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PROGRAMM AND ABSTRACT VOLUME

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12th Stable Isotope Network Austria Meeting

Graz, 15th-16th November 2013

Hosted by:

- Technical University Graz, Institute of Applied Geosciences
- Karl-Franzens University, Institute of Earth Sciences, Geology and Paleontology
- Joanneum Research, Graz, RESOURCES - Institute of Water, Energy and Sustainability

PROGRAMM

FRIDAY 15th NOVEMBER 2013

14:00–14:15 Welcome & Introduction

SESSION 1 (Chair: Martin Kralik and Albrecht Leis)

14:15 – 14:50 *Key Note Address*

Martin Elsner (Helmholtz Zentrum München; Forschungszentrum für Gesundheit und Umwelt):

Investigating degradation of groundwater contaminants with compound-specific isotope analysis

14:50 – 15:10 **Wolfgang Wanek** and Judith Prommer (Division of Terrestrial Ecosystem Research, University of Vienna): Isotopic composition of soluble organic N: an important player in soil N cycling

15:10 – 15:30 **Claudia Wrozyzna et al.** (Institute of Earth Sciences, Graz University): Stable isotopes in lacustrine ostracods – Calibration of a Neotropical proxy

15:30 – 15:50 **Albrecht Leis et al.** (RESOURCES - Institute of Water, Energy and Sustainability, Joanneum Research): Tracing anthropogenic inputs to a lagoon ecosystem by using a combined approach of hydrochemical and stable isotope investigations

15:50 – 16:20 Coffee and Tea Break

16:20 – 16:40 **Martin Kralik** (Environment Agency Austria): Water-Isotope Map Austria 2015: Isotope **distribution** in precipitation, surface water and groundwater.

16:40 – 17:00 **Till Harum et al.** (RESOURCES - Institute of Water, Energy and Sustainability, Joanneum Research): Interaction of lakes with local groundwater systems – environmental isotopes as tool for water balance investigations

17:00 – 18:00 **Posters of sessions 1** (includes a 3 min presentation for each poster)

18:00 – 18:40 **Lab Tours**

Laser ICPMS-MC facility, NAWI central laboratory for water, rock and minerals.

from 19:30 **Social dinner**

Gasthaus Karl-Franz – Zinzendorfgasse 30, 8010 Graz

SATURDAY 16th NOVEMBER 2013**SESSION 2** (Chair: Wolfgang Wanek and Martin Dietzel)

- 09:30 – 10:05 *Key Note Address* : **Anton Eisenhauer** (Geomar, Kiel):
Non-Traditional Isotope Systems: New scientific frontiers for the Earth and Live Sciences.
- 10:05 – 10:25 **Chloé Pretet et al.**, (Department of Environmental Geosciences, University of Vienna): Barium isotope fractionation in carbonates: ongoing research and future development
- 10:25 – 10:45 **Vassilis Mavromatis et al.**, (Institute of Applied Geosciences, Graz University of Technology): Tracing cyanobacteria-mediated hydrous magnesium carbonate precipitation using Mg isotopes: Experimental observations and fields studies
- 10:45 – 11:15 Coffee and Tea Break
- 11:15 – 11:35 **Dorothee Hippler et al.**, (Institute of Applied Geosciences, Graz University of Technology): Ca-isotope fractionation in modern and fossil bivalve shell carbonate
- 11:35 – 12:30 **Posters of sessions 2 and 3** (includes a 3 min presentation to each poster)
- 12:30 – 13:30 Lunch Buffet in front of the Lecture Hall

SESSION 3 (Chair: Ronny Boch and Sylvain Richoz)

- 13:30 – 14:00 *Key Note Address*: **Christoph Spötl** (Innsbruck University)
Stable isotopes and climate change: a geologist's view
- 14:00 – 14:20 **Filip Volders et al.**, (Elementar): Advancement in IRMS
- 14:20 – 14:40 H. Jost, **Andreas Hilkert et al.**, (Thermo Fisher Scientific): Performance of an Isotope Ratio Infrared Spectrometer for Simultaneous measurements of carbon and oxygen isotopologues OF CO₂
- 14:40 – 15:00 **Attila Demény et al.**, (Institute for Geological and Geochemical Research, Hungarian Academy of Sciences): Hydrogen and oxygen isotope analyses of inclusion-hosted waters in fluorites using laser spectroscopy: domination of crustal fluids in the formation of the Speewah fluorite deposit of NW Australia
- 15:00 – 15:20 **Lukasz Pytlak et al.**, (Chair Petroleum Geology, Montan University Leoben): Generation and Alteration of Gas in the Austrian Molasse Basin
- 15:00 – 15:40 **Florian Mittermayr et al.**, (Institute of Applied Geosciences, Graz University of Technology): Mechanisms of concrete attack revealed by stable isotopes
- 15:40 – 16:10 Coffee and Tea Break
- 16:10 **Generalversammlung SINA** --- Verein für Stabile Isotopen Forschung
(General assembly of the Stable Isotope Network Austria --- SINA)

Poster

Session 1

- Benjamin Bichler et al.** (Institute of Geology, University of Innsbruck): Insights and limitations of stable isotopes in groundwater research: a case study from the eastern side of the Untersberg, Salzburg.
- Melanie Hager et al.** (Austrian Institute of Technology, Tulln): Determination of the 12c/13c and H/D isotopic fractionation during biodegradation of decane in microcosms.
- Giorgio Höfer-Öllinger** (Geoconsult ZT GmbH) and B. Millen: Stable Isotope relationships of groundwater and runoff at high altitudes – A case study from the Andean Cordillera, Chile/Argentina.
- Martin Kralik** (Environment Agency Austria) and Stephan Wyhlidal: Water-Isotopes to trace the source and timing of recharge in a fractured granite aquifer in Western Kenya, Africa.
- Katharina Schott et al.** (Austrian Institute of Technology, Tulln): Analysis of isotopic signals in Danube River water at Tulln (Austria) based on daily grab samples 2012.
- Walter Schön et al.** (Institute of Applied Geosciences, Graz University of Technology): Chemical and isotopic composition of soil solutions from cambisols in Styria (Austria) – seasonal variations and experiments.
- Elisabeth Schwaiger et al.** (Austrian Institute of Technology, Tulln): Analysis of drought stress on winter wheat using Stable Isotope Ratio Spectrometry ($\delta^{13}\text{C}$).
- Andrea Watzinger et al.** (Austrian Institute of Technology, Tulln): Isomon - Isotope application for remediation, aftercare and monitoring of contaminated sites.

Session 2 and 3

- Daniel Birgel et al.** (Department for Geodynamics and Sedimentology, University of Vienna): Archaeal biomarkers and their compound-specific carbon isotopes record the onset of the Messinian Salinity Crisis.
- Ronny Boch et al.** (Institute of Applied Geosciences, Graz University of Technology): Nalps: Last Glacial climate changes recorded in the northern Alps.
- Magda Mandić et al.**, (University of Rijeka, Croatia): Moonmilk in Postojna Cave precipitates under isotopic equilibrium conditions.
- Stephanie Neuhuber et al.** (Institute of Applied Geosciences, BOKU Vienna): Stable and radiogenic carbon- and stable oxygen isotopes in authigenic carbonate from Lake Neusiedl, Austria.
- Barbara Pühr et al.**, (Institute of Earth Sciences, Graz University): Geochemistry and isotope-chemostratigraphy of medium-grade marbles from the Austroalpine Basement (Eastern Alps).
- Markus Reuter et al.**, (Institute of Earth Sciences, Graz University): Correlating Mediterranean shallow water deposits with global Oligocene–Miocene stratigraphy and oceanic events.
- Sylvain Richoz et al.**, (Institute of Earth Sciences, Graz University): Progress in integrated Late Triassic isotopic stratigraphy of the Northern Calcareous Alps.
- Daniel Thaller et al.**, (Institute of Applied Geosciences, Graz University of Technology): Crystal water of sulfate minerals – Fractionation of stable isotopes and its application.

NAWI-Graz sponsored a 300.-€ prize to be attributed to the best contribution of a young scientist

2 Oral Presentation

Isotopic composition of soluble organic N: an important player in soil N cycling

Wolfgang Wanek¹ and Judith Prommer¹

¹ Division of Terrestrial Ecosystem Research, Department of Microbiology and Ecosystem Science, Faculty of Life Sciences, University of Vienna, Althanstraße 14, 1090 Vienna, Austria

Introduction: Soluble organic N is a major component of global N transfer processes, contributing to atmospheric N deposition, to the extractable soil N pool, as well as to available N in aquatic and marine ecosystems. Given the prevalent focus on inorganic N as major N source to plants, to date only a few studies have investigated the N isotopic composition of soil extractable organic N, pointing to ¹⁵N enrichment of this relatively labile N pool relative to bulk soil N and to soil inorganic N. Soluble organic N in soils is produced by desorption of soil organic N and from microbial lysis, and the pool is mainly depleted by hydrological losses (all these processes exhibit no or marginal ¹⁵N fractionation) and by soil N mineralization. Soil N mineralization has been commonly assumed to have no or a small isotope effect (0-4‰) but might reach values of 10-14‰ (Pörtl et al. 2007). Depending on the degree of ¹⁵N isotope fractionation by soil N mineralization, we expect soluble organic N to become variably ¹⁵N-enriched relative to bulk soil N, and inorganic N (ammonium and nitrate) to become variably ¹⁵N-depleted relative to both, bulk soil N and soluble organic N.

Materials and Methods: In this study we therefore investigated the concentration and isotopic composition of bulk soil N, soluble organic N and inorganic N in a wide range of sites, covering arable, grassland and forest ecosystems in Austria from 100 to 2400 m elevation, and including different types of tropical forests in Costa Rica and a latitudinal transect in Siberia, extending from steppe to tundra ecosystems. To directly measure the isotopic composition of soluble organic N we optimized a method to release inorganic N in soil extracts, followed by alkaline persulfate digestion of soluble organic N to nitrate, and subsequent conversion to nitrous oxide, to be measured by purge-and-trap isotope ratio mass spectrometry.

