Using Zero Waste Approach for Extraction of Valuable Metals in the ESE Europe Region

Robert Šajn[1*] & Aleksandra Trenchovska[1]

[1] *Geological Survey of Slovenia, Dimičeva ulica 14, 1 000 Ljubljana, Slovenia*

* corresponding author: robert.sajn@geo-zs.si

Mining and processing tailings can present a substantial risk to the environment and represent valuable sources of secondary and in particular critical raw materials. Serbia and North Macedonia have an abundance of Cu mines which have been exploited since ancient times. These activities generated about 920 M tonnes of different types of mining, floatation and metallurgical tailings, containing approximately 1.3 M tonnes of Cu, 128 tonnes of Ag and 23 tonnes of Au, which could be a valuable resource for the European raw materials market sector. On the basis of aforementioned two projects were designed, RIS-CuRE and RIS-RECOVER.

The activities of the projects are based on an innovation model merging all relevant stakeholders within the knowledge triangle in the field of industry, research, and education in order to increase regional competitiveness based on a regional scale, taking into account the latest know-how of the RIS-CuRE consortium. This innovative approach is based on the zero waste paradigm, which means that, once valuable raw materials such as CRM and other metals are extracted, the residues can be recycled for the construction sector. Such a holistic eco-innovative approach to the extraction of valuable metals and the beneficial use of residues after the extraction of metals provides a guarantee for the successful development of a regional innovation scheme based on the exploitation of tailings, and is, from the economic, organizational, technological, environmental and social points of view, the most viable option. This will lead to the development of an encouraging environment for the boosting entrepreneurship and intrapreneurship in the region, based on the exploration of secondary deposits. The final output of the project will be a strong sustained regional network, based on validated and fact-based data, including a study of the potential economic, technological, organisational (legislative), environmental and social impacts of applying the innovative methodology of the zero waste extraction of valuable materials in Serbia and the North Macedonia. This will lead to development of encouraging environment for boosting entrepreneurship and entrepreneurship in the region based on exploration of secondary deposits.

Keywords: *raw materials, copper, tailings, RIS-CuRE, ESEE region*

Does Tuff Geochemistry Control its Diagenetic Rate? – Case Study of the Ugljevik Basin Tuffs From the Miocene Pannonian Basin System (NE Bosnia and Herzegovina)

Branimir Šegvić[1*], Luka Badurina[1], Giovanni Zanoni[1] & Oleg Mandic[2]

[1] *Texas Tech University, Department of Geosciences, 1200 Memorial Circle, Lubbock, Texas 79 409, U.S.A.*

[2] *Natural History Museum Vienna, Geological-Paleontological Department, Burgring 7, 1 010 Vienna, Austria*

* corresponding author: branimir.segvic@ttu.edu

The Ugljevik or Semberija Basin is located in the Sava Zone of the Dinarides fold-and-thrust belt at the southern margin of the Pannonian Basin System (UNEN et al., 2019, MANDIC et al., 2012). Numerous tuffs from early and middle Miocene are recovered in post-orogenic lacustrine deposits of the Dinarides Lake System (DLS) making a record of an extensive volcanic activity (DE LEEUW et al., 2012, KRSTIĆ et al., 2001). The Ugljevik Basin, in contrast to the most of Dinarides basins, has been affected by the Badenian marine transgression (MANDIC et al., 2019, PAVELIĆ & KOVAČIĆ, 2018). This created relatively stable marine environment, which made diage-

netic patterns of analyzed tuffs more robust compared to those weathered under altering depositional conditions (e.g. ZHAO et al., 2017).

