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28th Meeting of the Petrology group
of the Mineralogical Society of Poland



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Editorso f Volume51:

Łukasz KRUSZEWSKI, Jakub CIAŻELA
Institute of Geological Sciences, Polish Academy of Sciences, Twarda 51/55, 00-818
Warszawa, Poland; Podwale 75, 50-449 Wrocław, Poland

Wojciech STAWIKOWSKI
Institute of Geology, Adam Mickiewicz University
B. Krygowskiego 12, 61-680 Poznań, Poland

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Wydawnictwo Naukowe "Akapit", Kraków; Kom.608 024 572; e-mail: wn@akapit.krakow.pl;
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Layered gabbro near Wolibórz, Nowa Ruda Massif



Pillow lavas near Bożkówek, Nowa Ruda Massif

Professor Wojciech Narębski (14.04.1925 – 27.01.2023)



At the beginning of year 2023 passed away one of the most eminent Polish geochemists and petrologists, a honorary member of the Mineralogical Society of Poland, Professor Wojciech Narębski. He was not only an excellent scientist, who contributed to the better understanding of geology and petrogenesis of magmatic, metamorphic and sedimentary rocks in Poland, Antarctica, Spitsbergen, Andes, Mongolia and many other areas. At first, he was the exceptional man with unusually charming, friendly personality, who inspired people around him with the positive attitude to life and to other people, and brought good energy anywhere he appeared. On the occasion of this conference, which has the oceanic crust in its title, and which venue is located close to Ślęża Ophiolite Massif (the area of conference trip) and the other ophiolitic units of the Central Sudetic Ophiolite, we also want to point to important contributions of Professor Narębski to the research of this area and the issues related to the fossil oceanic crust rocks. By this short note, we want to pay a little homage to his memory. Below, we present an obituary note, which brings closer his long, uneasy and fruitful life. It was written by Dr. Grzegorz Leśniak, who knew Professor Narębski like hardly nobody.

Dear Professor, we will keep a good memory about you in our hearts,

Conference Organizers

Obituary note

Professor Wojciech Narębski was born as a son of an architect Stefan Narębski, professor at the Stefan Batory University (USB) in Vilnius (Wilno before the WW2). In April 1941, he was arrested by the Soviet secret police NKVD and deported to the Soviet Union. After the half year imprisonment he was released, pursuant to the Sikorski-Majski treaty. Just afterwards, he joined the ranks of the Polish Army in the East, which was later transformed into the 2nd Polish Corps. He participated in the Italian campaign 1944-45 (Monte Cassino, Ancona, the Gothic Line, Bologna). He finished secondary school in Italy, and passed the school leaving exams (A levels) in England. After the return to Poland, he finished chemical studies at the Nicolaus Copernicus University (UMK) in Toruń (master's degree in 1952). Later (1953-1955), he carried out doctoral studies in the Department of Geochemistry of the Jagiellonian University/AGH University in Kraków, under the supervision of professor Antoni Gawęł. He gained a doctorate (diploma of geological sciences candidate) on 11 February 1957, by presenting the PhD thesis entitled „Mineralogia i geochemiczne warunki genezy syderytów fliszu karpackiego” (“Mineralogy and geochemical conditions of the origin of siderites from the Carpathian flysch”. Since the year 1956 until his retirement (in 1995), he was employed at the Museum of the Earth, Polish Academy of Sciences (Muzeum Ziemi PAN), successively at the positions of an assistant professor (in Polish: adiunkt), associate professor (in Polish: docent – since 1965) and full professor (since 1972).

In the initial period of his scientific activity Wojciech Narębski continued the mineralogical and geochemical research on the concretions and the surrounding sediments, in the Outer Carpathians and Pieniny Klippen Belt. Among others, their result was the determination of distinct mineralogical variability of the so-called siderites and the discovery of phosphorites in the Flysch Carpathians. For the first time in the Polish scientific literature he demonstrated the strong relationship of this diversity with the evolution of physico-chemical conditions of the depositional environment and of the diagenesis in the sedimentary basins. This observation had a significant meaning for the palaeogeographic reconstructions. In the sixties, W. Narębski in accordance with the research subject area of the Museum of the Earth, undertook geochemical and petrological research of the Lower Palaeozoic metavolcanites in the Sudety Mts. (Kaczawskie Mts., Rudawy Janowickie, Kłodzko Metamorphic Unit, etc.). Its first effect was the habilitation thesis „Petrochemia law puklistych Gór Kaczawskich i niektóre ogólne problemy petrogenety spilitów („Petrochemistry of the pillow lavas from the Kaczawskie Mts. and the selected general problems in the petrogenesis of spillites”), based on which, in 1965 he obtained habilitation and the title of docent (associate professor) at the Jagiellonian University in Kraków. The thesis was awarded with the prize of the 3rd Department of the Polish Academy of Sciences (PAN). W. Narębski was the first author in the Polish literature, who applied and propagated geochemical methods for establishing the palaeotectonic position of metavolcanites, indicating their importance for modelling geodynamic evolution in the light of new global tectonics. He used those methods when conducting the simultaneous geochemical-petrological studies of the Precambrian amphibolites from Spitsbergen (participation in the scientific expedition 1959) and the amphibolites from the Western Tatra Mts.

His important achievements were setting-up of the research group, which carried out pioneer complex studies of the volcanic rocks from Cotopaxi (Ecuador) and King George

Island (Western Antarctica), as well as establishing the cooperation with the Italian research centres, which was related to isotopic dating of these rocks. The long-term collaboration in the research of volcanism manifestations in the polar countries was honoured by Professor Krzysztof Birkenmajer, who called one of the basaltic capes at the King George Island with the name "the Narębski Point". W. Narębski was for many years the member of the international research group active in the framework of socialist states partnership, which was focused on the studies of ophiolitic complexes in Eurasia. He participated in fieldworks at the Caucasus, Ural Mts., in Kazakhstan, Mongolia, Romania, Bulgaria, Slovakia, Czech Republic and Hungary. He was a co-author and co-editor of several monographs devoted to ophiolites and metabasites of the NE part of the Bohemian Massif, with special reference to the Central Sudetic Ophiolite in Poland, incl. the Ślęża Massif. W. Narębski was the author of about 150 scientific publications.

Professor Wojciech Narębski was also author of several dozen publications and presentations given at the conferences in Italy, which were focused on the history of fights of his native 2nd Corps in Italy during the World War II, and also on the military and comprehensive schools, which he graduated.

For several tens of years W. Narębski was an appreciated activist of the Mineralogical Society of Poland and the Polish Geological Society, both of which granted him honorary memberships. He made vast contributions in the fields of veterans of war community activity and in Poland-Italy relations. He continued to conduct these activities for about sixty years by performing responsible functions in different organisations, e.g. the president of the Kraków Chapter of the National Union of the Former Soldiers of the Polish Armed Forces in the West and the vice-president of the F. Nullo Polish-Italian Friendship Society (Towarzystwo Przyjaźni Polsko-Włoskiej im. płk. F. Nullo). He was also the president of the Kraków Chapter of the Society of Wilno and Ziemia Wileńska Enthusiasts (Towarzystwo Miłośników Wilna i Ziemi Wileńskiej). W. Narębski was a full member of the Natural Sciences Department of The Polish Academy of Arts and Sciences (Polska Akademia Umiejętności), and in the years 1955-1999 he held a function of secretary of this section. The University of Wrocław, in recognition of his contributions in the field of research in the Lower Silesia region and in reviewing numerous applications for professorship, habilitation and doctorate degree, awarded him with the Golden Medal "Merentibus". The Minister of National Defence distinguished him for dissemination and cultivation of the glorious traditions of the Polish army in the native country and abroad with the Honorary Badge and Commemorative Medal "The Custodian of Tradition, Glory and Fame of the Polish Army" (Kustosz Tradycji, Chwały i Sławy Oręża Polskiego). Wojciech Narębski was decorated with: four Crosses of the Order of Polonia Restituta: Commander's Cross with Star, Commander's Cross, Officer's Cross and Knight's Cross, with the Polish Army Medal (twice), with the Monte Cassino Commemorative Cross, the Cross of Home Army (Krzyż Armii Krajowej), the Military Cross of the Polish Armed Forces in the West (Krzyż Czynu Bojowego PSZ na Zachodzie), the Siberian Exiles Cross (Krzyż Zesłańców Sybiru), the Officer's Cross of the Order of Merit of the Italian Republic, and also with the Italian and British war stars and medals. Besides, he obtained the golden badges: Meritorious for Polish Geology, for the community service for the Kraków City, and for the merits for Ziemia Krakowska (Cracow Land) and was awarded medals „Pro Memoria”, „Pro Patria” and „Honoris Gratia”.

Grzegorz Leśniak

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9th Meeting of the Mineralogical Society of Poland
28th Meeting of the Petrology group
of the Mineralogical Society of Poland

Invited Speakers



Deep-sea minerals: a big challenge for the world sustainable future

Francisco Javier GONZÁLEZ¹, GEOMAR Research Group²

¹Geological Survey of Spain (IGME-CSIC), C/ Ríos Rosas, 23 Madrid (Spain); e-mail: fj.gonzalez@igme.es

²Marine Geology Resources and Extreme Environments, Geological Survey of Spain (IGME-CSIC), C/ Ríos Rosas, 23 Madrid (Spain)

Introduction

Minerals are major geopolitical players in today's world, facing the European and international research and sustainable development plans. Supply chains for strategic and critical raw materials such as cobalt, copper, lithium, nickel and rare earth elements are highly concentrated, creating risks. Demographic pressure on the environment and the exhausted status of many of the onshore mineral deposits, is leading to new developments to explore the seabed, from coastal areas to the deep abyssal plains. Spanning a large diversity of environments and resource style, including high and low temperature hydrothermal deposits (SMS, SEDEX), phosphorites, as well as ferromanganese crust and nodules, deep-sea deposits are particularly attractive for their polymetallic nature with high content of transition, rare and critical metals. The attractiveness and development of many of these deposits is hindered by the lack of constrain of their spatial variability, their continuity over area sufficient to sustain potential mining activity, and our poor understanding of the disturbance of marine environments associated with human activities. The International Seabed Authority (ISA) is the intergovernmental regulator of the exploration and future exploitation of seabed minerals beyond national jurisdictions. The Clarion-Clipperton Zone in the Pacific Ocean, the Mid-Atlantic Ridge and the Pacific Prime Crust Zone concentrate most of the exploration contracts with ISA for polymetallic nodules, sulphides and cobalt-rich crusts respectively. In Europe the EC is funding transnational projects (e.g., GeoERA, EMODnet-Geology, GSEU, TRIDENT, S34i) contributing to the best use and management of the subsurface including the seabed raw materials (González et al., 2023). The objective is to provide a better and more accurate basis for future exploration and exploitation, as well as sea-use management, and to provide high quality marine mineral intelligence data to the European data portals. The international community needs to increase knowledge about the seas and oceans prior to any commercial mining contract. New investments in exploration and research, including transdisciplinary studies on the geosphere, biosphere and hydrosphere, regulatory framework, spatial planning, social license and the development of more sustainable mining techniques are necessary to face this enormous challenge for humanity.

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Rare mineral assemblages in manganese-rich metasediments of the Stavelot Massif, Belgium

Frédéric HATERT¹

¹Laboratory of Mineralogy, University of Liège, B18, B-4000 Liège, Belgium; e-mail: fhatert@uliege.be

Introduction and geological context

The Stavelot Massif is a large geological unit located at the East of Belgium (Fig. 1), and constituted by Cambro-Ordovician rocks. Three different lithostratigraphic groups are defined in this area: the Deville Group characterized by greenish to grey quartzites of Lower Cambrian age; the Revin Group formed by dark grey to black schists and quartzites of Middle to Upper Cambrian age; the Salm Group showing schists of Lower to Middle Ordovician age. In the middle part of the Salm Group occurs the Otrré Formation, characterized by a very unusual geochemistry dominated by iron and manganese. Depending on the oxidation degree of these rocks, as well as on their mineralogical contents, the Otrré Formation is further divided in three members: the Meuville Member showing very oxidized red schists containing manganese oxides, the Les Plattes Member with purple schists of intermediate oxidation degree and containing *coticule* layers, and the Colanhan Member characterized by weakly-oxidized grey chloritoid-bearing schists.

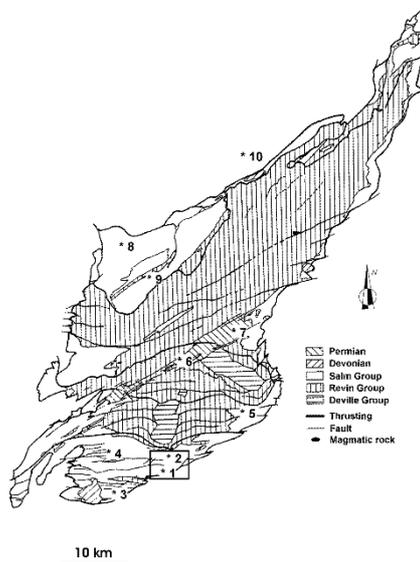


Fig. 1. Simplified geological map of the Stavelot Massif. (1) Salmchâteau, (2) Vielsalm, (3) Bihain, (4) Lierneux, (5) Recht, (6) Stavelot, (7) Malmedy, (8) Theux, (9) Spa, (10) Eupen.

The term *coticule* has been defined in the area to designate a whetstone constituted by tiny spessartine crystals (ca. 5-10 μm in diameter) enclosed in a matrix of phyllosilicates. These rocks occur in the Les Plattes Member (Fig. 2A), where it was mined for centuries, but very similar rocks named *pseudocoticules* occur in the Colanhan Member (Baijot *et al.*, 2011; Fig. 2B). These *pseudocoticules* also show spessartine grains, but of larger size (up to 50 μm in diameter), and enclosed in a matrix of quartz.

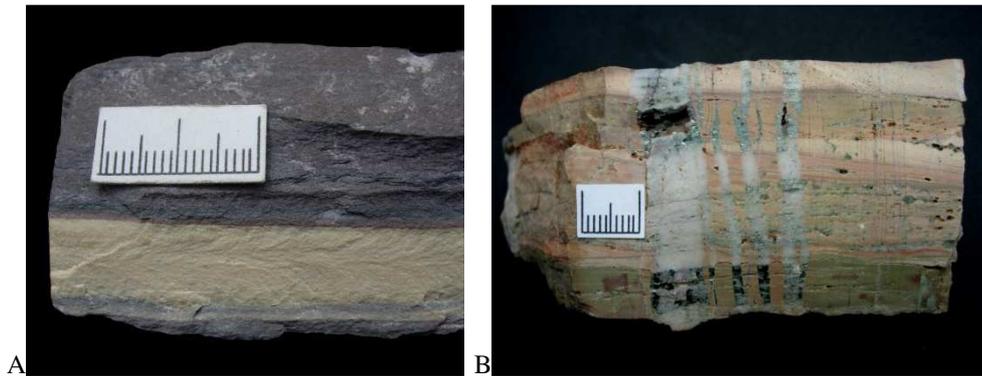


Fig. 2. A. Coticule layer (yellow) occurring in the red schists of the Les Plattes Member. B. Layer of pinkish pseudocoticule found in the Colanhan Member, and crosscut by quartz veins.

Variscan metamorphism in the Southern part of the Stavelot Massif

Mineral assemblages occurring in the rocks of the Otrré Formation allowed to estimate the metamorphic conditions prevailing in the Southern border of the Stavelot Massif. These rocks outcrop mainly in two valleys: the Salm valley, with the localities of Vielsalm, Salmchâteau, Bihain, Otrré, Sart, and Regné, and the Lienne valley with the localities of Lierneux, Chevron, Bierleux, and Moët-Fontaine.

In the Salm valley, the Otrré Formation is well exposed, and the three different members can easily be distinguished. The presence of the rhodochrosite + quartz assemblage, as well as the absence of rhodonite, indicate temperature and pressure conditions of 360-420°C / 2 kbar (Kramm, 1982). These conditions produced several metamorphic minerals, as for example spessartine, chlorite, hematite, andalusite, and Mn-rich chloritoid sometimes approaching the otrrélite end-member.

In the Lienne valley, the Otrré Formation is not so developed: the Colanhan Member seems to be absent, and the Meuville and Les Platte members are difficult to distinguish. In this area, we observe red schists that contain meter-sized layers of manganese ore, which was mined until the Second World War; at a few meters of these ores occur tiny layers of *coticule*. The presence of carpholite $[\text{Mn}^{2+}\text{Al}_2\text{Si}_2\text{O}_6(\text{OH})_4]$ in those red schists indicates metamorphic conditions lower than those occurring in the Salm valley. According to Theye *et al.* (1996), these conditions are close to 300°C and 1-2 kbar.

Genesis of coticule and pseudocoticule

Rocks of the Otré Formation are extremely enriched in iron and manganese, and these two chemical elements occur in variable amounts. For example, *coticule* layers are particularly rich in manganese, the reason why spessartine crystals occur in these rocks. On the other hand, the red schists enclosing *coticule* layers are iron-rich, thus explaining their color produced by the presence of hematite.

The geochemical investigation by Krosse & Schreyer (1993) revealed that both sediments originated from the same source, since the trace elements occurring in the *coticules* and in the red schists show the same fingerprints. The origin of these elements is hydrothermal, indicating that probably, both iron and manganese were produced by submarine hydrothermal springs. These exhalations are certainly correlated to the magmatic rocks found in direct contact with the *coticule* (Fig. 3A). According to Baijot *et al.* (2011), the origin of *pseudocoticule* in the Colanhan Member is certainly comparable.



Fig. 3. A. Magmatic rock (grey), occurring in direct contact with the *coticule* (yellow). B. Sample of ardennite-(As) (yellow fibres) included in quartz from Salmchâteau (collection ULiège n° 13619).

The reason why iron and manganese are separated in different layers is still unclear. Indeed, some authors (Lamens *et al.*, 1986) identify sedimentary textures typical of density currents, thus explaining the manganese-rich layers by turbiditic deposition processes. However, a more realistic model was developed by Krosse & Schreyer (1993), who suggested that Eh-pH variations in the sedimentary basin would lead to a periodical precipitation of manganese oxides, thus producing manganese-rich *coticule* layers during metamorphism. These variations of Eh-pH conditions would be produced by periodical flux and influx of water in a relatively closed sedimentary basin, as observed actually in some area of the Baltic see.

Quartz vein mineralizations

The quartz veins crosscutting rocks of the Otré Formation show a very unusual mineralogy. Indeed, the manganese-rich sediments, coupled with a very low metamorphism that affected the area during the Variscan orogeny, produced a plethora of rare minerals. Most quartz veins show a simple mineralogy, with quartz, hematite, and chlorite. But some of them may contain other species as for example otrérite $[\text{Mn}^{2+}_2\text{Al}_4(\text{Si}_2\text{O}_{10})(\text{OH})_4]$, the manganese equivalent of chloritoid which was defined in the locality of Otré. Other rare species were first described in the quartz veins of the Stavelot Massif, as for example dauvexite $[\text{Mn}^{2+}\text{Al}_6(\text{Si}_4\text{O}_{17})(\text{OH})_2]$, a manganese aluminosilicate structurally related to

sillimanite, as well as ardennite-(As) $[\text{Mn}^{2+}_4(\text{Al,Mg})_6(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})[\text{AsO}_4](\text{OH})_6]$, which was named for the Ardenne mountains (Fig. 3B).

The mineralogy of the quartz veins is sometimes strictly correlated with the geochemistry of the enclosing rocks. For example, in the extremely oxidized Meuville Member occur quartz veins containing manganese oxides, as for example lithiophorite, cryptomelane, nsutite, hollandite-strontiomelane, pyrolusite, and braunite. In those quartz veins was defined stavelotite-(La) $[\text{La}_3\text{Mn}^{2+}_3\text{Cu}(\text{Mn}^{3+},\text{Fe}^{3+},\text{Mn}^{4+})_{26}(\text{Si}_2\text{O}_7)_6\text{O}_{30}]$, a species with one of the most complex crystal structure known in the mineral kingdom (Bernhardt *et al.*, 2005).

In the Colanhan Member, characterized by a low oxidation degree, occur quartz veins mineralized with copper sulfides (Hatert, 2003, 2005). It seems that the source for copper is constituted by the pseudocoticules occurring in those rocks. The primary sulfides crystallizing in these veins are bornite, chalcocite, and chalcopyrite, but they progressively transform to supergene sulfides like covellite, idaite, digenite, djurleite, anilite, spionkopite, and yarrowite. Tiny mineral inclusions in the copper sulfides are constituted by tellurides as for example native tellurium, melonite, tellurobismuthite, and altaite. The presence of these minerals, which are generally a signature for a magmatic origin, confirm that the pseudocoticule are probably related to the hydrothermal exhalations produced by the volcanic rocks observed in the area.

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How fast-spreading oceanic crust is created: benefits from large-scale sampling in the Oman ophiolite in combination with cores drilled by the ICDP Oman Drilling Project

Jürgen KOEPKE¹, Dominik MOCK¹, Sven MERSEBURGER¹, Dieter GARBE-SCHÖNBERG²

¹*Institute of Mineralogy, University Hannover, Callinstr. 3, 30167 Hannover; e-mail: koepke@mineralogie.uni-hannover.de*

²*Institute of Geosciences, University Kiel, Olshausenstr. 40, 24118 Kiel; e-mail:dgs@gpi.uni-kiel.de*

The Oman Ophiolite is the largest, best-exposed section of oceanic lithosphere on our planet and is regarded as a former fast-spreading ridge in the environment of subduction zone initiation. The Oman Drilling Project (OmanDP; Kelemen et al., 2020) within the frame of ICDP (International Continental Scientific Drilling Program) is a comprehensive drilling program within the Oman ophiolite, aimed in understanding essential processes related to the geodynamics of mid-ocean ridges, including the magmatic formation, their aging and the cooling/alteration by seawater-derived fluids, and their past and ongoing weathering with focus on the carbonatization of peridotites.

Over two drilling seasons (winter 2016/17 and 2017/18), the OmanDP has sampled the Samail Ophiolite sequence from crust to basal thrust in nine diamond-cored and six rotary-drilled boreholes. The total cumulative drilled length is 5458 m, with 3221 m of which was cored at more or less 100% recovery. These cores were logged to IODP standards aboard the Japanese drilling vessel "Chikyu" during two description campaigns in summer 2017 and 2018. In addition to sampling and analysis of rock core and cuttings, the operations include ongoing geophysical logging, fluid sampling, hydrological measurements and microbiological sampling.

Here we present a summary of the finding of the working group of the Universities Hannover and Kiel which focused on the theme accretion and cooling of the lower Oman palaeocrust, based on results of investigating the crustal drill cores GT1 (lower layered gabbros), GT2 (mid-gabbro crust) and GT3 (dike/gabbro transition), as well as the drill cores CM1 and CM2 penetrating the crust/mantle boundary. In addition, we established a 5 km long profile through the whole plutonic crust of the Oman ophiolite by systematic outcrop sampling in the Wadi Gideah (Wadi Tayin Block near Ibra), providing the reference frame for the 300 to 400 m long OmanDP drill cores GT1 and GT2 (deep and mid gabbro crust), as well as CM1 and CM2 (crust/mantle boundary) drilled into the same area. Based on the newly established reference profile through fast-spreading oceanic crust of the Oman ophiolite and on the cores mentioned above, we present here the results of 12 years research, focusing on the nature of the magmatic accretion of the deep crust beneath fast-spreading mid-ocean ridges.

The results allow implication on the mechanism of accretion of fast-spreading lower oceanic crust. Depth profiles on bulk rock and mineral compositions, crystallization temperature and microstructures combined with petrological modelling reveal insights into the mode of magmatic formation of fast-spreading lower oceanic crust, implying a hybrid accretion mechanism. The lower 2/3 of the crust (mainly layered gabbros) was formed via the injection of melt sills and in situ crystallization. Here, upward moving fractionated melts mixed with more primitive melts through melt replenishments, resulting in an upward differentiation trend. Since the fraction of crystallization is only small, upmoving melts could easily transport the latent heat produced by deep crystallization upward. The upper third of the gabbroic crust is significantly more differentiated, in accord with a model of downward differentiation of a parental melt originated from the axial melt lens sandwiched between the gabbroic crust and the sheeted dike complex. These results are summarized in Garbe-Schönberg et al. (2022), Koepke et al. (2022), Mock et al. (2021), and Müller et al. (2022).

While the 5 km long profile shed light on the overall magmatic accretion process, the Oman DP drill cores with ~100% recovery allowing high density sampling provide incredible details on the magmatic accretion process. Key results of the core investigations are the identification of individual melt sills from which the layered gabbro section has been formed (drill core GT1), manifesting the model of sheeted sill intrusions. Concerning the crust/mantle boundary, detailed investigations of the drill cores CM1 and CM2 revealed that the main process of the formation of 150 m thick massive dunites was a result of olivine accumulation in individual melt sills, and not the consequence of melt/mantle interaction at the base of the crust. This implies that the massive dunites sandwiched between the layered gabbros and the mantle harzburgites are formed by the same process than the whole lower gabbroic crust, hereby indicating that the massive dunites at the base of the crust are those "missing" cumulates, which are responsible for the early differentiation of the very primitive parental mantle melts to those slightly differentiated melts enabling the crystallization of clinopyroxene in order to produce olivine gabbros, which form the main part of the lower crust.

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Sources and fates of water oceans on primordial Earth, Mars, (maybe) Venus and beyond the solar system

Stephen J. MOJZSIS¹

¹Research Centre for Astronomy and Earth Sciences, MTA Centre for Excellence, Konkoly Thege Miklós út 15-17, H-1121 Budapest, Hungary; e-mail: stephen.mojzsis@csfk.org

Water is abundant in the universe and is primordial to Earth, Mars and Venus (Mojzsis 2021). Water and its dissociated forms modulate the physical, chemical and mechanical properties of silicate mantles and crusts of the rocky planets (Spaargaren et al., 2023), and acts as the medium for biological processes. Just as nothing in biology makes sense except in light of evolution, nothing in planetary science makes sense in except in light of a planet's ingredients, including water (Mojzsis, 2022). I will discuss some developments that have sharpened our focus on the appearance of water on Earth and clues about its manifestation on Mars, possibly Venus and even in rocky exoplanets (Wang et al., 2022).