Results and Discussion: The results clearly show that soluble organic N is ¹⁵N-enriched relative to bulk soil N by 5‰, and that inorganic N (the sum of extractable ammonium and nitrate) is ¹⁵N-depleted relative to soluble organic N, the mean difference being 9‰. Ecosystem-specific differences (arable, grassland and forest ecosystems in Austria) as well as biome-specific differences (boreal, temperate and tropical forests) in these patterns are investigated, in relation to climatic and soil environmental drivers. Models of soil ¹⁵N fractionation in the coupled processes of production and losses of extractable organic N and of inorganic N will be applied to advance our understanding of the terrestrial N cycle. In terrestrial ecosystems the isotopic composition of this soluble (dissolved) organic N pool has strong repercussions on global isotope-based models of gaseous N losses and ecosystem N cycling, given that soluble organic N losses cause ecosystems to become ¹⁵N depleted (as in undisturbed, low N ecosystems), while inorganic N losses cause ecosystems to become ¹⁵N-enriched (as in managed or N saturated ecosystems with open N cycle).

3 Oral Presentation

Stable isotopes in lacustrine ostracods – Calibration of a Neotropical proxy

Claudia Wrozyna¹, Werner E. Piller¹, Martin Gross²

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² Universalmuseum Joanneum, Department for Geology & Palaeontology, Weinzöttlstrasse 16, A-8045 Graz

Ostracods are common constituents of lake sediments and their low-Mg-calcite valves are often used as authigenic carbonate sources in palaeolimnological research. Although application of stable isotopes geochemistry of lacustrine ostracods has become a standard procedure in palaeoclimatological and –ecological studies there are, however, still limitations precluding complete understanding of obtained isotopic signatures, e.g., vital effects. The majority of proxy-based palaeoenvironmental reconstructions in the Neotropics are based on botanical indicators.

Based on actualistic-ecological analyses of *Cytheridella*, we want to investigate the relationships between ecology and stable oxygen and carbon isotopes on a spatial range. *Cytheridella* is a common freshwater ostracod taxon in the Neotropics and study areas will cover its whole geographical range.

The compilation of an extensive ecological data set will allow us to identify species specific ecological tolerances. Moreover, geochemical signatures of the ostracods' calcitic valves and host water chemistry (major and trace elements, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) will enable us to determine population specific and site specific basic chemical conditions and, in particular, oxygen and carbon isotope signatures and isotopic offsets (vital effects). These data will, thus, provide essential understanding of the geochemistry of ostracod valves and extend the potential of ostracods as proxies in the Neotropics.

4 Oral Presentation

Tracing anthropogenic inputs to a lagoon ecosystem by using a combined approach of hydrochemical and stable isotope investigations

Pierpaolo Saccon¹, Albrecht Leis¹, Alina Marca², Jan Kaiser², Laura Campisi², Michael E. Böttcher³, Joël Savarino⁴, Peter Escher³, Anton Eisenhauer⁵, Joseph Erbland⁴

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³Leibniz Institute for Baltic Sea Research (IOW), Geochemistry & Isotope Geochemistry Group, D-18119 Rostock, German

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⁵GEOMAR, Helmholtz Zentrum für Ozean Forschung Kiel, Wischhofstr. 1-3, 24148 Kiel, Germany

Traditional approaches for environmental management and control of water quality are commonly focused on the monitoring of pollutant concentrations. However, chemical data alone does not enable one to establish unambiguously the type, location and contribution of different pollution sources. The present study therefore represents a modern approach, which, beside the traditional hydrochemical analyses (major ions and nutrients) also uses the stable isotopes of water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$), nitrate ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$), boron ($\delta^{11}\text{B}$) and sulphate ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$).

Nitrates detected in groundwater and along the groundwater up-welling line are mainly related to the use of manure (both liquid and solid), while other nitrate is released from untreated urban wastewaters as detected in some rivers like, for instance, Cormor and Corno rivers. In the lagoon the characterization of the origins and fate of nitrate was in general much more difficult to achieve because of complex mixing processes among different water types like seawater, river water and rain water. However since the $\delta^{18}\text{O}$ of seawater is higher than that of freshwater, the nitrate produced in the lagoon from nitrification of ammonium will have a higher $\delta^{18}\text{O}$ value. This may mean that nitrate with $\delta^{18}\text{O} > 8\text{‰}$ mainly originates from nitrification processes within the lagoon itself, especially since the small $\Delta^{17}\text{O}$ values (mean 0.65 ‰, maximum 3 ‰) indicate an direct atmospheric nitrate contribution of less than 3 % on average (but up to 10 % locally).

The $\delta^{11}\text{B}$ values of the upwelling groundwater samples analysed in this study showed large variations from 4 to 22.7 ‰ (median value 17.7 ‰). In contrast, urban waste water has higher boron concentrations (0.46 to 1.1 mg/l) and lower $\delta^{11}\text{B}$ values from 0 to 12.9 ‰. No significant differences in boron contents and isotopic compositions have been found between raw and treated sewage. Therefore, boron isotope variations can be applied for tracing contamination of groundwater by both raw and treated sewage effluents. However, the higher boron concentrations in the seawater end-member result in non-linear (hyperbolic) boron concentration versus $\delta^{11}\text{B}$ mixing curves. That complicates the identification of the other pollution sources especially in the lagoon itself. Therefore, $\delta^{11}\text{B}$ values have been normalized using bromide concentration in water as second tracer for admixing of seawater. Moreover, the data are showing that in some areas of the lagoon the waters are less affected by these pollution sources. This identifies rain water as an additional mixing end-member.

5 Oral Presentation

Water-Isotope Map Austria 2015: Isotope distribution in precipitation, surface water and groundwater.

Martin Kralik¹

¹Environment Agency Austria & Univ. Vienna 1090 Vienna/Austria

Water-Isotopes are a useful tool to elucidate the origin of waters in the water cycle or to identify the origin of food or trading goods. In addition, water-Isotopes are an important tool in climate research and the main key to palaeo-climatology.

The measurements of water-isotopes started in the early 60th of the last century and has steadily increased up to now and has in Austria due to complicated meteorological and hydrological cycles and a well developed monitoring network (ANIP) a relative higher frequency of application than in other countries.

The oxygen-18 and hydrogen-2 (deuterium) values fractionate along precipitation lines and depend mainly on the temperatures and the quantities in the receiving areas as well as on the original evaporation source. In the case of groundwater the seasonal evapo-transpiration before groundwater recharge may play an important role. Most mean values range between delta -15 and -110 ‰ in high altitude snow up to -8 and -60‰ (SMOW) in the low laying areas in the East of Austria. In winter snow delta -22 and -170 ‰ and in evaporating surface waters like the lake Neusiedel values of up to -1 and -10 ‰ (SMOW) can be reached.

Based on an initiative of the Ministry of Agriculture and Forestry and the Environment Agency Austria water-isotope measurements of precipitation (e.g. ANIP), surface water and groundwater (e.g. "Grundwasseralter") of the past 50 years should be collected and presented in a digital(paper)-map of Austria. The present status will be presented and all owners of water isotope data are invited to contribute to this map by full reference to the original publication or the contributor of the data.

BRIELMANN, H. & KRALIK, M. (2013): ANIP: Österreichisches Messnetz für Isotope im Niederschlag und in Oberflächengewässern. 74-75, In: Wassergüte in Österreich: Jahresbericht 2012. 86 S., Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, Wien. http://www.lebensministerium.at/wasser/wasserqualitaet/wasserguete_jb2012.html

KRALIK, M., WENTER, F., HUMER, F. & GRATH, J. (2011): Grundwasseralter ausgewählter Grundwasserkörper, 2009/2010: Grazer Becken, Jauntal, Leibnitzer Feld, Rheintal, Unteres Salzachtal, Wulkatal. 205 S., Ber. S259, Umweltbundesamt, Wien (<http://www.lebensministerium.at/publikationen/wasser/grundwasser.html>).

6 Oral Presentation

Interaction of lakes with local groundwater systems – environmental isotopes as tool for water balance investigations

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²Carinthian Institute for Lake Research, Kirchengasse 43, 9020 Klagenfurt am Wörthersee / Austria

With the example of two small alpine lakes with totally different hydrogeological boundary conditions (Karst and pore groundwater) and circulation behaviour it is demonstrated that the stable isotopes oxygen-18 and deuterium can deliver relevant information concerning evaporation processes, in- and outflow of groundwater and the circulation conditions in lakes. Furthermore the analyses of the radioactive isotope tritium and its decay product helium enable the determination of the mean residence time of lake water in the deeper zones.

On the basis of long term isotope monitoring data the connection between a lake and a spring is proved (Fig. 1), the portion of lake water on spring discharge quantified and groundwater inflows in lakes detected.

This important information is used for the water balance calculations by means of a hydrological model which allows the estimation of past changes of water balance parameters as well as the development of future scenarios with changed climatic conditions.

The combination of isotopic investigations and hydrological water balance modelling delivers important parameters for the limnological assessment of lakes and their possible climate change induced changes.