Six middle Miocene tuffaceous horizons (13.86 to 12.6 Ma, MANDIC et al., 2019) intercalated between the marls and limestones were sampled for the purpose of this research. Tuffs show high levels of alteration giving rise to the formation of ubiquitous clay matrix in which only the remnants of volcanic glass are preserved. The loss of ignition values (16.5 to 36.5 wt. %) are in line with the high content of authigenic clay minerals, which are largely consisted of illite and different intermediates of illite-smectite. Calcite is another major mineral, while quartz, muscovite, biotite, plagioclase, K-feldspars and amphiboles represent minor phases. Presence of calcite and aragonite is likely linked to the abundance of fossiliferous content. Chemical composition of tuffs is featured by low amounts of K (K_2O = 0.53-3.18 wt. %) and Na (NaO = 0.05-1.28 wt. %), and strong variations in the content of Ti (TiO_2 = 0.07-0.23 wt. %) and Si (SiO_2 = 20.29-54.90 wt. %). The Nb/Y vs Zr/Ti (PEARCE et al., 1996) discrimination diagram largely defines these tuffs as intermediate rocks, with only one sample classified as rhyolite. Concentrations of HFS elements seem to decrease with time (Hf = 4.63-1.22 ppm, Ta = 2.6-0.28 ppm), while the Mg# and Cr concentrations exhibit the opposite trend (Mg# = 33.63-89.5; Cr = 9.3-118 ppm). Generally, the original magmatism must have been evolved (~6-40 times chondrite concentrations) with a modest enrichment of LREE over HREE [$(La/Lu)_{cn}$ = 6.00-11.34].

A clear trend has been documented between the crystallinity of the main alteration product of tuffs – illite-smectite – and the age of tuffs, which in turns reflects a decrease in magmatic evolution of tuffaceous geochemistry (Fig. 1). Thus, well-crystallized but disordered illite-smectite (FWHM = ~0.8°) dominates in younger and less evolved tuffs, while in the older ones, more evolved in nature, a poorly crystallized illite-smectite (FWHM = ~1.42°) renders a major alteration product. We hypothesize that the reactiveness of less evolved magmatic material, prone to deuteric alterations, may explain the correlation patterns presented herein. Future research which will include larger dataset and additional techniques will lend further insights into the problematic of diagenetic evolution of Miocene tuffs from DLS.

Keywords: *tuffs, diagenesis, Dinarides, southern Pannonian Basin, clays, mineralogy*

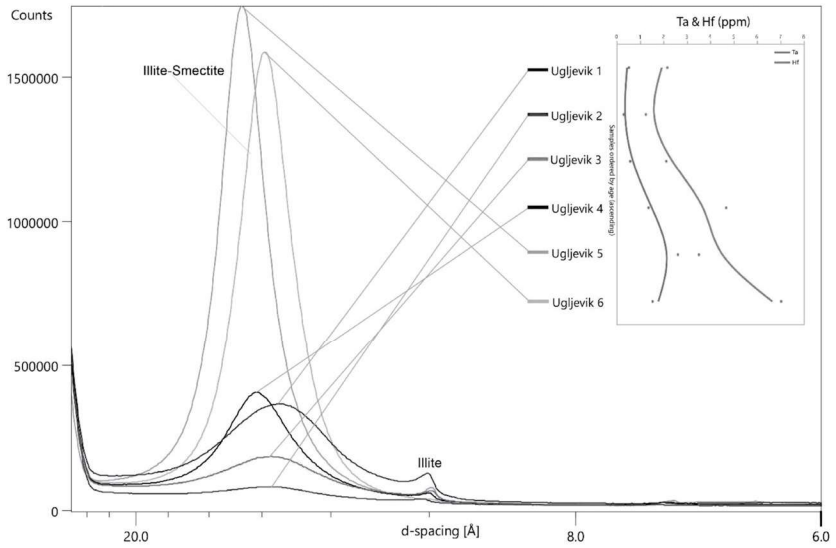

Figure 1. The correlation between the illite-smectite crystallinity and concentrations of HFS elements (samples ordered by ascending age).

References

DE LEEUW, A., MANDIC, O., KRIJGSMAN, W., KUIPER, K. & HRVATOVIĆ, H. (2012): Paleomagnetic and geochronologic constraints on the geodynamic evolution of the Central Dinarides. Tectonophysics, 530-531, 286-298.

KRSTIĆ, N., DUMURDŽANOV, N., OLUJIĆ, J., VUJNOVIĆ, L. & JANKOVIĆ-GOLUBOVIĆ, J. (2001): Interbedded tuff and bentonite in the Neogene lacustrine sediments of the central part of the Balkan Peninsula. A review. Acta Vulc., 13, 91-99.

MANDIC, O., DE LEEUW, A., BULIĆ, J., KUIPER, K., KRIJGSMAN, W. & JURIŠIĆ-POLŠAK, Z. (2012): Paleogeographic evolution of the Southern Pannonian Basin: 40Ar/39Ar age constraints on the Miocene continental series of northern Croatia. Int. J. Earth Sci. (Geol. Rundsch.), 101, 1033-1046.

