discrimination based on the Cr-Nb concentrations shows that 79% of the detrital rutile grains originated from metapelitic and 21% from metamafic rocks. The calculated rutile formation temperatures vary from 471 °C to 798 °C with an average temperature of 635 °C at P=10 kbar. Zr-in-rutile thermometer gives overlapping temperatures for all detrital rutile grains from both the metapelitic and metamafic sources. This demonstrates that most of the detrital rutiles sourced from metapelitic and metamafic rocks underwent similar metamorphic conditions and have similar metamorphic history. The U-Pb rutile dating yielded ages for the detrital rutiles in the time range of 346 Ma to 319 Ma, which gives the age of metamorphism for the potential source rocks. Trace element compositions, Zr-in-rutile thermometer and U-Pb rutile geochronology show that detrital rutile grains were predominantly derived from rocks that underwent early Carboniferous metamorphism in amphibolite-facies conditions. Amphibolite-facies rocks of the Sarıcakaya Massif in the central Sakarya Zone seem to be the primary source lithologies for the detrital rutiles in the Jurassic Bayırköy Formation as it comprises previously-mentioned source lithologies and has a close geographic position to the area studied. Carboniferous Variscan metamorphism was followed by emplacement of numerous post-collisional granitoids in the central Sakarya Zone.

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The in situ Rb-Sr dating of detrital muscovite from the Jurassic sandstones in the Central Sakarya Zone, NW Anatolia

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The Rb-Sr isotopic system of muscovite is generally interpreted to constrain the formation and/or cooling age. In this study, muscovite grains from the Jurassic sandstones were dated by Rb-Sr method. Fine- to medium-grained Jurassic sandstones that unconformably overly Paleozoic granitic basement are exposed in the Central Sakarya Zone. Higher in the stratigraphy, the Jurassic sandstones are unconformably overlain by the Bilecik Limestone. The sandstones are compositionally immature and are composed of quartz, K-feldspar, muscovite, biotite and rock fragments. The presence of muscovite in the detritus enables to apply in-situ LA-ICP-MS/MS Rb-Sr dating to constrain age information from the source. Single-spot Rb-Sr ages calculated of the detrital muscovite grains are between 290 Ma and 780 Ma. The isochron calculated from the same dataset is 297 ± 12 Ma. This age implies a Late Paleozoic thermal event in the source area(s). The immature composition of the sandstones implies a local source rather than long-distance sedimentary transport. The presence of muscovite, biotite and feldspar also indicates direct erosion of basement, rather than recycling of sedimentary cover sequences. Muscovite-bearing Silurian, Devonian and Carboniferous magmatic and metamorphic rocks are common in the western Sakarya Zone. Interestingly, the main group of Rb-Sr muscovite ages at ~300 Ma is younger than the Silurian and Devonian basement. This may indicate that the source area was pervasively thermally overprinted during the Variscan orogenic event. Finally, our study shows that in situ detrital muscovite Rb-Sr isotopic characteristics could be a potential indicator for the provenance of geological complex areas.

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Variscan metamorphism and deformation affecting the Sakar Unit of the Strandja Zone (SE Bulgaria/NE Turkey)

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The Sakar Unit of the Strandja Zone (SE Bulgaria/NW Turkey) consists mainly of variably deformed and metamorphosed Late Carboniferous to Triassic felsic to intermediate magmatic rocks intruding pre-Late Carboniferous basement. The protolith of the country rocks include Neoproterozoic-Cambrian and Ordovician magmatic rocks, and sedimentary rocks with maximum Cambrian depositional ages, interpreted to represent parts of peri-Gondwanan terrane(s). The country rocks are overlain by a Permian to Triassic meta-sedimentary sequence (Topolovgrad Group). These units were affected by upper greenschist- to amphibolite-facies Late Jurassic to Early Cretaceous (Early Alpine or Cimmerian) metamorphism, which in many places obliterated earlier Variscan metamorphism and deformation.

Here we present evidence of the Variscan event affecting the Sakar Unit, and provide constraints for its timing based on LA-ICP-MS U-Pb zircon dating of the orthogneisses, metagranitoids and granitoids. Country-rock orthogneisses yielded Ordovician crystallization ages of ~459 Ma (SAK-29, near Shishmanovo) and ~457 Ma (SAK-30, near Branitsa). Sample SAK-30 is cut by a ~308 Ma undeformed leucocratic dyke (SAK-31), which includes an older (~456 Ma) zircon population inherited from the country rock. A similar leucocratic dyke (SAK-09) intrudes country-rock amphibolites near the north-western part of the Sakar Batholith (close to Kanarata quarry) and was dated at ~304 Ma. These leucocratic dykes are interpreted as cogenetic with a minor leucocratic component of the Sakar Batholith occurring mostly as elongated bodies along its peripheries. The ~319 Ma Levka Pluton is the oldest intrusion postdating Variscan deformation in the Strandja Zone. Both the ~306 Ma Sakar Batholith and ~319 Ma Levka Pluton contain large xenoliths, which internally show features of older metamorphism and deformation. It is observed in the Kanarata quarry, where almost undeformed Sakar granitoids contain strongly deformed and metamorphosed amphibolite xenoliths, similar to the country rocks near the quarry. Amphibolite country rock (SAK-39) collected near Mladinovo contains a zircon population with ages scattered between ~600 Ma and ~2700 Ma, with the youngest cluster yielding an age of ~613 Ma. Migmatite (SAK-32) sampled in a low-strain window of the country rock (along the road from Studena to Radovets), contains a zircon population with a core-rim structure. Dating the zircon cores reveal a major population of Cadomian (540–600 Ma) ages, a second population up to ~830 Ma and a few Paleoproterozoic to Neoarchean ages (2000–2600 Ma). The outermost parts of the zircon were analyzed using depth profiling, and almost all the zircon rims revealed Variscan components. However, the Late Carboniferous ages show some scatter, and do not provide an exact timing for the Variscan metamorphism. Such scatter can be attributed to potential Pb loss during the Early Alpine thermal event, also detected as a minor component in the zircon rims. Our results show that Variscan metamorphism and deformation took place between 459-456 Ma and > ~319 Ma, the most probable in the Late Carboniferous.