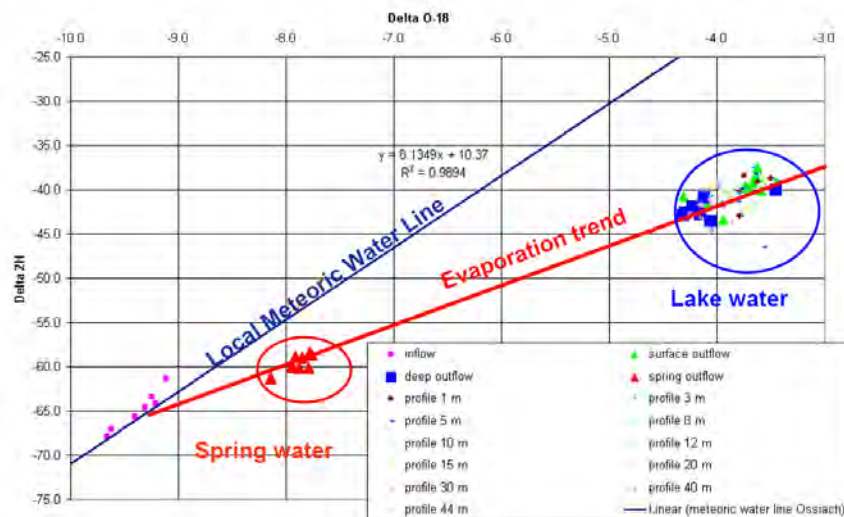


Fig. 1: Local Meteoric Water Line for precipitation and evaporation trend of lake water as natural tracer to prove the connection with a spring.

7 Oral Presentation

Non-Traditional Isotope Systems: New scientific frontiers for the Earth and Live Sciences

Anton Eisenhauer¹

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Efforts to unravel the complex web of biologic and inorganic processes that characterize low-temperature biogeochemical reactions which is a primary goal in the Earth sciences, have benefited from continual improvement of analytical techniques and conceptual approaches like the invention of plasma mass-spectrometry and the development of the double spike technique. Furthermore, precise determination of trace element and isotope ratios are combined with high spatial resolution via the application of laser-ablation and other micro-analytical tools and techniques. In this regard during the past 15 years, an exponentially increasing number of studies have demonstrated that the application of non-traditional isotope systems of several metallic elements like Mg, Ca, Fe, Cu, Zn and others varies significantly in nature up to a few permill and that this variability can be used to understand low temperature biogeochemistry from a totally new perspective. Thereby, the application of non-traditional isotopes extend across the borders of several science disciplines: geology, hydrology, biology, environmental science, and biomedicine opening up new research fields.

8 Oral Presentation

Barium isotope fractionation in carbonates: ongoing research and future development

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² Institut für Geologie, University of Bern, Switzerland

³ Centre Scientifique de Monaco, Monaco

The interest on Ba isotope fractionation in terrestrial sample is very recent but the first results obtained so far seem promising. Here we present a Ba isotope fractionation ($\delta^{137/134}\text{Ba}$) study on marine carbonates and the future development of Ba isotope.

The present work on marine carbonates and seawater was initiated to gain a first order view of the marine Ba isotope cycle. A special focus is the question whether the nutrient-type distribution of Ba in the water column, as well as different Ba sources, are reflected in Ba isotope ratios of carbonate archives. Barium in the ocean originates from various sources, e.g. terrestrial weathering and hydrothermal input.

The dataset consists of seawater and coral skeleton originating from different natural (shallow and warm water corals from the Bahamas/Florida -Sample set 1- and cold water corals from the Norwegian shelf -Sample set 2-) and monitored (CSM, Monaco) environments. The analytical procedure includes the application of a $^{130}\text{Ba}/^{135}\text{Ba}$ double spike, a cation exchange column followed by isotope measurements on a Nu Instruments Multicollector ICP-MS. The Ba isotope fractionation of the samples is compared to a Ba nitrate standard ($\text{Ba}(\text{NO}_3)_2$).

All coral skeletons show a significant enrichment in heavy isotopes compared to the standard. However, differences between natural samples (mean natural samples: Sample set 1: 0.5 ± 0.06 ‰, 2 SEM; N=18; Sample set 2: 0.1 ± 0.03 ‰, 2 SEM; N=9) and cultured samples (mean cultured samples: 0.3 ± 0.06 ‰, 2 SEM; N=13) are observed. Potential influence of diagenetic alteration on Ba isotopic composition was further tested on 5 natural samples with varying calcite to aragonite ratios (0 to 0.3). No significant effect was observed. Moreover, the Ba isotopic composition seems independent from the Ba concentration in the studied coral skeleton, within our measurement resolution of ± 0.1 ‰ (2SD). The $\delta^{137/134}\text{Ba}$ of seawater (0.3 ± 0.14 ‰, SD) from the monitored environment suggests that no significant fractionation occurs during skeleton formation. If this important finding is confirmed by more seawater data, the $\delta^{137/134}\text{Ba}$ of coral skeleton is a potential proxy for Ba isotopic composition of seawater.

These results clearly encourage further investigation of Ba isotope variations in marine settings to evaluate the Ba cycle and associated Ba isotope fractionation of marine carbonate material in other locations. To widen our understanding of the terrestrial Ba cycle, different environments should be investigated. Future development of this research in Vienna will focus on lacustrine environments, in particular waters and authigenic precipitates such as amorphous carbonates. By studying the Ba isotopic composition of these precipitates and the fate of Ba in lakes, we aim to better constrain the Ba cycle and the processes involved.

9 Oral Presentation

**Tracing cyanobacteria-mediated hydrous magnesium carbonate precipitation using Mg isotopes:
Experimental observations and fields studies**

Vassilis Mavromatis^{1*}, L.S. Shirokova¹, I. Bundeleva¹, P. Bénézeth¹, E. H. Oelkers¹, O. S. Pokrovsky¹

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Magnesium carbonate is commonly occurring on Earth's surface environments in the form of hydrated minerals. Hydrous Mg-carbonates are usually secondary products during the weathering of mafic and ultramafic rocks and their formation is mediated via microbiological activity. As a result these rocks are widely considered as primary candidates for both in-situ and ex-situ mineralogical CO₂ sequestration. To date however very little attention has been done on the mechanistic characterization of biological activity on hydrous Mg-carbonate mineral precipitation and furthermore to the potential for Mg isotopic fractionation during bacterially induced carbonate precipitation. To this end and in order to fill the existing knowledge gap, in this study we combine experimental biomineralization experiments, with isotopic measurements on samples from Lake Salda (SW Turkey). This lake is one of the few modern environments where hydrous Mg-carbonates formation occurs.

The Mg-isotopic cycle of the Lake Salda, constrained via Mg isotope analyses performed both on natural samples (incoming streams, groundwaters, lake waters, stromatolites, and hydromagnesite-rich sediments) and laboratory bio-precipitates grown in the presence of *Chroococcales* sp. cyanobacteria isolated from the lake waters. The obtained results show that the difference between the isotopic composition of stream waters feeding the lake ($\delta^{26}\text{Mg} \approx -1.1$ to -1.4 ‰) and the lake water samples ($\delta^{26}\text{Mg} \approx 0.0$ to 0.1 ‰) might be explained by the formation of hydromagnesite with $\delta^{26}\text{Mg} \approx -0.8$ to -1.1 ‰ relative to DSM3 international standard. The suggested fractionation factor exhibits similar fractionation factor $\Delta^{26}\text{Mg}_{\text{Solid-solution}}$ to the one observed in our laboratory bio-precipitates.

10 Oral Presentation

Ca-isotope fractionation in modern and fossil bivalve shell carbonate

Dorothee Hippler¹, Rob Witbaard², Thomas Nægler³ and Dieter Buhl⁴

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² Royal Netherlands Institute for Sea Research, Landsdiep 4, 1797 SZ 't Horntje (Texel), Netherlands

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⁴ Institute of Geology, Mineralogy and Geophysics, Ruhr-University, Universitätsstr. 150, 44801 Bochum, Germany

The geochemistry of bivalve shell carbonate (e.g. stable isotopes, metal/Ca ratios) may provide a useful archive of annual and seasonal parameters such as temperature, salinity or nutrient level, and therefore for high-resolution palaeoclimate reconstructions, but the reliability of these proxies remains questionable given potential vital and microenvironmental effects. Furthermore, in order to test the applicability of shell carbonate-based environmental proxies on geological time-scales, it is of crucial importance to assess the sensitivity of the shell geochemistry to early diagenesis.

We investigated these potential effects for the non-traditional stable isotope system of Ca, first by using laboratory and field-cultured bivalve species, second by examining a historical shell record of *Arctica islandica*, and third by using selected fossil bivalve shells from the Pleistocene (MIS 5e). Cultured individuals offer the chance to compare time series of instrumental environmental data directly to growth increment width (and thus growth rate), as well as shell chemistry, whereas fossil samples, which were exposed to meteoric conditions for an extended period, are perfect for studying potential diagenetic influences on their shell geochemistry and Ca-isotope signature, respectively.

The Ca-isotope composition of laboratory and field-cultured bivalve species are positively correlated with ambient seawater temperature, defining a linear relationship between 0 to 15°C with a slope similar to inorganic calcite and aragonite precipitates. The Ca-isotope values are however offset from the inorganic curves. The most likely explanation for this offset is a biological induced fractionation, which can be attributed to growth rate, precipitation rate or transport kinetics of Ca through different cell layers to the site of calcification. The study of Ca isotopes and Sr/Ca ratios within an *A. islandica* shell in sub-annual resolution yet revealed the finding that seasonal temperature changes might be mimicked by these kinetic effects. The studied fossil shells show little variations in Ca-isotope composition, with fossil biogenic aragonite from the same chronostratigraphic unit is considerably less fractionated than fossil biogenic calcite. This finding might suggest considerable Ca-isotope fractionation during diagenesis. To summarize, Ca-isotope signatures within multi-proxy approaches can thus be a powerful tool for the investigation of biomineralization, palaeo-seawater chemistry or diagenesis.

12 Oral Presentation

Advancement in IRMS

Filip Volders¹, Marian de Reus¹, Mike Seed², Paul Wheeler², Lutz Lange¹

¹Elementar Analysensysteme GmbH, Hanau, GmbH

²Isoprime Ltd, Cheadle Hulme, UK

Up until the present moment, the operation of an IRMS required the skilled presence of a trained technician to get good data out of the system. The setup and monitoring of the system required a high level of knowledge of the workings of such a system. The operation of a complete system requires a massive investment in time and money to get a new laboratory up and running. Together with our range of inlet products we present a solution that takes user error out of the equation and lets you concentrate on the important part, generating excellent data.