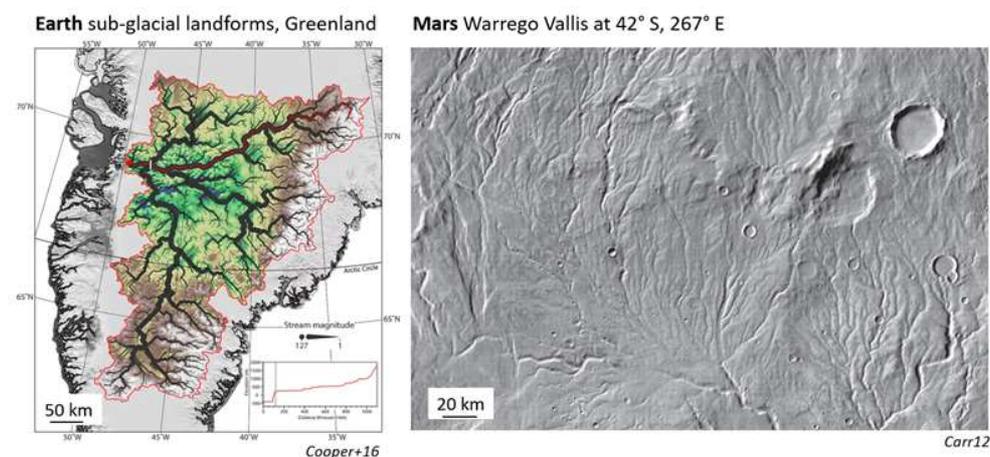


Fig. 1. How prevalent was liquid water on other planets in our solar system? Dynamical simulations and climate models predict that the ancient Martian surface was always cold. Previous interpretations of drainage patterns on Mars argued for precipitation and surface water runoff to form valley networks in the southern highlands terrain. If, on the other hand, ice sheets covered early Mars, subglacial and fluvial (outwash and outburst) erosion were the predominant geomorphic agents (e.g., Graugalofreet al., 2020).

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Origin and tectonic setting of the Alpine-Apennine ophiolites

Riccardo TRIBUZIO¹, Alessandra MONTANINI², Maria Rosaria RENNA³, Alessio SANFILIPPO¹

¹Department of Earth and Environmental Sciences, University of Pavia, Italy; e-mail: riccardo.tribuzio@unipv.it

²Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Italy; e-mail: alessandra.montanini@unipr.it

³Department of Mathematics and Computer Sciences, Physical Sciences and Earth Sciences, University of Messina, Italy; e-mail: mariarosaria.renna@unime.it

¹Department of Earth and Environmental Sciences, University of Pavia, Italy; e-mail: alessio.sanfilippo@unipv.it

The Jurassic ophiolites from the Alpine-Apennine belt are dismembered lithospheric fragments of the Alpine Tethys, also known as Ligurian-Piedmontese basin. This basin separated the Europe-Iberia plate to the northwest from the Africa-Adria plate to the southeast. Despite the orogenic evolution, some of the Alpine-Apennine ophiolites preserve the original lithostratigraphy, particularly those with no high-pressure tectono-metamorphic overprint. Overall, these ophiolites consist of a substrate made up of a mantle section that is intruded by gabbroic bodies providing U-Pb zircon ages clustering at 158-166 Ma, and a heterogeneous basalt-sedimentary cover, which includes MORB-type lava flows, Middle-Upper Jurassic radiolarian cherts and/or polymict sedimentary breccias.

Some of the Alpine-Apennine ophiolites are primarily associated with continental crust material, such as Permian granitoids or quartz-rich clastic sediments, and include mantle sections of subcontinental lithospheric origin. These mantle sections typically consist of spinel- and amphibole-bearing lherzolites with frequent pyroxenite layers (Fig. 1), which in turn locally contain garnet relics. Additionally, the ultramafic rocks record a plagioclase-facies decompression, which occurred under subsolidus conditions or was associated with reactive melt infiltration. These ophiolites have been characteristically related to a magma-poor rifting evolution, which led to uplift and denudation of subcontinental lithospheric mantle, similar to what was proposed for the ocean-continent transitions of the Iberia-Newfoundland margins.



Fig. 1. Protomylonitic lherzolite enclosing boudinaged pyroxenite layers in the mantle section of the External Ligurian ophiolites (northern Apennine, Italy).

Other ophiolites from the Alpine-Apennine belt, typically attributed to oceanward domains of the Jurassic basin, have no relationship with continental crust material and include mantle sections displaying a depleted geochemical signature. These mantle sections are mostly composed of spinel-bearing harzburgites to clinopyroxene-poor lherzolites, which characteristically record a plagioclase-facies melt-peridotite reaction event and locally enclose dunite bodies of replacive origin. The oceanward ophiolites frequently comprise km-scale gabbroic bodies that are structurally and compositionally similar to those exposed along Mid Atlantic and Southwest Indian Ridges. The ophiolitic gabbroic bodies mostly consist of olivine gabbros and gabbros, locally associated with oxide-gabbros and felsic veins, and in places include up to tens of meters thick olivine-rich troctolite and mantle peridotite lenses. The gabbros also provide evidence for a polyphase tectono-metamorphic evolution related to their exhumation to the Jurassic seafloor. This evolution initially comprised granulite- to amphibolite-facies ductile shearing, followed by hornblende veining (Fig. 2) associated with downward migration of seawater-derived fluids.



Fig. 2. Hornblende vein crosscutting a pegmatoid gabbro in the Internal Ligurian ophiolites (northern Apennine, Italy). Close to the vein, for few mm, the magmatic clinopyroxene is replaced by hornblende.

The tectonic setting of the oceanward Alpine-Apennine ophiolites is debated. They could have formed at a slow- or ultraslow-spreading centre, similar to modern oceanic core complexes. Alternatively, the oceanward ophiolites correspond to distal sectors of a magma-poor ocean-continent transition. Following this idea, the depleted mantle sections are of subcontinental lithospheric origin, and record a melt extraction event occurred during the early Permian post-collisional Variscan evolution. This interpretation implies the lack of any genetic mantle-crust link for the Alpine-Apennine ophiolites.



Quantum Crystallographic Studies of Minerals under Pressure

Krzysztof WOŹNIAK¹, Michał L. CHODKIEWICZ¹, Roman GAJDA¹, Marcin STACHOWICZ², Jan PARAFINIUK², Vitali B. PRAKAPENKA³, Przemysław DERA⁴

¹University of Warsaw, Chemistry Department, Pasteura 1, 02093 Warszawa, Poland; kwozniak@chem.uw.edu.pl

²University of Warsaw, Department of Geology, Żwirki i Wigury 93, 02-089 Warszawa, Poland

³APS, Argonne National Laboratory, 9700 South Cass Avenue, Lemont, IL 60439, USA,

⁴Hawai'i Institute of Geophysics and Planetology, Université d'hawaii à mānoa, 1680 East-West Road, Honolulu, HI 96822, USA

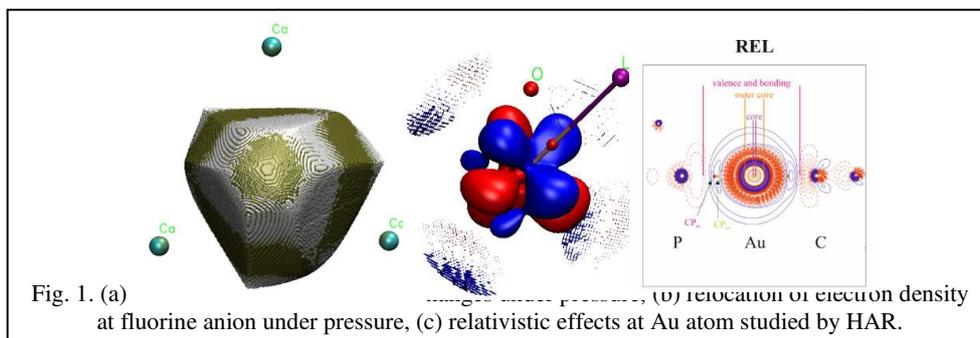
Introduction

This is quite a paradox that almost all structures of minerals have been refined with the spherical Independent Atom Model (IAM, 1914 [1]) which suffers from severe methodological deficiencies. Far better results can be obtained when new approaches of Quantum Crystallography (QCr) utilizing aspherical atomic scattering factors are applied. In short, QCr is crystallography beyond IAM. QCr includes among others refinement of quantitative distributions of electron density in minerals and so called Hirshfeld Atom refinement (HAR). In this contribution will present examples of such refinements. In particular, we will present changes of electron density in minerals under pressure such as hsianghualite[2] and langbeinite[3], and structures of ices such as ice VI, ice VII and hexagonal ice. Despite ca. 5 mln papers published on ices, still their structures have not been fully established yet. We have applied modern approaches of Quantum Crystallography such as Hirshfeld Atom Refinement (HAR) of single crystal high pressure (sc HP) X-ray synchrotron and laboratory X-ray and electron diffraction data to obtain and refine structures of ice VI, VII and hexagonal ice. This method utilizes aspherical atomic scattering factors (X-rays), and aspherical atomic electrostatic potentials (ED), based on so called stockholder (Hirshfeld) partition and is especially effective in the case of refinement of crystals of H-rich compounds.

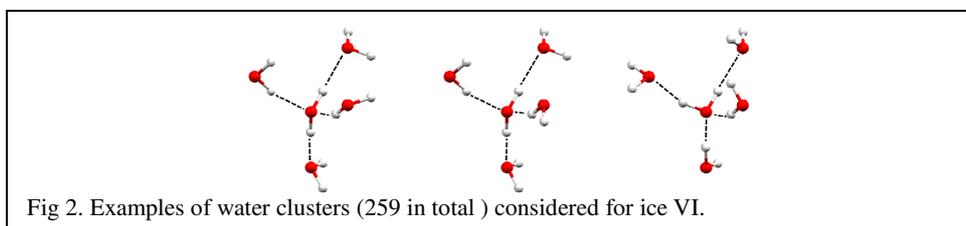
Results

We will present details of electron density distribution in hsianghualite and langbeinite and their changes under pressure (Fig. 1). Will trace how atomic basins and atomic charges change for particular ions when pressure is applied. Additionally we will analyze detailed changes of electron density of particular ions under pressure.

The second part of the lecture will be focused on structures of ices (Fig. 2). We will present accurate crystal structures of H₂O, D₂O and mixed (50%H₂O/50%D₂O) ice VI and ice VII obtained by HAR against sc HP synchrotron and laboratory X-ray diffraction data as well as results of refinement of hexagonal ice obtained by HAR against electron diffraction data (Fig. 1). It was possible to obtain the O-H bond lengths and anisotropic ADPs for disordered hydrogen atoms which are in good agreement with the corresponding results of single crystal neutron diffraction data.[2]



Our results show that HAR against X-ray diffraction and electron diffraction data is a tool which can compete with neutron diffraction in detailed studies of polymorphic forms of ice and crystals of other hydrogen rich compounds.



Conclusions

A century after the Braggs, it is possible to obtain H-atom positions from X-ray diffraction studies which are equally reliable as those from neutron diffraction. It is also possible to get reliable positions of H-atoms in the closest neighbourhood of very heavy atoms, to study tiny redistribution of electron density in minerals under pressure, or to estimate consequences of relativistic effects using X-ray diffraction data. So users of X-ray crystallography can do far better than just routinely refining poor IAM model against precise, accurate and very often very dear diffractometer/synchrotron/ XFEL X-ray data. Cheaper and more accessible X-ray measurements combined with HAR do facilitate the verification of the existing ice polymorphs and the quest for the new ones.[4]

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9th Meeting of the Mineralogical Society of Poland
28th Meeting of the Petrology group
of the Mineralogical Society of Poland

Abstracts



The Góry Suche Rhyolitic Tuffs, a large-scale, caldera-related ignimbrite deposit in the Intra-Sudetic Basin: U-Pb SHRIMP zircon dating, regional correlations and stratigraphic implications

Marek AWDANKIEWICZ¹, Magdalena PAŃCZYK², Izabela PLOCH², Paweł RACZYŃSKI¹, Honorata AWDANKIEWICZ², Anna GÓRECKA-NOWAK¹, Wojciech PAWLAK³, Tadeusz PERYT²

¹University of Wrocław, Institute of Geological Sciences, Pl. M. Borna 9, 50-204 Wrocław, Poland, marek.awdankiewicz@uwr.edu.pl, pawel.raczynski@uwr.edu.pl, anna.gorecka-nowak@uwr.edu.pl

²Polish Geological Institute - National Research Institute, Rakowiecka 4, 00-975 Warszawa, Poland, mpan@pgi.gov.pl, iplo@pgi.gov.pl, hawd@pgi.gov.pl, tadeusz.peryt@pgi.gov.pl

³University of Warsaw, Faculty of Biology, Institute of Evolutionary Biology, Biological and Chemical Research Centre, Żwirki i Wigury 101, 02-089 Warszawa, Poland, wojciech.pawlak@uw.edu.pl

The intracontinental sedimentary succession of the Intra-Sudetic Basin, a Permo-Carboniferous intramontane trough (NE margin of the Bohemian Massif), provides a record of intense, late- to post-orogenic volcanism. The most voluminous volcanic unit (c. 100 km³ of erupted magma), the Góry Suche Rhyolitic Tuffs (GSRT), reflect a climactic phase of explosive activity which resulted in the formation of a caldera c. 10-15 km in diameter, deposition of fall and surge tuffs and widespread ignimbrites, and subsequent intrusion of trachyandesite and rhyolite laccoliths along the caldera margins. To constrain the age of this activity we have collected 9 samples from various levels within GSRT and from selected subvolcanic intrusions. Zircon separates and mounts were prepared using standard techniques. U-Pb dating was carried out using SHRIMP IIe/MC at the Polish Geological Institute - National Research Institute, Warszawa. Four ignimbrite samples were dated at 300.5±1.4, 300.5±2, 298±1.6 and 296±3 Ma and three other, strongly dominated with xenocrysts, contain sparse juvenile zircon dated at c. 300 Ma. Two rhyolite samples were dated at 298±1.5 and 292±1.7 Ma. These results indicate that the GSRT volcanism was initiated at c. 300.5 Ma, most intense activity occurred in the following 2-4 Ma, the emplacement of rhyolitic laccoliths partly overlapped the ignimbrite volcanism and terminated at 292 Ma, c. 8 Ma after the onset of activity. The new ages correlate the GSRT to the peak of post-Variscan volcanism in Central Europe at the Carboniferous/Permian transition. Several Ma of GSRT volcanism, as indicated by our results, is a prolonged time span, but silicic calderas are the longest-lived volcanic systems in general, and similar spans of activity are recognized in other Late Palaeozoic magmatic systems in the region (e.g., the Teplice-Altenberg Caldera, or the Strzegom-Sobótka granitic pluton). Our ages obtained for GSRT are 5-10 Ma older than assumed in the existing, informal lithostratigraphic schemes. This strongly suggest that the stratigraphic position of the reddish-brown rocks of the uppermost Carboniferous/lowermost Permian of the Intrasudetic Basin, which have poor biostratigraphic documentation, should be revised: the Carboniferous/Permian boundary is most probably located above the GSRT, within the “Walchia shales”, in the top part of the “Słupiec Formation”, not in the underlying formations, as supposed so far. *Acknowledgements: The research was funded by the NCN grant 2017/26/M/ST10/00646.*



Growth of ThSiO_4 phases during experiments as a result of interaction of hydrothermal fluids with chevkinite-(Ce): element mobility, textural features and variable crystal structure

Bogusław BAGIŃSKI¹, Ray MACDONALD¹, Marcin STACHOWICZ¹, Petras JOKUBAUSKAS¹, Jakub KOTOWSKI¹, Witold MATYSZCZAK¹, Daniel HARLOV²

¹Department of Geochemistry, Mineralogy and Petrology, Faculty of Geology, University of Warsaw, ul. Żwirki i Wigury 93, 02-089 Warszawa; e-mail: b.baginski@uw.edu.pl

²GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany; e-mail: dharlov@gfz-potsdam.de

The high contents of Th and U in thorium silicates make them prone to metamictization by radiation damage and thus to hydrothermal alteration. Petrological and experimental studies have shown that Th is mobile during such alteration but generally with short transport distances (micrometres to millimetres). Results of the series of high T-P (500-600 °C; 200-400 MPa) experiments aimed at examining the fluid-induced alteration of the REE,Ti-silicate chevkinite has provided valuable data for the following conclusions:

- (i) Thorium released during hydrothermal experiments on chevkinite-(Ce) containing 0.54-2.89 wt% ThO_2 showed significant solubility and mobility in the fluids, achieved in ≤ 84 days. Thorium solubility was enhanced in alkaline fluids.
- (ii) Thorium may have been transported as hydroxyl complexes.
- (ii) ThSiO_4 crystallized as either huttonite or thorite, both forms being present in single chevkinite-(Ce) grains. The thorite is shown to be the stable crystalline phase under the experimental conditions, with huttonite being metastable.
- (iv) An amorphous variety was a result of hydration of the crystalline forms.

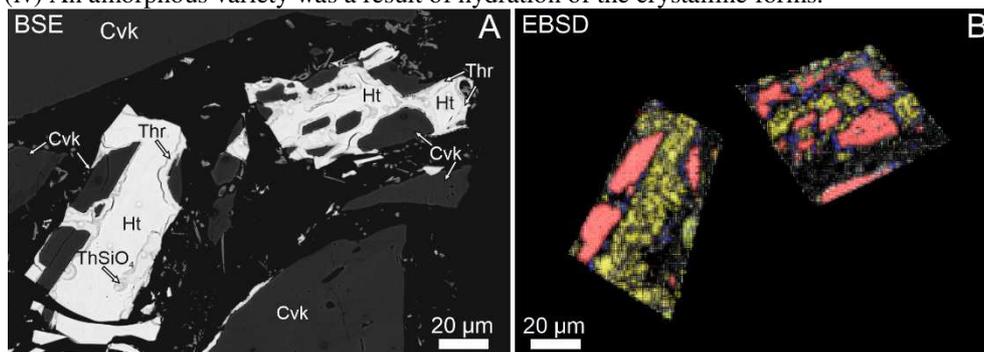


Fig. 1. A – BSE image showing huttonite (Ht) to be the dominant Th phase, with thin rims of thorite and amorphous ThSiO_4 . B – EBSD image of same crystals. Red is chevkinite-(Ce), yellow = huttonite, and blue = thorite.

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Environmental application of the magnetic nanoparticles decorated with zeolite synthesized from coal fly ash

Tomasz BAJDA¹, Santhana Krishna Kumar ALAGARSAMY¹, Eugeniusz ŚWISTUŃ¹, Maciej SOBCZYK¹

¹Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Krakow, al. A. Mickiewicza 30, 30-059 Krakow, Poland, e-mail: bajda@agh.edu.pl

Fly ash (FA), produced during coal combustion for energy making, and recognized as an industrial by-product, could lead to environmental health hazards. Subsequently, FA was found to have an exceptional adsorption performance for removing various toxic pollutants. The adsorption capacity of FA might be altered by introducing physical/chemical stimulation. Successively converting FA into zeolites recovers their disposal difficulties and transforms unwanted material into merchandisable products for various industrial applications. NaX-UP zeolite was successfully prepared from FA by molten hydrothermal treatment. The prepared NaX-UP zeolites exhibited a high mesoporous structure with a specific surface area of 104.6 m²/g and a pore volume of 0.13 cm³/g. The FA was converted into zeolites and then modified with amino propylimidazole (ionic liquid). The imidazole-based zeolites were used as templates for loading Fe₃O₄ nanoparticles (Fe₃O₄ NPs) and decorated on the surface of the zeolites. Polystyrene sulphonate (PSS), polyvinyl alcohol (PVA), and chitosan were also incorporated into the fabrication of magnetic film (Fe₃O₄ NPs@zeolite film) to produce a variety of functional groups. The fabricated magnetic films exhibited excellent functionality and durability in the adsorption of Cr(VI), Se(IV), Congo Red, and Rhodamine B (RhB). These contaminants are electrostatically bound to the magnetic films due to (i) their protonation with different functional groups from imidazole cationic groups (R-N⁺), (ii) amino groups from chitosan (-N, -NH and -NH₂), and (iii) hydroxyl groups from Fe-OH. The magnetic films are suitable for practical applications, achieving maximum removal performance over a wide pH range. According to the pseudo-second-order kinetic model, the magnetic films have fast adsorption kinetics compared to earlier literature evidence. The magnetic films' adsorption of Cr(VI), Se(IV), Congo red and RhB coincided well with the Langmuir adsorption isotherm, indicating a relatively prominent homogeneous adsorption process. The magnetic films have greater adsorption capacities for Cr(VI), Se(IV), Congo red, and RhB than reported in the literature. This magnetic membrane technology is a cost-effective platform for producing potable water for various uses, depending on the requirements. Moreover, this technology has high efficiency in practical applications in the near future to create sustainable clean water in commercial activities.

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Local or imported? The mineralogical study of casting molds from the metallurgical workshop in Grzybiany, S-W Poland

Wojciech BARTZ¹, Kamil NOWAK², Tomasz STOLARCZYK³, Justyna BARON⁴

¹University of Wrocław, Institute of Geological Sciences, pl. M. Borna 9, 50-204 Wrocław, Poland; e-mail: wojciech.bartz@uwr.edu.pl

²Nicolaus Copernicus University in Toruń, Institute of Archaeology, ul. Szosa Bydgoska 44/48, 87-100 Toruń, Poland, e-mail: kamil.nowak@umk.pl

³Museum of Copper in Legnica, ul. Partyzantów 3, 59-220 Legnica, Poland, e-mail: tomasz_stolarczyk@wp.pl

⁴University of Wrocław, Institute of Archaeology, ul. Szewska 48, 50-139 Wrocław, Poland; e-mail: justyna.baron@uwr.edu.pl

The prehistoric lost-wax ceramic molds are highly specialized tools, which demand proper material selection and specialized production. Although they are common finds across many prehistoric and early historic sites in central Europe, their production remains unclear. Hence, our research aimed to shed more light on this topic. All the analyzed artefacts come from the Late Bronze and Early Iron Age Lake settlement in Grzybiany, SW Poland (ca. 9/8th–5th c. BC). They have been characterized using combined use of optical polarizing microscopy, scanning electron microscopy, X-ray powder diffraction and thermal analysis. Our main goal was to describe the composition of the ceramic paste used in these refractory ceramics and identify the potential source of raw material. The second purpose was to determine whether or not the Early Iron Age community used the local raw material and how they prepared it for the pyrometallurgical process.

The analyses of the sampled material demonstrated that the molds were made from locally accessible raw material (the “Poznań clays”, Neogene), which was processed entirely differently than in other ceramic items (kitchenware) from the site. The raw material was rich in illite and smectite. Aplastic components were dominated by subordinate amounts of silt-sized grains (quartz). The paste was tempered with fine-grained quartz sand and an exceptional amount of organic material, i.e., remnants of straw or horse dung and plastic enough to form molds around the wax models. The molds were fired in well-controlled conditions (presumably kiln-firing), as indicated by the colour of the mold surfaces at relatively high temperatures (700-950°C). Through this sequence of operations, the Grzybiany community obtained high-quality products designed specifically for metallurgical purposes. The presence of lead (alloying additive) suggests that at least some molds were used in the casting process, most likely the casting of tin-lead bronze.

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Chemical composition of currently forming carbonate tufas in the Pieniny Klippen Belt area - preliminary results

Jakub BAZARNIK¹, Piotr LENIK¹, Grażyna STAŃCZAK¹

¹*Carpathian Branch, Polish Geological Institute – National Research Institute; Skrzatów 1, 31-560 Kraków, Poland; jakub.bazarnik@pgi.gov.pl; piotr.lenik@pgi.gov.pl; grazyna.stanczak@pgi.gov.pl*

Evidence of currently forming carbonate tufas has already been found in many places in the western part of the Polish Carpathian flysch – e.g., in the area of the Mszana Dolna tectonic window and the Podhale region (e.g., Wiśniowski, 1908; Halicki & Lilpop, 1932, Gruszczyński & Mastella, 1986). The existence of modern tufas was also found in the Pieniny Klippen Belt area. They are often associated with the presence of mineral water in this region. The origin of the mineral water is commonly connected with the locations of Neogene intrusive igneous rocks (e.g., Birkenmajer, 1956, Chowaniec et al., 2007) – based on the coincidence of spatial distribution of mineral water springs and andesites. The line of occurrence of andesite bodies are present in the Magura Nappe belonging to the Outer Carpathians along the border with the Pieniny Klippen Belt. The Pieniny Klippen Belt is built of rocks from the Jurassic to the Palaeogene and forms a narrow tectonic zone separating the Outer Carpathians from the Inner Carpathians. The Magura Nappe is built of flysch rocks (mainly sandstones and claystones) deposited from the Upper Cretaceous to the Neogene.

The highest mineral water trace element content was observed in a sample from the Maria mineral water spring in Krościenko nad Dunajcem. This is especially evident in the case of elements such as Sr, Te, Ba, Au, Mn, Cu, Ge, and Mo, which may provide a genetic link to magmatic intrusions. In the case of other tufas collected from small springs, much lower contents of individual elements were observed. However, the increased content of such elements as Sr and Ba is clearly visible. The content of REE in both groups was at the level of hundreds to tens of ppm.

The research is supported by the National Fund for Environmental Protection and Water Management project No. 22.2301.2001.00.1.