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Early Cretaceous thermal event of the Sakar Unit (Strandja Zone, SE Bulgaria/NE Turkey)

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The Strandja Zone (SE Bulgaria/NW Turkey) is a northwest-southeast-trending mountain belt consisting of pre-Late Cretaceous autochthonous and allochthonous units affected by two metamorphic events. An older high-grade Late Carboniferous Variscan metamorphism and deformation is strongly obliterated by an upper greenschist- to amphibolite-facies Late Jurassic to Early Cretaceous event, called Early Alpine or Cimmerian orogenesis. The timing of the younger event is estimated between ~170–120 Ma. Additionally, the north-western part of the Strandja Zone (northern part of Sakar Unit) was locally affected by superimposed albitization.

Here we present U-Pb zircon, titanite and rutile dating by LA-ICP-MS coupled with petrographic and geochemical studies of various rocks (granitoids and amphibolite xenoliths) from the Kanarata deposit (near Hlaybovo, northern part of Sakar Batholith), and country-rock orthogneiss cut by quartz vein (near Levka). The samples from the Kanarata deposit represent granodiorite, leucodiorite, melanodiorite and amphibolite xenoliths which are albitized to various degrees. The less altered granodiorite shows a strong resemblance to typical equigranular Sakar granite. Leucodiorite represents albitized leucogranite occurring as elongated bodies mainly in the peripheries of the Sakar Batholith. The chemical composition of the melanodiorite indicates contamination of felsic magma by assimilation of country-rock amphibolites. Amphibolite xenoliths show the features of older deformation and metamorphism in their internal parts, whereas close to the contact with granitoids, xenoliths are albitized and surrounded by rutile-rich rims.

U-Pb zircon dating of granitoids revealed Late Carboniferous crystallization ages (~304–301 Ma) consistent with previous studies of Sakar Batholith. U-Pb titanite dating from the less altered granodiorite gave an age of ~297 Ma. Fluid migration caused the alteration of primary igneous titanite to rutile-rich aggregates during albitization. Petrographic observation and geochemical studies indicate that albitization was associated with removal of quartz. U-Pb rutile dating of these aggregates from altered granitoids (leucodiorite and melanodiorite) yielded ~125–116 Ma ages. In comparison, rutiles from country-rock orthogneiss are significantly older (~154 Ma). Our results confirm that amphibolite-facies metamorphism in the Strandja Zone occurred in the Late Jurassic (~154 Ma) and prove that at least the northwest part of the area was reheated to similar temperatures (~550–620 ^{o}C, Zr-in-rutile geothermometry) in the Early Cretaceous (~125–116 Ma). Therefore, the albitization is the youngest thermal event locally affecting Strandja Zone.

The long time interval of the Early Alpine metamorphism was obtained by previous authors using various isotopic systems and minerals with different closure temperatures. Our study suggest that previously published results do not need to represent slow cooling over 50 Myr, but various isotopic systems could be at least partially disturbed by Early Cretaceous thermal event.

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Thermochronological investigations of orogenic belts

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Thermal history analysis using radiometric dating methods, called thermochronology, showed a rapid growth since 1970s and has been applied to a variety of geoscientific problems in which temperature elevation is a critical parameter. It has been particularly successful with fission-track and noble gas dating methods, exhibiting a wide range of applications to orogenic belts, lifted continental margins, sedimentary basins, etc. The classical way of reconstructing orogenic uplift-exhumation-cooling is to plot apparent ages vs (1) closure temperatures of individual thermochronometries for each rock or (2) elevations of host rocks for a certain thermochronometry (*e.g*., Wagner *et al*., 1977). Subsequently, thermal history inversion techniques were developed and sophisticated (*e.g*., Green *et al*., 1989), revealing more detailed tectono-thermal features of geological terrains including orogenic belts.

Recent progress of low-temperature thermochronology, *e.g*., developments of (U-Th-Sm)/He method and fission-track inversion modeling, also enables to analyze uplift-exhumation-cooling histories of the island-arc mountains with good confidence. This is particularly fruitful for studying the topographic evolution of the Japan Arc, because many of the Japanese mountains are started to uplift in recent time (*e.g*., late Pliocene to Quaternary) after an extended period of tectonic quiescence, and hence the resultant amount of total denudation is relatively small. This was first demonstrated by elucidating the uplift-exhumation-cooling process for some of the Japan Alps, in which average topographic changes of the tilted mountain block were quantitatively reconstructed by low-temperature thermochronology (*e.g*., Sueoka *et al*., 2012). Such analyses also allow to estimate the background paleo-depth of neo-tectonic faulting episodes.