13 Oral Presentation

Performance of an isotope ratio infrared spectrometer for simultaneous measurements of carbon and oxygen isotopologues of CO₂

H.J. Jost¹, Eric Wapelhorst², Hans-Juergen Schlueter², Andreas W. Hilkert²

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Laser-based Isotope Ratio Infrared Spectrometers (IRIS) offer the potential to perform precise, continuous, *in-situ* monitoring of isotopologues of trace gases at ambient concentration. We are presenting a mid-infrared laser-based sensor platform that is capable of simultaneously determining both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope ratios of carbon dioxide. Specifically, we access the fundamental bands of CO₂ at 4.2 microns using a difference frequency generation (DFG) laser combined with a simple, direct absorption approach that makes use of a robust multi pass cell and a cryogen free setup.

This novel analyzer offers precision and accuracy of less than <0.1 ‰ for many applications such as atmospheric monitoring, ecosystem fluxes, plant research, or volcanology. We are presenting performance data of sensitivity, stability, and accuracy demonstrating the performance relevant to the different applications.

14 Oral Presentation

Hydrogen and oxygen isotope analyses of inclusion-hosted waters in fluorites using laser spectroscopy: domination of crustal fluids in the formation of the Speewah fluorite deposit of NW Australia

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Application of laser spectroscopy in stable isotope analyses has revitalized isotope geochemistry in the last decade. In the present study a novel method, coupled H and O isotope analyses of water from fluid inclusions was established using a vacuum-based liquid water isotope analyser (Los Gatos Research, LWIA-24d). Inclusion-bearing samples were vacuum-crushed and the released water was cryogenically transferred to the spectroscope's inlet using a vacuum line. Memory and amount effects were determined by introducing standard waters injected into glass capillaries. Amount effects for both H and O isotope compositions were quantified by analyses of varying amounts of distilled water and fluorite samples. On the basis of a set of fluorite samples, whose H isotope compositions had been measured by IRMS it can be stated that the precision of H isotope analyses achieves or even exceeds that of the IRMS analyses with a significant reduction in analysis time and cost. The strength of the method was demonstrated by analysing H₂O extracted from the Speewah fluorites deposit (NW Australia). The H and O isotope data form an array on the δD - $\delta^{18}O$ plot from local meteoric water compositions to D- and ¹⁸O-enriched ones, which may indicate the coupled effects of evaporation and high-temperature rock/water isotope exchange. The data provide evidence for the ultimately crustal origin of fluids whose migration brought about the formation of fluorite veins.

15 Oral Presentation

Generation and Alteration of Gas in the Austrian Molasse Basin

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The Molasse Basin, extending from Geneva to Vienna, is the northern foreland basin of the Alps and a minor oil and gas province. It formed due to overthrusting of the Alpine nappes on the European foreland and was filled with shallow to deep marine sediments since Eocene time. Within the Austrian sector two petroleum systems can be distinguished: A thermal petroleum system comprising Lower Oligocene source and Cenomanian and Eocene reservoirs rocks; A biogenic (bacterial) gas system in Oligocene and Miocene strata.

Typically the thermogenic gas contains significant amounts of higher hydrocarbons (C₂H₆, C₃H₈) and is classified as “wet”. Moreover the hydrocarbons are isotopically heavy ($\delta^{13}\text{C} > -45\text{‰}$). In contrast, the primary biogenic gas consists almost exclusively of methane (“dry”) and is isotopically light ($\delta^{13}\text{C} < -50\text{‰}$ relative to PDB). Biodegradation of pre-existing oils leads to formation of relatively dry “secondary” biogenic gas, which is isotopically heavier than primary biogenic gas.

The aim of the present study is to understand the generation, migration and alteration of gaseous hydrocarbons in the Molasse Basin. To reach this goal, both analysis of hydrocarbon gases and CO₂ and diagenetic studies on potential reservoir rocks have been performed.

The molecular composition and C (-50 to -70‰) and H isotope ratios (-200 to -250‰) of gas and condensate samples from Oligocene and Miocene reservoirs have been determined. These data show that some gas deposits, considered bacterial in origin, contain wet gas (C₁/[C₂+C₃]: 20-300) and locally even liquid hydrocarbons. The results from GC and IRMS point out that chemical characteristics of gas fields in the Molasse Basin are a result of interplay of different processes, like thermogenic gas generation, primary (from solid organic matter) and secondary biogenic gas generation (from biodegradation of pre-existing oils), migration and alteration.

16 Oral Presentation**MECHANISMS OF CONCRETE ATTACK REVEALED BY STABLE ISOTOPES**

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Understanding the underlying complex reaction mechanisms leading to concrete deterioration by e.g. sulfate attack and thaumasite formation from field observations is highly challenging. This study aims to contribute to a deeper understanding by introducing a novel multi-proxy approach that comprises mineralogical methods such as X-ray diffraction with Rietveld refinement and electron microprobe, hydrogeochemical measurements including ion chromatography and inductively-coupled plasma-mass spectrometry, hydrogeochemical modelling and analyses of stable isotope ratios. While stable sulphur isotopes were successfully applied to investigate the origin of sulfate in damaged concrete, stable hydrogen and oxygen isotope ratios were feasible to verify evaporation effects and to quantify evaporation degrees at distinct relative humidity. Evaporation was found to be to the main mechanism for the enrichment of SO₄ and other dissolved, potential harmful ions such as Cl. An enormous and consistent accumulation of incompatible dissolved ions (e.g. K, Rb and Li) in expressed interstitial solutions from deteriorated concrete clearly indicated that numerous wetting and drying cycles had been occurring. Our results show a highly dynamic system to be responsible for severe concrete damage. Actual causes and counter measures will be discussed.

17 Poster Presentation

Insights and limitations of stable isotopes in groundwater research: a case study from the eastern side of the Untersberg, Salzburg

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In the Salzburg Basin fluvial sediments form a porous aquifer which is regarded as coherent and unconfined. The Untersberg consists mainly of carbonate rocks forming a large karst aquifer. Tracer tests have shown that large parts of the Untersberg are drained to the Fürstenbrunn spring, the main karst spring of this massif. A deep karst has previously been postulated below the spring assuming that karst water infiltrates directly into the porous aquifer.

Between 01.02.2012 and 26.03.2013, 60 sites (springs, streams and monitoring wells) were sampled monthly. In addition to temperature, electrical conductivity and discharge stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$) were measured on these samples. Precipitation was collected in rain gougues and snow profiles were sampled as well.

The isotopic composition of precipitation in the Untersberg area shows an altitude gradient of -0.14 ‰/ 100 m. This provides the basis for assessing the mean altitude of the springs' catchments. A mean residence time of ca. 0.4 yr was obtained for water emerging at the Fürstenbrunn spring using an exponential model.

The isotope data confirm the infiltration of the Berchtesgadener Ache into the porous aquifer at St. Leonhard. In this area, monitoring wells and the nearby Berchtesgadener Ache show the same mean $\delta^{18}\text{O}$ values and a very similar pattern throughout the year. Further towards the basin, rain is the main source of recharge. Secondly, water from the Untersberg (Rosittenbach, Fürstenbrunn spring) infiltrates - partly artificially - into the porous aquifer. A distinction between these waters from the Untersberg is not possible because of their similar $\delta^{18}\text{O}$ values. Consequently the hypothesis of an additional infiltration via a deep karst aquifer cannot be tested using stable isotope data, because this source would have an isotopic composition indistinguishable from that of the Fürstenbrunn spring.

The data of this study show, however, that large fluctuations of the groundwater body do also occur in winter when the discharge from the karst system is very low. This leads to the conclusion that precipitation in the Salzburg Basin is more important for recharging the porous aquifer than was previously assumed. Furthermore, neither temperature nor electrical conductivity showed evidence of infiltration of cold and low-mineralized waters into this aquifer.

18 Poster Presentation

Determination of the $^{12}\text{C}/^{13}\text{C}$ and H/D isotopic fractionation during biodegradation of decane in microcosms

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Bioremediation is a cost-effective solution for the clean-up of soil and groundwater environments polluted with hydrocarbons. During biodegradation the isotopic composition of a specific pollutant may change, therefore evidence of the clean-up process is provided and calculation of its extent is possible. At a contaminated site in Vienna the suitability of constructed wetlands filled with differing substrates for the removal of diesel hydrocarbons from groundwater is currently tested in at pilot scale. In this experiment the biodegradation process was simulated in the laboratory in gastight bottles filled with material from the filter bodies and groundwater or groundwater only from the pilot-site. The decane or a decane-ethanol solution was added and the concentration of decane and its $^{12}\text{C}/^{13}\text{C}$ as well as H/D isotopic ratio were measured by GC-IRMS during. Microcosms with sand or clay pellets from the constructed wetlands showed immense growth of microbes for two weeks but no degradation of decane occurred. The δ -value of decane remained constant at $\delta^{13}\text{C} = -32\text{‰}$ and $\delta\text{D} = -82\text{‰}$. Furthermore, these microcosms showed anaerobic conditions after three weeks. The bottles filled only with groundwater from the polluted site showed degradation of decane and the decane-ethanol solution, but nevertheless no shift in the δD -value of decane. All assumed decane degraders were cultivated and sequenced and their growth with decane as sole carbon source was tested. Eight strains of closely related *Pseudomonas* species and one strain of *Serratia* sp. could be identified.