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Clay minerals in Permian (Upper Rotliegend) aeolian sandstones of SW Poland: Distribution and origin

Julita BIERNACKA¹

¹*Institute of Geology, Adam Mickiewicz University in Poznan, Krygowskiego 12, 61-680 Poznan, PL; e-mail: julbier@amu.edu.pl*

Permian aeolian sandstones, the primary focus of gas prospecting in SW Poland, are buried at depths ranging from approximately 1 to 4 km. Clay minerals are the predominant authigenic components of the sandstones, significantly influencing their reservoir properties. Additionally, clay minerals can serve as indicators of environmental conditions during diagenesis as they formed at various stages of sedimentary basin development, from subaerial settings to deep burial. A total of 180 sandstone samples were collected from 30 borehole cores coming from the Fore-Sudetic Monocline region. These samples were studied using various methods (polarising microscopy, XRD, SEM, microprobe, illite K-Ar dating) to identify patterns in the diversity and distribution of clay minerals in Permian aeolian sandstones.

Illite, chlorite, and kaolin minerals occur in varying proportions. Both aerial and depth variations in clay mineral types were observed. Porosity-conserving chlorite (sudoite, Mg-chlorite) is prevalent in the northern region of the Fore-Sudetic Monocline, to the north of the Wolsztyn High, a buried regional hill composed of volcanic and metamorphic rocks. Conversely, kaolin minerals (kaolinite, dickite) dominate in the shallowly buried areas to the south and southwest of the Wolsztyn High. Illite (a mixture of several illitic minerals) is widespread, occasionally being the sole clay mineral present in a sandstone. It is concluded that clay minerals formed in pulses at the expense of primary sandstone components/early diagenetic phases. Their crystallization was triggered by fluid flows of varying chemistry along fault zones.



Crust-mantle interaction at near ultra-high pressure conditions recorded by a melt inclusions-bearing eclogite lens in Pfaffenberg, Bohemian Massif

Alessia BORGHINI¹, Silvio FERRERO^{2,3}, Patrick O'BRIEN⁴, Bernd WUNDER⁵, Peter TOLLAN⁶, Jarosław MAJKA^{1,7}, Rico FUCHS⁴, Kerstin GRESKY⁴

¹Department of Mineralogy, Petrography and Geochemistry, AGH University in Krakow, 30-059 Krakow, Poland; borghini@agh.edu.pl

²Dipartimento di Scienze Chimiche e Geologiche, University of Cagliari, 09042 Monserrato, Italy; silvio.ferrero@unica.it

³Museum für Naturkunde (MfN), Leibniz-Institut für Evolutions- und Biodiversitätsforschung, 10115 Berlin, Germany

⁴Institute of Geoscience, University of Potsdam, 14476 Potsdam, Germany; obrien@uni-potsdam.de

⁵Helmholtz-Zentrum Potsdam, Deutsches GeoForschungsZentrum (GFZ), D-14473 Potsdam, Germany; wunder@gfz-potsdam.de

⁶Eidgenössische Technische Hochschule, ETH, 8092 Zürich, Switzerland; peter.tollan@gubelingemlab.com

⁷Department of Earth Sciences, Uppsala University, 752-36 Uppsala, Sweden; jmajka@agh.edu.pl

The eclogite lens in the peridotite body of Pfaffenberg, Granulitgebirge (Bohemian Massif, Germany), represents a nice example of crust-mantle interaction during the subduction of the crust at mantle depth, near ultra-high pressure conditions. The eclogite garnets contain in fact primary granitic melt inclusions with a composition akin to the continental crust. The inclusions are polycrystalline, up to 30 μm in diameter and they were investigated with microRaman spectroscopy and EDS mapping in order to determine the main mineral assemblage. They contain: phlogopite/biotite, kumdykolite, quartz/rare cristobalite, a phase with a main Raman peak at 412 cm^{-1} , a phase with a main Raman peak at 430 cm^{-1} , osumilite and plagioclase and a minor amount of white mica, K-feldspar, amphibole and kokchetavite. Interestingly they locally contain, beside accessory phases (graphite, apatite and rutile), a fluid phase rich in CO_2 , CH_4 and N_2 . The melt chemical signature is similar to melts produced by the partial melting of metasediments part of the continental crust in fact the melt is granitic, peraluminous, hydrous and rich in Cl, F, Cs, Pb, Rb, Th, U, Li and B. Hence, the melt described above most likely originated from the continental crust during the subduction at mantle depth and interacted with the mantle producing the Pfaffenberg eclogite lens. Moreover, the enrichment in Cl and F of the melt suggests a possible involvement of brines during partial melting. This crustal melt is now trapped in a mantle body and therefore it can be regarded as a metasomatizing agent responsible for the interaction and transfer of elements between the crust and the mantle. The similarities between the melt trapped in Pfaffenberg eclogite with other melts trapped in other eclogites of the Granulitgebirge and the Erzgebirge and with the trace elements signatures of metasomatized mantle rocks in different localities of the Bohemian Massif suggest that lithospheric mantle contamination by the continental crust was widespread during the Variscan orogeny.



Multi-stage retrogression of garnet peridotites recorded by amphibole – Lejarfjället Retrogressed Garnet Peridotite, Scandinavian Caledonides case study

Daniel BUCZKO^{1,2}, Jarosław MAJKA^{2,3}, Magdalena MATUSIAK-MAŁEK¹, Sonja AULBACH⁴

¹*Institute of Geological Sciences, University of Wrocław, pl. Maxa Borna 9, 50-204 Wrocław, Poland; daniel.buczko@uwr.edu.pl*

²*Department of Earth Sciences, Uppsala University, Villavägen 16, 752 36 Uppsala, Sweden*

³*Faculty of Geology, Geophysics and Environ. Protection, AGH UST, al. Mickiewicza 30, 30-059 Kraków, Poland*

⁴*Institute of Geosciences, Goethe University, Altenhöferallee 1, 60438 Frankfurt am Main, Germany*

Exhumed garnet (Grt) peridotite bodies provide important insights into processes operating in the deep lithosphere during orogenesis. In contrast to the well-known parautochthonous Western Gneiss Region, the occurrences of Grt-facies peridotites in the allochthonous nappes of the Scandinavian Caledonides are scarce. This study focuses on newly discovered amphibole (Amph)-bearing, retrogressed Grt peridotites from Lejarfjället, Seve Nappe Complex, Sweden. While the general mechanisms of exhumation of Grt peridotite bodies are well understood, their secondary mineralogy can provide new, detailed information on the exhumation path and attendant metasomatic processes.

The Lejarfjället body is formed of foliated, kelyphite-bearing dunites with Amph present in different textural positions: type 1) as patches of zoned Amph, type 2) as “healing” of the cracks after Grt brittle deformation, type 3) as a major constituent of post-garnet kelyphites (+Opx, Chl, Al-Spl), type 4) as pressure shadows around kelyphites, and type 5) as single Amph crystals dispersed in the dunite. Preliminary studies show that each Amph textural type records distinctive characteristics, best expressed by a change in total alkali and Ca content (parameter A: $\text{Na}+\text{K}+2\text{Ca}$ [apfu]; Hawthorne et al., 2012). Variations in A and textural evidence allow reconstruction of Amph formation conditions and relations between types. Type 1 and 2 Amph (Mg-hornblende; $A=0.43-0.50$) have high alkali content, tentatively ascribed to fluid-flux at Grt-facies conditions in the supra-subduction zone in the continental(-like?) lithospheric mantle, simultaneous with brittle deformation of Grt. Type 3 records lower A values (0.18-0.37) and gradual transition from hornblende to tremolite, typical for spinel-facies conditions (consistent with exhumation). Types 4, 5 and the outermost zones observed in type 1 are represented by tremolite with $A<0.20$, representing Amph forming in shallow, sub-oceanic lithospheric mantle. Collectively, the secondary mineralogy of the Lejarfjället body records retrogression (exhumation) from Grt facies down to shallow, sub-oceanic spinel-facies mantle conditions. Trace element and isotopic systematics of different textural types of Amph will be further investigated to tackle details of the origin of each generation and the implications for the tectonic evolution of the body and hosting nappe. This study is a part of NCN Poland grant no. 2019/35/N/ST10/00519.

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Preliminary results on the petrology of mica schists from the AMINv K-1 borehole in Kobierzyce (Lower Silesia, SW Poland)

Kamil BULCEWICZ^{1,2}, Rafał SIKORA², Jacek SZCZEPAŃSKI¹, Piotr LENIK², Grzegorz ZIELIŃSKI²

¹*Institute of Geological Sciences, University of Wrocław, Pl. Maksa Borna 9, Wrocław 50-204, Poland, e-mail: kamil.bulcewicz@uwr.edu.pl*

²*Polish Geological Institute – Polish National Institute, ul. Rakowiecka 4, Warszawa 00-975, Poland*

The AMINv K-1 borehole has been located near Kobierzyce, approx. 20 km SW of Wrocław. The crystalline rocks has been at depth interval 100.00 - 434.80 m below the terrain surface (b.t.s.). The obtained material gives a unique insight into the geology of the Variscan basement in the area where the surface exposures are scarce. In our study, we have taken a closer look at the mica schists from this borehole in order to reveal their petrological evolution and to correlate their tectonic position.

Three samples of garnet-bearing mica schists have been analyzed to date, all from the interval between 250 and 300 m b.t.s. In the most carefully studied sample, from a depth of 256.60 m b.t.s., inquiry on SEM and EMPA studies have revealed the following observations: 1) garnet preserves a zoning indicative of progressive metamorphism, with Mn enrichment in the core; 2) numerous inclusions in garnet, including, e.g., chloritoid, kyanite, staurolite, margarite, biotite, rutile; 3) white mica with diverse chemical composition, including phengitic white mica; 4) peculiar overgrowths of Ti-bearing phases: rutile, ilmenite and titanite are present in both garnet and matrix. U–Th–total Pb chemical dating of 44 analyzed monazite grains yields an age of 342 ± 10 Ma.

Our preliminary results show that the mica schists from the AMINv K-1 borehole have a complex metamorphic history. We interpret the mineral assemblage consisting of chloritoid, kyanite, rutile and phengitic white mica as a well-preserved relic of the HP-LT metamorphism. On the other hand, the mineral assemblage represented by staurolite, muscovite, margarite, biotite, titanite and ilmenite most likely crystallized later, at much lower P and higher temperatures. Petrological characteristics of the studied rocks clearly match those of their counterparts in the Kamieniec Metamorphic Belt (KMB; Szczepański et al., 2022), indicating that the KMB may extend further north. Certainly, this requires further intensive research. However, it may have an impact on our understanding of the geometry of this part of the Variscan belt in Europe.

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Metasomatic alterations of xenotime and their geochronological implications (Ås pegmatite, Evje and Hornnes, S Norway)

Bartosz BUDZYŃ¹, Richard WIRTH², Jiří SLÁMA³, Gabriela A. KOZUB-BUDZYŃ⁴,
Patrik KONEČNÝ⁵, Grzegorz RZEPA⁴, Anja SCHREIBER²

¹Institute of Geological Sciences, Polish Academy of Sciences, Kraków, Poland; e-mail: nbudzyn@cyf-kr.edu.pl

²GeoForschungsZentrum Potsdam (GFZ), Section 3.5 Interface Geochemistry, Potsdam, Germany

³The Czech Academy of Sciences, Institute of Geology, Rozvojová 269, Prague 6, 16500, Czech Republic

⁴AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Kraków, Poland

⁵Dionýz Štúr State Geological Institute, Bratislava, Slovakia

Fluid-mediated alterations and their geochronological implications were studied in altered crystals of pegmatitic xenotime from Ås II feldspar quarry (Evje, S Norway) using microscale to nanoscale analytical methods. The “unaltered” domains yielded LA-ICPMS data with a reverse discordance (-10.5 to -2.6%) constraining $^{208}\text{Pb}/^{232}\text{Th}$ mean age 988.4 ± 5.9 Ma (all data) and $^{207}\text{Pb}/^{235}\text{U}$ mean age 979.1 ± 5.0 Ma (data filtered to below $\pm 5\%$ discordance). The altered domains yielded highly scattered $^{208}\text{Pb}/^{232}\text{Th}$ dates from 200 ± 14 to 2135 ± 120 Ma, whereas discordant U-Pb data constrained upper intercept age 909 ± 16 Ma. TEM investigations revealed submicron-scale alterations in the “unaltered” domains. Alterations progressed mostly along parallel submicron- to nanoscale fractures, including segregation of U-, Th- and Si-enriched material in ca. 15–20 nm thick and up to several hundred nm-long dislocations. The other fractures are partially open grain boundaries that are empty or filled with secondary inclusions of (Th, U)-silicates, UO_2 or coffinite. In contrast to “unaltered” domains with moderate degree of radiation damage, altered xenotime is well crystalline in TEM imaging and electron diffraction patterns. The (Th, U)-depleted xenotime domains contain numerous microinclusions of (Th, U)-silicate, UO_2 and minor galena. Th- and U-bearing phases are nanocrystalline or amorphous, and contain nano-inclusions of Pb_3O_4 or metallic Pb. Also, <100 nm-sized inclusions of (Pb,Sb)-oxide formed in altered xenotime. To summarize, this study sheds new light on our understanding of coupled dissolution-precipitation processes that affect xenotime. The presence of nano-inclusions of Pb_3O_4 , (Pb, Sb)-oxide and metallic Pb, as well as removal of U from xenotime structure may strongly contribute to geochronological data and explain reverse discordance and disturbance towards older ages. Complete results of this study are available in Budzyń et al. (2023a, b). *Acknowledgements:* This work was supported by the NCN grant no. 2017/27/B/ST10/00813.

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Lunar ilmenite as a host of helium: a new source for clean energy

Agnieszka BYLINA¹, Tomasz KRZYKAWSKI¹, Hakim RABIA¹, Kamila BANASIK¹, Jakub CIAŻELA², Krzysztof SZOPA¹

¹Faculty of Natural Sciences, University of Silesia in Katowice, Będzińska 60, 41-200 Sosnowiec, Poland; e-mail: abylina@us.edu.pl

²Institute of Geological Sciences, Polish Academy of Sciences, Podwale 75, 50-449 Wrocław, Poland

Ilmenite (FeTiO_3), like most minerals, occurs on the Earth and the Moon. However, the lunar regolith containing ilmenite is subjected to space weathering, including bombarding by solar wind, which changes its structure and chemistry. Due to its crystallographic structure, ilmenite captures more solar wind elements, including helium, than other minerals (e.g., Fa and Jin, 2007; Eberhart et al., 1970). The isotope of helium, helium-3, is attractive as a clean energy source for future thermonuclear fusion power plants. However, to transport helium-3 from the Moon to Earth, methods of helium extraction from lunar ilmenite need to be developed, which is the long-term aim of this project.

Despite the need to implement helium into the Earth ilmenite, terrestrial samples are easier to work with than scarce lunar material. Finding optimal terrestrial samples resembling the lunar material is necessary for high-quality results. Five samples have been selected for the experiments: (1) the Skalna Brama pegmatite, Poland; (2) Jezioro Okrągłe 2 (borehole), Poland; (3) ferrogabbro from the Ślęza Massif, Poland; (4) ilmenite crystals, Zagi mountain, Pakistan, and (5) lunar regolith simulant LMS-1. After separating ilmenite grains, we performed a set of chemical (SEM-EDS and EMPA) and mineralogical (Raman spectroscopy and XRD) analyses to characterize these samples.

We revealed chemical differences, especially the degree of Mn substitution in the structure. Due to the related structural changes, such cation substitutions affect how efficiently helium is released from ilmenite. Our data will be compared to sample data reported from Apollo missions and the most similar samples selected for future steps. These include experimental helium implantation using an ion implanter and an experimental helium extraction through sample heating.

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Lunar ore geology and feasibility of ore mineral detection using MIRORES far-IR spectrometer

Jakub CIAŻELA¹, Jarosław BAKAŁA², Mirosław KOWALIŃSKI², Marta CIAŻELA¹, Weronika PATALAS¹, Natalia ZALEWSKA², Łukasz KRUSZEWSKI¹, Albert WIECZYSTY³, and MIRORES team³

¹Institute of Geological Sciences, Polish Academy of Sciences, Warsaw, Poland; j.ciazela@twarda.pan.pl

²Space Research Centre, Polish Academy of Sciences, Warsaw, Poland;

³Department of Geology, University of Warsaw, Warsaw, Poland;;

⁴A team involving scientists from ¹⁻³ as well as European Science Foundation, SKA Polska, Wrocław University of Technology, Adam Mickiewicz University in Poznań, Nicolaus Copernicus University in Toruń and others.

Lunar sulfides and oxides are a significant source of noble and base metals and will be vital for future human colonies' self-sustainability. Sulfide detection (pyrite and troilite) applies to many technological fields and use cases, for example, as a raw material source (available in situ on the Lunar surface) for new solar panel production methods. Ilmenite is the primary iron and titanium ore on the Moon and can provide helium-3 for nuclear fusion (Bylina et al., this issue) and oxygen for rocket fuel. The most important ore minerals have prominent absorption peaks in a narrow far-infrared (FIR) wavelength range of 20–40 μm , much stronger than the spectral features of other common minerals, including significant silicates, sulfates, and carbonates. Our simulations based on both the linear mixing and the single-scattering albedo/Hapke modeling of ore minerals with the silicates mentioned above indicated that areas containing at least 10–20 vol.% pyrite or ilmenite could be detected from the orbit in the FIR range. MIRORES, Multiplanetary far-IR ORE Spectrometer, proposed here, would operate with a resolution down to <5 m, enabling the detection of areas covered by 2–3 m^2 of pyrite (or ilmenite) on a surface of $\sim 17 \text{ m}^2$ from an altitude of 50 km, creating possibilities for detecting large and local smaller orebodies along with their stockworks. The use of the Cassegrain optical system achieves this capability. MIRORES will measure radiation in eight narrow bands (0.3 μm in width) that can include up to five bands centered on the ore mineral absorption bands, for example, 24.3, 24.9, 27.6, 34.2, and 38.8 μm for pyrite, marcasite, chalcopyrite, ilmenite, and troilite, respectively. The instrument size is 32 x 32 x 42 cm, and the mass is <10 kg, which fits the standard microsatellite requirements. The instrument was selected as the priority payload for the Polish Lunar Mission (Ciazela et al. 2023) and should be integrated into a satellite launched to the Moon by the Polish Space Agency between 2028 and 2029. Prototype construction for Earth-based tests started in 2021, and its laboratory testing began in 2022. The Earth test of the prototype from the drone will start in the *Polski lupek serycytowy* open-pitmine in Orłowice this Autumn (Wieczysty et al., this issue).

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Conditions for larger SMS deposits along slow-spread mid-ocean ridges: implications for the Polish contract area at the MAR

Jakub CIAŻELA¹, Agata KOZŁOWSKA-ROMAN², Michał TOMCZAK², Eman ELSHERIF¹, Piotr WOJTULEK³

¹*Institute of Geological Sciences, Polish Academy of Sciences, ul. Podwale 75, 50-449 Wrocław, Poland; e-mail: j.ciazela@twarda.pan.pl*

²*Polish Geological Institute – National Research Institute, ul. Rakowiecka 4, 00-975 Warsaw, Poland*

³*Institute of Geological Sciences, University of Wrocław, M. Borna 9, 50-204 Wrocław*

Slow-spreading ridges host much larger seafloor massive sulfide (SMS) deposits than fast-spreading ridges. The highest-tonnage SMS deposits are hosted in plutonic rocks from oceanic core complexes (OCC), which expose the lower crust and mantle uplifted to the seafloor along detachment faults at slow-spreading ridges. All seven contractors of the International Seabed Authority for sulfide exploration, including Poland, operate on slow-to intermediate-spreading ridge segments with OCCs.

Slow-spread oceanic crust is thinner and often more heterogeneous than fast-spread oceanic crust, which may affect sulfide differentiation during magmatic processes and metal transport between the mantle and the ocean floor. In large gabbroic bodies of the Atlantis Bank OCC (57°E, Southwest Indian Ridge), sulfides differentiate mainly through fractional crystallization. Sulfides fractionate early and accumulate at the lower part of gabbroic bodies. In the Kane Megamullion OCC (23°N, Mid-Atlantic Ridge) with low magma supply, sulfides typically differentiate through melt-mantle reaction, which leads to high sulfide enrichment at the contacts of gabbro and peridotite, often shallow under the ocean floor. This enrichment in melt-mantle reaction could explain why most large SMSs occur along slow-spread oceanic lithosphere with relatively low magma supply.

The study aims to understand the migration of metals from the mantle to the seafloor and the formation of seafloor massive sulfide deposits along the slow-spreading ridges based on the Central Sudetic Ophiolite (CSO). CSO is a well-preserved slow-spreading ridge-related ophiolite with a lithosphere architecture similar to the Polish sulfide exploration area along the 26–33°N Mid-Atlantic Ridge (MAR) (Elsharif et al.; Wojtulek et al.; Woźniak et al., this issue). Our results will aid in searching for SMSs within the Polish contracted area along the MAR (26–33°N), where a low magma supply shapes the lithosphere structure (Kozłowska-Roman et al., this issue). The first Polish expedition in the Summer of 2022 performed acoustic imaging, including multi-beam bathymetry and backscatter supported with sub-bottom profiling to characterize three known OCCs (Atlantis Massif, the Southern OCC, Dante's Domes) and two new OCCs in the area. These sites' precise bathymetry (25 cm/pixel) and geophysical features are being investigated using Autonomous Underwater Vehicles this year, followed by sampling with Remotely Operated Vehicles next year.

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Ore prospecting using satellite data in planetary analogs

Marta CIAŻELA¹, Jakub CIAŻELA¹

¹Institute of Geological Sciences, Polish Academy of Sciences, Podwale 75, 50-449 Wrocław; e-mail: marta.ciazela@twarda.pan.pl

Large-scale exploration of ore deposits in the world using satellite data is becoming more and more available thanks to the high-quality remote sensing data sets. The presented research aimed to find ore minerals (sulfides and oxides) and their weathering products such as sulfates in two open pit mine areas: Rio Tinto in Andalusia, Spain, and Sierra Gorda in Atacama, Chile. We have been using satellite data (Sentinel-2, PRISMA, Landsat, ASTER) to find detection thresholds for selected minerals. The research were carried out using: 1) RGB bands composites, 2) spectral coefficients (e.g., ASTER 4/6 for hydrothermal sites), 3) logical operators (e.g., ASTER bands: $(4 + 6) / 5$ indicates alunite and kaolinite rich zones), 4) minerals indices, 5) Principal Component Analysis. Besides remote analysis, we have validated the results with geological mapping *in situ*. During one week stays in more preliminary research Rio Tinto (17-27.03.2022) and more advanced research in the Sierra Gorda mine (14-18 August 2023), we performed geological mapping on a selected study area (of approximately 50 x 50 m) with a large number of ore mineral outcrops in a regular grid of points (separated by 3 m) to estimate macroscopically the content of the desired minerals. At each point, we have estimated the contents of critical minerals in five random samples. The essential minerals for this study were: sulfides such as pyrite, chalcocite, chalcopyrite, sphalerite, and galena, oxides such as hematite or magnetite, as well as other hydrothermal minerals such as goethite, jarosite, alunite, copiapite, chrysocolla, or atacamite. In addition, we collected samples of the investigated rocks to analyze them further with X-ray diffractometry. The preliminary results will be presented at the conference. Sierra Gorda and Rio Tinto has been chosen for this investigation due to the exposures of both ore minerals and other hydrothermal minerals used as a proxy for ore prospecting, arid climate, lack of vegetation, and the availability of a long series of satellite images. Besides ore prospecting on Earth, this research will facilitate the upcoming prospecting of ore minerals on the Moon and Mars in the following years, including that planned in the Polish Lunar Mission (2028-2032) (see also Wieczysty et al., 2023, this issue).



Ophiolite-hosted carbonate mineralization in the Braszowice – Brzeźnica Massif: new LA-ICP-MS data and initial concepts

Błażej CIEŚLIK¹, Anna PIETRANIK¹, Jakub KIERCZAK¹, Alicja ŁACIŃSKA², Simon CHENERY²

¹*Institute of Geological Sciences, University of Wrocław, Pl. Maksa Borna 9, 50-204 Wrocław, Poland; blazej.cieslik2@uwr.edu.pl*

²*Environmental Science Center, British Geological Survey, Keyworth, Nottingham NG125GG, UK*

In the Central-Sudetic Ophiolite (CSO), carbonate mineralization appears mostly as extensive magnesite veins and vein-like structures within peridotites and serpentinites. Since the early 1900s, there has been a contentious discussion regarding the origin of magnesite mineralization in CSO, which continued until the very first carbon and oxygen isotope analyses were performed (see Jędrysek & Sachanbiński, 1994). The obtained results have suggested that magnesite veins were formed by low-temperature hydrolysis of ultramafic rocks, affected by groundwaters of meteoric origin saturated with biogenic CO₂.

Second-largest magnesite deposit in CSO, and the only one in operation, is located in the Braszowice – Brzeźnica Massif (BBM). Combining SEM-BSE observations with EMPA analysis unveiled the intricate, multi-phase composition of carbonate veins, especially in samples from the lowermost parts of the pit. The ophicarbonates examined in the study exhibit a very high modal abundance of cryptocrystalline magnesite. The second most common phase is dolomite, typically manifesting as irregular intergrowths with magnesite. Pore-filling clusters of saddle dolomite were found in magnesite-rich veins, but also in calcite-bearing veins. Calcite, in the form of euhedral crystals, occurs in veins sampled from the mine pit floor. Trace elements of carbonates and U-Pb isotopic ages of micritic calcite were acquired by LA-ICP-MS. White and rusty brown magnesites, calcite, and dolomite exhibit distinct variations in the concentrations of Ca, Sr, Ba, Mn, Ni, Co, and Fe. A single fragment of the micritic calcite yielded an isochron age of 15 ± 20 Ma (2σ), which may be attributed to Cenozoic tropical weathering events in a very general sense.

Initial textural and geochemical data of carbonate mineralization in BBM suggests that ophicarbonates formation is not solely related to the circulation of CO₂-rich meteoric waters. It is rather consistent with carbonation by both hydrothermal and supergene fluids, a similar origin to that proposed by Kowarz (1965). However, additional isotope analyses are required to fully confirm this hypothesis.