In this presentation, we give a brief overview of the low-temperature thermochronology and its application to orogenic belts, and then highlight some of the ongoing thermochronologic researches of the Japan Arc, such as:

(1) Compilation of previously reported thermochronologic data from the Japan Arc (Sueoka and Tagami, 2019);

(2) (U-Th-Sm)/He and fission-track analyses of the NE Japan Arc (*e.g*., Fukuda *et al*., 2020), which is a well-known example of the modern island arcs formed in plate subduction zones;

(3) (U-Th-Sm)/He, fission-track and U-Pb analyses of the Hida Mountain, which is a part of the Japan Alps that are formed by recent tectonic convergence between the NE and SW Japan Arcs and may have suffered widespread deformations with rapid exhumation, as deduced from the exposure of youngest granites on the Earth (Ito *et al*., 2013).

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Investigating exhumation of the High Tatra Mountains: Implications for the Western Carpathians, Slovakia by Zircon and Apatite (U-Th)/He thermochronometry

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The Carpathian Mountains form the large collisional orocline stretching from Vienna, Austria to Bucharest, Romania. The Western and Inner Carpathians include the High Tatra mountains, which exhibit the highest elevation peaks of the entire mountain belt. Here we studied the exhumation history of an area near Gerlachovský štít, the topographically highest point of the High Tatras. Granitoid samples from different elevations were collected and analyzed for apatite (U-Th)/He (n=12; 5-6 aliquots) and zircon (U-Th)/He ages (n=22; 2-4 aliquots). In addition, apatite U-Pb dating by LA-ICPMS was conducted to complement existing zircon U-Pb dates to track the evolution of the High Tatra Mountains from the onset of magmatism during the Variscan orogeny. The (U-Th)/He apatite ages show a general increase from 9.6 ± 0.6 Ma to 31.9 ± 2.0 Ma to from lower to higher elevations. The zircon (U-Th)/He ages are more scattered and range from 13.5 ± 1.1 Ma to 47.8 ± 3.9 Ma. These reported ages agree with published low-temperature thermochronometric results. However, the apparent average exhumation rates for zircon and apatite (U-Th)/He data derived from the age-to-elevation profile near Gerlachovský štít are inconsistent with a proposed rapid early Miocene exhumation pulse. Apatite U-Pb ages obtained in this study are between 337.61 ± 2.21 Ma and 372.74 ± 3.09 Ma. These ages agree with previously reported zircon dates from the same or nearby samples. This observation is indicative of rapid cooling of the granitoids following crystallization. However, the greatest variance in both data sets were observed from samples collected near the sub-Tatra fault and along the Ružbachy fault. This observation was used to confine regions about these major structures that have distinct exhumation records. The results of the (U-Th)/He ages captures both pre- and post-Miocene slow cooling interrupted by early Miocene tectonic unroofing. Overall, these results are used to outline the earliest tectonic history of the High Tatra Mountains until the onset of more recent exhumation and impacts our understanding of the origin and development of this section of the arcuate mountain belt.

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Detrital zircon geochronology and sedimentary provenance of the Lower Danube River

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A highly ranged spectrum of ages was identified by U-Pb geochronology on detrital zircons (DZ) from the Danube River and several sites located up to 300 m upstream, at the confluence with major tributaries, which deliver terrigenous material from the Southern and Eastern Carpathians. Most of the DZ exhibit three major populations ages, which are: *i*) Cambrian–Ordovician, associated to back-arc basins and island arcs, linked to the Peri-Gondwana subduction (600–440 Ma); *ii*) Lower to Middle Carboniferous, from magmatic and metamorphic Variscan units (350–320 Ma), represented by dominant peaks in most analyzed samples; *iii*) Upper Cretaceous to Tertiary, younger than 100 Ma, possibly related to the Southern Carpathian Late Cretaceous Banatitic arc and to the Neogene volcanism of the Eastern Carpathians and Apuseni Mountains.

For the Lower Danube western tributaries, such as Cerna, Topolnița and Jiu, our results show that the main source of the DZ are the metamorphic rocks characteristic for the Upper and Lower Danubian tectonic units of the Southern Carpathians (~300 Ma). These Danubian units are identified as components of Dacia mega-unit (Roban *et al*., 2020) and consist of high-grade metamorphic rocks (Medaris *et al*., 2003). Weak signals of Variscan events (340–325 Ma) were identified by Ducea *et al*. (2018) and Roban *et al*. (2020), while in the present study the investigated samples show stronger indication of a regional Variscan metamorphism. The analysis performed on both western samples (Cerna, Topolnița, Jiu and Olt rivers) and easternmost sample from the Danube sediments show a strong Variscan peaks that could be principally correlated with the former Ceahlău-Severin oceanic basin (Roban *et al*., 2020).