19 Poster Presentation

Stable isotope relationships of groundwater and runoff at high altitudes – a case study from the Andean Cordillera, Chile/ArgentinaGiorgio Höfer-Öllinger¹ and B. Millen¹¹GEOCONSULT ZT GmbH, Wals bei Salzburg

The Andean Cordillera forms a 7.000 km long and 50 to 500 km wide mountain chain with elevations up to more than 7.000 m a.s.l. It works as drainage and weather divide. Groundwater flow is governed by permafrost activities at altitudes above 4.000 m a.s.l., porous aquifers exist along the valleys, joint aquifers in crystalline and volcanic rock mass and – in special cases – karst aquifers in calcareous or gypsum rock mass.

Between 2008 and 2011 water samples have been taken and analysed for their isotopic characteristics. The sampling sites are distributed throughout the provinces of San Juan and Mendoza in Argentina and IV Región in Chile in arid and semiarid terrain at different altitudes. The results were compared with existing studies and the data published by the IAEA.

On one hand, the results provided well fitting lines with both regional as well as world-wide approaches. On the other hand, some values deviated from the expected ones but are worth mentioning and discussing.

Due to high variations in altitude, the most important effect on $\delta^{18}\text{O}$ and ^2H is the altitude effect in combination with seasonal temperature changes and precipitation. In addition, there exists an important effect between Pacific Ocean and South American continental precipitation.

By estimating the altitude of recharge zones, local altitude regression lines were calculated. They show similar slopes, but do deviate from each other (Fig. 1).

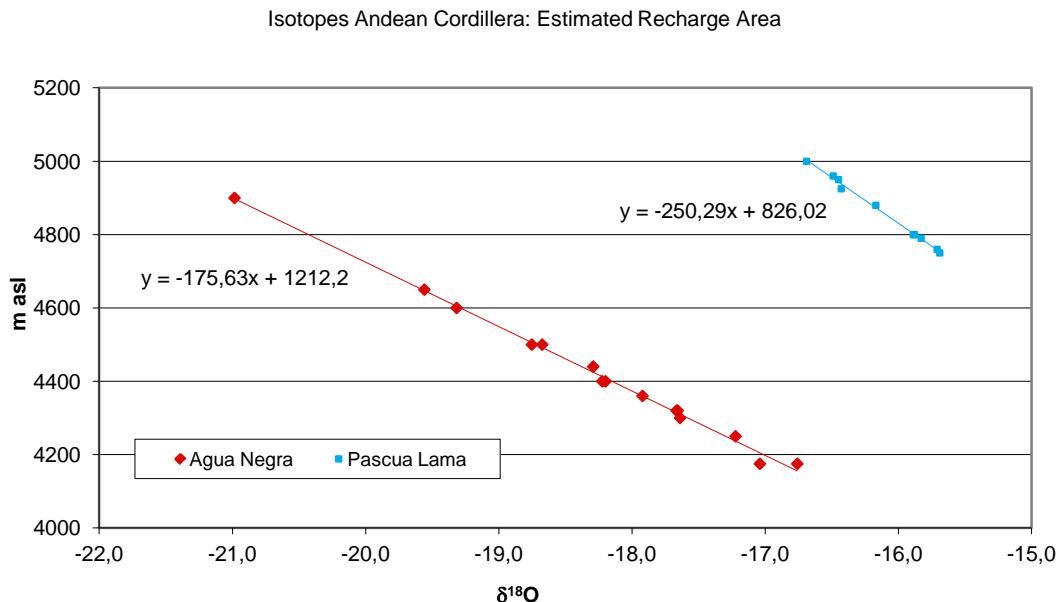


Fig. 1: $\delta^{18}\text{O}$ values against estimated absolute altitude of recharge areas. The Agua Negra ($\sim 31^\circ\text{S}$) area is located around 100 km south of the Pascua Lama zone ($\sim 30^\circ\text{S}$).

20 Poster Presentation

Water-Isotopes to trace the source and timing of recharge in a fractured granite aquifer in Western Kenya, Africa.**Martin Kralik¹, S. Wyhlidal², F. Asunah³ & J. Sültenfuß⁴**

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Sub-Sahara Africa has variable precipitation patterns from tropical high precipitation regimes to semi arid to arid areas. However, in most areas drink water supply is hampered by poor infrastructure. Large parts of the population is forced to drink water from rivers or poorly serviced water wells sometimes far away from their houses. Therefore gastro enteritis infections through consumption of contaminated water are common. Water quality data as chemical or isotope analyses used as a tool to improve the knowledge about the hydrological cycle and to help to find the best position of new wells are relatively rare.

The Vihiga District in West Kenya North-West of Lake Victoria is one of the most densely populated areas in Kenya with 1033 person per square kilometer. To supply a Primary School in this district with an own well as a start the closest springs, school wells and creeks were sampled to get information about the hydrological cycle in the area. The own well should help to avoid that 600 schoolchildren have to walk twice a day to the next spring or creek to get water for their lunch, sanitary facilities and watering the school owned vegetable garden during dry season.

The Waluka Primary school (0.02134°N, 34.64311°E) is situated at the North slope of the Maragoli Hills 20 km North-West of the provincial capital Kisumu at the East shore of Lake Victoria. The hilly relief varies between 1535 – 1675m. The yearly precipitation is between 1200-1600 mm/a (23°C mean temperature) with a dipole rainy season in which the long rains are generally from March to May as the Inter-Tropical Convergence Zone (ITCZ) moves northwards, and the short rains are typically from October to December as the ITCZ retreats southwards. A lateritic soil covers a thin alteration zone above the Precambrian Maragoli-Granite (SAGGERSON, 1952).

Water circulates either in the thin alteration zone or in fault zones cutting through the Precambrian granite. From the measured discharge at the end of the dry season (February 2012) of the two springs and the creek a minimum discharge of ca. 10-20 L/s km² (300-600 mm) can be estimated. The water is with one exception of the earth-alkaline to alkaline sulfate-nitrate type with low mineralization (70-150 µS/cm, 25°C) and a low pH of about 5 to 6. The delta oxygen-18 and deuterium value range between -2.84 to -1.98 ‰ and -8.5 to -3.9 ‰ (VSMOW). The deuterium excess ranges from 11.7-14.2 ‰. The water of the Anzaya spring and the Hobunaka well have a tritium content of 1.42 – 1.62 TU.

All waters are typical low mineralized groundwater in granitic areas with low arsenium, fluorine and uranium content, which did not pass long distances through soils. The relatively elevated, but not problematic content in nitrate (10 – 16 mg/L) probably reflects the intensive agricultural activities in this area. As the mean $\delta^{18}\text{O}$ values during the rainy seasons are significantly lower (-3 to -4 ‰) than in the mean precipitation during the rest of the year (-2.5 to -1.9 ‰; MWANGO, 2003) one can conclude that the main spring "Anzaya" and the well in the Naboka Secondary School are recharged from deeper faults with water supplied more during the rainy season. This is also supported by the significantly higher d-excess of 13.4-14.2 ‰ compared to 11.7-12.6 ‰ in the rest of the samples. These are rather recharged from rain in the rest of the year with more enriched oxygen values. This slightly higher d-excess indicate also a somewhat higher recharge area with recycling vapor effects around the Liailhunuu peak (ca. 1675m). This effect is supported by spring-water measurements at the Kilimanjaro (d-excess 13.4-16.6 ‰) 400 km SE. Similarly, the tritium content of 1.42 – 1.62 TU

indicate that compared to a mean tritium content of 2 TU in the rain of this area (MWANGO, 2003) the mean residence time can be in the range of recent to few years only.

A combination of chemical analyses, stable isotopes and tritium helps to improve the hydrological model and the strategy to site potential drill holes to drill through water containing fracture zones.

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21 Poster Presentation

Analysis of isotopic signals in Danube River water at Tulln (Austria) based on daily grab samples 2012Katharina Schott¹, S. Wyhlidal¹, D. Rank², G. Heiss¹¹ Austrian Institute of Technology – AIT, 3430 Tulln, Austria² Center for Earth Sciences, University of Vienna, 1090 Wien, Austria

Results of stable isotope measurements ($\delta^2\text{H}$, $\delta^{18}\text{O}$) of daily grab samples, taken from the Danube at Tulln (river km 1963) during 2012, show seasonal and short term variations depending on the climatic/hydrological conditions and changes in the catchment area (temperature changes, heavy rains, snowmelt processes). Isotope ratios of river water clearly reflect the isotopic composition of precipitation water in the catchment area since evaporation influences play a minor role. Average $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values 2012 are -78 ‰ and -11.0 ‰, respectively, deuterium-excess averages 10 ‰. The entire variation amounts to 1.8 ‰ in $\delta^{18}\text{O}$ (Fig. 1) and 15 ‰ in $\delta^2\text{H}$. Quick changes of the isotopic composition within a few days emphasise the necessity of daily sampling for the investigation of hydrological events, while monthly grab sampling seems to be sufficient for the investigation of long-term hydro-climatic trends. ^3H results show peaks (half-width 1-2 days, up to about 150 TU) exceeding the regional environmental level of about 9 TU, probably due to releases of nuclear power plants.