MANDIC, O., SANT, K., KALLANXHI, M.-E., ĆORIĆ, S., THEOBALT, D., GRUNERT, P., DE LEEUW, A. & KRIJGSMAN, W. (2019): Integrated bio-magnetostratigraphy of the Badenian reference section Ugljevik in southern Pannonian Basin - implications for the Paratethys history (middle Miocene, Central Europe). Glob. Planet. Chan., 172, 374-395.

PAVELIĆ, D. & KOVAČIĆ, M. (2018). Sedimentology and stratigraphy of the Neogene rift-type North Croatian Basin (Pannonian Basin System, Croatia): A review. Mar. Petrol. Geol., 91, 455-469.

References

PEARCE, J.A. (1996): A users guide to basalt discrimination diagrams. In: WYMAN, D. A. (ed.): Trace Element Geochemistry of Volcanic Rocks: Applications for Massive Sulphide Exploration. Short Course Notes 12. St. John's, Canada, Geol. Assoc. Can., 79-113.

VAN UNEN, M., MATENCO, L., NADER, F.H., DARNAULT, R., MANDIC, O. & DEMIR, V. (2019): Kinematics of foreland-vergent crustal accretion: inferences from the Dinarides evolution. Tectonics, 38, 49-76.

ZHAO, L., ZHU, Q., JIA, S., ZOU, J., NECHAEV, V. & DAI, S. (2017). Origin of Minerals and Critical Metals in an Argillized Tuff from the Huayingshan Coalfield, Southwestern China. Minerals, 7, 92.

Subaerial Exposure Surface Within the Palaeocene Carbonates of the Likva Cove, the Island of Brač

Natalia Šenolt[1*], Maja Martinuš[1], Blanka Cvetko Tešović[1] & Igor Vlahović[2]

[1] *University of Zagreb, Faculty of Science, Horvatovac 102a, 10 000 Zagreb, Croatia*

[2] *University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6, 10 000 Zagreb, Croatia*

* corresponding author: nataliesenolt@hotmail.com

Discontinuity surfaces are common in successions of carbonate platforms, including the Adriatic Carbonate Platform (AdCP). The end of the AdCP deposition is marked by a regional unconformity between the Cretaceous and Palaeogene, but in some parts of the platform sedimentation was more or less continuous across the K/Pg boundary, like in the Likva Cove, NW part of the Island of Brač. In the Likva Cove the youngest deposits of the Sumartin formation belong to the early Palaeocene, corresponding to the lower part of the Liburnian deposits of Slovenia and marking the Maastrichtian-Palaeocene transition.

The studied section of the Palaeocene part of the Sumartin formation is 15.70 m thick and is characterized by lacustrine and shallow marine carbonates with freshwater influence. These carbonates are poor in fossil remains, such as benthic foraminifera, which would enable exact age determination, but the younger Palaeocene-Eocene? age is assumed since the studied section overlies the oldest Palaeocene (Danian) strata previously dated. In its lower part, the studied section comprises subaerial exposure surface characterized by the processes of soil formation in a terrain rich in vegetation under conditions of semiarid climate. The surface is characterized by irregular relief, biogenic calcretes with rhizoliths, *Microcodium* aggregates, alveolar septal fabric, micrite nodules, black pebbles and laminated calcretes and pisoids, indicating long-term subaerial exposure. It may be assumed that a complete meteoric diagenetic zone has been developed under the emerging surface. The subaerial exposure was followed by the transgression resulting in incorporation of fragments of terrestrial carbonates into the clayey calcareous matrix, forming transgressive breccia (including bauxite occurrences) most likely preserved in the palaeodepressions. Above the transgressive breccia brackish to freshwater limestones with ostracods, gastropods, cyanobacteria and charophytaceans have been deposited, indicating a very shallow and restrictive lacustrine environments, as well as certain marine influence. Within the brackish and freshwater limestones several subaerial exposure surfaces have been identified, probably as a consequence of a synsedimentary tectonic activity.

The studied subaerial exposure and erosion surface probably formed under the influence of the Late Cretaceous synsedimentary tectonics caused by initial stages of the collision of the Adriatic microplate and Eurasian plate, and is recognized as a regional event over the entire Adriatic Carbonate Platform, marking the end of the typical carbonate shallow-marine sedimentation.

Keywords: *subaerial exposure surface, Palaeocene carbonates, Adriatic Carbonate Platform, Island of Brač*