Some larger tributaries in the eastern (downstream) Lower Danube, such as Olt, Argeș, Ialomița and Siret rivers show temporal disperse peaks on the DZ geochronology, feature probably reflecting successive processes of recycling. Notably, the most representative sources of DZ identified in the samples from easternmost Lower Danube tributaries (Siret and Prut rivers) are the Variscan metamorphites.

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Plio-Pleistocene volcanic activity in the Mariovo basin, N. Macedonia

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Intense volcanic activity between ~ 8 Ma and 1.5 Ma characterized the Vardar Zone south of Scutari-Peć transverse zone that is strongly connected to the tectonic evolution of the Aegean extensional province (Yanev *et al*., 2008, Molnár *et al*., 2022). Contemporaneously, small-volume volcanic centers developed along deep structures and the large SW-NE trending Kožuf-Voras volcanic system was formed comprising lava domes and various pyroclastics. The volcanic evolution of Kožuf-Voras is characterized by increasing K-content with decrease in eruption age towards the southwest. It is bounded by the Mariovo, Tikveš and Almopia basins towards the northwest, northeast and south, respectively, with thick basin-filling pyroclastic deposits present on all sites. While on the southern site three large explosive eruptions were identified at ~4.9 Ma, 4.2 Ma and 2.6 Ma (Vougioukalakis, 2002), the eruptive products in the Mariovo basin were studied only to a lesser extent.

The pyroclastics of Mariovo basin outcrop at two main localities, at Gradešnica and at around Polčište and Vitolište villages. In both cases the deposits start with an agglomerate layer consisting of clasts both from the basement (mainly gneiss) and volcanics. It is followed by tuff-lapilli layers with variable pumice content. Alluvial deposits and/or travertine layers occur intercalated with the pyroclastics. Blocks and boulders of lava rocks top the successions. Besides these layers, a massive lapilli tuff deposit can be identified along the road cut towards Šumovit Greben. This is the westernmost lava dome of Kožuf-Voras volcanic system, which was formed at ~2.9–2.8 Ma.

Petrography, whole rock geochemistry and combined sanidine Ar-Ar, zircon (U-Th)/He and groundmass K-Ar methods were applied to unravel the eruptive history in the Mariovo basin and to correlate these pyroclastics with the already identified centers. The lowermost layer shows similarities to a small cluster of lava domes along the Macedonian-Greek border, whereas the topmost layer at Gradešnica resembles in composition the youngest lava rocks on the southern site. Based on the preliminary zircon (U-Th)/He ages, the explosive eruptions occurred between ~3.8 Ma and 2.2 Ma, which represent additional events to the previously identified explosive activities.

The massive lapilli tuff layer overlaps both in age and composition with the rhyolitic Šumovit Greben lava dome, confirming that it had explosive activity besides its dome forming phases.

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Thermochronological constraints on fault activities. Examples from Kraishte area (West Bulgaria)

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Low-temperature thermochronological analysis has been applied to answer a wide range of geologic problems. Apart from the reconstruction of large-scale regional cooling histories, these methods may provide time constraints on a smaller scale defining the amount and timing of fault movement in the uppermost few kilometres of the crust (*e.g.*, Malusà and Fitzgerald, 2019). Thermochronologic age distributions across major faults may reveal not only the sense of movement along the tectonic structure but also constrain the timing of the deformation based on modelling the exhumation paths experienced by the different fault blocks through time. Low-temperature thermochronology may also define the amount of stratigraphic burial and/or the tectonic load exerted by now-eroded thrust sheets. Reconstructed configuration of eroded rocks will be based on the distribution of unreset, partly annealed and fully reset samples in a present day landscape.

Here we present some examples determining the time and sense of movement along fault structures constrained by fission-track analysis from the Kraishte area of Western Bulgaria. The zone is part of the Alpine orogenic system at the junction of the Balkanides and Hellenides-Dinarides tectonic belts in south-eastern Europe. The tectonic history of this area includes Early Cretaceous north-eastward thrusting of the Morava unit (pre-Silurian continental basement rocks and Lower Palaeozoic metasediments) onto the Struma unit (pre-Permian basement rocks and Mesozoic sediments), both part of the generally north vergent Balkanide thrust system. During the Cenozoic the Kraishte zone was dominated by extension related to the exhumation of the Crnook-Osogovo-Lisets complex along a system of detachment faults.

Our fission-track analysis show that faults, previously described as thrusts (Zagorchev, 2001), are Cenozoic normal faults. Consistent Eocene-Oligocene zircon and apatite fission-track ages between 47 Ma and 27 Ma together with thermal modelling of rocks from the footwall of major detachment faults reveal cooling of these rocks during the Cenozoic. The much older zircon fission-track ages, between 298 Ma and 69 Ma, from the hanging wall, point to normal fault movement along the detachments. Apatite fission-track ages between 31 Ma and 29 Ma, observed on both sides of the detachment faults, suggest that at that time these structures were inactive.

Additionally, fission-track data from different structural domains of the Morava thrust sheet and its footwall sequences constrain the Cretaceous tectonothermal evolution of this structure. In this case, low-temperature thermochronological analyses reveal the time interval of the main thrusting event as well as the original thickness and extent of the thrust sheet. Varying ages along the footwall and hanging wall of the thrust define different structural levels associated with the thermal evolution during this major tectonic event in the area.