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Traces of Alpine convergence in the External Western Carpathians based on detrital rutile U-Pb geochronology

Ludwik DE DOLIWA ZIELIŃSKI¹, Jakub BAZARNIK², Ellen KOOIJMAN³, Karolina KOŚMIŃSKA¹, Tomáš POTOČNÝ¹, Stanisław MAZUR⁴, Jarosław MAJKA^{1,5}

¹Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Kraków, Poland lzielins@agh.edu.pl, kkosm@agh.edu.pl, pococny@agh.edu.pl

²Polish Geological Institute – National Research Institute, Kraków, Poland Jakub.Bazarnik@pgi.gov.pl

³Department of Geosciences, Swedish Museum of Natural History, Stockholm, Sweden Ellen.Kooijman@nrm.se

⁴Institute of Geological Sciences, Polish Academy of Sciences, Kraków, Poland ndmazur@cyf-kr.edu.pl

⁵Department of Earth Sciences, Uppsala University, Uppsala, Sweden jaroslaw.majka@geo.uu.se

In order to better understand the closure of the Alpine Tethys Ocean in the Western Carpathians, U-Pb geochronology was applied to detrital rutile of the Magura Superunit. Ten medium-sized sandstone samples were collected across the Bystrica and Krynica units. Approximately 200 rutile grains were separated from each sandstone and half of them were selected for further analyses. The age and appearance (shape, inclusions, zoning etc.) of the dated rutile show significant variations, suggesting derivation from various sources. The most prominent age peaks represent the Variscan (c. 400-280 Ma) and Alpine (c. 160-90 Ma) tectonic events which are well-pronounced in all but the oldest dated sample. It is noteworthy that four distinct Alpine maxima were detected in the rutile data set. The two most prominent peaks of 137-126 Ma and 115-105 Ma are found in majority of the samples. In two sandstone samples, deposited between the Eocene – Oligocene and the Late Cretaceous – Palaeocene, the youngest peak of 94-90 Ma appears. Another peak of 193-184 Ma is also present in these two samples, as well as in another sandstone deposited between the Palaeocene and Eocene. In addition, majority of the dated sandstones show some Proterozoic ages (approx. 1770 Ma, 1200 Ma, 680 Ma and 600 Ma). Since metamorphic rutile requires relatively high pressure to crystallize, its formation in the course of an orogeny is possible in a subduction setting. Tentatively, we propose that recognizable events include the Jurassic subduction of the Meliata Ocean (~180-155 Ma), and the Cretaceous thrust stacking and exhumation of the Veporic and Gemeric domains (140-90 Ma). The Zr content of the dated rutile formed during the Alpine orogeny was measured. The Zr content varies between 37-11000 ppm, but 96% of the analysed grains varies in between 37-400 ppm. The Zr in rutile thermometer was used to calculate the forming metamorphic conditions at 450-650 °C and >7.5 kbar. This data set corroborates formation of the Alpine rutile under relatively high pressure and rather low to moderate pressure/temperature gradient, i.e. typical of subduction-related tectonic environments. In a broader sense, we claim that synorogenic deposits of the Magura Superunit contain detritus from the formerly subducted, exhumed and imbricated oceanic and continental crustal domains at the southern margin of the Alcapa microcontinent. Interestingly, the abundance of Alpine rutile in all but the oldest dated sandstone suggests no physical barrier for supply of detrital material derived from the southern and central Alcapa to a sedimentary basin developed north of the alleged Oravic (Czorsztyn) continental sliver within the Alpine Tethys. This research is funded by the National Science Centre, Poland, project no. 2021/43/B/ST10/02312.



New high-pressure phase of CaSiO_3 wollastonite with penta-coordinated silicon

Przemysław DERA^{1,2}, Robert RAPP¹, Sasithorn CHORNKRATHOK¹, Dongzhou ZHANG¹, Vitali B. PRAKAPENKA³, Krzysztof WOŹNIAK²

¹Hawaii Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, 1680 East West Road, POST Bldg, Office 819E, Honolulu, Hawaii 96822; pdera@hawaii.edu

²University of Warsaw, Chemistry Department, Pasteura 1, 02093 Warszawa, Poland; kwozniak@chem.uw.edu.pl

³APS, Argonne National Laboratory, 9700 South Cass Avenue, Lemont, IL 60439, USA,

Introduction CaSiO_3 is one of the most important chemical compounds in the Earth's lower mantle, with the Ca-silicate perovskite accounting for almost 10% of the rocks by volume in the lower mantle.[1] At lower pressures and shallower depths, other, less dense wollastonite pyroxenoid polymorphs with CaSiO_3 composition are more thermodynamically stable. In this study we examined the behavior of wollastonite-1A under hydrostatic compression and ambient temperature up to a maximum pressure of 35 GPa, using synchrotron single-crystal X-ray diffraction.

Results The sample underwent a series of two displacive phase transitions that took place at approximately 9 and 24 GPa, and were accompanied by slight but discontinuous increases in density. Crystal structures of the two new triclinic high-pressure polymorphs have been solved from in situ single crystal data. The highest pressure phase, Hb shows a change in coordination number of silicon from ^{IV}Si to a mixture of ^{IV}Si and ^VSi. During these two phase changes, wollastonite retains its triclinic symmetry, though the inversion centre is lost in phase Ha. The unit cell of wollastonite undergoes two consecutive doublings at the two phase transitions, first along the (100) direction, then also in the (010) direction. Unlike the phase transitions reported on cold compression of both CaGeO_3 and MgSiO_3 in which the corrugation period increased along the tetrahedral chains, the 1A – Hb transition in CaSiO_3 wollastonite preserves the 3-polyhedra repeat motif.

Conclusions The two new metastable polymorphs constitute intermediate steps for densification towards denser, fully octahedral structure. In the pyroxene inosilicates, similar sequences of displacive phase transitions have been found to lead to intermediate phases with mixed 4 and 5, and 4 and 6 coordinated Si, gradually transforming the tetrahedral chain structure towards ilmentite-type high pressure octahedral polymorphs. Penta-coordinated silicon side has a trigonal bipyramid geometry, also found in metastable high-pressure gamma polymorph of diopside, $\text{CaMgSi}_2\text{O}_6$.

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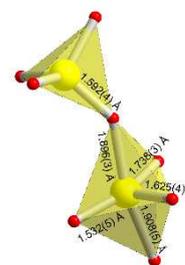


Fig. 1. In the Hb phase of CaSiO_3 one of the Si atoms assumes a rare intermediate 5-coordinated trigonal bipyramid geometry.



Lead isotopic composition of the oxidized materials from the North Sudetic Basin, Poland and its implications for metal-provenance and environmental research

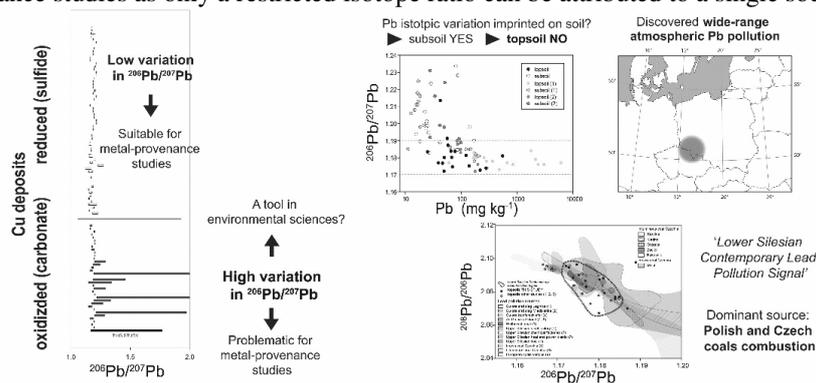
Katarzyna DERKOWSKA^{1,2}, Anna PIETRANIK¹, Jakub KIERCZAK¹, Paweł DERKOWSKI², Vojtěch ETTLER³, Martin MIHALJEVIČ³

¹ Institute of Geological Sciences, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław, Poland; katarzyna.derkowska@uwr.edu.pl

² Polish Geological Institute - National Research Institute, Poland, ul. Rakowiecka 4, 00-975 Warszawa, Poland;

³ Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Albertov 6, 128 00 Prague, Czechia

Lead isotopic compositions of oxidized Cu ores, host rocks, slags, and soils associated with the Zechstein Ca1 formation were analyzed for this study. Results presented surprisingly diverse array of Pb isotope ratios, particularly when juxtaposed with prior studies on Cu ores and related materials from Poland. Specifically, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio has exhibited a range from 1.094 to 2.092 for ores and from 1.151 to 1.240 for slags. The variation is related to the process of the oxidized ore formation (Pb sourced from U-rich surrounding rocks) and translates to significant differences in Pb isotope records between oxidized and sulfide ores. Furthermore, analyzed soils have displayed considerably fluctuating range of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios within the lower horizons (1.184-1.234). In contrast, topsoil Pb isotope ratios are typical for a whole Lower Silesia region (approx. 1.170-1.190 $^{206}\text{Pb}/^{207}\text{Pb}$). This observation implies the predominance of contemporary atmospheric lead contributions within the surface soil environment. We identify this phenomenon as *Lower Silesian Contemporary Pollution Signal*, attributing its origin to coal combustion processes. Consequently, we present that strong Pb isotopic variation affects both environmental and provenance studies as only a restricted isotope ratio can be attributed to a single source.



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Massive Cu mineralization from Lublin-Sierszowice copper district - new data on the mineralogy and geochemistry of the veins

Katarzyna DERKOWSKA^{1,2}, Piotr WOJTULEK¹, Jakub KIERCZAK¹, Liliana AUGUSTYNIAK¹

¹ Institute of Geological Sciences, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław, Poland; katarzyna.derkowska@uwr.edu.pl

² Polish Geological Institute - National Research Institute Poland, ul. Rakowiecka 4, 00-975 Warszawa, Poland; katarzyna.derkowska@pgi.gov.pl

The Fore-Sudetic Monocline hosts one of the world's premier sediment-hosted copper deposits associated with the Kupferschiefer formation. The formation spreads from southwestern Poland to central Germany, forming one of the largest ore bodies in the world. Among the various mineralization events that have occurred during the development of the deposit, the formation of massive mineralized veins is believed to have taken place during one of the latest stages, specifically in the Jurassic era (Pieczonka et al., 2010) and the aim of our study is to add new data to identify details of their origins.

The copper deposit in the Lublin-Sierszowice district primarily comprises dispersed mineralization occurring in successive layers of sandstone, black shale, and dolomite. The occurrence of massive mineralization within the Kupferschiefer has been rarely documented (Król and Sawłowicz 2017). The vein examined in this study extends over a distance of 240 meters, with variable widths ranging from 6 to 38 meters. Multiple sampling locations were chosen to assess mineralogical and geochemical variations within this vein. Additionally, two profiles displaying greater mineralization thickness were meticulously studied to compare vertical disparities. The mineral composition of the massive mineralization is intricate and exhibits variations in different regions. In general, three distinct mineralogical types have been identified: pyrite-chalcopyrite, galena, and chalcocite veins, with minor occurrences of marcasite, tennantite, sphalerite and other phases. The minerals often exhibit overgrowths and can be found in nest-like aggregates or spherulitic clusters, occasionally displaying mineral-related zonation. Parallel to the mineralogical variations, differences in geochemistry have been observed among different mineralogical types of veins manifesting as variations in trace element concentrations, especially Co, Zn, Cr, Mo, As, Hg, and Re. Within the minerals, strong variations in Pb, Cd, Ag, As, Sn, Zn, Ni and In are noted, depending on the mineral.

The study is funded by the National Science Centre grant to KD (2019/35/N/ST10/04524).

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Phosphate minerals in the Baszkówka meteorite

Paweł DERKOWSKI¹

¹Polish Geological Institute – NRI, Address: Rakowiecka 4 00-975 Warsaw; e-mail: pder@pgi.gov.pl

The Baszkówka meteorite was found on August 25, 1994, ca. 20 km south of Warsaw, shortly after its fall which was observed by multiple witnesses. Its petrology and chemistry was thoroughly studied (e.g., Stępniewski et al 1996, Przylibski et al 2003) and it was classified as a L5 chondrite, with a unusually high porosity. Textural features indicate that the Baszkówka meteorite was formed between 1 and 2 M years after the origin of solar system, as a result of a collision of two bigger planetoids (Przylibski et al 2003).

We analysed multiple polished cross-sections in search of phosphate minerals and high-alumina spinels. Two phosphate phases were found – (chlor)apatite $\text{Ca}_5(\text{PO}_4)_3(\text{Cl}/\text{F})$ and merrillite $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$. Apatite was found both inside chondrules and as idiomorphic crystals between them. Single-point analyses by EMPA demonstrated that apatite contains 0,16% to 1,56% (average of 0,61%) F and 1,41 to 5,01% (average of 2,72%) Cl. Both F and Cl contents vary strongly from grain to grain. Merrillite composition was fairly constant, but it was found only within the chondrules.

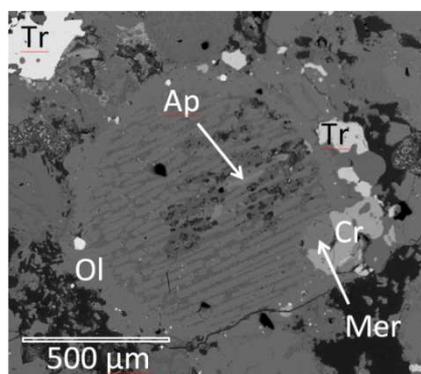


Fig. 1. Barred chondrule from Baszkówka meteorite, containing two different phosphate minerals (Apatite Ap and Merrillite Me); (Cr – chromite, Ol – olivine, Tr – troilite)

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Rare Earth Elements in heavy minerals from ion adsorption deposits, an example from Syrymbet ore district, Northern Kazakhstan

Agata DUCZMAL-CZERNIKIEWICZ¹, Madina KURMANGHAZINA², Kuanysh TOGIZOV², Ludmiła ISSAEVA², Daulet MURATKHANOV², Maciej SWĘD³

¹Institute of Geology, Adam Mickiewicz University in Poznań, Address Krygowskiego 12, 61-686 Poznań, Poland; e-mail: agata.duczmal-czernikiewicz@amu.edu.pl

², Satbayev University Almaty, Kazkhstan Institute of Geological Sciences Almaty 050010, Kazakhstan; e-mail k.togizov@satbayev.university, m.kurmanghazina@satbayev.university, l.issaeva@satbayev.university, daulet.muratkhanov@satbayev.university; m.kurmanghazina@satbayev.university

³ Polish Academy of Sciences. ul. Twarda 5 Warszawa, m.swed@pan.edu.pl

Rare earth elements deposit are the subject of flood literature (e.g., Goodenough et al. 2019) and are still. The deposits in Northern Kazakhstan, located within the Syrymbet ore cluster is characterised by rare-metal and rare earth mineralisation. The deposit was discovered in 1961 during deep prospecting for uranium in the Syrymbet deposit area (Issayeva et al. 2022).

The deposit accumulated in the weathering crusts of the Upper Oligocene sediments, and the main share of the deposit's REE is hosted in clays. At South part of the deposits the cumulative content of REE is in the range of 0.1–0.6 wt.%; approximately 20% of yttrium is at North's site, and the sum of rare earth elements' content ranges from 0.1–0.4% (the maximum is 0.8 wt.%). Although residual REE clays likely constitute >80% of the world's economic HREE resources, the studied deposit LREE predominates among rare earth elements. The deposit is economically attractive for its association with clays.

The dominant rare earth mineral is monazite, and the secondary one is parisite. Radioactive minerals include thorite and orangite. Rare and accessory minerals include ilmenite, magnetite, titanomagnetite, zircon, hematite, pyrite, chalcopyrite, arsenopyrite, rutile, galena, and chromospinels. The major gangue minerals are common quartz, chlorite, mica, and rarely potassium feldspar, whereas secondary minerals include tourmaline, garnet, amphibole, epidote-zoisite, and different mica varieties.

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Ore minerals of the Central Sudetic Ophiolite: preliminary insight from field observations and petrographic study

Eman ELSHERIF¹, Jakub CIAŻELA¹, Piotr WOJTULEK², Maciej FITT¹, Magdalena PAŃCZYK³, Wojciech STAWIKOWSKI⁴, Anna KUKUŁA¹, Marta PRELL²

¹Institute of Geological Sciences, Polish Academy of Sciences, Wrocław; e-mail: eman-elsherif@twarda.pan.pl

²Institute of Geological Sciences, University of Wrocław, Wrocław

³Polish Geological Institute, National Research Institute, Warsaw

⁴Institute of Geology, Adam Mickiewicz University, Poznań

The study aims to understand the migration of metals from the mantle to the seafloor and the formation of seafloor massive sulfide deposits along the slow-spreading ridges based on the case study of the Central Sudetic Ophiolite (CSO). CSO is a well-preserved slow-spreading ridge-related ophiolite with a lithosphere architecture similar to the Polish sulfide exploration area along the 26–33°N Mid-Atlantic Ridge (MAR). During 18 sampling campaigns, we have collected 292 samples, including 15 chromitites, 124 mantle peridotites, 8 ultramafic cumulates from the former crust-mantle boundary, 132 gabbros, 21 diabases, 18 basalts, and 23 ocean-floor sediments. Mineral modes and textural features of fifteen representative samples of different lithologies have been investigated under an optical microscope, including reflected and transmitted light and using SEM-EDS analyses. Sulfides are irregular or globular grains, from tens of micrometers up to 1–2 cm in diameter. Magmatic sulfides are typically <500 μm polyphase grains of pyrrhotite, chalcopyrite, and pentlandite, with pentlandite predominating in the mantle and pyrrhotite in the crust. The magmatic sulfides dissolved during serpentinization are often reprecipitated as secondary pentlandite or heazlewoodite. Hydrothermal sulfides in the crust (<1 cm) are mainly pyrite, chalcopyrite, and minor pyrrhotite. The crust's magmatic oxides (2–3 cm) are mostly ilmenite and titanomagnetite. Magmatic mantle oxides are mostly chromites, especially in chromitite horizons, partially altered to ferrichromites (see also Wojtulek et al., this issue). Sulfide enrichment occurs mainly in dikes in the middle crust and ferrogabbro horizons in the lower crust. The BSE images of those sulfides revealed pyrite exsolutions within pyrrhotite grains and massive up to 50 μm chalcopyrite crystals on the rims. Average major element contents in pyrrhotite (Fe_{0.91}S), chalcopyrite (Cu_{0.97}Fe_{1.09}S₂), pyrite (Fe_{1.05}S₂), sphalerite (Zn_{0.94}Fe_{0.17}S), and ilmenite ((Fe²⁺_{0.92}Mn_{0.07})(Fe³⁺_{0.03}Ti_{0.99})O₃) have been determined in ten representative samples of dikes and gabbro. We are currently determining the whole-rock major element, trace metal, and sulfur contents, as well as S isotopic compositions of these rocks, which will be partially presented on the poster. Sulfides, oxides, and other relevant phases are analyzed *in situ* for major-, chalcophile-, and highly-siderophile elements (HSE) along with S, Cu, Fe, and Ni isotopic compositions. Thanks to this, we should be able to determine the distribution of chalcophile- and HSE metals, S, and their isotopes for the entire CSO, its magmatic centres, individual outcrops, specimens, and thin sections (see also J. Ciałęła et al.; Wojtulek et al.; W. Woźniak et al.; this issue).



Organic compounds in karstic water (Rovte region, Slovenia)

Monika J. FABIAŃSKA¹, Justyna CIESIELCZUK¹, Vanessa E. JOHNSTON², Bojan OTONIČAR², Filip ŠARC², Andrzej TYC¹, Beata GEBUS-CZUPYT³, Krzysztof GAIDZIK¹

¹Faculty of Natural Sciences, University of Silesia in Katowice, Będzińska 60, Sosnowiec, Poland;
e-mail: monika.fabianska@us.edu.pl

²Karst Research Institute ZRC SAZU, Titov trg 2, Postojna, Slovenia

³Institute of Geological Sciences, Polish Academy of Sciences, Twarda 51/55, 00-818 Warszawa, Poland

Sedimentary organic matter plays a significant role in several processes in the geosphere favouring reducing conditions within sediments. Its components show different water solubilities from almost insoluble aliphatic hydrocarbons to relatively well-soluble phenolic derivatives. However, transport in solution is not the only way for mature organic matter to move within the geosphere since its bituminous fraction can be expelled and moved with pore water as crude oil or in suspension eroded from rocks containing organic matter. The distribution of organic compounds in eight samples, 1.5 litres each, of spring and deep well water collected in the Rovte region in central Slovenia was investigated to contribute to establishing speleogenetic processes. The organic phase was separated from the water phase by solid phase extraction on Bakerbond C18 SPE pre-conditioned columns and analysed by gas chromatography-mass spectrometry (GC-MS) (Agilent Techn). All organic compounds in the waters investigated, despite different sampling sites, show striking distribution similarity suggesting the same geological source. *n*-Alkanes in the range *n*-C₁₅-*n*-C₃₅ dominate, with *n*-C₁₈ being the maximum of distribution. This feature is typical for planktonic kerogen (I or IIA type). Low Pr/Ph values (ca. 0.5) testify to the reducing depositional environment but not hypersaline since gammacerane is absent and C₃₄ and C₃₅ hopanes show lower contents than C₃₃ hopanes. This agrees with the sterane relative percentage distribution that suggests the marine shelf environment. The diagram of Pr/(Pr+Ph) ratio versus steranes/diasteranes indicates an environment poor in clay minerals, thus possibly carbonates, relatively poor in organic matter and anoxic. This is confirmed by the Hedges diagram of Pr/Ph versus MPI-1/phenanthrene. CPI and other biomarker and aromatic hydrocarbon ratio values point to mature organic matter at the advanced catagenesis, corresponding to vitrinite reflectance ca. 0.80%–0.95% (calculated from MPI-1 values). Only a slight elevation of CPI values was registered for the WEL-B sample, probably due to contamination by the recent soil material. Partial removal of lighter *n*-alkanes in the range from *n*-C₁₁-*n*-C₁₄, more soluble in water than heavier compounds, suggests organic compound leaching prior to the mobilisation of compounds found in the samples analysed. After such removal, heavier compounds sorbed on the inorganic phase were mobilised, possibly as suspension.

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Weathering alterations of coal wastes geochemistry, organic petrology and mineralogy, a case study from the Janina and Marcel Coal Mines, Upper Silesian Coal Basin (Poland)

Monika J. FABIAŃSKA¹, Justyna CIESIELCZUK¹, Marek SZCZERBA², Magdalena MISZ-KENNAN¹, Dariusz WIĘCŁAW³, Ewa SZRAM¹, Ádám NÁDUDVARI¹, Zuzanna CIESIELSKA²

¹Institute of Earth Sciences, University of Silesia in Katowice, Poland; e-mail: monika.fabiańska@us.edu.pl

²Institute of Geological Sciences, Polish Academy of Science, Cracow, Poland

³Faculty of Geology, Geophysics and Environmental Protection, AGH University of Krakow, Krakow, Poland

Weathering-caused alterations in coal waste geochemistry, organic petrology and mineralogy occurring in the known time span of 1998-2018 and in the temperate climate of Poland were investigated. The regional variability of gangue Pennsylvanian rocks is represented by the low mature (sub-bituminous) coal exploited in the Janina Coal Mine (Eastern part of the Upper Silesian Coal Basin, USCB) and mid-mature (coking) coal exploited in the Marcel Coal Mine (Southwestern part of the USCB).

Two series of coal waste rocks deposited on the heaps of both mines have been investigated to find how the level of organic matter (OM) maturity impacts weathering. Differences in OM content and petrography, gangue rock mineralogy and inorganic geochemistry were also taken into account. Whereas OM petrography, including vitrinite reflectance values, does not show significant weathering signs, apart from irregular cracks and in very rare cases paler in colour oxidation rims, organic geochemistry evidences low-temperature secondary processes, including increased oxygen index values, particularly for the coal wastes containing low-mature OM. Biomarker distributions of these samples have been changed considerably, with partial removal of *n*-alkanes, possibly due to biodegradation of OM; water-washing of lighter polycyclic aromatic hydrocarbons, including alkyl naphthalenes was recorded as well. The low-mature OM of coal wastes from the USCB eastern part, as more reactive, showed a higher level of secondary transformations than the higher-mature ones (Marcel Mine). Minerals, that were formed during weathering of the stored wastes were found; they are mainly oxidation products of iron sulphides: goethite and jarosite. However, most of the minerals have been not altered. Thus, despite physical changes in coal wastes such as increased brittleness, decreasing fragment size, and surface colour change, there are only limited changes in their inorganic and mineralogical composition. The results indicate that weathering processes lasting up to 20. years do not favour elements' release to the environment and point out that measures to prevent self-heating within the dumps are the most vital part of post-mining activity leading to the best scenario: slow low-temperature weathering of coal wastes.

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Mafic, ultramafic and carbonatic clasts in a migmatitic matrix: a HT-mélange marking a Variscan suture in the Helvetic-Dauphinois-Provençal domains of Western Alps?

Marco FILIPPI¹, Maria Iole SPALLA¹, Massimo TIEPOLO¹, Davide ZANONI¹, Manuel RODA¹, Luca SPAGGIARI¹, Silvia VOLANTE², Guido GOSSO¹, Jean-Marc LARDEAUX^{3,4}

¹Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano, Via Mangiagalli 34, Milano; e-mail: marco.filippi@unimi.it

²Structural Geology and Tectonics Group, Geological Institute, Department of Earth Sciences, ETH Zürich

³UMR Géozur, Université Côte d'Azur, Observatoire de la Côte d'Azur, CNRS, IRD, Valbonne, 06560, France

⁴Centre for Lithospheric Research, Czech Geological Survey, Prague 1, 118 21, Czech Republic

The Variscan metamorphic and igneous signatures observed in the pre-Alpine crust of the Southalpine, Austroalpine, Penninic, and Helvetic-Dauphinois-Provençal domains, along with their ages, well align with those found in the other sections of the European Variscan belt. Moreover, the presence of meta-ophiolite remnants provides evidence that parts of Variscan suture zone(s) are preserved in the Alps. Uncertainties persist on which and how many of the proposed Variscan suture zones recognized from the Bohemian Massif to Southern Iberia are actually present within the Alps.