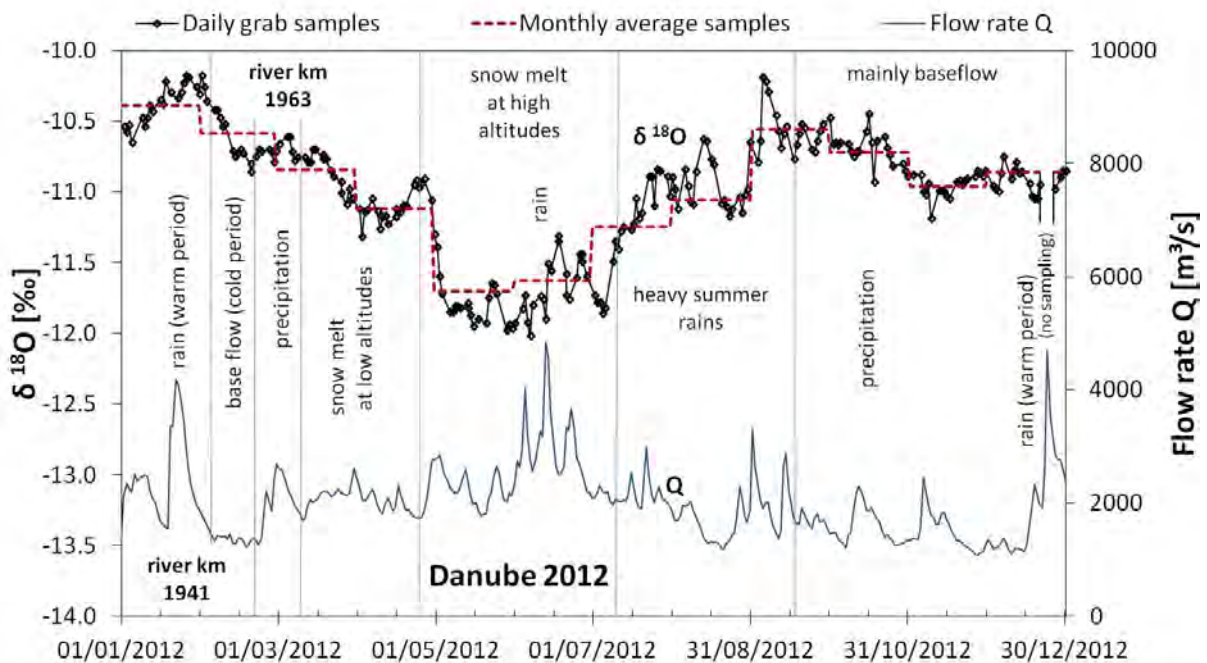


Fig. 1: $\delta^{18}\text{O}$ variations of daily Danube river samples at river km 1963 (dashed line: monthly means) during 2012 based on flow rates.

22 Poster Presentation

Chemical and isotopic composition of soil solutions from cambisols in Styria (Austria) – seasonal variations and experiments

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In most natural surroundings soil solutions are primarily gained from the uptake of meteoric water. Subsequently infiltration, capillary exchange, bioresponse, evaporation etc. result in complex and individual gas-water-solid systems. Knowledge on the chemical and isotopic composition of soil solutions and its evolution is highly relevant for environmental and forensic studies, but respective systematic and combined field and experiment studies are rare. Hence we investigated the composition of solids and interstitial solutions of individual soil horizons for three sampled cambisols in Styria (Austria).

The soil solutions were separated from the soils by compaction method at hydraulic pressures of 27.4 and 54.9 MPa, corresponding to pF values of 5.43 and 5.73, respectively (Böttcher et al., 1996, modified). The soils consist mainly of quartz, chlorite, muscovite and plagioclase with minor amounts of kaolinite, vermiculite and smectite due to weathering processes without any carbonates and without significant vertical variability in composition. The soil solutions contain Ca^{2+} , Na^+ , K^+ , Mg^{2+} , NO_3^- , Cl^- and SO_4^{2-} ions in decreasing order of concentrations. The pH ranges from 5.8 to 7.8. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values vary from -11.9 to -4.0 ‰ and -90.4 to -34.4 ‰ respectively. In principal, solutes, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are higher concentrated and isotopically heavier, respectively, at pF 5.73 vs. 5.43.

Concerning seasonal variations two sampling campaigns were carried out (April and October, 2012). $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values from October plot on the local meteoric water line, whereas values from April indicate an evaporation trend. Current degrees of evaporation can be calculated for distinct horizons of the three soils according to the approach by Mittermayr et al. (2013). The evaporation approach was verified by evaporation lab experiments using the above soils at a given humidity and temperature.

Moreover wetting experiments using deionized water with high $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were conducted to observe changes regarding pH, ion content, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the interstitial solutions as a function of matrix potential. Field-related and experimental results are discussed with respect to the impact of seasonality, evaporation, wetting and matrix potential-related interstitial distribution of the isotope-geochemical compositions of the separated soil solutions.

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23 Poster Presentation

Analysis of drought stress on winter wheat using stable isotope ratio spectrometry ($\delta^{13}\text{C}$)

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Regional climate change scenarios for Eastern Austria (Pannonian Region) predict fewer but heavier rains during the vegetation period without substantial changes in the total annual amount of rainfall. In order to assess whether winter wheat on three different soil types (sandy calcareous phaeozem, gleyic phaeozem and calcic chernozem) are differently affected by rainfall patterns an experiment at the AGES lysimeter station using 18 3 m² lysimeters was conducted. Simulated rainfall amounts and patterns were calculated using a weather generator software (LARS-WG) according to regional climate change scenarios (current 'C-climate' vs. predicted 'D-climate').

As a measure of drought stress, $\delta^{13}\text{C}$ isotope ratios were determined on different parts of winter wheat plants, such as senescent leaves, the youngest fully developed leaves, and the grain. Drought stressed plant parts of winter wheat were more enriched with ¹³C under the D-climate than under the C-climate. Soil type did not significantly influence drought stress on winter wheat.

The $\delta^{13}\text{C}$ values of senescent leaves for the 29th day after seeding (DAS) range from -27.0‰ to -25.7‰ (D-climate) and from -27.2‰ to -26.6‰ (C-climate). The $\delta^{13}\text{C}$ values for the 58th DAS range from -26.9‰ to -26.0‰ (D-climate) and from -27.0‰ to -26.4‰ (C-climate). The $\delta^{13}\text{C}$ values for the 89th DAS range from -27.5‰ to -25.9‰ (D-climate) and from -27.7‰ to -26.4‰ (C-climate). The values for youngest fully developed leaves for the 29th DAS values range from -25.9‰ to -24.4‰ (D-climate) and from -26.6‰ to -25.2‰ (C-climate). The $\delta^{13}\text{C}$ values for the 58th DAS range from -25.7‰ to -24.4‰ (D-climate) and from -26.0‰ to -24.4‰ (C-climate). The $\delta^{13}\text{C}$ values for the 89th DAS range from -26.3‰ to -24.5‰ (D-climate) and from -26.7‰ to -25.5‰ (C-climate). The $\delta^{13}\text{C}$ values of the grain for the 100th DAS range from -25.5‰ to -23.4‰ (D-climate) and from -26.2‰ to -25.0‰ (C-climate).

Carbon isotope discrimination has been proposed as an indirect selection criterion for water use efficiency and grain yield in wheat. Results suggest that soil types have little influence on $\delta^{13}\text{C}$ values of winter wheat leaves and grain. The advantage of this analysis is that more drought resistant varieties can already be identified in the growth phase with no need to wait for grain yield results. The aim of this research is predicting the response of winter wheat to future rainfall scenarios, specifically for the most important soil types found in eastern Austria.

24 Poster Presentation

ISOMON - Isotope application for remediation, aftercare and monitoring of contaminated sites

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The project ISOMON aims to develop and adapt stable isotope methods for their use in monitoring in-situ remediation of contaminated land. It brings together four Austrian research groups working in the field of site and soil remediation and SMEs offering services related to this area. The project is supported by the county of Lower Austria. Various aspects are elaborated in four work packages. Work package 1 aims to refine an elaborated stable isotope method for characterizing the biological stability of landfilled municipal waste in a landfill simulation reactor - which allows controlled and accelerated degradation – and validate its suitability under field conditions (closed landfill sites). Furthermore the stable isotope signatures are compared to FTIR (Fourier Transform Infrared) spectra and chemical parameters traditionally used to describe the stability of landfill sites. Work package 2 aims at improving the quantification of natural biodegradation of chlorinated hydrocarbons in the groundwater by looking at the spatial and time dependent changes in the carbon and hydrogen isotope fractionation factors in the field and in a simulated aquifer (Aqua-box). Results from the stable isotope methods will be compared to conventional investigations including groundwater modelling. Additionally, the application of electron donors i.e. enhanced natural attenuation and their effect on the carbon and hydrogen isotope fractionation factor will be explored. Work package 3 aims at ameliorating the effect of heavy metals on the biodegradation of organic contaminants by soil amendments, i.e. by immobilization of heavy metals. Biodegradation is quantified by monitoring the stable isotope fractionation of carbon in the soil-contaminant. To define degrading microorganisms ¹³C labeled contaminants are used and the uptake in the microbial biomass is followed by ¹³C phospholipid fatty acid analysis. Work package 4 aims to quantify degradation of petroleum hydrocarbons after in-situ biodegradation by monitoring the stable isotopic ratios of the electron acceptors used (nitrate and sulfate). The gained knowledge will be shared with SMEs offering services related to soil remediation and strengthen their market position and competitiveness.

25 Poster Presentation

Archaeal biomarkers and their compound-specific carbon isotopes record the onset of the Messinian salinity crisis

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Seven carbonate-rich beds of the Pollenzo section (Tertiary Piedmont Basin, NW Italy) interbedded with euxinic shale/marl couplets record the onset of the Messinian Salinity Crisis (MSC). Their great variability of sedimentological features is accompanied by major changes in the archaeal lipids. The archaeal lipids are predominantly represented by glycerol dibiphytanyl glycerol tetraethers (GDGTs). The $\delta^{13}\text{C}$ values of the GDGT-derived biphytanes mostly range between -22 and -20‰ in the pre-MSC carbonate beds, agreeing with planktic thaumarchaea as major source. Only in the lowermost bed, GDGT-0 shows a $\Delta\delta^{13}\text{C}$ of -9‰ compared to the other, cyclic biphytanes, which most likely reflects a contribution from sedimentary archaea, probably methanogens. Archaeol was found in all pre-MSC beds. In all pre-MSC samples, archaeol was slightly depleted in ^{13}C compared to the GDGT-derived biphytanes (av. $\Delta\delta^{13}\text{C}$: -4‰), possibly also pointing to input from methanogens.