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Thermochronological evolution of the Plovdiv pluton, Bulgaria

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The Plovdiv pluton is intruding the Maritsa strike-slip fault zone, situated in the southern part of the Sredna Gora Zone, in the area of the town of Plovdiv. Here, we present the first thermochronological results from this pluton in order to reveal the thermal and tectonic evolution since its emplacement in the Late Cretaceous. A monzonite rock sample was collected from the Sahat Tepe Hill in Plovdiv (N 42.1452, E 24.7473) for $^{40}Ar/^{39}Ar$ multiple single grain fusion dating, and apatite and zircon fission-track (FT) analyses.

$^{40}Ar/^{39}Ar$ data obtained from twelve amphibole grains are ranging between 83.3 Ma and 78.5 Ma. The total fusion experiments of 8 grains give a weighted mean age of 80.43 ± 0.43 Ma (MSWD 4.08, inverse isochron age 87.22 ± 1.26) with an initial $^{40}Ar/^{36}Ar$ estimate of 299.69 ± 111.42. Eighteen zircon and 28 apatite grains were used for the FT age calculation. The sample yields zircon FT age of 55.6 ± 2.8 Ma and apatite FT age of 36.1 ± 3.1 Ma, where both passed the Chi-square (χ^2) test. The apatite mean track length is 13.45 μm with standard deviation of 1.76. The average Dpar value is 1.61 μm (with standard deviation of 0.17 μm).

The obtained thermal model using HeFTy software reveals very fast cooling to ~90 °C at ~44–42 Ma followed by moderate cooling to ~60 °C between 42 Ma and 22 Ma.

The obtained $^{40}Ar/^{39}Ar$ amphibole weighted mean age of 80.43 ± 0.43 Ma is identical with the earlier obtained zircon U-Pb age from the Plovdiv pluton (80.02 ± 0.33 Ma, Georgiev and Balkanska, 2018) and is related to cooling of the magmatic body to temperatures below ~490 °C immediately after its emplacement. This cooling could be associated with some activities along the Maritsa fault zone and its segments. As suggested by the zircon FT age the Plovdiv pluton cooled bellow 250 °C in the early Eocene (55.6 ± 2.8 Ma). This cooling could be related to thermal relaxation following the early Eocene magmatic pulse in the Rhodope Zone. Another possibility is to be associated with post-orogenic cooling following the middle to late Paleocene Late Alpine compressional event in the central parts of the Sredna Gora Zone. The Eocene cooling and exhumation of the Plovdiv pluton between 44 Ma and 42 Ma, suggested by the apatite thermal modelling, could be related to the period of denudation and extension, associated with the formation of the Thrace basin. Such scenario is in accordance with the thermochronological data from the neighbouring areas (*e.g.*, Kounov *et al*., 2020).

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Chemical abrasion in application to high U metamict zircons

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Chemical abrasion is a perfect approach for getting precise and accurate U-Pb data for zircons, affected by post-crystallization Pb-loss. However, it is believed that this approach is not applicable for zircons with heavy self-irradiation damages (with self-irradiation α-dose of $D\alpha > 2 \times 10^{18}$ α-decay/g) (Mattinson, 2005; Huyskens *et al*., 2016; Widmann *et al*., 2019). Here we present an example of dating several alkaline granitoid massifs via U-Pb (ID-TIMS) technique, using high-uranium metamictized zircons, with a high degree of radiation. These alkaline granitoids are from the area of Eastern Transbaikalia and Eastern Sayan (Siberia) and are related to REE-Nb-Ta-Zr-Th-U deposit. The pretreatment conditions for those zircons with high dose of autoradiation was as follows: i) high-temperature annealing (850 °C) and ii) HF acid leaching (mainly soft treatment at 180 °C for 4 h and less often regular treatment at 220 °C for 2 h) and iii) fluxing of the residue overnight at 220 °C in the oven in 11 N HCl. This way of pretreatment ensures, almost complete removal of the metamict phase and preservation of sufficient amount of material – dust-like zircon (sometimes, size of fragments <20 µm) for U-Pb (ID-TIMS) dating. Using this approach, we have been able to obtain mostly concordant ages from the Aryskan (H)REE-Nb-Ta-Zr-Th-U deposit, Snezhnoye phenakite-beryl deposit, pegmatites of the Mamskoye deposit and Suprunovskoye deposit exhibiting unique beryllium mineralization.

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Special session SS11

Geochemistry and hazardous substances (HS) evaluation in river basins

Conveners:

Zlatka Milakovska, Georgi Zhelezov

Radiological risk assessment and spatial distribution of naturally occurring radionuclides within riverbed sediments in the Ditrău alkaline Massif, Eastern Carpathians (Romania)

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The main objective of this study is to determine the spatial distribution of naturally occurring ^{238}U, ^{232}Th and ^{40}K radionuclides within riverbed sediments of the Jolotca and Ditrău rivers from the Ditrău Alkaline Massif (DAM) and to assess their associated radiological risk.