In the External Crystalline Massifs (ECMs) of the Western Alps (Helvetic-Dauphinois-Provençal domain), numerous mafic, ultramafic, and sedimentary protoliths have been affected by Variscan metamorphism. In the Argentera-Mercantour, Pelvoux-Belledonne, Aiguilles Rouges and Mt Blanc Massifs (ECM) footprints of Variscan subduction, collision and late-orogenic extension (up to Early Permian times) are testified by the widespread occurrence of eclogite-facies rocks, granulites, amphibolites, high-grade metasediments and metagranitoids in tectonic units weakly affected by the localized Alpine overprint.

This contribution focuses on the Argentera-Mercantour Massif, which is the southernmost of the ECMs. The Variscan basement of this massif is primarily composed of migmatitic metaintrusives and paragneisses, containing lenses and boudins of mafic and ultramafic rocks that have been transposed within the migmatitic foliation. Metabasites consist of amphibolites, eclogites, and granulites, whereas ultramafics occur as variably serpentinized peridotites and pyroxenites. These rocks are associated with calc-silicate lenses (clinopyroxene- and garnet-bearing) and marble layers. In this contribution, we present new structural, petrological, geochemical, and chronological data for this mixture of lithologies, which is embedded within the Variscan migmatites. Our goal is to uncover the original lithostratigraphic context and unravel their complex, tectonic evolutionary history.



Petrographic and geochemical study of 16 Martian meteorites: implications for ore-forming processes

Maciej FITT¹, Jakub CIAŻELA¹, Malte JUNGE², Melanie KALIWODA², Stephen MOJZSIS³, Levente PATKÓ⁴, Mateusz SZCZEŚNIEWICZ⁵, Katarzyna ŁUSZCZEK⁵, Petras JAKUBAUSKAS⁶, Marta PRELL⁷

¹*Institute of Geological Sciences, Polish Academy of Sciences, Poland; m.fitt@twarda.pan.pl;*

²*Mineralogische Staatssammlung, München, Germany;*

³*Research Centre for Astronomy and Earth Sciences, HUN-REN, Hungarian Academy of Sciences, Hungary;*

⁴*Institute of Earth Physics and Space Science, HUN-REN, Hungary;*

⁵*Faculty of Geoenvironment, Mining and Geology, Wrocław University of Science and Technology, Poland;*

⁶*Faculty of Geology, University of Warsaw, Poland;*

⁷*Institute of Geological Sciences, University of Wrocław, Poland.*

We report on the investigation of a set of 16 ore-bearing Martian meteorites to understand the course of ore-forming processes on Mars. Ten shergottites (four basaltic, three olivine-phyric, three poikilitic), three nakhlites, chassignite, an orthopyroxenite, and regolith breccia were analyzed using ore microscopy, scanning electron microscopy (SEM), electron probe microanalysis (EPMA), and Raman spectroscopy.

Basaltic shergottites are composed of 46.3–75.6 vol.% clinopyroxene (Cpx), 19.3–44.4% maskelynite (Mask), 1.6–4.3% merrillite (Mer), 0.8–2.4% oxides (ox): titanomagnetite (Ti-Mag), and ilmenite (Ilm), 0.2–1.4% pyrrhotite (Pyh). Poikilitic: 32.6–48.0% olivine (Ol), 38.0–48.4% Cpx, 9.6–13.2% Mask, 0.5–1.5% Mer, 3.0–3.3% Ox (Ti-Mag, Ilm, chromite – Chr), 0.9–1.1% Pyh, with rare, very fine pentlandite (Pn) grains (5–10 μm). Olivine-phyric: 45.7–70.1% Cpx, 10.9–38.1% Ol, 14.9–18.0% Mask, <1.1% Mer, 0.7–3.6%, ox (Ti-Mag, Ilm, Chr), 0.3–2.7% Pyh (+Pn grains). Nakhlites comprise 76.1–83.3 vol.% Cpx, 1.8–10.6% Ol, 7.1–17.8% mesostasis (Meso), 0.8–3.9% Ti-Mag, 0.2–0.4% Pyh. Chassignite is 95.0 vol.% Ol, 1.2% Cpx, 0.7% plagioclase (Pl), 1.7% Meso, 1.3% Chr, <0.1% pyrite (Py). Orthopyroxenite is 95.4 vol.% orthopyroxene, 2.6% Mask, 0.3% Mer, 1.7% Chr, and <0.1% Py. Regolith breccia is polymictic, but most clasts are basaltic.

The dominance of Fe sulfides displays enrichment of Martian magma in Fe, while being depleted in Cu and Ni compared to typical terrestrial systems. The predominance of pyrrhotite, rarely associated with pentlandite, points to a magmatic origin of the sulfides. Nakhlites, regolith breccia, and orthopyroxenite, however, also show some degree of alteration due to the post-magmatic hydrothermal activity. This is manifested by veins and secondary mineral assemblages such as hydrothermal pyrite in regolith breccia NWA 7034.

³²S and ³⁴S isotopes, which we will measure in target sulfides this Autumn, may allow us to distinguish between hydrothermal and mantle sources. Iron isotopes, measured in sulfides and other phases, will be used to test equilibrium with primary silicates, secondary silicates, high-temperature oxides, or low-temperature oxides and hydroxides. These studies will reveal new insights into ore-forming processes in the ancient Martian crust.

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Tracing acid mine drainage contamination with chemical and isotopic methods

Agnieszka GAŁUSZKA¹, Zdzisław M. MIGASZEWSKI¹

¹*Institute of Chemistry, Jan Kochanowski University in Kielce, 7 Świętokrzyska St., 25-406 Kielce; e-mail: agnieszka.galuszka@ujk.edu.pl (A. Gałuszka), e-mail: zmig@ujk.edu.pl (Z.M. Migaszewski)*

Microbially-catalyzed oxidation of pyrite and other iron-bearing sulfide minerals in surface environments leads to the formation of strongly acidic and contaminated waters. This process, known as the acid mine drainage (AMD), is one of the most serious hazards to the environmental quality in areas of currently operating or historic metal-ore and coal mines. The typical features of AMD waters are their orange-brown colour, low pH, and high concentrations of sulfate and metal ions often reaching tens of grams per litre (Nordstrom et al. 2000). High concentrations of As are also common in AMD and they lead to deterioration of ground- and surface waters causing health risk to humans (Migaszewski et al. 2019). An assessment of AMD impact on the environment is usually employed for surface waters and shallow aquifers in the vicinity of the mine. Close to abandoned mine tailings piles or in areas of accidental spills of acidic waters, soils should be also examined. Elevated levels of SO_4^{2-} , Fe, Al, As, Ni, Co, Cu and other trace elements point to a potential impact of AMD on the samples examined. Another possibility is the use of rare earth element (REE)-normalized patterns in waters and soils impacted by AMD because they usually show middle REE (Sm-Dy) enrichments and a positive Gd anomaly (Grawunder et al. 2014; Migaszewski et al. 2016, 2019). Stable sulfur and oxygen isotopes are used to study water-rock/mineral interactions. The $\delta^{34}\text{S}\text{-SO}_4^{2-}$ and $\delta^{18}\text{O}\text{-SO}_4^{2-}$ values in waters and the $\delta^{34}\text{S}$ values in soils are one of the best markers of the AMD impact on the environment (Migaszewski et al. 2018). This study discusses advantages and disadvantages of employing the aforementioned markers in the assessment of the AMD potential threats to neighbouring waters, soils and biota.

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Ultrabasites of the easternmost Góry Sowie massif: a fragment of the Devonian oceanic lithosphere of the Central Sudetes?

Grzegorz GIL¹, Piotr M. WOJTULEK², Sławomir ILNICKI¹, Petras JOKUBAUSKAS¹

¹Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, 02-089 Warszawa; g.gil2@uw.edu.pl

²Institute of Geological Sciences, University of Wrocław, M. Borna 9, 50-204 Wrocław; piotr.wojtulek@uwr.edu.pl

The metamorphic Góry Sowie massif (Central Sudetes, SW Poland) hosts variably serpentinized ultrabasic bodies. In the easternmost part of the massif, near the Gilów village, completely serpentinized peridotites are prevailing. Bulk $\text{Al}_2\text{O}_3/\text{SiO}_2$ (0.03-0.04) and MgO/SiO_2 (0.77-0.79) ratios of these serpentinites (Gil et al. 2022) are similar to that of abyssal peridotites affected by an intermediate degree of partial melting and extensive sea-floor weathering, and are similar as in serpentinites of the Devonian Central Sudetic Ophiolite (CSO) (Wojtulek et al. 2022). Stable isotope ratios of serpentinites from Gilów ($\delta^{18}\text{O} = 5.7$ to 7.1‰ ; $\delta\text{D} = -64$ to -48‰) (Gil et al. 2022) are similar to those of the CSO ($\delta^{18}\text{O} = 4.3$ to 7.1‰ ; $\delta\text{D} = -104$ to -46‰), and comparable with typical abyssal and ophiolitic ultrabasites.

Serpentinites from Gilów host chromian spinel grains, with Mg-, Cr- and Al-rich cores, and metamorphic magnetite rims. Spinel cores are characterized by $\text{Mg}\# = 0.08$ - 0.42 , $\text{Cr}\# = 0.58$ - 0.82 and $\text{Fe}^{3+}/(\text{Al}+\text{Cr}+\text{Fe}^{3+})$ ratio = 0.01 - 0.99 (Gil et al. 2022), and presence of sulfides, chlorite, phlogopite and wonesite inclusions. Phlogopite and wonesite inclusions are rounded, irregular in shape or euhedral, and seem to be unaffected by metamorphic processes and undeformed. Spinel cores from ultrabasites of the CSO, similar to that of the back-arc basin and fore-arc peridotites (Wojtulek et al. 2022), are also undeformed, have comparable $\text{Cr}\#$ (≈ 0.41 - 0.70) and contain sulfides and phlogopite inclusions (Wojtulek et al. 2019, 2022). Chemical and isotopic composition of serpentinites from Gilów is similar to those of the CSO, and typical abyssal and ophiolitic ultrabasites. Serpentinites from Gilów are characterized by a $\text{Cr}\#$ value of spinel cores, and a set of undeformed inclusions in spinels, similar to those of the CSO. Moreover, a preservation of phlogopite and wonesite, sensitive to PT changes, implies formation in low-P conditions, not exceeding those of the sea-floor metamorphism, similar as in the case of the CSO spinels.

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Characteristics of organic matter in hydrothermally altered Ediacaran volcanics from Volyn (Ukraine)

Magdalena GORYL¹, Leszek MARYNOWSKI², Jan ŚRODOŃ¹

¹*Institute of Geological Sciences, Polish Academy of Sciences, Research Centre in Kraków, Poland; e-mail: m.goryl@ingpan.krakow.pl*

²*Faculty of Natural Sciences, University of Silesia, Sosnowiec, Poland*

The Ediacaran continental flood basalts and associated tuffs were studied by Środoń et al. (2019) to identify and quantify alteration processes. Two alteration processes were identified: hydrothermal alteration caused by meteoric waters, heated and set in motion by cooling basalt, and Caledonian and/or Variscan potassic alteration.

Here, we present the results of an organic geochemistry investigation on the Ediacaran volcanics. All samples were organic-lean (total organic carbon content did not exceed 0.2%). The low level of thermal maturity promotes the preservation of the original character of the distribution of organic compounds (Goryl et al., 2018). The main constituents of organic matter (OM) were *n*-alkanes and *n*-fatty acids. However, the distribution of these biomarkers in the basalt differs significantly from fanglomerates and caverns in basalts. In basalt sample long-chain *n*-alkanes and *n*-alkanoic acids are present in relatively high concentration, while in other samples they are insignificant. This pattern is characteristic for terrestrial higher plants. However, Bobrovskiy et al. (2018) propose that spherical cyanobacterial colonies may be a possible origin for long-chain *n*-alkanes found in Ediacaran rocks.

OM from the basalt sample represents non-oxidized or only slightly oxidized remnants of the activity of Ediacaran cyanobacteria (and other microorganisms?) in the basalt hydrothermal system. The observed more reducing conditions at the final stages of basalt alteration may be explained by the activities of cyanobacteria.

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Lead nanospheres identified in Acasta gneiss from northwestern Canada

Ewelina GRABIAS-BLICHARZ¹, Monika A. KUSIAK¹, Richard WIRTH², Tsuyoshi IIZUKA³

¹Department of Polar and Marine Research, Institute of Geophysics, Polish Academy of Sciences, 64 Księcia Janusza Str., 01-452 Warszawa, Poland, e-mail: monika.kusiak@igf.edu.pl; ewelina.grabias@igf.edu.pl

²GeoForschungsZentrum Potsdam, Section 3.5 Surface Geochemistry, D-14473 Potsdam, Germany, e-mail: richard.wirth@gfz-potsdam.de

³Department of Earth and Planetary Science, The University of Tokyo, Tokyo 152-8551, Japan, e-mail: iizuka@eps.s.u-tokyo.ac.jp

Zircon is the most widely used geochronometer, which preserves geochemical transformations and age data. Nevertheless, the reliability of zircon U-Pb geochronology findings can be disturbed by the redistribution of radiogenic lead. The formation of the Pb-enriched domains is attributed to high-temperature metamorphism of zircon crystals. Moreover, it has been determined that the non-uniform redistribution of lead in metamorphic zircon can reduce the precision and accuracy of U-Pb isotopic data, in some extreme cases leading to false ages. Thus, investigating the composition and mineralogy of Pb-enriched zircon grains is essential for understanding Pb redistribution processes in zircon and its impact on geochronology.

The evidence for the presence of lead nanospheres in zircon was first recognized from ultra-high temperature (UHT) rocks in Antarctica (Kusiak et al., 2015). Recent study documented metallic Pb nanospheres from well recognized Jack Hills zircon irrespectively of their age and U content (Kusiak et al., 2023), where no UHT was documented. Now, we present a discovery of tiny Pb nanospheres in zircons from the ancient xenocrystic core (4.2 Ga) of Acasta gneiss from the northwestern Canada (Iizuka et al. 2006). The Pb spheres up to 3-5 nm in diameter, as identified by high-resolution transmission electron microscopy (TEM), occur in concert with nanopores containing traces of Y and U. Moreover, there are small dark Fe crystals present, probably Fe oxide. These results confirm that the UHT conditions are not a requirement for the Pb nanosphere formation and that their presence is much more common than initially thought.

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Volatile organic compounds from self-heating of coal waste dump (USCB, Bytom); passive sampling experiment

Julia GRZEGORCZYK¹, Monika J. FABIAŃSKA¹

¹*Institute of Earth Sciences, University of Silesia in Katowice, Poland; e-mail: monika.fabiana@us.edu.pl*

Introduction

Volatile organic compounds (VOCs) comprise a wide range of substances, many of them harmful to the environment and human health. It is known that VOCs are emitted to the atmosphere during spontaneous fires occurring on the coal waste dumps, however the size of emission and its dynamics are not well recognized. The aim of this project was to test the passive method of VOCs sampling that will allow to find their amounts and composition on numerous sites of coal waste dump at the same time.

Methods

The Bytom coal waste dump (USCB) has been thermally active since 2015 at least due to its opening and subsequent interior oxygenation when its material was taken during the A1 highway construction. A site with visible self-heating signs (vents, efflorescences, fumes etc) was selected for the experiment. Four activated sorbents were applied in 1 cm thick layer placed over the vent - charcoal, diatomic earth, silica gel, and alumina. The sorbents were left for 3 hours and 3 days to find the optimal time of VOCs sorption. Next, they were extracted with dichloromethane, sulphur removed, and extracts analyzed with GC-MS.

Results

Main VOCs identified included *n*-alkanes in the range *n*-C₁₁ do *n*-C₂₉ with maximum at *n*-C₂₀ to *n*-C₂₃, and the Gaussian distribution outline, characteristic for pyrolytical products, 2-5 rings polycyclic aromatic hydrocarbons (PAHs) with maximum for 3-ring compounds, and phenols (phenol and cresols present).

Generally, 3 hour experiment yielded satisfactory results; however 3-day sorption gave extracts with lower contamination levels, especially sulphur. Moreover, low-concentration compounds were present in amounts allowing their identification what was not always the case in 3 hour extracts. Sorbents had different affinity to different compound groups. Charcoal extracts were the richest in *n*-alkanes and phenols, and lowest in S content. This sorbent preferentially sorbed 2-3-ring PAHs, with heavier compounds absent. Diatomic earth, silica gel and alumina extracts showed a PAHs wider range and similar amounts of sorbed VOCs, with silica gel the best for 3h procedure.

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The deciphering of chemical and isotopic genesis and fluctuations of fine and ultra-fine PM_x in the coastal area of Tri-city (Poland)

Maciej GÓRKA¹, Jaroslav BEZYK^{2,3}, Martyna MALINOWSKA⁴, Izabela SÓWKA², Anita LEWANDOWSKA⁴

¹*Institute of Geological Sciences, Faculty of Earth Science and Environmental Management, University of Wrocław, Cybulskiego 32, 50-205 Wrocław, Poland; e-mail: maciej.gorka@uwr.edu.pl*

²*Faculty of Environmental Engineering, Wrocław University of Science and Technology, Plac Grunwaldzki 13, 50-377 Wrocław, Poland;*

³*Faculty of Physics and Applied Computer Science, AGH University of Kraków, Mickiewicza 30, 30-059 Kraków, Poland*

⁴*Faculty of Oceanography and Geography, University of Gdańsk, al. J. Piłsudskiego 46, 81-378 Gdynia, Poland*

PM₁ and PM_{2.5} samples were collected by HYDRA Dual Sampler in Gdynia (N Poland) during January-March 2022 and September-October 2022 campaigns to evaluate seasonal concentration differences and to identify the potential sources/processes that influenced the chemical composition of both aerosol fractions. To decipher the environment, complicated matrix coupled methods have been applied. For measuring carbonaceous fractions (TC/OC/EC) Sunset Laboratory Dual-Optical Carbonaceous Analyzer has been used. Ion chromatograph (Metrohm 850 Professional IC) equipped with a conductometric detector was applied for detecting selected ions concentration. Picarro G2201-i CRDS has been used for characterization of carbon isotopic signatures ($\delta^{13}\text{C}_{\text{TC}}$). In addition for specific PM_x high concentration episodes, HYSPLIT backward trajectories (NOAA HYSPLIT model) were calculated and interpreted with dedicated synoptic charts (KNMI).

Statistical tests (Spearman rank) between analyzed chemical parameters and meteorological conditions indicated relationships related to: (i) fossil fuel combustion; (ii) agriculture activity; and (iii) natural sea surface influence. Moreover, statistically significant differences (ANOVA) in the short monthly scale as well as between seasons (the heating and vegetative period) were noted. Seasonal discrimination indicated significant differences for ions (NO_3^- , Cl^- , K^+ , Ca^{2+} , Mg^{2+}) for both PM₁ and PM_{2.5}, while for carbon isotopes only for PM₁ fraction. Similarly to the Spearman rank correlations, the ANOVA test allowed to decipher different fuel combustion/agricultural activities during different measurement periods. Moreover, carbon fractions analyses (OC/EC ratio), $\delta^{13}\text{C}_{\text{TC}}$ values (with calculated dominant source), as well as K^+ ion (a biomass burning tracer), showed variations on a monthly and seasonal scale with different coal/liquid fuel and biomass inputs.

Finally, both similarities as well as some differences in the chemical composition of fine and ultra-fine aerosols were noted during the measurement period in Gdynia, depending on the source's influence, alteration processes, and meteorological conditions. Thus we suggest that broad look at air pollution and a multi-proxy approach seems to be prerequisites for drawing reliable conclusions in relation to environmental research.



Metamorphic record of eclogites and associated mica schist from the Kamieniec metamorphic belt (NE Bohemian Massif, SW Poland)

Sławomir ILNICKI¹, Jacek SZCZEPAŃSKI², Xin ZHONG³, Robert ANCZKIEWICZ⁴

¹Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, 02-089 Warszawa; slawomir.ilnicki@uw.edu.pl

²Institute of Geological Sciences, University of Wrocław, Poland.

³Department of Earth Sciences, Freie Universität Berlin, Germany.

⁴Institute of Geological Sciences, Polish Academy of Sciences, Research Centre in Cracow, Poland.

The Kamieniec Metamorphic Belt (KMB) is a supracrustal succession exposed at the NE part of the Bohemian Massif (Fore-Sudetic Block, SW Poland) and is considered a section of the Variscan collision zone between the Saxothuringian and Brunovistulian domains. The KMB is dominated by mica schists with dispersed small bodies of paragneisses, quartz-graphite schists, calc-silicate rocks, amphibolites and eclogites. Our study focused on reconstructing the full P–T trajectory recorded by eclogites coupled with geochronological constraints, and comparison with the P–T path of the accompanying mica schist.

The textural evidence combined with mineral–chemical composition indicates a prograde mineral succession starting with high-Mn garnet cores (with inclusions of Omp, Ph, Amp, Rt, Qz) followed by poor-Mn garnet rims and matrix minerals: Omp (X_{jd} up to 0.49) + Ph (Si^{4+} up to 3.48 a./p.f.u.) + Rt + Qz + Lws. On retrogression, these minerals were variously pseudomorphed by symplectites or poly-mineral aggregates. Specifically, Amp has developed a considerable compositional variation which in strongly retrogressed eclogites correlates with changes in Pl composition. Combining the estimation of conditions of metamorphism from thermodynamic modelling and conventional geothermobarometry we obtained a clockwise P–T trajectory for eclogites starting at 470°C and 12–13 kbar (M1), then 24–27 kbar at temperatures of ca. 550–560°C (M2), followed by decompression to low pressure greenschist/amphibolite facies conditions and subsequently an increase up to 690–700°C at 6.3–7.9 kbar (M3) and final retrogression to ca. 570–450°C and <5 kbar. The Raman geobarometry for inclusions of apatite in garnet porphyroblasts (AiG) coupled with Zr-in-Rt geothermometer suggest baric peak conditions of ca. 22–23 kbar. In terms of geochronological record, the age of HP metamorphism is ca. 347 ± 4.3 Ma (Lu-Hf method based on garnet porphyroblasts). Nearly identical metamorphic evolution and a shape of P–T path were produced for mica schists collected from the same outcrop as eclogite samples. Despite some discrepancies (baric peak ca. 20–21 kbar for mica schist vs. 24–27 kbar for eclogites, thermal peak ca. 640°C for mica schists vs. <700°C for eclogites), both lithologies registered HP-LT episode (cold subduction) then decompression followed by LP-HT episode and exhumation to shallow crustal levels. The multistage metamorphic evolution in the KMG either mirrors cycling within subduction channel or depicts tectonic transport (i.e., burial and exhumation coeval with folding) in the Variscan collision zone.

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Insights into the paragenesis of recently forming weathering minerals in acid mine drainage: a case study from world-class polymetallic deposits of the Carpathian Mountains

Anna JANUSZEWSKA^{1,2}, Łukasz KRUSZEWSKI³, Rafał SIUDA⁴, Paweł ŻOCHOWSKI, Patryk KOSAŁKA, Wojciech SIERNY

^{1,4} Department of Geochemistry, Mineralogy and Petrology, Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, 02-089 Warsaw; a.januszewska3@uw.edu.pl; rsiuda@uw.edu.pl

² Polish Geological Institute - National Research Institute, Rakowiecka 4, 00-975 Warsaw; anna.januszewska@pgi.gov.pl

³ Institute of Geological Sciences of the Polish Academy of Sciences, Twarda 51/55, 00-818 Warsaw; lkruszewski@twarda.pan.pl

The Baia Mare area deposits in Romania serve as a globally renowned exemplar of a classic polymetallic ore mineralization. The Băiuț village, nestled in Maramureș County, is home to mineralized veins distinguished by their abundant inventory of valuable ore minerals (e.g., Kovács & Tămaș 2017). Prevalence of sulfide minerals has instigated acid mine drainage, hastening weathering processes and engendering a diverse array of secondary minerals. Samples were gathered at four mines in the area: Johan Hell, Poiana Botizii, Cisma, and Văratec. They were analyzed using PXRD. TOPAS software with Rietveld method were used for the structural and qualitative phase analysis. Approximately 40 distinct secondary minerals or groups have been identified. The composition of the supergene parageneses is variable, contingent on specific environmental conditions. The Johan Hell mine boasted the most extensive diversity of supergene minerals (25 species). Prevalent minerals belong to the halotrichite group, followed by the melanterite group. Additionally, some rare minerals, with somewhat unsure crystal structures were documented. This includes lausenite, $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, with calculated lattice parameters: $a=10.771(9)$, $b=11.014(19)$, $c=5.630(9)$ Å, $\beta=98.62(11)^\circ$. Data for paracoquimbite, $\text{Fe}_4(\text{SO}_4)_6(\text{H}_2\text{O})_{12} \cdot 6\text{H}_2\text{O}$, is: $a=10.961(13)$, $c=51.66(12)$ Å. Minerals of the voltaite group and römerite formulate a separate paragenesis. Within the Poiana Botizii (Cisma, gall. XII) mine, Fe arsenate mineralization was uncovered, with diverse copper sulphates such as wroewolfeite, devilline group, chalcantite, and langite. The Cizma mine mirrored similar copper mineralization, with secondary zinc sulphates, namuwite and ktenasite, in addition. Conversely, the Văratec mine exhibited the most limited secondary mineralization, primarily characterized by common supergene Cu sulfates. Specific recognized mineral species possess capability to store and subsequently release particular toxic elements, thus being of a great environmental importance.