Major changes in the biomarker inventory are (1) a gradual shift of the GDGT-0/Ar ratio from 4 to 0.5 which is accompanied by (2) a minor shift of the GDGT-0/crenarchaeol ratio from 1 to 2, ultimately rising to 13 in the uppermost bed. The $\delta^{13}\text{C}$ values of the thaumarchaeal biphytanes (bp-2 and bp-3) and archaeol are by 3‰ heavier than in pre-MSC times. In contrast, GDGT-0 is enriched in ^{12}C by 5 to 10‰ . As envisaged for the lowermost pre-MSC bed, sedimentary archaea (possibly methanogens) may have contributed to this isotope pattern. The pre-MSC signature of marine planktic thaumarchaea admixed with sedimentary archaea has consequently changed after the MSC onset to a signature typified by halophilic archaea (archaeol) with contributions from sedimentary archaea (GDGT-0).

26 Poster Presentation

NALPS: Last Glacial climate changes recorded in the northern Alps

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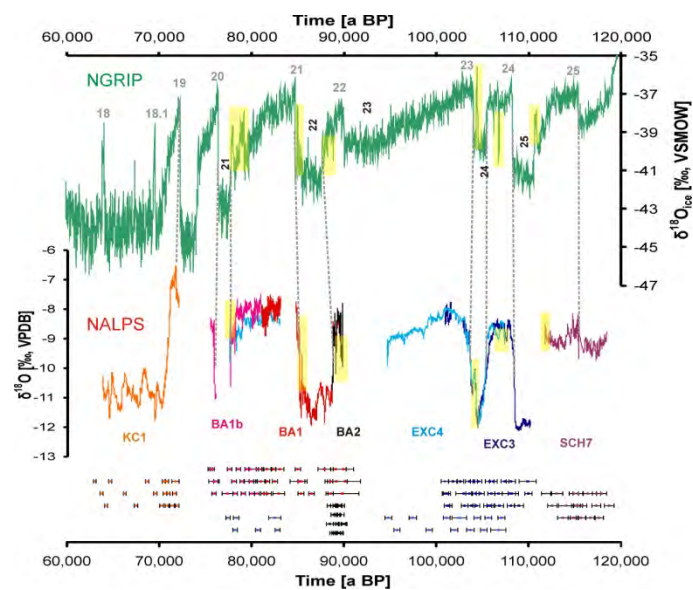
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In Greenland ice-cores drastic climate changes are documented during the Last Glacial period. Rapid and recurrent variations – known as Dansgaard-Oeschger (D-O) events – are expressed as relatively warm and humid Greenland Interstadials (GI) and cold and dry Greenland Stadials (GS). These successions had a global effect on climate, i.e. large air temperature changes, greenhouse gases and global sea-level. Accurate and precise chronologies are essential for interpreting climate signals from ice-core records and to study global teleconnections. Radiometric U-Th-based speleothem chronologies are promising in reducing these uncertainties substantially.

The NALPS stack consists of seven stalagmites from carefully selected Swiss and Austrian caves. All caves are located at the northern rim of the Alps and are exposed to a dominant Atlantic moisture advection, favouring a comparison of the speleothem- and ice-core oxygen isotope signals. Moreover, the caves developed in the same carbonate host rock providing stalagmites with excellent geochemical conditions for U-Th dating. NALPS covers most of the time interval from 120-60 thousand years (ka) ago and is temporally constrained by 154 U-Th ages (20-30/stalagmite). Typical 2σ -age-uncertainties range from 200-500 years (0.2-0.6 %). The stable isotope curves consist of ca. 8200 individual analyses and the temporal resolution ranges from 2-22 years.

The alpine speleothem O isotopic signal is highly reminiscent of Greenland. Interstadials dominate the record reflecting favourable conditions with regard to speleothem growth. Oxygen isotope values primarily reflect the isotopic composition of regional meteoric precipitation and in the Alps this variable is strongly correlated with air temperature. Rapid and large isotope shifts of 1-4.5 ‰ occurred within decades to centuries. Compared to an updated ice-core timescale (GI17.5-18.1) NALPS confirms the timing of rapid warming and cooling transitions between 118 and 106 ka, but suggests younger ages for D-O events between 106 and 60 ka. There is a discrepancy in the duration of the stadial following GI 22 between the ice-core and the stalagmite chronology (2900 vs. 3650 years). The short-lived D-O events 18 and 18.1 are not recorded in NALPS, provoking questions with regard to the nature and the regional expression of these events. NALPS further resolves recurrent short-lived climate changes superimposed on the stadial and interstadial successions that have not been documented outside Greenland before.



Oxygen isotope and age data available at: <http://www.clim-past.net/7/1247/2011/cp-7-1247-2011.html>

27 Poster Presentation

MOONMILK IN POSTOJNA CAVE PRECIPITATES UNDER ISOTOPIC EQUILIBRIUM CONDITIONS**Magda Mandić¹, Andrej Mihevc², Albrecht Leis³, Tea Zubin Ferri⁴, Ines Krajcar Bronić⁵**¹ Department of Physics, University of Rijeka, Rijeka, Croatia; mmandic@phy.uniri.hr² Karst Research Institute, Postojna, Slovenia;³ Joanneum Research Institute, Graz, Austria;⁴ Research Centre METRIS, Istrian Development Agency (IDA) Ltd.⁵ Ruđer Bošković Institute, Zagreb, Croatia

Here we present a part of a comprehensive multidisciplinary study of Postojna Cave, the largest known cave in Europe and most visited cave in Slovenia, related to modern speleothem formation conditions (Mandić, 2013). One year monitoring was conducted at nine locations within Postojna Cave in order to determine environmental conditions of carbonate deposition. Modern carbonates, mostly soda-straw samples, were collected and their stable isotope composition ($\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$) was determined. The assessment of process (equilibrium or kinetic) of precipitation for modern carbonates was done by comparing these values with isotopic composition of water ($\delta^{18}\text{O}_w$) and of dissolved inorganic carbon (DIC, $\delta^{13}\text{C}_{\text{DIC}}$): measured difference between $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_c$ was compared with the theoretical fractionation ϵ value; fractionation factor (α) calculated from the measured $\delta^{18}\text{O}_w$ and $\delta^{18}\text{O}_c$ values was compared with the equilibrium fractionation factor α_{eq} for the measured temperature; temperature of carbonate precipitation was calculated from the isotopic ^{18}O composition of carbonate and water and compared with the measured temperature.

Even though the temperatures of calcite precipitation calculated by using different equations generally do not agree with the measured temperatures at given locations, research has resulted in finding locations and samples which are promising candidates for palaeoclimate investigations. One of such samples is moonmilk from location Zgornji Tartar. Monitored environmental parameters of location microclimate and requirements for carbonate deposition under isotopic equilibrium on this location are fulfilled. All these parameters indicate that the moonmilk is a promising candidate for palaeotemperature reconstruction.

Because this is the first time that moonmilk is described in Postojna Cave, the investigation of its origin has started. Petrographically, the moonmilk is composed of calcite needles approximately 100 μm long, and 10 μm wide. SEM micrographs of moonmilk show evidence of microbial biomediation or bioprecipitation. Also, attenuated total reflectance Fourier transform infrared (ATR-FTIR) analysis pertains to presence of organic compounds.

Since Postojna Cave is a tourist cave it has to be distinguished whether the organic compounds found in moonmilk sample are results of cave microorganisms (native) or they are allochthonous species. To rule out these two possibilities sample is given for RNA sequencing.

Mandić M., 2013. Determination of equilibrium conditions of carbonate precipitation in Postojna Cave with possible application to paleoclimatology. Ph.D. Thesis, Zagreb, University of Zagreb, 205 p.

28 Poster Presentation

Stable and Radiogenic Carbon- and Stable Oxygen Isotopes in Authigenic Carbonate from Lake Neusiedl, Austria

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Due to its low sedimentation rate and constant sediment remixing the age of Lake Neusiedl has never been determined analytically. Formation of authigenic carbonate in Lake Neusiedl has been reported since the 1960^{ies}. Dating of these authigenic carbonate is an alternative method to determine the minimum age of water present – even episodically - at the lake.

To characterize the mineralogy we use X-Ray Diffractometry, Simultaneous Thermo Analysis, and Fourier Transform Infra Red Spectroscopy. The stable C and O isotopes were determined on a ThermoFisher Delta^{plus}XL with a Gasbench II (University of Innsbruck) and ¹⁴C activities at the accelerator VERA (Vienna).

In this poster we present the results from one sample taken at the west shore of the lake north of Rust. The sample consists of 60% clay. To characterize the authigenic carbonates and find the fractions with highest authigenic carbonate minerals we investigate the size fractions <4 µm, <3 µm, <2 µm, <1 µm, <0.5 µm and <0.2 µm. The “coarser” fractions (4 µm to 2 µm) contain detrital minerals such as chlorite, muscovite, quartz, feldspar, stoichiometric calcite and stoichiometric dolomite as well as authigenic high Mg calcite. In contrast, the smaller size fractions (1 and 0,5 µm) lack well-crystallized detrital carbonate - just authigenic carbonate phases are found.

Stable carbon isotopes (vs. VBDB) show a mixing line between -3.8 ‰ in the finest fraction and -2.9 ‰ in the coarsest fraction. Stable oxygen isotopes also show a mixing line between -0.8 ‰ in the finest fraction and coarser samples (-3.85 ‰). The exception is the fraction <0.5 µm with aberrant δ¹⁸O of + 8‰ that might be attributed to a new mineral formed possibly under evaporitic conditions. Radiogenic carbon ages lie at 89 %pMC (0,2 and 0,5 µm fraction) and 72 %pMC (4µm fraction) this corresponds to an approximate age of 850 yBP for the fine fractions and 2 300 yBP for the coarsest fraction.