The DAM comprises a sequence of ultramafic rocks, alkali gabbros, diorites, syenites, nepheline syenites and alkali granites, which are cut by secondary mafic dykes. The massif is enriched in rare earth elements (REEs), Nb and Mo, monazite being the main REE-bearing phase (Honour *et al*., 2018). Borcoş *et al.* (1984) mentioned three mineralizations in the DAM: Jolotca-Ditrău (pneumatolytic-hydrothermal Mo-Pb-Zn $\pm$ Au, Ag deposit), Aurora-Ditrău (hydrothermal Mo deposit) and Ditrău (alluvial Ti, Zr deposit, zircon, ilmenite, titanite, magnetite and monazite being the main minerals found). According to Constantinescu and Anastasiu (2004), the mineralization from Jolotca-Ditrău consists of oxides, sulphides, carbonates, phosphates and subordinate silicates and native elements, *i.e.*, uraninite, Mn-rich ilmenite, pseudobrookite, anatase, brookite, bismuthinite, isocubanite, joséite, mackinawite, valleriite, tetradymite, monazite-(Ce), monazite-(Nd), apatite, thorite, allanite-(Y), titanite, native silver, copper.

A total number of 45 samples (23 from the Jolotca River and 22 from the Ditrău River) were collected from the riverbed sediments. The analyses were done by using gamma-ray spectrometry (HP Ge – detector ORTEC). The results show average values of 38.16 Bq/kg for ^{238}U, 46.38 Bq/kg for ^{232}Th and 1239.23 Bq/kg for ^{40}K. When comparing the above values with those of the Upper Continental Crust, we observe an enrichment trend, for some samples even 1.7 times above the UCC for ^{232}Th or two times higher for ^{238}U and ^{40}K. This is due to the presence in the studied area of minerals such as monazite, thorite or uraninite that show high Th and U values, respectively. Also, by comparison of the average absorbed gamma dose rate from our study 98.85 nGy/h with the world average (UNSCEAR, 200) 84 nGy/h, we notice a visible upward trend. The average values of the calculated parameters for the radiological effects, such as the internal and external hazard indexes, are as follows: H_{in} = 0.65 and H_{ex} = 0.54, which is lower than 1 mSv/y (acceptable limit as of ICRP-65, 1993).

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Spatial geochemical distribution of some potentially toxic elements within riverbed sediments from the Rodna Mountains, Eastern Carpathians, Romania

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The main objective of this study is to determine the spatial distribution of some potentially toxic elements (As, Cd, Co, Cr, Cu, Ni, Pb, Sn and Zn) within riverbed sediments of the Izvorul Roşu and Izvorul Băilor rivers with their tributaries (Rodna mining area) from the Rodna Mountains (RM) and to assess the contamination degree of sediments using some widely used pollution indices.

The RM, included in the Rodna National Park and Biosphere Reserve and located in northern Romania, comprises a structurally higher Rebra Unit correlated with the Subbucovinian Nappe in the East Carpathians, and a lower Bretila Unit assigned to the Infrabucovinian Nappe. Both units are made of Late Cambrian–Ordovician medium-grade rock assemblages and had a complex metamorphic evolution during three discrete events: two amphibolite-facies overprints of similar grade, followed by greenschist-facies retrogression (Reiser *et al*., 2013; Balintoni *et al*., 2014). Borcoş *et al*. (1983) mentioned the Izvorul Roşu and Valea Vinului mineralizations in the studied area, hosted by the Rebra Unit (Voşlobeni carbonate formation) as Pb, Zn + Au, Ag deposits, pyrite (FeS_2), pyrrhotite (Fe_7S_8), arsenopyrite (FeAsS), sphalerite (ZnS), galena (PbS), magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$), chalcopyrite ($CuFeS_2$), bournonite ($CuPbSbS_3$), semseyite ($Pb_9Sb_8S_{21}$), mackinawite ($(Fe,Ni)_9S_8$), cubanite ($CuFe_2S_3$) being the most common minerals. A total number of 20 samples were collected from the river sediments and further analyzed by Four-Acid Digestion procedures and ICP-MS at ALS Geochemistry Roșia Montană. The average value (Av) and the geochemical background value (Bv) for every element are as follows (mg/kg): Av 56.21 and Bv 28.02 for As, Av 1.66 and Bv 0.86 for Cd, Av 27.50 and Bv 24.81 for Co, Av 86.67 and Bv 83.27 for Cr, Av 38.62 and Bv 36.64 for Cu, Av 45.46 and Bv 44.32 for Ni, Av 205.25 and Bv 65.15 for Pb, Av 2.65 and Bv 2.57 for Sn, Av 449.70 and Bv 231 for Zn. The geochemical background was calculated using the Median±2 MAD procedure (Reimann *et al*., 2005). From the evaluation of the sediment's pollution indices, EF, CF, Igeo, PLI and RI, it can be seen that the studied river sediments, in most cases, are either not contaminated or slightly contaminated. However, there are a few samples with moderate contamination by As, Cd, Pb and Zn due to former mining activities.

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Main steps of a protocol for mapping metal contamination of soil in river floodplains using geographical data

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The concentration of heavy metals in the soil of contaminated river floodplains usually shows significant variations at small distances. It greatly hinders the elaboration of reliable and detailed maps using classical methods. Geographical data on topography, hydrological dynamics, land use, and irrigation practices can be applied to predict the heavy metal dispersal within mine waste contaminated floodplains. We combined these data with the geomorphological-geochemical approach developed by Macklin *et al*. (2006) to investigate the metal pollution in the Ogosta River valley, NW Bulgaria, caused by historical mining. Based on our 10-year long investigation, we suggest below the main steps for mapping soil contamination in mining-affected river floodplains.