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Apatite and zircon petrochronological constraints on the metamorphic evolution of eclogites from the Scandinavian Caledonides

Maciej JARANOWSKI¹, Bartosz BUDZYŃ¹, Christopher BARNES¹, Jarosław MAJKA^{2,3}, Jiří SLÁMA⁴, Gabriela A. KOZUB-BUDZYŃ³, Karolina KOŚMIŃSKA³

¹Polish Academy of Sciences, Institute of Geological Sciences, Kraków, Poland; e-mail: ndjarano@cyf-kr.edu.pl

²Uppsala University, Department of Earth Sciences, Uppsala, Sweden

³AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Kraków, Poland

⁴The Czech Academy of Sciences, Institute of Geology, Prague, Czech Republic

U-Pb and trace element zircon and apatite petrochronology of eclogites from the Scandinavian Caledonides were conducted using LA-ICPMS, EPMA and whole rock analysis to resolve their metamorphic evolution. Two samples from the Lofoten Archipelago (Lofoten-Vesterålen complex - LVC), two samples from Northern Jämtland (Lower Seve Nappe - LSN) and one sample from the Nordøyane Archipelago (Blåhø Nappe) were studied. Chemical zoning of zircon was revealed by CL imaging coupled with chondrite-normalized REE data, which distinguished inherited and metamorphic domains. U-Pb dating of inherited domains provided a cluster at ca. 1800 Ma for the Lofoten eclogites. For one of the LSN eclogites, dates are scattered from ca. 883 to 1986 Ma with a cluster at ca. 1000 Ma. Metamorphic zircon domains from the collective eclogites date different histories along the pressure-temperature pathways for the different regions. Zircon geochronology resolves the timing of prograde metamorphism in eclogites from the LVC at 427.8 ± 5.7 Ma, and in one eclogite from the LSN at 467.2 ± 5.9 Ma. A zircon age representing retrograde metamorphism at 444.5 ± 5.5 Ma is yielded by the second eclogite from the LSN. In contrast, protracted high-grade metamorphic event(s) from ca. 430 to 395 Ma are recorded in the Blåhø Nappe eclogite. Apatite U-Pb geochronology, combined with geochemical data, constrained the timing of the late metamorphic stages or cooling during exhumation. These results also indicated metasomatic alteration of apatite in some eclogites. For the LVC eclogites, apatite U-Pb dates of ca. 354–322 Ma represent retrogressive metamorphism and fluid-induced alteration during exhumation. The dates of 436 ± 18 Ma and 415 ± 25 Ma, yielded by apatite from the LSN eclogites, correspond well to previously determined exhumation stages, with apatite recording fluid alteration in one of the samples. The 390 ± 12 Ma date of apatite from the Blåhø Nappe eclogite resolves cooling of the eclogite after periodic or prolonged (U)HP-HT metamorphism.

In summary, this work demonstrates the high potential for applying zircon and apatite petrochronology in eclogite to reconstruct the metamorphic histories of (U)HP terranes. The results are published in Jaranowski et al. (2023, Contrib Mineral Petrol).

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Strategy of the Republic of Poland for the research of the seabed and negotiations for exploitation regulations in the Area

Bartosz JASIŃSKI¹, Piotr NOWAK¹

¹*Department of Geological Supervision and Raw Materials Policy, Ministry of Climate and Environment*

In the EU the supply of most raw and critical metals depends on imports, which exposes the supply chain to a number of external factors and instability. This condition affects technological development, the production of advanced technologies, or energy transition. Some of the necessary raw materials, after proper identification, assessment, and development of appropriate technology, may be exploited from the bottom of the sea in the future. It is estimated that oceanic sulphide and oxide deposits have a particularly high concentration of metals in the ore – some of them have been classified as critical raw materials. Therefore, the topic of deep-sea mining can be considered as prospective, taking into account the constantly growing demand for metals that are necessary for the green transformation. In view of those challenges, the Government of the Republic of Poland found it important to take this area into account when developing the National Raw Materials Policy (PSP2050). As indicated in this document, sustainable development, economic progress, and increased raw material security of both, Poland and Europe, are not possible without responsible and effective management of the resources, including mineral resources. The PSP2050, following the European Commission, indicates a projected significant increase in demand for some raw materials, necessary for a successful energy transition, up to 1000% by 2050. An opportunity to become independent and increase Poland's recognized raw material base are activities involving the implementation of research programs under the auspices of the International Seabed Authority (ISA), conducted in accordance with the United Nations Convention on the Law of the Sea. Therefore, in 2018, Poland signed a 15-year contract with the ISA for the exploration of polymetallic sulphides, under which two research cruises have been organized in the Mid-Atlantic Ridge. These studies, commissioned by the Ministry of Climate and Environment, are carried out by the Polish Geological Institute – National Research Institute, in cooperation with other scientific units in Poland and abroad. It should be noted, that current research and development of the deep-sea mining industry is still in its initial phase. There is no certainty that Poland will exploit the seabed, but the government administration is preparing for such a scenario by conducting exploration and research to verify potential deposits, and is actively involved in preparing regulations governing environmental protection and mining rules. Poland presents the position that the framework for any activities related to deep-sea mining is set by the United Nations Convention on the Law of the Sea, which takes into account both the protection of the marine environment and the possibility of benefiting from the exploitation of the mineral resources located in areas beyond national jurisdiction. Poland has confidence in that efforts to develop exploitation regulations should be continued, based on the Convention and science- and evidence-based knowledge, taking into account the precautionary approach and principles of non-discrimination among contractors.



BaZr-silicate, a potentially new mineral from the Löhley quarry, Germany

Rafał JUROSZEK¹, Biljana KRÜGER², Günter BLAß³, Günter FRENZ⁴

¹Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland; rafal.juroszek@us.edu.pl

²Institute of Mineralogy and Petrography, University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria; biljana.krueger@uibk.ac.at

³Merzbachstr. 6, D-52249 Eschweiler, Germany; nc-blaszgu@netcologne.de

⁴Börschgasse 16a, D-51143 Köln, Germany; guefz@freenet.de

A potentially new BaZr-silicate was found within the fissures and crevices of the leucite-melilite-bearing nephelinite in the Löhley quarry in the Eifel volcanic area, Germany. A new phase forms idiomorphic, thick tabular crystals of a maximum diameter of about 1 mm. The crystals are colourless or cloudy-white and exhibit vitreous lustre. The BaZr-silicate usually crystallizes on perovskite crystals or in direct contact with them, and it is also associated with leucite, nepheline, minerals of the pyroxene group, fluorapatite, titanite, magnetite, fresnoite, and minerals belonging to the pyrochlore group. The ideal chemical composition BaZrSi₂O₇ shows slight variations due to the substitution of Ba primarily by K and Ca and of Zr by Nb according to the SEM-EDX analyses.

The crystal structure of BaZrSi₂O₇ phase was refined in *P4/mbm* space group with the following unit-cell parameters: $a = 8.894(2) \text{ \AA}$, $c = 8.051(2) \text{ \AA}$, $V = 636.8(3) \text{ \AA}^3$, and $Z = 4$. The structure consists of ten-fold coordinated Ba-polyhedra, which are connected to the ZrO₆ octahedra and SiO₄ tetrahedra. The corner-sharing ZrO₆ octahedra form chains along the [001] and are connected to the SiO₄ tetrahedra, merging into Si₄O₁₀ rings arranged parallel to the [110]. In chains, each octahedron shares four corners with four SiO₄ tetrahedra belonging to four different Si₄O₁₀ units to yield a three-dimensional framework. This arrangement causes the presence of pentagonal channels extended through the structure along the *c*-axis and occupied solely by Ba atoms. According to the SC-XRD data, Ba atoms are partially substituted by K, which correlates with the chemical composition.

The occurrence within the fissures and cavities of nephelinite country rock, as well as mineral association, may indicate that the BaZr-silicate formed under hydrothermal conditions.

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The significance of Palaeoarchean ferroan calc-alkaline granitoids from the Saglek Block, Labrador, Canada

Tanmay KELUSKAR¹, Monika A. KUSIAK¹, Daniel J. DUNKLEY¹, Martin J. WHITEHOUSE², Simon A. WILDE³, Keewook YI⁴, and Shinae LEE⁴

¹Department of Polar and Marine Research, Institute of Geophysics Polish Academy of Sciences, ul. Księcia Janusza 64, PL-01452 Warszawa; Poland; email: tanmay.keluskar@igf.edu.pl

²Department of Geosciences, Swedish Museum of Natural History, SE-10405 Stockholm, Sweden

³School of Earth and Planetary Sciences, Curtin University, Kent St, Bentley, Western Australia 6102, Australia

⁴Korea Basic Science Institute (KBSI), Ochang Campus, Republic of Korea

The term A-type granite was first coined by Loiselle and Wones (1979) for anorogenic granites. Frost et al. (2011) suggested replacing the term ‘A-type’ with ‘Ferroan’ as the former refers to the tectonic setting of the source magma, which is not always applicable. Instead, the latter authors suggested various origins for ferroan granitoids. Here we report U-Pb zircon geochronology and geochemical data from Mentzel and Maidmonts Islands off the Labrador coast of Canada. Augen gneiss samples from both islands yield ages of ca. 3.3 Ga from rocks originally classified as ca. 3.6 Ga Uivak II Gneiss (Wasilewski et al. 2021), fitting the definition of Maidmonts Gneiss. The augen gneisses are ferroan calc-alkaline granite and granodiorite. On Maidmonts Island, augen gneiss intrudes ca. 3.7 Ga Uivak I gneiss, indicating deformation and metamorphism before ca. 3.3 Ga. Other granitic bodies intruded the augen gneiss at ca. 2.7 Ga and 2.5 Ga during high-T metamorphism. The ferroan calc-alkaline granitoid character of the augen gneiss can be generated by low-pressure differentiation of tholeiitic magmas derived from the mantle, mixed with an older crustal component. This interpretation is consistent with Hf data from gneisses of equivalent age in the Saglek Block (Wasilewski et al. 2021). Similar iron-rich granitoids are found in the Itsaq Gneiss Complex (IGC) of SW Greenland, pointing to widespread magmatic activity at ca. 3.3 Ga, possibly associated with continental rifting or back-arc activity in the Palaeoarchean.

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Mineral carbonation of ultramafic rocks from the Central Sudetic Ophiolite: an experimental approach.

Jakub KIERCZAK¹, Błażej CIEŚLIK¹, Anna PIETRANIK¹, Krzysztof TURNIAK¹, Alicja LACINSKA²Keith BATEMAN²

¹Institute of Geological Sciences, University of Wrocław, Pl. Maksa Borna 9, 50-204 Wrocław, Poland;

²Environmental Science Center, British Geological Survey, Keyworth, Nottingham NG125GG, UK

Ultramafic rocks are considered one of the best substrates for mineral carbonation – a potential solution to sequester CO₂. This is because they consist of magnesium silicates (olivine, serpentine) that readily react with CO₂-rich fluids to form Mg-carbonates and silica. In this study, we have chosen three samples of ultramafic rocks of similar chemical composition but different mineralogy. Two rocks represent partially serpentinized peridotites containing olivine and serpentine as major phases. The third rock is serpentinite, composed almost exclusively of serpentine group minerals. The purpose of the study was to determine the suitability of different samples for mineral carbonation and, to find the conditions under which the process will be most effective.

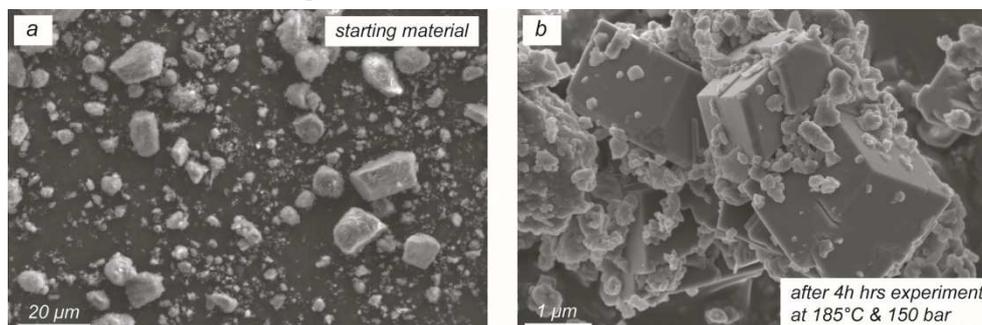


Fig. 1. Pulverized sample of serpentinized peridotite (a) before and (b) after a 48-hour mineral carbonation experiment. Image (b) shows newly formed (during the experiment) magnesite crystals.

The carbonation experiments were performed under a range of conditions. In each case, the material was pulverized to < 50 µm fraction. Short-term experiments lasted 4, 17, and 48 hours and were performed at 150 bar and 185°C. Long-term experiments lasted 7 days and were conducted at 20 bars and 50°C. Analysis of the samples before and after the experiments (SEM observations and XRD analyses) showed that the best conditions for carbonation were achieved during the 48-hour experiment at elevated pressure and temperature. The main solid product of all experiments was magnesite (Fig. 1). Partially serpentinized peridotite proved to be most suitable for mineral carbonation at the conditions tested in our study.

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Fluid inclusions with liquid hydrocarbons in carbonates from the copper-bearing shale of the Rudna Deposit – origin and correlation with ore mineralization.

Piotr KLECZYŃSKI¹, Krzysztof NEJBERT², Wojciech KACZMAREK³

¹ Polish Geological Institute National Research Institute, Address ul. Rakowiecka 4, 00-975 Warsaw; e-mail: Piotr.Kleczynski@pgi.gov.pl

² Department of Geology, University of Warsaw, Address ul. Żwirki i Wigury 93, 02-089 Warsaw; e-mail: knejbert@uw.edu.pl

³KGHM Polska Miedź S.A., Address ul. M. Skłodowskiej-Curie 48, 59-301 Lubin; e-mail: Wojciech.Kaczmarek@kghm.com

The study area is situated in the southern part of the Fore-Sudetic Monocline, where the Permian deposits are developed in the Rotliegend and Zechstein facies. The samples were collected in the Rudna mine, where a rich stratabound Cu-Ag deposit is mined around the horizon of copper-bearing shale (Kupferschiefer). Organic matter (OM) is one of the most important component of the geochemical barrier, where economic concentrations of Cu-Ag sulfides occur. Its content in the ore-bearing shales varies in a wide range from 1% to 30% wt. The role of organic matter in the Kupferschiefer ores of the Lubin-Sieroszowice area has been always considered in genetical models explaining the genesis of Cu-Ag ore mineralization. Its role in the mineralization processes was probably limited to controlling the physicochemical conditions of formation waters and also could support the processes of sulphate sulphur reduction. The aim of this presentation is to document the occurrence and genesis of liquid hydrocarbons present during the formation of the economic concentration of Cu-Ag sulphides.

The Kupferschiefer samples collected from the Rudna mine show strong lithological diversity in the vertical section. The content of organic matter (OM) gradually decreases towards the top of the shale section. In the examined samples, in addition to liptinite, vitrinite and inertinite group macerals, the presence of solid bitumens and liquid hydrocarbons was documented. The solid bitumens fill pore spaces of the shale, while liquid hydrocarbons were found in fluid inclusions within calcite and dolomite that form paragenetic associations with Cu-Ag sulphides. The degree of maturity of OM in the shale samples is insufficient to generate liquid and gaseous hydrocarbons. Data collected indicate that the genesis of accumulations of these hydrocarbons are related to the migration of hydrothermal waters responsible for the origin of the Cu-Ag sulphides. As a potential source of liquid and gaseous hydrocarbons can be indicated strongly thermally altered Lower Carboniferous deposits and/or locally thermally altered Lower Zechstein formations rich in OM, strongly affected by oxidizing hydrothermal solutions genetically related to the development of the Rote Fäule facies.



Ce-allanite from isotropic metagabbroes of the Nowa Ruda massif (SW Poland) – preliminary results

Michał KLUKOWSKI¹

¹General Directorate for National Roads and Highways, Address: Warszawska str. 89, 10-443, Olsztyn, Poland; e-mail: mklukowski@gddkia.gov.pl

The first occurrence of REE-minerals has been discovered in the Central Sudetic ophiolites. Disseminated, up to 50 μm in diameter automorphic Ce-allanite grains are related to Ca-amphibole (Mg-hornblende to actinolite) + pumpellyite + zircon masses developed at the expense of primary magmatic plagioclase of isotropic metagabbroes of the SW part of the Nowa Ruda massif.

The chemical composition of allanite demonstrate profound variation in CaO, FeO^{tot} , Al_2O_3 and SiO_2 (11,8 – 16 wt %, 10,5 – 14,1 wt %, 14,9 – 19,4 wt %, 31,3 – 34,0 wt %, respectively). MgO range between 0,4 – 0,6 wt % and TiO_2 between 0,3 – 1,0 wt %. Na_2O , K_2O and MnO exhibit concentrations below detection limit. The REE demonstrates the following ranges: 7,1 – 10,9 wt % of Ce_2O_3 , 1,6 – 5,2 wt % of Nd_2O_3 , 3,9 – 6,3 wt % of La_2O_3 , 0,4 – 1,1 wt % of Pr_2O_3 , 0,1 – 0,5 wt % of Sm_2O_3 , 0,1 – 0,4 wt % of Gd_2O_3 and up to 0,2 wt of Dy_2O_3 . Y_2O_3 , UO_2 , ThO_2 and F are under detection limit. Abovementioned variations are strictly connected with zonation of a given grain.

Ti-in-amphibole geothermometric estimates for paragenetic amphibole reveal the crystallization temperature of 670 - 550°C. On the Al^{tot} vs. REE + Y + U + Th diagram Ce-allanite from the Nowa Ruda massifs located within the field of hydrothermal (juvenile) plagiogranite-related allanite of the Troodos ophiolite. Analyzed points are located roughly along the 0,5 to 0,6 Fe_{OX} isoline.

Both mineral assemblage, chemical composition, crystallization conditions and geological context are analogue to Troodos, plagiogranite-related REE mineralization. The presence of Ce-allanite in the Nowa Ruda massif can be thus considered as an evidence of hydrothermal alteration promoted by REE-bearing juvenile fluids exsolved by crystallizing plagiogranites (concurrently with pervasive seawater-derived, ocean-floor hydrothermal activity). High concentration of the REEs indicates Ce-allanite crystallization direct from exsolved juvenile fluids. Finally, a direct link between the REE mineralization in ophiolites and the epidiosation indicates the possibility of epidosite formation in the Nowa Ruda ophiolite (especially plagiogranite hosted).

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Multiple *P-T-t* paths revealed by granular zircon open new horizons in impact research

Elizaveta KOVALEVA^{1,2}, Matthew S. HUBER², Anja SCHREIBER¹, Vladimir RODDATIS¹, Nicolai KLITSCHER¹, Richard WIRTH¹

¹Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany; e-mail: kovaleva@gfz-potsdam.de; ekovaleva@uwc.ac.za

²University of the Western Cape, Department of Earth Sciences, Robert Sobukwe Road, 7535 Bellville, South Africa

Hypervelocity impact events result in shock metamorphism recorded in mineral grains, which can be used to reconstruct the peak *P-T* conditions and the post-impact history of the target. Shocked zircons with granular textures document and preserve both shock conditions and ages of impact events. The mechanisms creating these granular textures, however, have not been fully explored. Three mechanisms were suggested by Wittmann et al. (2006): (i) shock-induced solid-state transformation of zircon to reidite and back under high post-impact temperatures; (ii) decomposition of zircon into ZrO₂ and SiO₂ due to shock heating, and back-reaction of these oxides to form new zircon; and (iii) crystallization of amorphous zircon into granular texture. Mechanism (i) of zircon neoblast formation (“former reidite in granular neoblastic,” or “FRIGN” zircon) has been explored in literature in recent years (e.g., Cavosie et al., 2018). We completed a comprehensive transmission electron microscopy (TEM) analysis of a variety of granular zircon aggregates from two complex peak-ring impact structures (Kara, Russia, and Araguainha, Brazil), and demonstrated that there are multiple discernible types of zircon neoblasts formation: (i) granular neoblastic zircon reverted from reidite (i.e., FRIGN); (ii) incongruent melting/dissociation and new crystallization of zircon from oxides; (iii) solid-state recrystallization of damaged zircon by grain boundary migration; (iv) shearing of zircon under elevated differential stress. Moreover, shocked zircon can produce (v) high-pressure, low-symmetry intermediate polymorph of ZrSiO₄ (Mihailova et al., 2019) that can be quenched. The polymorph forms characteristic porous lamellar texture and is easily confused with zircon. Each granular type has a unique *P-T-t*-cooling path related to shock metamorphic conditions. Thus, we confirm that the FRIGN zircon model it is not the only pathway to generate granular zircon. Moreover, granular ZrSiO₄ is not only an indicator of the shock process, but the types of its granules or lamellae record a wider variety of extreme conditions than any other common mineral phase.

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Geological settings of the Polish massive sulfides exploration area in the Mid-Atlantic Ridge – morpho-structural analysis from regional scale to perspective deposits areas

Agata KOZŁOWSKA-ROMAN¹, Michał TOMCZAK¹, Jakub CIAŻELA², Mateusz DAMRAT¹

¹*Polish Geological Institute – National Research Institute, ul. Rakowiecka 4, 00-975 Warsaw, Poland; agata.kozłowska@pgi.gov.pl*

²*Institute of Geological Sciences, Polish Academy of Sciences, ul. Podwale 75, 50-449 Wrocław, Poland*

The Polish exploration area between 26°09'–32°50' N along the Mid-Atlantic Ridge (MAR) spreads across two segments between the Hayes, Atlantis, and Kane fracture zones. The total length of the area is 876 km, and it is a part of the international seabed area beyond the limits of the national jurisdiction of any State, under the International Seabed Authority jurisdiction. It borders the Portuguese submission for an extended continental shelf from the north, and from the south, it borders the IFREMER (France) exploration area.

The Mid-Atlantic Ridge is one of the most promising areas for the possible occurrence of seafloor massive sulfides (SMS), but the critical challenge is to depict the location of the most significant deposits of a mining value, considering the technical and legal frame.

The following study selects areas within exploration blocks that, due to their morphological structure, may indicate the presence of hydrothermal fields. Analysis of the morphology of the ocean floor made it possible to identify structures like flat-topped volcanoes, scarps, faults, axial volcanic ridges, and oceanic core complex (OCC), which are indicators of the probable occurrence of large hydrothermal fields (Ellefmo, Søreide, 2019).

Most currently studied SMS deposits, especially those most significant, are associated with uplifted lower crust and mantle rocks (OCC) at the MAR segments with asymmetric accretion mode (tectonic segment). Others, typically smaller, are hosted in basalts (magmatic segments). It is assumed that at least half of the SMS deposits in the Polish exploration area are associated with asymmetrical modes of accretion and gabbro peridotite rocks (tectonic segments), and this type of geological setting is considered promising for the large high-grade SMS deposits.

The morpho-structural analysis of the Polish exploration area based on high-resolution bathymetric data acquired during the 1st Polish cruise in the Summer of 2022 allowed us to recognize promising areas associated with uplifted lower crust and mantle rocks in various OCCs. Except for three OCCs previously known from the area (Atlantis Massif, Southern OCC, and Dantes' Domes), we have identified and characterized two previously unknown OCCs thanks to the new bathymetric data with a resolution of ~30 m acquired by our expedition. These areas will be subjected to detailed studies i.e. with ultra-high bathymetric data (down to 25 cm) and synthetic aperture sonar (SAS) that will provide a better understanding of the geological settings and reveal key seabed structures related to hydrothermal features and SMS deposits.



Zircon reveals complex polymetamorphic and magmatic history in Napier Complex, East Antarctica

Piotr KRÓL¹, Monika A. KUSIAK¹, Daniel J. DUNKLEY¹, Martin J. WHITEHOUSE², Simon A. WILDE³

¹*Institute of Geophysics, Polish Academy of Sciences, Address Warsaw 01-452, Poland;
e-mail: piotr.krol@igf.edu.pl;*

²*Department of Geosciences, Swedish Museum of Natural History, Address Stockholm 114 18, Sweden;*

³*School of Earth and Planetary Sciences, Curtin University, Address Perth 6845, Australia.*

The Napier Complex is one of the least studied regions where early Earth rocks have been preserved. It is a unique component of the East Antarctic Shield because it archives a timeline of crustal growth from the Eo- to Neoproterozoic, with protoliths dating back to 3.75 Ga (Harley et al., 2019). It is primarily composed of gneisses and granulites that underwent high- to ultra-high-temperature (UHT) metamorphism at ~2.5 Ga (Harley et al., 2019) and locally at ~2.8 Ga (Hokada et al., 2003). Although the UHT rocks are spatially related to convergent plate margins and assembly of supercontinents (Jiao et al. 2023), there is still no consensus when the final assembly of the Napier Complex occurred.

To gain more insights into the crustal evolution of the Napier Complex, samples from the inland Napier Mountains were selected for zircon imaging and U-Pb dating. They record metamorphic growth, modification of zircon and recrystallization at 2800-2770, 2740-2720 and 2490-2460 Ma. The ~2800 Ma metamorphism is recorded in zircon grains with ages as young as 2770 Ma, thus extending the duration of the event by 20 Myr when compared to the earlier date of 2790 Ma proposed by Hokada et al. (2003). For the first time, evidence of fluid-related alteration at ~2730 Ma has been observed in the complex. At the same time, the formation of dioritic protoliths occurred. Furthermore, protolith crystallization ages of ~3210 and ~2825 Ma, were determined for tonalitic and granitic gneisses, respectively. The generation of granitic gneiss was coeval with ~2800 Ma metamorphism in the area. All the samples show significant zircon modification due to the 2490-2460 Ma metamorphism. Based on available data, the ~2500 Ma event likely represents the cumulation of tectonothermal processes that juxtaposed the various crustal domains.