29 Poster Presentation

Geochemistry and isotope-chemostratigraphy of medium-grade marbles from the Austroalpine Basement (Eastern Alps)Barbara Pühr¹, Sylvain Richoz¹, Ralph Schuster², Georg Hoinkes¹, Beatrix Moshhammer²¹ University of Graz, Institute of Earth Sciences, 8010 Graz, Austria (barbara.puhr@uni-graz.at)² Geological Survey of Austria, 1030 Wien, Austria

Calcitic marbles of different tectonic units of the Koralpe-Wölz nappe pile (Austroalpine Basement, Eastern Alps) were studied regarding their geochemical and isotope characteristics.

For stratigraphic purposes samples with primary compositions were selected using Mn/Sr- and Rb/Sr-ratios and Sr-, C, and O-isotope signals. Limits for Mn/Sr are ≤ 2 and for Rb/Sr ≤ 0.02 . Primary isotope ratios are given by the spread of Phanerozoic seawater curves. Marbles reflecting primary signals do not exceed 0.70925 for $^{87}\text{Sr}/^{86}\text{Sr}$ and O- and C-values scatter between -8 to 0 and -1 to 6‰ respectively (V-PDB).

Although high-P/T metamorphic conditions may facilitate post-depositional changes of the signals, a sufficient quantity of samples falls within the primary fields. Mn/Sr-ratios vary between 0.036 and 2.814 and Rb/Sr-ratios between 0 and 0.132. $\Delta^{18}\text{O}$ - and $\Delta^{13}\text{C}$ -values range from -12.95 to 0.10‰ and -1.58 to 4.78‰ respectively.

The evaluation of the signals allows distinguishing two distinct groups of marbles. The Rappold, Plankogel and Koralpe-Sauzalpe Complexes are summarized within group I which is characterized by low and less variable Sr-values (between 0.707997 and 0.708465). O- and C-data are scattering between -11.08 and 0.10‰ and -1.58 and 4.78‰ respectively. Just a few samples show altered values. Group II, including the Wölz, Greim, Millstatt and Radenthein Complexes, shows variable and relatively high Sr-ratios from 0.708556 and 0.711090, most of them exceeding the values provided by the seawater curve. Oxygen-isotopes fluctuate within -12.95 and -4.01‰ and carbon-ratios scatter from -0.9 and 2.02‰.

For group I a deposition age in the late Early to Middle Devonian is likely. Marble-chemistries of group II point to sedimentation ages from the late Silurian to the earliest Devonian.

The obtained deposition ages as well as lithologic successions allow comparing both groups with un- or weakly metamorphosed Paleozoic counterparts from the Austroalpine and Southalpine. The lack of an Ordovician magmatic event and a minor influence of the Variscan evolution are characteristic for group I and are similar to the evolution of the Paleozoic of Graz. Group II however shows similarities with the other Austro- and Southalpine Paleozoic units including the Greywacke Zone, Gurktal nappes, Carnic Alps and the Karawanken.

30 Poster Presentation

Correlating Mediterranean shallow water deposits with global Oligocene–Miocene stratigraphy und oceanic events

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Shallow marine sediment records have the strong potential to display sensitive environmental changes in sedimentary geometries and skeletal content. However, the time resolution of most neritic carbonate records is not high enough to be compared with climatic events as recorded in the deep sea sediment archives. In order to resolve the palaeoceanographic and palaeoclimatic changes during the Oligocene–Miocene transition in the Mediterranean shallow water carbonate systems with the best possible time resolution, we re-evaluated the Decontra section on the Maiella Platform (central Apennines, Italy), which acts as a reference for the correlation of Oligocene–Miocene shallow water deposits in the Mediterranean region. The 120-m-thick late Oligocene–late Miocene carbonate succession is composed of larger foraminiferal, bryozoan and corallinean limestones interlayered with distinct planktonic foraminiferal carbonates representing a mostly outer neritic setting. Integrated multi-proxy and facies analyses indicate that CaCO₃ and total organic carbon contents as well as gamma-ray display only local to regional processes on the carbonate platform and are not suited for stratigraphic correlation on a wider scale. In contrast, new biostratigraphic data correlate the Decontra stable carbon isotope record to the global deep sea carbon isotope record. This links relative sea level fluctuations, which are reflected by facies and magnetic susceptibility changes, to third-order eustatic cycles. The new integrated bio-, chemo-, and sequence stratigraphic framework enables a more precise timing of environmental changes within the studied time interval and identifies Decontra as an important locality for correlating not only shallow and deep water sediments of the Mediterranean region but also on a global scale.

31 Poster Presentation

Progress in integrated Late Triassic carbon isotopic stratigraphy of the Northern Calcareous Alps

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During the Late Triassic, despite new important originations a general decline in biodiversity was marked by a series of steps between the Carnian and the Rhaetian, with the T-J boundary event as final strike. The Reingraben Event and the Julian-Tuvalian boundary are two first massive turnovers; the Carnian-Norian boundary records a major vertebrate turnover, the early to middle Norian boundary comes up with a turnover in both the reefal and pelagic fauna and the most dramatic loss (70%) in biodiversity among Late Triassic molluscs. Around the Norian-Rhaetian boundary, the pelagic fauna of higher trophic level starts declining, whereas the reefs experience a blooming time. A refined stratigraphy and a construction of a well-calibrated carbon isotope reference curve are necessary to decipher between gradual environmental changes and abrupt or even catastrophic events during the Late Triassic.

Improvement in the Upper Triassic $d^{13}C_{carb}$ curve shows that after a gentle increase until the base of the Carnian, the early Carnian records three negative excursions of 2 to 3‰ amplitude. The two first excursions rebound to previous values, whereas the third negative excursion, at the Julian-Tuvalian boundary, is followed by a positive excursion up to +5‰. The remaining Upper Carnian displays stable values around 2‰. The Carnian-Norian boundary interval is marked by a minor increase of less than 1‰. The Early to Middle Norian crisis is marked by a turning point from Early Norian slowly increasing carbon isotope values (up to 3.5‰) to gradually decreasing ones until 1.8‰ at the base of the Rhaetian. This Norian decrease display two accelerated steps, one in the middle Norian and the other one just after the Norian-Rhaetian Boundary. This last 1‰ decrease correspond however to a important change in lithology. The values show then a small increase during the early Rhaetian, with a maximum in the middle Rhaetian (at 2.4‰). The isotopic record remains constant until the top of the Rhaetian with its significant negative shift identified in a number of marine sections in close proximity to the extinction event. The general stability of the curve even through the Norian-Rhaetian boundary crisis event describes a stable oceanic structure prior the mass extinction. From an isotopic point of view, only the two Lower Carnian excursions, the Early Late-Upper Carnian Boundary and the Triassic-Jurassic Boundary can be interpreted as events, whereas other biotic crises of the Late Triassic seem to have occurred during periods of gradual changes in the carbon isotopic composition of seawater.

Superposed to this long-term trend, the $\delta^{13}C$ isotopic curve in the Rhaetian Zambach Formation records distinctive cycles. First results of the spectral analyses reveal prominent long eccentricity (400 kyr.) Milankovitch cyclicity. Cycles occurring in our record resemble those observed in several Cenozoic and Cretaceous records, suggesting that a link between orbital forcing and carbonate cycling existed also in the Late Triassic time. These 400kyr cycles in the Late Triassic could have been linked to sea-level changes influencing the carbonate export from the platform or, as during the Cretaceous, be related to a fluctuating monsoonal regime.

32 Poster Presentation

Crystal water of sulfate minerals – fractionation of stable isotopes and its application

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In the past decades numerous studies on concrete damage due to the secondary formation of sulfate hydrate minerals such as thaumasite had been published. For instance thaumasite formation causes a disintegration of the concrete matrix, mostly based on CSH-phases, which reduces the durability of the concrete. Despite of intensive research, the key factors leading to concrete damage, in particular the formation conditions of sulfate hydrate minerals and individual reaction mechanisms are still uncertain (Neville, 2004). Therefore, material damaged by the thaumasite form of sulfate attack (TSA) was collected in Austrian tunnels (Mittermayr et al., 2013). In this case evaporation of interstitial solutions recharged by groundwater has led to a massive increase of the SO_4^{2-} concentration triggering the formation of sulfate minerals.

In the present study the above described damaged concrete material containing thaumasite $\text{Ca}_3\text{Si}(\text{OH})_6(\text{CO}_3)(\text{SO}_4)\cdot 12\text{H}_2\text{O}$ and gypsum $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ was used to separate crystal water by extraction via a clod trap setup. Subsequently the extracted crystal water was analysed for its isotope composition. Lab-synthesized gypsum and ettringite $(\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O})$ were used as internal standards. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were measured by wavelength scanned cavity ring-down spectroscopy.

The crystal water from 5 damaged concrete samples was successfully and quantitatively recovered. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ analyses yielded in -57.1 ± 4.0 and $-3.4 \pm 1.0\text{‰}$ (VSMOW), respectively. Compared to the average isotope values of the local groundwater ($\delta^2\text{H} = -83.0\text{‰}$; $\delta^{18}\text{O} = -12.0\text{‰}$) the extracted crystal water indicates a significant discrimination of the light vs. heavy stable isotopes. As a result evaporation degrees of SO_4^{2-} rich interstitial solutions (5000 up to 50000 mg L^{-1}) can be validated from the isotope composition of crystal water tracing the individual formation conditions of damaging sulfate minerals. An isotope fractionation factor for thaumasite was assessed ($\alpha(^2\text{H})_{\text{thaumasite-water}} = 0.987$; $\alpha(^{18}\text{O})_{\text{thaumasite-water}} = 1.003$) since so far only the respective isotope fractionation factor between gypsum and water is known (Horita, 1989).

In forthcoming studies, the first successfully lab-synthesized thaumasite will be analysed, where the results have to be compared to the presented data to verify the above described isotope fractionation factor.

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