Step 1. Collecting information on mining history, pollution sources, major floods during the mining period, floodplain geomorphology, soil cover, land use, irrigation practices and previous studies on the contamination in the valley.

Step 2. Selection of representative sections along the valley to reveal the patterns of contaminant-metal dispersal in soil. Identifying a site in a clean neighboring valley of similar size and geology to determine the geochemical background.

Step 3. Acquisition of detailed topography and land cover data by aerial laser scanning and photography.

Step 4. Elaboration of geo-products as precise digital terrain models, flood models, detailed maps of land use and irrigated areas for the selected valley sections.

Step 5. Spatial analysis of geodata using GIS to calculate morphometric variables as vertical distance to river channel network and lateral distance to the river, and to delineate the boundaries of the major morphographic units within the valley floor by classification of the vertical distance values.

Step 6. Extensive soil sampling considering the morphographic units.

Step 7. Measurement of heavy metals and particle size distribution in the collected soil samples.

Step 8. Statistical analyses to determine the local reference values for selected heavy metals in floodplain soil and explore the relationship between geographical predictors and metal concentrations.

Step 9. Elaboration of maps of soil pollution, considering the major morphological units of the valley floor.

Using the described protocol, we assessed the aggregated excess over the local geochemical background in the Lom River valley for As, Cu, Pb, Zn, Fe, Mn and Sn using the PLI index. More than 30% of the land in the Upper Ogosta valley between the town of Chiprovtsi and the Ogosta dam was likely to be contaminated more than twice above the reference level. The soil in the lower stretch of the Ogosta River was less polluted with PLI>2 for 8% of the valley floor in the vicinity of the village of Mihaylovo. The elaborated maps can be used by decision-makers and farm managers to ensure low levels of heavy metals in agricultural production and diminish the health risks for the local population.

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Danube River – on the path of the scientific knowledge

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The Danube is a home to many plant (1000 species) and animal (over 4000) species. The river is also associated with the development of fishing, not only as a hobby but also as a way to feed many people. The Danube also provides opportunities for tourism development. The Danube Park in Silistra is the oldest in Bulgaria, and the sunsets over the river are extremely beautiful. Walking in the park and the coolness of the river are a favorite for all Silistra residents and guests of the city. It is important for me to keep sustainable the river ecosystem. In my previous research, I studied biodiversity in two protected areas in the Silistra region – Srebarna Lake and Malak Preslavets Swamp, which are of great importance for biodiversity conservation. That is why I decided to engage in a monitoring study on the water and sediments of the Danube River.

I was invited from the Bulgarian team of Project SIMONA (System for Information, Monitoring and Evaluation of Sediment Quality) to participate in a Workshop with Training in Silistra, Bulgaria. On June, 29, 2021 – the Danube Day, the SIMONA Transnationally Harmonized Sediment Sampling Protocol was discussed and demonstrated.

The monitoring included the three test areas (Drava and Tisza Rivers and the Southern Danube) with over 50 sampling sites. Several types of river sediments were sampled and studied – bottom, flood and suspended for hazardous substances and evaluated if they are harmful to the organisms living on or at the bottom of the water basins. The Danube can be called the bloodstream of Europe and the Danube sediments are the ones that sustain rivers' life. Their quality can affect the ecological balance. Contamination of the sediments with hazardous substances is a problem on the Danube River. Most countries cannot deal with the problem on their own due to lack of experience, technological capacity, harmonized international protocols and others. Therefore, it is necessary to develop a common system for quality control of sediments by stakeholders and this is the SIMONA project.

Using everything I learned from the presentations and training, I decided to do my own study of water and sediment quality in the Silistra sector of the Danube. For this purpose, I asked various institutes of BAS for assistance – the Institute of Inorganic Chemistry, the Geological Institute, the Institute of Organic Chemistry with Centre of Phytochemistry, and also the scientific consultant of SIMONA project, Dr. Gyozo Jordan – for more information. So, I decided to follow the path of scientific knowledge on environmental issues related to the Danube River and call for its protection.

It was a challenge for me to get involved in the SIMONA trainings. In this way, I want to prove that I do care in what environment I live in and I want to make more young people follow my experience.

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Variation of the geochemistry of alluvial sands along the river basins. Case study: Mureș River, Romania

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Sand and gravel represent the most widely used building materials in the world. For example, the natural aggregates (including here the crushed stone and the river aggregates) currently represent up to 80% of the mass of concrete or hydraulically bound/unbound materials for use in the civil engineering work and road construction. Thus, the properties of this component considerably influence the behaviour of the final product, in terms of strengths and durability. Consequently, the knowledge on the variation of the physical, chemical and mechanical characteristics of the aggregates is a defining step in the selection of a perimeter as a specific source of raw material.

The present research focused on alluvial aggregates, knowing that a large number of researches and laboratory tests have documented a significant variation of the sand and gravel characteristics along a river basin. According to the European standards, the river aggregates which, for intended use, are subjected to nothing more than mechanical processing, are tested to determine their general characteristics, the geometric properties of clasts, respectively the physical, chemical and mechanical behavior.