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Bismuth-halogen-rich “gryphons” of the Radlin burning coal-mining heap and their geochemical position against other Upper Silesian fumarolic sites

Łukasz KRUSZEWSKI¹

¹Institute of Geological Sciences, Polish Academy of Sciences, Twarda 51/55, PL-00-818 Warszawa; e-mail: lkruszewski@twarda.pan.pl

13 years of study in the continuously burning post-coal-mining heap in Radlin (Rybnik Coal Area, Upper Silesia, S Poland) allowed to detect numerous mineral species, including those also known from the Moon, and some potentially new ones. recently also confirmed to exist on the Moon. Under current study is an ammonium iodobismuthate forming orange-red microcrystals covering salamoniac crusts. Temperature within the parent fumarole reaches 345 °C but most gas exhausts show 80 °C (as of February 2023). The gas bears ~1 ppm I₂, <100 ppm H₂S (Indicator Tubes). Similar content of I₂ was detected in FeCl-rich fumaroles in the nearby “Szarłota” heap (T_{max} of 120 °C), where a similar Bi-I mineral was also observed. Variations in gas-phase composition were addressed by GASMET DX4000 FTIR spectrometer (06.2022 study): CO₂ 4400-4600, CO 476-551 (reaching 5045 in a new fire zone of the heap), NO₂ 7.2-10, SO₂ 32, NH₃ 0.59, HF 0.06-0.36, AsH₃ 0.13-0.31, CH₄ 148-181, ethane 7.4, ethene 0.79-6.2, *o*-cresol 1.5-4.8, furan 64-86, dimethyl sulfide 9.8-14, dimethyl disulfide 3.6-5.1, thiophene 16, pyridine 5.6-7.9, CCl₄ 1.6-1.7, 1,1-dichloroethane 24, 1,2-dichloroethane 63-80, 1,2-dichloropropane 3.8-5.4, (fully quantitative mode); *n*-butane 7.3-8.8(24), *i*-butane 5.4-6.7(18-19), *n*-pentane 6.4-7.8(25-26), *i*-pentane 6.7-8.2(21), octane 4.0-4.8(26), 1,3-butadiene 60-69(5-7), propene 52-82(35-43), 1-butene 24-28(38-40), toluene 32-38(37-39), 1,2,3-trimethylbenzene (TMB) 21-26(45-46), 1,2,4-TMB 28-33(44-45), 1,3,5-TMB 26-31(43-44), *m*-xylene 34-39(38-40), *p*-xylene 36-39(37-39), *o*-xylene 32-37(39-41), 3-carene 12-14(35-38), *n*-propanol 9.4(33), methanethiol 89-110(34-36), isocyanic acid 9.9-11(39-42), acrylonitrile 67(61), cyclohexanone 6.3(35), methyl ethyl ketone 25(33), C₂Cl₄ 0.46(47), OCS 5.1-5.3(88), and probable SF₆, 0.65-0.66(36-40) (External Library Search mode, fit in parentheses). The most likely admixing trace gases (qualitative analysis of residual spectra) include thiirene, dihydroxycarbene; dioxygen monofluoride and/or digermane / VH₂ / Mg₂H₂ / Si(NO)₂; Mo(CO)₃ and/or *c*-(NO)₂; MoH₂ / peroxyethyl nitrate; Cu(NO)₂ / (chloromethylidene)phosphine / perfluorinated iodinated *p*-benzynes; Zn₂H₂ / selenoacetic acid / *t*-ClO₂ (chlorine nitrate); INS (thiazyl iodide) / diindane / H₂InNH₂; H₂GeCl / Sb₂H / GaH₂ / dihydroxyacetylene; and In(OH) / Cr(OH)₃. The source of Bi is the coal itself, with clearly elevated 0.17 ppm Bi detected in coal from “Szarłota”. Compared to the above fumaroles, ones at Wojkowice-Krzyżówka (T_{max} of 25 °C) represent a fire-cease allowing for a relative species-rich plant (e.g., *Helichrysum arenarium*, *Erigeron annuus*, *Matricaria discoidea*, *Echium vulgare*, *Lepidium densiflorum*, *Solidago gigantea*, *Verbascum*, *Centaurea*; *Rorippa silvestris*, *Lamium amplexicaule*, *Plantago alfa*) coverage of the burning pile.



⁵⁷Fe Mössbauer studies of Fe²⁺-phyllosilicates dehydrogenation

Małgorzata LEMPART-DROZD¹, Artur BŁACHOWSKI²

¹Institute of Geological Sciences, Polish Academy of Sciences, Kraków, Poland;

ndlempar@cyf-kr.edu.pl

²AGH University, Faculty of Geology, Geophysics and Environmental Protection, Kraków, Poland;

artur.blachowski@agh.edu.pl

The oxidation in Banded Iron Formation (BIF) are debated between biotic and abiotic, and/or primary and secondary oxidation. In contrast to the model of oxidation by incorporation of oxygen, Fe²⁺ oxidation of phyllosilicates is driven by a thermally induced dehydrogenation reaction. Dehydrogenation does not require the presence of external oxygen and occurs via electron transfer between OH⁻ and Fe²⁺, resulting in H₂ and H₂O release during heating. ⁵⁷Fe Mössbauer spectroscopy was used to study dehydrogenation during thermal decomposition of minnesotaite (Lempart-Drozdz et al., 2022) and chlorites (Lempart et al., 2018) as a potential abiotic secondary oxidation reaction of Fe²⁺-rich silicates in BIFs. The redox state of iron, structural changes, and the alteration products were studied. The results may be important in the context of the current interest in the potential H₂ generation from BIFs and the oxidative dehydrogenation of Fe²⁺-bearing minerals on Mars.

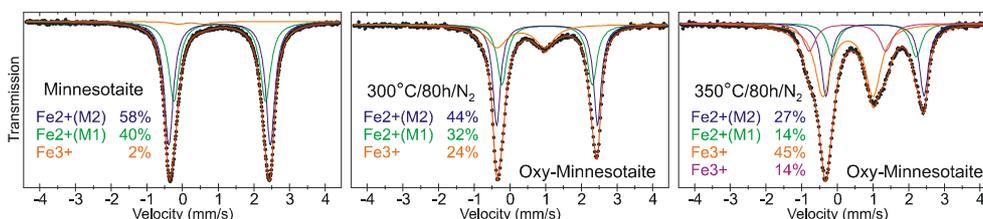


Fig. 1. ⁵⁷Fe Mössbauer spectra of minnesotaite Fe₃Si₄O₁₀(OH)₂ measured ex-situ at room temperature before and after isothermal heating at 300°C and 350°C for 80h under N₂ inert atmosphere conditions.

The colours mean: black dots – experimental, red line – fitted, green – octahedral Fe²⁺ in site M1 (*cis*), blue – octahedral Fe²⁺ in site M2 (*trans*), and orange/magenta – Fe³⁺.

Relative percentage distribution of the iron atoms are shown.

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Optimization of a new method for the recovery of rare earth elements by crystallization from solutions

Mikołaj LEŚ¹, Kacper STASZEL¹, Julia SORDYL^{1,2}, Maciej MANECKI¹

¹Department of Geology, geophysics and Environmental Protection, AGH University of Kraków, al. Mickiewicza 30, 30-059 Kraków, Poland; e-mail: mles@student.agh.edu.pl

²Department of Earth Sciences, Uppsala University, Villavägen 16, SE-752 36, Uppsala, Sweden

Introduction

There is growing demand for novel REE recovery methods from alternative ores and previously economically unavailable sources, due to the Chinas' continuous domination of the REE market. One of the recently developed methods is leaching of apatite using phosphoric acid followed by coprecipitation of REE phosphates in the presence of Pb (Sordyl et al. 2023). In this research, laboratory experiments were conducted which involved precipitation of crystalline Pb-phosphates from mixed solution containing ~24mg/L of each REE (La-Lu, Y and Sc) and Th. To optimize precipitation, the experiments were carried out at pH 2, 4 and 6 with varying Pb content with respect to REE concentration (molar fraction Pb:REE equal to 1:4, 1:1, and 4:1).

Results and discussion

The efficiency of REE recovery was quantified by the percentage removal from solution, defined as the ratio of the amount removed to the initial concentration of each element in solution. The most efficient reaction was at pH = 4 and 6, with removal rate exceeding 95%. The optimal Pb:REE molar ratio was established at 1:1. Regardless of initial conditions of experiments, Sc and Th were removed almost completely from each solution. In all experiments, removal of REE from solution is driven by coprecipitation of Pb and REE phosphates. Determining the phase composition is difficult due to the fine grain size of the poorly crystalline sediments, particularly at elevated pH and low Pb concentrations. Most abundant phase was pyromorphite $Pb_5(PO_4)_3Cl$ substituted with REE. It was accompanied with Pb-REE-phosphates of low crystallinity. Complementary experiments involving synthesis with selected individual REEs indicate that La to Sm elements (LREE) form structurally identical Pb-LREE phosphates, while Tb to Lu (and Y) elements (HREE) coprecipitate with Pb to form different phosphate phases. Despite these differences, the efficiency of recovery is very high and co-precipitation of Pb and REE phosphates is a promising method for the beneficiation of REE using hydrometallurgy.

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Relations between REE-phosphates in the Alum Shale Formation at the Caledonian Foreland in Sweden

Jarosław MAJKA^{1,2}, Julia SORDYL^{1,2}, Maciej MANECKI^{1,2}, Chris MARK³

¹ Department of Earth Sciences, Uppsala University, Uppsala, Sweden

² Faculty of Geology, Geophysics and Environmental Protection, AGH University of Kraków, Poland

³ The Swedish Museum of Natural History, Stockholm, Sweden

The Cambrian Alum Shale Formation in the Caledonian Autochthon is recognized as a potential source for various metals including Uranium, Vanadium and Rare Earth Elements (REE). However, the knowledge about the occurrence and distribution of the REE-carriers, mostly phosphates in phosphoritic varieties of the Alum Shale, is vastly limited. Neither is known the potential mechanism behind enrichment in REE of these minerals. A coupled textural, chemical and isotopic characterization of REE-carriers was applied in this study. The main REE-phosphates recognized within the phosphoritic shale are monazite, xenotime and apatite. Monazite reveals complex zoning with apparent dissolution reprecipitation features. It is mostly detrital in origin yielding Proterozoic to early Cambrian ages. However, reprecipitated zones yielded Early Devonian age. Xenotime is also interpreted to be detrital. Dissolution-reprecipitation features of xenotime have also been noticed. Some apatite grains are detrital yielding Proterozoic ages, while majority have clearly bio- and diagenetic origin. REE enrichment within the two latter types reaches 2 wt% of total oxide. Such REE-apatite also yielded Early Devonian age, interpreted as the timing of fluid-induced dissolution-reprecipitation. This is supported by REE distribution when normalized to post-Archaeon average shale revealing no Ce-anomaly, which confirms non-diagenetic origin of REE-enrichment. Additionally, Fe-Mg carbonates have been identified as another carrier of REE. Tentatively, we propose the following sequence of events leading to the development of REE-mineral assemblage in the phosphoritic Alum Shale at the Caledonian Front in Sweden: (1) detrital monazite, xenotime, and apatite were deposited in shale protolith at the Baltica passive margin; (2) biogenic and diagenetic apatite was co-deposited within the same protolith; (3) the Alum Shale underwent metamorphism in greenschist facies during the Early Devonian Scandian phase of the Caledonian Orogeny; (4) this prograde metamorphism triggered partial dissolution of metastable detrital monazite (and potentially xenotime) in a vastly similar mode and similar conditions to monazite (and xenotime) behavior within the so-called allanite window defined for common pelites; (5) the latter process resulted in mobilization of REE in a fluid that caused dissolution-reprecipitation of apatite (and carbonates); (6) further increase of metamorphic conditions brought monazite (and xenotime) back to its stability field as demonstrated by the development of newly grown Early Devonian metamorphic domains.

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The occurrence and provenance of TiO₂ polymorphs in a pyrite-REE stratiform deposit of the Wiśniówka area (south-central Poland)

Zdzisław M. MIGASZEWSKI¹, Agnieszka GAŁUSZKA¹

¹Institute of Chemistry, Jan Kochanowski University in Kielce, 7 Świętokrzyska St., 25-406 Kielce; e-mail: zmig@ujk.edu.pl (Z. Migaszewski), mail: agnieszka.galuszka@ujk.edu.pl (A. Gałuszka)

The Wiśniówka Massif of the western part of the Holy Cross Mts. is highlighted by the presence of unique sediment-hosted pyrite-REE mineralization zones that occur within the Upper Cambrian siliciclastic formation. Results derived from many years of geochemical, mineralogical and petrographic studies have been summarized by Migaszewski and Gałuszka (2019, 2023ab). The more recent investigation has been centred on the occurrence and provenance of TiO₂ polymorphs and their relationship with associated pyrite and REE minerals (Migaszewski, Gałuszka, 2023b). In most sedimentary studies, predominant rutile is recognized as a detrital accessory mineral originated from weathering of igneous, metamorphic and older sedimentary rocks or hydrothermal deposits. Identification and geochemical characteristics of TiO₂ polymorphs were determined using optical and electron microscopy, electron microprobe analysis and laser Raman microspectrometry. The last technique showed that anatase (56%) prevailed over rutile (30%), mixed phases of rutile-anatase (11%) and rutile-brookite (2%), and brookite (1%). TiO₂ polymorphs occur mostly in the form of interstitial massive or skeletal grains averaging 30–50 μm across, in places attaining 110 μm in size. They commonly co-occur with pyrite, goethite/hematite, REE minerals (APS group, xenotime, most monazite) and nacrite. The hitherto study has shown that all these minerals formed as a results of multiphase hydrothermal vent activity in the Wiśniówka Late Cambrian depositional basin. In spite of the overlapping mineral generations, the authors identified two basic phases of their crystallization:

- (i) Pyrite and TiO₂ polymorphs (primarily anatase) under reducing conditions;
- (ii) Goethite/hematite and TiO₂ polymorphs (mostly rutile) under oxidizing conditions.

This study places under a question mark both the microscope identification of TiO₂ polymorphs and the provenance of titanium in unmetamorphosed siliciclastic formations.

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Not fertile, but refertilized - melt impregnation in Puke massif, Mirdita Ophiolite, Albania

Jakub MIKRUT¹, Magdalena MATUSIAK-MAŁEK¹, Benoit ILDEFONSE², Andrea TOMMASI², Georges CEULENEER³, Michel GRÉGOIRE³, Kujtim ONUZI⁴

¹University of Wrocław, Institute of Geological Sciences, Wrocław, Poland, e-mail: jakub.mikrut@uwr.edu.pl,

²Géosciences Montpellier, CNRS & Université de Montpellier, 34095 Montpellier, France

³Géosciences Environnement Toulouse, Toulouse University, CNRS, IRD, CNES, 31400 Toulouse, France

⁴Institute of GeoSciences, Rr.Don Bosko, Nr.60, Tirana, Albania

Mirdita ophiolite (N Albania) is formed of Jurassic Neothetian lithosphere. It consists of two N-S trending belts of ultramafic massifs, separated by a zone of crustal volcanic and plutonic rocks. The western belt and adjacent crustal rocks show dominant MORB affinity, whereas eastern belt has SSZ affinity. This study focuses on the Puke massif located in the western belt.

The Puke massif is interpreted as an ancient Oceanic Core Complex forming a mantle dome. The supposed primary lithology – coarse grained, plagioclase-free spinel harzburgite – is restricted to the eastern part of the massif. Strong olivine CPO (J-index above 2.76), and microstructures indicate high temperature deformation conditions. Other parts of the massif are composed of mylonitic, plagioclase- and amphibole-bearing peridotites, mostly lherzolites. Two types of reactional microstructures occur in those rocks. The first one displays very fine-grained clusters of intermixed olivine and orthopyroxene, the second one consists in ortho- and clinopyroxene, amphibole and plagioclase grains dispersed among coarser olivine. CPO in mylonitic olivine is weakened (J-index 1.06-2.11), which points to low-temperature deformation. Mylonites are often cross-cut by gabbroic and pyroxenitic veins, locally forming intercalating layers with peridotites.

The mylonites and harzburgites also differ in chemical composition. Clinopyroxene in mylonites is HREE- (>1xPM) and TiO₂-rich (<0.1 wt.%), while in harzburgites it is HREE- and TiO₂-poor (<1xPM, <0.1 wt.%). Similar REE trends are observed in gabbros cross-cutting peridotites, and observed within crustal material, which indicates their related affinity. Only some harzburgites escaped magmatic impregnation, and exhibit depleted LREE trend, pointing to partial melting.

Textural and chemical observations suggest magmatic impregnation of Puke mylonites, during deformation. Evolution from high temperature to low temperature texture in peridotites is observed from the east to the west. MORB-like composition of mylonitic peridotites developed as a secondary feature, and is restricted to the uppermost part of Puke mantle dome.

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Distribution of elements in post-magmatic titanite on the example of granitic pegmatite in Szklarska Poręba (Sudetes, Poland)

Karolina MIL¹, Bożena GOŁĘBIEWSKA¹

¹Faculty of Geology, Geophysics and Environmental Protection, AGH-University of Science and Technology, al. Mickiewicza 30, 30-059 Kraków, Poland; mil@agh.edu.pl, goleb@agh.edu.pl

Titanite is a widespread accessory mineral, crystallizing in a wide range of physicochemical conditions, in both igneous and metamorphic rocks.

In our research, we focus on changes in the chemical composition of titanite from granite pegmatite in the Szklarska Poręba quarry (Karkonosze granite massif, southwestern Poland), where, numerous minerals representing W–Sn–Mo–Bi and Th–U–REE associations have been found. Substitutions in the composition of titanite can provide information about the evolution of postmagmatic processes. Analyzed titanite grains display significant chemical heterogeneity. On the basis of microprobe results (obtained by JEOL SuperProbe JXA-8230), we determined the following chemical titanite varieties:

- Sn-rich titanite with a maximum Sn content of 14.78 wt% (0.21 apfu).
- (Sn, Nb, Ta, Sc)-rich titanite; the highest concentration of Sn (15.88 wt%; 0.23 apfu) was recorded in the bright region of the zoned titanite crystal associated with stokesite (CaSnSi₃O₉·2H₂O). Sc enrichment (up to 1.9 wt.%; 0.06 apfu) is present in all analyses of this titanite variety, with the highest concentration being associated with Sn and Nb-rich zones (up to 14.41 and 9.85 wt.%, respectively). The content of Ta in this variety of titanite reached 7.88 wt.% (0.08 apfu).
- (Y, REE)-rich titanite; the highest concentrations of Y (up to 6.83 wt.%; 0.12 apfu), with high Al content (up to 9.27 wt %; 0.37 apfu), were observed in titanite association with hingganite-(Ce) Be(Ce,Y)(SiO₄)(OH). The content of REE (up to 2.39 wt.% - excluding Y) exhibits a clear prevalence of HREE (from Gd to Lu) compared to LREE (from La to Sm).

Various substitutions in titanite from pegmatitic assemblage show the path of evolution of postmagmatic processes. Titanite grains enriched in Nb, Ta evolve towards zabińskiite compositions, a mineral of the titanite group. In addition to the principal substitution mechanisms, our focus should also encompass the content of scandium within the titanite structure.

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Pyroxenites diversity in the subcontinental mantle: the example of the External Ligurian ophiolites (northern Apennine, Italy)

Alessandra MONTANINI¹, Riccardo TRIBUZIO², Elisa FERRARI^{1,3}, Ambre LUGUET⁴, David VAN ACKEN⁵

¹ Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Italy

² Department of Earth and Environmental Sciences, University of Pavia, Italy

³ INGV - Istituto Nazionale di Geofisica e Vulcanologia, Milano, Italy

⁴ Institute for Geosciences, University of Bonn, Germany

⁵ School of Earth Sciences University College Dublin, Ireland

The ocean-continent transition exemplified by the External Ligurian mantle section consists of three distinct domains, developed in response to the Mesozoic extension of continental lithosphere (Ferrari et al. 2022): (1) a spinel tectonite domain (ST), characterized by sub-solidus static formation of plagioclase, (2) a plagioclase mylonite domain (PM) experiencing melt-absent deformation, and (3) a nearly undeformed domain (PI) that underwent reactive melt infiltration under plagioclase-facies conditions. All domains are characterized by the presence of distinct types of pyroxenite layers with variable origin, age and evolution.

In the ST domain, spinel pyroxenites crystallized at $P > 1.5$ GPa from melts derived from a eclogite-bearing peridotite source, which reacted with their host peridotite to form hybrid pyroxenites, presumably in the Lower Palaeozoic (~430 Ma, Borghini et al. 2016). The PM domain locally preserves the occurrence of UHP (~2.8 GPa) garnet clinopyroxenites and websterites. The garnet clinopyroxenites were related to recycling of crustal mafic protoliths through partial melting of eclogitized gabbros, whereas the garnet websterites were interpreted as reaction products between eclogite-derived melts and peridotites. Nd-Hf-Pb isotope systematics indicate that the mafic precursors of the garnet pyroxenites experienced a long-term evolution of recycling into the mantle, developing an isotope signature close to the HIMU component of oceanic basalt sources. Re-Os isotope systematics constrains the formation of garnet pyroxenite gabbroic precursors at ~2.6 Ga. In the PI domain, spinel pyroxenites include Fe-rich clinopyroxenites and Mg-rich websterites. Reactive melt infiltration involved both peridotites and pyroxenite layers, causing extensive mineral and chemical transformations. Lower Palaeozoic Re-Os model ages for the Fe-rich clinopyroxenites (~0.4-0.5 Ga) likely represent their age of crystallization, whereas a Sm-Nd isochron at ~210 Ma is interpreted to record an isotopic homogenization due to melt-rock interaction.

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Preliminary results of U-Pb isotope studies of detrital zircons from the Cretaceous sedimentary rocks of the Outer Western Carpathians in Poland

Magdalena PAŃCZYK¹, Jerzy NAWROCKI², Tomasz MALATA³, Piotr DZIADZIO⁴, Leszek BALICKI³, Dominik GURBA¹

¹Micro-area Analysis Laboratory, Polish Geological Institute-National Research Institute, Address: 4 Rakowiecka St., 00-975 Warsaw, Poland; e-mail: Magdalena.panczyk@pgi.gov.pl

²Regional Geology Department, Polish Geological Institute-National Research Institute, Address: 4 Rakowiecka St., 00-975 Warsaw, Poland; e-mail: Jerzy.nawrocki@pgi.gov.pl

³Geohazards Center, Polish Geological Institute-National Research Institute, Address: 1 Skrzatów St., 31-560 Krakow, Poland;

⁴Oil and Gas Institute – National Research Institute, Address: 25A Lubicz St., 31-503 Krakow, Poland

A set of U-Pb isotope ages of detrital zircons from 20 samples of the Berriasian to Maastrichtian sediments taken from the Silesian, Sub-Silesian, Dukla and Magura structural units in various regions of the Polish Outer Western Carpathians was obtained and interpreted in terms of their sources. In the Silesian and Sub-Silesian and Dukla units the most frequent are mid-Variscan zircons derived from the Variscan Internides. On the other hand, detrital zircons originally derived from the Cadomian and Caledonian sources are equally or even more frequent in the samples from Magura unit only. Samples from this unit contains also a significant amount of Cretaceous zircons. Further studies of the whole sample set collected from all mentioned structural units should allow to recognize changes of zircons sources in time and space, and link them with Cretaceous palaeogeographic frames of the Carpathian domain. The issue of whether the transport directions inferred from sedimentological evidences are in agreement with delivery paths of detrital zircons will also be examined.

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Detection of HCl and CH₄ in the Martian atmosphere: a geological perspective

Weronika PATALAS¹, Jakub CIAŻELA¹

¹Institute of Geological Sciences, Polish Academy of Sciences, ul. Podwale 75, 50-449 Wrocław, Poland; w.patalas@twarda.pan.pl

This research aims to find volcanic and hydrothermal gases such as HCl, CH₄, H₂S, and SO₂ in the atmosphere of Mars. As these are known from volcanic and hydrothermal activity areas on Earth, they might be essential in detecting potential high-temperature geological processes on Mars.

ExoMars Trace Gas Orbiter (TGO) currently tracks down several volcanic trace gases using two instruments, Atmospheric Chemistry Suite (ACS) and Nadir and Occultation for Mars Discovery (NOMAD), which can detect volcanic trace gases on a ppt to ppb level with a spatial resolution of 15 km. NOMAD is a suite of three spectrometers, among which the Solar Occultation (SO) spectrometer is the most capable of detecting volcanic trace gases. In this study, we use the NOMAD spectrometer in the SO mode.

We have found nine detections of HCl (e.g., Fig. 1A) and one of potential CH₄ non-associated with HCl in the atmosphere of Mars (Fig. 1B) in Mars years 34 and 35. Most HCl occurs in the southern high latitudes, where water vapour sublimates from the southern polar cap and permafrost during the southern hemisphere summer. The vertical distribution of HCl resembles the vertical distribution of water vapour. In the next step, we need to verify whether HCl is associated with other gases (CH₄, H₂S, and SO₂) in the atmosphere and how the seasonal appearance of HCl is connected with the ice caps or permafrost on Mars. Answering these questions will allow us to determine whether it originates from hydrothermal activity or other geological processes.

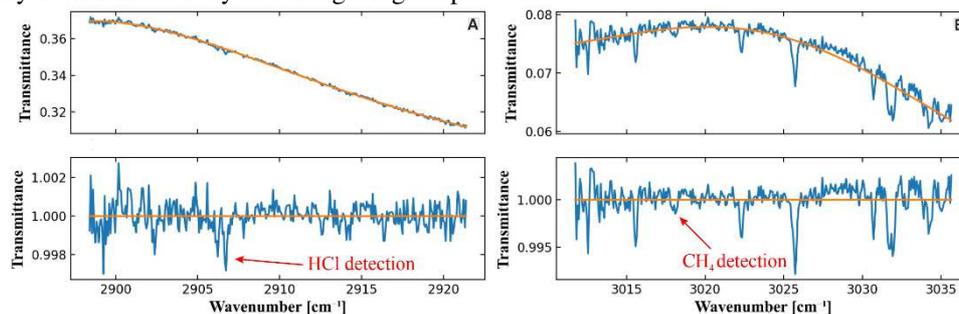


Fig. 1. Example of the (A) HCl detection in the atmosphere of Mars: measurements in the diffraction order 129 performed on November 7, 2018; ($L_s = 284.5^\circ$, Latitude = 63°S , Longitude = 149°E); altitude = 20,1 km. (B) CH₄ in the atmosphere of Mars: measurements in the diffraction order 129 performed on July 21, 2021; altitude = 4,4 km. The best-fit synthetic spectra are shown by the blue curves and orange line as transmittance, normalized to 1 on the lower panels.