The petrography of coarse clasts has the main influence on the quality of aggregates, followed by the mineralogy of the fine aggregates and the percentage of the fine fraction (described in the sand fraction through the presence of humus, discrete unbound grains of mica and other foreign bodies). Other properties, important for establishing the performance of the final product, are particle size distribution, shape and flakiness index, density, porosity, permeability, water absorption, thermal and weathering characteristics and mechanical resistances to wear and fragmentation. For the sand fraction, the oxide compounds, the content of soluble salts and the sulfur containing compounds could be specific indicators for different segments of a river and partially influenced by the local geological frame, temperature, humidity and precipitation of each season.

Mureș is the second river in Romania, having 761 km in length and a 27,890 km² of hydrographic area, and crossing the central-western parts of the country. In the official inventory of the National Agency for Mineral Resources, 75 sand and gravel perimeters are inventoried along the Mureș River, from which 38 were included in the present research. For these perimeters, values of the chemical characteristics of the fine fraction were available, as: oxide compounds (where applicable) and impurity content. In addition, an analysis of the shape index and angularity of the clasts from upstream to downstream was performed, as an important indicator of the capacity and competence of hydrodynamic transport along the river bed.

The results obtained were correlated with the impact of normal seasonal climatic variations and those with catastrophic potential, so that they can be used by the responsible authorities in local and regional planning and for intervention programs. The main beneficiaries are the companies acting in exploitation and capitalization of river aggregates on the construction materials market. These companies thus have access to additional indicators on the efficiency in the selection of perimeters with sand and gravel, which are sustainable raw materials, partially renewable and with low impact on the environment.

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Hydrochemical peculiarities of Ogosta River catchment, Northwestern Bulgaria

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Waters are one of the key components for the determination, differentiation, and classification of the landscape diversity. The research interprets the problems related with hydrochemical peculiarities in Ogosta River catchments, NW Bulgaria. It is one of the main river basins in Northern Bulgaria (3157,1 km^2). The Ogosta River springs from the high parts of the Stara Planina Mts, passes through the Fore-Balkan Mts and the Danube Plain. A number of natural and anthropogenic factors, affecting the formation of the chemical composition of its waters, have been identified in the river's watershed. The aim of the present research is to clarify and differentiate the influence of these factors. For this purpose, twelve points were selected, where water samples were taken twice (in the years 2020 and 2021) and analyzed. Eight of them are positioned along of the Ogosta River, from its upper course to the mouth, and four, on the more important tributaries.

The results allow for a spatial analysis of the hydrochemical parameters, their change over time and determination. This is essential for clarifying the role of natural and anthropogenic factors for the water quality. First of all, the pH and conductivity data were processed, which are formed by complex factors. The waters are neutral, both in 2020 (pH = 6.75–7.95) and in 2021 (pH = 6.95–8.45). The maximal pH values were established at the confluence of the Ogosta River with the Danube River, and the tributaries, mainly Skat and Ribine rivers, are essential for this. The conductivity increases along the river, as the lowest values (83–195 µS/cm) measured in the mountainous parts of the catchment, gradually increase towards the mouth where reach values of almost 1000 µS/cm. The increase is due to both the contact of the water with the environment, and the inflow of waters with higher mineralization from the Skat and Ribine tributaries, formed in watersheds located at a lower altitude.

An analysis was made of the changes of the hydrochemical parameters, such as nitrates, nitrites, ammonium, whose presence is most often associated with human activity, Cu and Zn (associated with the abandoned mining activities), Ca (often associated with natural input from the rocks through which the river waters pass, and mainly several karst areas crossed by the river), and sulfates, the presence of which is a consequence of various factors. A different nature of the change in the parameters values along the course of the river and over time was established. The analysis gave reasons to differentiate the meaning of the specific natural features from the human impact. The most significant importance for the formation of the chemical composition of Ogosta waters among the natural factors has the contact of the river waters with the rocks and river sediments, as well as the tributaries waters with a different chemical composition. Another factor of this group is the differing chemical composition of each of the tributaries and the different mixing ratios with the main river. A determining artificial factor that is necessary to note on the first place is Ogosta Dam. On one hand, the accumulation and retention of large volumes of water in the dam evokes to processes leading to the precipitation and dissolution of various mineral phases. On the other hand, the irregular release of water over time from the dam leads to sharp changes in the water quantities of the Ogosta River, respectively different movement speeds and mixing ratios with its tributaries. The trails of the old mining activities still play a role, having the strongest impact in the upper reaches of the Ogosta River. There are no data for significant impacts on settlements and agricultural activities. The final results and conclusion of the research can be used during the regional planning. They should also be applied in the activities for optimization of the environment and quality of the life in investigated region.

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XXII International Congress
Carpathian-Balkan Geological Association
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The 22nd Congress of the Carpathian-Balkan Geological Association (CBGA) will be held from 7 to 11 September 2022 in Plovdiv, Bulgaria. It will celebrate the 100th anniversary of the Association. CBGA2022 aims to bring together geoscientists from Southeastern Europe with geoscientists from all over the world, for a meeting covering all disciplines of Earth sciences. The congress is a forum where scientists can present and discuss their latest results not only from the Carpathian-Balkan region, but also beyond it.

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