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Cassiterites from the Western Sudetes, SW Poland

Adam PIESTRZYŃSKI¹, Władysław ZYGO¹, Krzysztof FOLTYN¹, Tonny Bernt THOMSEN², Benjamin DOMINGUEZ HEREDIA²

¹Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Krakow, al. A. Mickiewicza 30, 30-059 Kraków, Poland; piestrz@agh.edu.pl

²Geological Survey of Denmark and Greenland (GEUS), Department for Mapping and Mineral Resources, Copenhagen, Denmark

Cassiterite occurs in several localities in the Western Sudetes in SW Poland, most notably in the Stara Kamienica Schist Belt (SKSB). The SKSB hosts low-grade cassiterite mineralization disseminated in the chlorite–mica–quartz schist forming a stratabound body and locally accompanied by a polymetallic sulphide/sulphosalt association.

Three cassiterite occurrences were studied: 1) cassiterite from the Gierczyn-Przecznica deposit area; 2) alluvial material collected in the foreground of the aforementioned deposit; and 3) samples from pegmatite: related to the intrusion of the Karkonosze Granite and from Piława Górna. Cassiterites from schist deposit have very similar chemical composition to those from alluvial complex but EPMA and LA-ICP-MS analyses of cassiterites reveal significant differences between pegmatites and samples from the SKSB. The cassiterites from Piława Górna are enriched in Ta and Nb, whereas in Czarnów the cassiterite is enriched in W and V. In the Gierczyn-Przecznica area, Hf and Mn are depleted, while these elements are enriched in the other types

Investigated cassiterite from the Gierczyn-Przecznica area are in general poor in Nb and Ta but in some cases contain elevated content of In (up to 0.73 wt.% In₂O₃ in samples from Przecznica area).

The small grain size of cassiterite from Gierczyn and Przecznica made U-Pb analyses challenging, and those that were successful, yield lower intercept dates of 353±14 and 360±5 Ma for the “translucent” cassiterite, whereas “spongy” grains yielded younger dates towards 318±6 Ma. These results of “translucent” cassiterite are clearly older than the Karkonosze Granite intrusion and may likely represent the age of resetting during regional metamorphism.

This activity was carried out under the project “Enhanced Use of Heavy Mineral Chemistry in Exploration Targeting (MinExTarget)” that received funding from the European Institute of Innovation and Technology (EIT)



Newly discovered LCP-rich volcanoes in Claritas Fossae shed new light on the evolution of Martian magma

Bartosz PIETEREK^{1,2}, Petr BROŽ³, Ernst HAUBER⁴, Katrin STEPHAN⁴, Andrzej MUSZYŃSKI¹

¹Geohazard Lab, Institute of Geology, Adam Mickiewicz University, Poznań, Poland, email: barpie@amu.edu.pl

²Polish Geological Institute – National Research Institute, Warsaw, Poland

³Institute of Geophysics of the Czech Academy of Sciences, Prague, Czech Republic

⁴Institute of Planetary Research, DLR, Berlin, Germany

Despite the fact that Martian volcanoes have been intensively studied for several decades, they still keep unexplored records of the magmatic evolution of Mars. Currently, our insight into the compositional evolution of Martian magmas is limited, as most volcanic regions were modified by the widespread younger plain-style volcanic activity of basaltic composition dominated by high-calcium pyroxenes (HCP). However, some regions in Tharsis, the largest Martian volcanic province, escaped resurfacing events and maintained the possibility of preserving volcanic landforms that may keep still unrevealed data about magmatic processes. Therefore, we explored a region of an old fractured crust of Claritas Fossae located in the southern part of Tharsis and searched there for signs of volcanic activity.

By using data from Context Camera (CTX) and High Resolution Imaging Science Experiment (HiRISE), we discovered and mapped 39 mounds superimposed on the ancient (Noachian-age) highly fractured crust. We deciphered that the edifices are characterized by the fresh-looking appearance being consistent with the volcanic origin (Pieterek et al., 2024). We interpreted that these volcanoes have been emplaced by an effusion of relatively viscous lavas incapable of significant movement. As these volcanoes do not reveal significant modification by erosion and postdate the main N-S-trending fracturing of Claritas Fossae, we concluded that they cannot be ancient (e.g., Noachian). However, a spectral investigation utilizing the data from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) shows a distinctly different mineral composition of the studied edifices from most other young volcanoes and lava flows found elsewhere on Mars. We found that investigated small-scale volcanoes are associated with high concentrations of low-calcium pyroxenes (LCP). Such composition contradicts the typical thoughts about the global mineral transition from LCP- to HCP-dominated magma that is dated at approximately 3.5 Ga. Finding LCP associated with pristine and hence likely young volcanoes (< 3 Ga) evidence that, at least locally, relatively young volcanic eruptions might have been fed by magmas depleted in aluminum and calcium that are produced by a high degree of partial melting. This suggests that Mars might have maintained enough heat to produce local zones of high degree of partial melting which occurred much later in Martian evolution than previously thought.

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The polygenetic character of Martian fissure eruptions and their progressive subsurface flow channelization

Bartosz PIETEREK^{1,2}, Thomas JONES³

¹Geohazard Lab, Institute of Geology, Adam Mickiewicz University, Poznań, Poland, email: barpie@amu.edu.pl

²Polish Geological Institute – National Research Institute, Warsaw, Poland

³Lancaster Environment Centre, Lancaster University, Lancaster, United Kingdom

Although almost the entire surface of Mars is targeted by the Context Camera (CTX) images providing sufficient resolution (~6 m/px) for detailed studies of spatiotemporal reconstructions of volcanic systems, fissure-fed volcanic systems remain poorly understood. On Earth, the dynamics of magma in the fissure plumbing system might be directly investigated by real-time field observations and laboratory-based analyses which results provide fundamental insights into the style, behaviour, and longevity of eruptions. However, on Mars, such analysis and investigation of fissure eruptions and their accompanying magmatic plumbing systems are solely limited to remotely sensed data. Therefore, the spatiotemporal investigation of Martian volcanic edifices on a high-resolution scale provides a means to unravel insights into, the otherwise inaccessible, magmatic subvolcanic plumbing systems. Here, using the combination of the CTX images and digital elevation models, we conducted a detailed mapping and age dating allowing us to shed more light on the spatiotemporal evolution of the fissure system south of Pavonis Mons, Mars. Such an approach enabled us to be the first who evidence the Martian eruption localization process and place quantitative constraints on the lifetime and lengthscales of Martian fissure-controlled plumbing systems (Pieterek and Jones, 2023).

In the studied region, we mapped and dated 30 volcanic units that constitute a larger volcanic field comprising low shield volcanoes and fissure vents associated with lava flows. However, to decipher the channelization process within the subsurface dyke, we focused on the > 90-km-length prominent NE-SW trending volcanic fissure accompanied by lava flows and a steep summit cone at its northern end. Using CTX-based 3D visualizations, we showed that the steep-summit cone is stratigraphically the highest followed by the associated finger-shaped lava flows and lastly, the central fissure lava flows that are stratigraphically the lowest. These constraints were further verified by crater counting revealing that the central fissure system experienced multiple eruptions of a period of several million years (64.3 through to 47.3 Ma), and thus, likely had a long-lived (minimum ≥ 9 Ma) and active magmatic plumbing system. These results of progressive localization and the increase in viscosity of erupted products suggest that, over time, this fissure system had a plumbing system experienced progressive subsurface flow focussing, and evolved chemically by crystallization and/or magmatic differentiation. This indicate that studied fissure system was fed by multiple eruptions producing volcanic edifices with a polygenetic character.

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Crystallographic EBSD-based characterization of palisade quartz-coesite inclusions (Dora Maira, Western Alps)

Tomáš POTOČNÝ¹, Karolina KOŚMIŃSKA¹ and Jarosław MAJKA^{1,2}

¹Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Kraków, Poland ; e-mail: potocny@agh.edu.pl

²Department of Earth Sciences, Uppsala University, Uppsala, Sweden

Introduction

Coesite represents one of the strongly limited evidences of ultra-high pressure (UHP) metamorphism. There are still large gaps in the understanding of mineral reactions under such extreme conditions. Finding of coesite is often the only possibility to detect predominantly felsic UHP terranes. It rapidly transforms to so called "palisade" quartz during exhumation and decompression and it is usually preserved only in form of inclusions in other minerals acting as pressure vessels (e.g. garnet).

This study is focused on electron backscatter diffraction (EBSD) and misorientation analysis of palisade quartz from archetypal UHP locality Dora Maira Massif in the Western Alps. The aim was to define crystallographic characteristics of palisade quartz with regard to the transformation of coesite in pyrope-quartzite from Dora Maira. Our observations provide systematic criteria to coesite-quartz transformation and palisade quartz crystallization.

Results and discussion

Crystallographic analysis based on EBSD yielded several criteria that define the conversion of coesite to palisade quartz during exhumation. Generally the orientation of quartz crystals often look randomly distributed. If we use the orientation distribution function, the effect of larger grains, will of course be apparent. The problem, however, is the numerous smaller grains, the effect of which disappears. Nonetheless, certain regularities can be seen in crystallographic preferred orientation of the quartz, interestingly changing from inclusion to inclusion. Hence, the features that have been clearly observed so far can be summarized as follows:

- (1) Coesite always represents a single crystal in the core of the inclusion;
- (2) Misorientation analysis of palisade quartz defined the difference between individual quartz grains and their sub-grains boundaries;
- (3) The misorientation between two neighbouring (???) quartz grains falls into the interval of 5-59° and 61-100°/[0001];
- (4) Within each quartz grain, sub-grain boundaries have intra- and intergranular misorientations of exactly 60°/[0001].

In the course of our further research we will aim to define the growth behaviour of palisade quartz, as pseudomorphs after coesite and link it to rates and style of exhumation processes.

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Th-U-Pb dating of rare euhedral postkinematic monazite - Jurassic to Paleogene tectonometamorphic evolution of the Meliatic accretionary wedge in the Western Carpathians

Tomáš POTOČNÝ¹ and Štefan MÉRES^{†2}

¹Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Kraków, Poland; e-mail: potocny@agh.edu.pl

²Department of Geochemistry, Faculty of Natural Sciences, Comenius University Bratislava, Slovakia

Introduction

The Meliata Superunit of the Western Carpathians incorporates the blueschists-facies Bôrka Nappe and the low-grade polygenous mélange – Meliata Unit s.s., both occurring as dismembered tectonic slices in a complicated accretionary wedge overlying the Gemer Superunit. The Meliata Unit is located in the lowermost structural position among the Inner Carpathian cover nappes. The high pressure-low temperature (HP/LT) Bôrka Nappe includes Permian to Triassic clastic formation with volcanics. The HP/LT metamorphism was directly related to subduction, whose age was estimated to 160-150 Ma. The subsequent exhumation of the Bôrka Nappe and its transformation to a system of dismembered nappes was accompanied by retrogressive metamorphism under the greenschist facies conditions. The mélange character of the Meliata Unit s.s. is defined by a co-existence of Triassic ophiolite, and undoubtedly Lower-Middle Jurassic dark shales containing olistoliths of mostly Triassic rocks.

Results

In the low grade metamorphosed probably Jurassic dark shales dominated by Q-Ab-Ms, a presence of numerous post-tectonic euhedral porphyroblasts of monazite was revealed (30-500 µm in size), all exhibiting oscillatory zoning. The number of cavities and varying chemistry indicate a very rapid growth of monazite. Based on the shape of its crystals it continued even under post-kinematic conditions. The cores of oscillatory zoned monazite show relatively lower contents of Ce₂O₃ (27 wt. %) and higher contents of Nd₂O₃ (19.2 wt. %), Sm₂O₃ (3.7 wt. %), and ThO₂ (4.8 wt. %), while the rims contain lower values of Nd₂O₃ (16 wt. %), Sm₂O₃ (0.7 wt. %), and ThO₂ (0.1 wt. %) and increased values of Ce₂O₃ (36.6 wt. %). The monazite see, to record the entire tectonometamorphic story of the Meliata Superunit. The incoming northern passive margin into the subduction channel and HP/LT metamorphism was dated to ca. 200-160Ma. Exhumation and formation of the accretionary complex was estimated to ca. 150-100 Ma. Collapse of the accretionary complex has happened at ca. 90-80 Ma. The final phase of the nappe stacking and emplacement of the nappes was eventually achieved at ca. 70-50 Ma.

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Siderophore producing bacteria affect stability of metallurgical wastes

Anna POTYSZ¹

¹Institute of Geological Sciences, University of Wrocław, Address: Cybulskiego 30, 50-205 Wrocław, Poland; e-mail: anna.potysz@uwro.edu.pl

Some microorganisms excrete metabolites namely siderophores that reveal high affinity towards iron and other elements. The existence of these bacteria in the environment is abundant. Therefore, implementation of such microorganisms to track bioweathering processes is crucial to understand element migration. This study evaluated experimentally the influence of *Pseudomonas fluorescens* on dissolution of mineral phases being a components of metallurgical residues (slag and matte).

A 119 days long experiment was carried out in semi-open pass flow through the reactor. Element release was assessed by an inductively coupled plasma atomic mass spectrometer, whereas phase dissolution and secondary phase formation was determined using scanning electron microscope and geochemical modelling.

This study proved the contribution of siderophore-producing bacteria to bioweathering of metallurgical residues. The leachates resulting from solid exposure to bacteria were enriched in elements as compared to leachates resulting from abiotic treatments with sterile medium and water. Metallurgical matte was found to be more susceptible to dissolution than slag because of higher element leaching (11% of Pb) and more pronounced weathering signatures. Overall, bacterially mediated mobilization of the metals took place in the following order: Cu > Pb > Zn. The formation of secondary phases was more evident on the surface of the mat. Geochemical model proved formation of precipitates and determined the type of secondary phases formed.

Based on this study, it is concluded that the presence of siderophore-producing bacteria at the dumping sites cannot be ignored. Even though microorganisms are acting at the microscale, their contribution to bioweathering might become important mechanisms driving elements mobility in a long-term perspective. Upcoming work aims to evaluate other strains representing the group of siderophore-producing bacteria. In addition, implementation of more advanced techniques such as X-ray near edge absorption structure spectroscopy is in progress to quantify the secondary phases formed.

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Metallurgical slags and mining wastes – metal mobility in the environment under exposure to biotic conditions

Anna POTYSZ¹, Artur PĘDZIWIATR², Jakub KIERCZAK¹, Sebastian HEDWIG³, Markus LENZ^{3,4}

¹Institute of Geological Sciences, University of Wrocław, Address: Cybulskiego 30, 50-205 Wrocław, Poland; e-mail: anna.potysz@uwr.edu.pl, jakub.kierczak@uwr.edu.pl

²Institute of Agriculture, Warsaw University of Life Sciences, Address: Nowoursynowska 159 b.37,02-787 Warszawa, Poland; e-mail: artur_pedziwiatr@sggw.edu.pl

³Institute for Ecopreneurship, School of Life Sciences, University of Applied Sciences and Arts Northwestern Switzerland, Switzerland; e-mail: markus.lenz.fhnw.ch, Sebastian.hedwig@sggw.edu.pl

⁴Sub-Department of Environmental Technology, Wageningen University, 6700 Wageningen AA, The Netherlands

Smelting and mining operations lead to the generation of by-products such as slags and mining wastes. Slags and ores, that have no value from the economical point of view, are gathered on dumps. Nevertheless, such wastes still contain minerals (i.e., pyrite, galena) that are metal(loid)s carriers. Exposure of slags and mining wastes to the environmental factors (i.e. bacteria, fungi, plants and root exudates, rain) poses serious environmental risk due to the potential weathering of such wastes and subsequent metal(loid)s leaching. Therefore, in this study we used a combined experimental approach demonstrating bioweathering (native microorganisms and bacteria *Acidithiobacillus thiooxidans*) of slags and mining wastes. For this study, historical fayalite bearing Cu-slugs (HS) and mining wastes were collected from the dump located in Miedzianka (Lower Silesia). Diopside bearing slags (SFS) originating from modern industry were also used for experiments. The toxicity of slags for plants was assessed by means of acute seeds germination test and pot experiments.

Our study demonstrated that both slags undergo bioweathering with native bacteria generating leachates enriched in metal(loid)s: (a) Zn and Pb for SFS and (b) Zn and Cu for HS. Root exudates were proven to affect the stability of slags in the environment, but the concentration of root exudates constitutes a pivotal factor that governs the degree of mobilization of metal(loid)s from slags. In turn, deposition of mining wastes on dumps led to the formation of soil profile in which accumulation of organic matter in the surface horizon and intense weathering traits of mining wastes in the deepest horizon were observed. In the deepest horizon, where the pH was 4.7, the highest metal(loid)s mobilization by *Acidithiobacillus thiooxidans* was noted amongst all evaluated horizons. The seeds germination test revealed that the interaction of slags with soil solution limits the seeds germination relative to contact of slags with water. The pot experiment with monocot and dicot plants revealed that monocot plant (*Festuca rubra*) is suitable for phytostabilization of dumps, whereas dicot plant (*Brassica juncea*) is promising plant species for phytoextraction of metal(loid)s from dumps.

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Structural and metamorphic study of the metaophiolite of Val d'Ala (Lanzo Valleys, Piemontese Zone, Western Alps – Italy)

Manuel RODA¹, Marco FILIPPI¹, Matteo ASSANELLI¹

¹Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano, Via Mangiagalli, 34 - 20133 Milano, Italy; e-mail: manuel.roda@unimi.it

This contribution presents a structural and metamorphic study of the Val d'Ala metaophiolite complex (Lower Piemonte Zone) at the southern boundary of the Gran Paradiso Massif. Although this area was known since the 18th century for mining activity, a complete and modern multiscale structural study of the metaophiolite is still lacking. For this reason, we realized a structural study along the northern slope of middle Val d'Ala and we completed the study with a microstructural analysis. Here, serpentinites and metabasites are the dominant rocks and host hectometre-sized calcschist bodies, meter to decametre-sized metagabbro bodies, and some meter-sized eclogite lenses. All these lithologies belong to the Lower Piemonte Zone. In the upper part of the northern slope of the valley the tectonic contact with the gneisses of the Gran Paradiso Massif occurs. Four groups of superposed structures have been recognized by the multiscale investigation of the cross-cutting relationships between minerals, foliations, and folds. D1 relict fabrics occur in eclogites, metagabbros, and metabasites and are marked by omphacite, garnet, rutile, and glaucophane. Oldest metamorphic relicts in serpentinites are serpentine and rare amphibole, in calcschists are quartz and calcite, and in gneisses are quartz, garnet, and plagioclase. D2 structures consist of isoclinal folds and the S2 axial plane foliation that represents the dominant fabric and developed within all rock types. The S2 foliation is marked by glaucophane and epidote in the metabasites, metagabbros, and eclogites, serpentine and chlorite in the serpentinites, carbonate, quartz, white mica in the calcschists and quartz, plagioclase, and white mica in the gneisses. Locally green amphibole, chlorite and plagioclase replace omphacite and glaucophane. The lithological boundaries and the tectonic contact between the Piemonte Zone metaophiolite and the gneisses of the Gran Paradiso Massif is parallel to S2. The D3 structures consist of a fold system with sub-horizontal axial plane (PA3) and axis (A3). The D4 fabric consists of isoclinal to open folds with sub-vertical dipping axial plane (PA4) and sub-horizontal axis (A4). D1 mineral assemblage suggests a metamorphic peak under eclogite-facies conditions for the metaophiolite complex, followed by re-equilibration under blueschist-facies conditions in which the contact with the gneisses of the Gran Paradiso Massif developed. The two units evolved together in lower pressure and temperature conditions.



Fungal spore tracers in road dust, soils and aerosols from Sosnowiec, Poland

Maciej RYBICKI¹, Leszek MARYNOWSKI¹, Doris GROSS²

¹University of Silesia in Katowice, Faculty of Natural Sciences, Institute of Earth Sciences, Będzińska 60, Sosnowiec 41-200, Poland; e-mail: maciej.rybicki@us.edu.pl

²Montanuniversität Leoben, Department of Applied Geosciences and Geophysics, Peter-Tunner-Str. 5, A-8700 Leoben, Austria

Road dust, soil and aerosol PM₁₀ samples were collected seasonally from the city of Sosnowiec, southern Poland and analyzed using gas-chromatography – mass spectrometry (GC-MS). Sugars were the most abundant compounds in all extracts, among which, a disaccharide (trehalose) and two sugar alcohols (mannitol and arabitol) were predominant in all samples with their highest concentrations in summer and autumn at the peak of fungal spore production and most active growth (Marynowski et al., 2020).

Trehalose together with arabitol and mannitol are generally considered as fungal-specific saccharides and are known from road dust, soil and aerosol samples (Simoneit et al., 2004, Marynowski et al., 2019). Some investigators believe that resuspension of soil and unpaved road dust might be a major ingredient of aerosol particles and the saccharides (including trehalose, arabitol and mannitol) can be considered as the source specific tracers (Simoneit et al., 2004; Rogge et al., 2007). However, trehalose-specific stable carbon isotope compositions differ significantly between soil/road dust and PM₁₀ samples from Sosnowiec indicating that resuspension of soil and road dust has little if any impact to aerosol particles in Sosnowiec. Our results indicate that ambient saccharides are most likely associated with direct biological particle emissions (including pollen and fungal spores) rather than with the microorganism-containing soil/road dust resuspension.

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Influence of the surface structure of goethite on the kinetics of DNA adsorption and particle aggregation

Mateusz SKALNY¹, Tomasz BAJDA¹

¹Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Kraków, Poland; mskalny@agh.edu.pl

Introduction

DNA is a ubiquitous component of various natural settings such as sediments, soils, aquatic environments, and biofilms. After cell lysis, DNA is liberated into the surroundings, and for the most part, it experiences denaturation, unless it is adsorbed to mineral particles. Consequently, the interactions between DNA and minerals assume a critical role in fundamental processes such as DNA preservation, horizontal gene transfer, and the formation of biofilms [1].

This study investigates how the textural properties of goethite affect the kinetics of DNA adsorption and the aggregation of DNA and goethite particles. It was shown that goethite particles with well-developed macroporosity exhibit a substantially greater DNA adsorption capacity when compared to mesoporous and low-porous goethite particles. The highest DNA adsorption capacity was related to the longest time to reach equilibrium. Indicating the pore diffusion plays an important role in the adsorption mechanism. Furthermore, upon introducing DNA into the goethite suspension, the entire system experiences aggregation indicating the occurrence of bridging phenomena between DNA and goethite particles. Also, the mechanism of the aggregation process is related to the surface structure of the mineral particles. We observed that the addition of DNA enhanced the aggregation kinetics of macroporous goethite, whereas, for meso- and low-porous goethite, it was diminished. Further, we investigated the influence of Ca²⁺ cation on the adsorption of DNA on goethite. The presence of divalent cations like Ca²⁺ influence the structure of DNA causing the compaction of a chain of DNA and a decrease in molecule diameter. Such compacted DNA molecules are more efficiently adsorbed on the surface of goethite particles, primarily owing to the facilitated diffusion within the material pores.

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High-aluminum phillipsite-Ca from the pyrometamorphic rocks of the Hatrurim Complex, Israel

Katarzyna SKRZYŃSKA¹, Georgia CAMETTI², Irina GALUSKINA¹

¹Faculty of Natural Sciences, University of Silesia in Katowice, Address Będzińska street 60, 41-200 Sosnowiec, Poland; e-mail: katarzyna.skrzynska@us.edu.pl, irina.galuskina@us.edu.pl

²Institute of Geological Science, University of Bern, Address Baltzerstrasse 1+3, 3012 Bern, Switzerland; e-mail: georgia.cametti@unibe.ch

The phillipsite series minerals are among the most widespread zeolites. They occur in diverse geological environments from volcanic rocks to deep-sea sediments (Sheppard, Hay 2001). The variety of crystallization environments is reflected in the wide range of the extra-framework population and Si/Al ratio (Passaglia, Sheppard 2001). So far, the zeolitic mineralization of pyrometamorphic rocks of the Hatrurim Complex, Israel remained unexplored. The investigation of amygdaloidal voids in latiumite-esseneite paralava reveals the occurrence of zeolites from the phillipsite series overgrown by flörkeite. The quantitative chemical analyses of phillipsite series minerals resulted in the following empirical formula: $\text{Ca}_{2.73}\text{K}_{1.37}\text{Na}_{0.61}\text{Ba}_{0.07}\text{Sr}_{0.02}(\text{Al}_{7.48}\text{Fe}_{0.04}\text{Si}_{8.48}\text{O}_{32.05}) \cdot 12\text{H}_2\text{O}$, with the highest known Al content among natural phillipsites. The presence of high-aluminum zeolites in pyrometamorphic rocks of the Hatrurim Complex indicates low aqueous silica activity and a strongly alkaline environment during crystallization. Conceivably, the desert climate supported the high pH conditions (Novembre et al. 2021). The investigated zeolite mineralization probably formed as a result of meteoric water circulations within pyrometamorphic rocks (Skrzyńska et al. 2022; Kruszewski et al. 2021; Spürgin et al. 2019).

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Minerals with GIS-type structure: garronite-Na and gobbinsite problem

Katarzyna SKRZYŃSKA¹, Georgia CAMETTI², Irina GALUSKINA¹

¹Faculty of Natural Sciences, University of Silesia in Katowice, Address Będzińska street 60, 41-200 Sosnowiec, Poland; e-mail: katarzyna.skrzynska@us.edu.pl, irina.galuskina@us.edu.pl

²Institute of Geological Science, University of Bern, Address Baltzerstrasse 1+3, 3012 Bern, Switzerland; e-mail: georgia.cametti@unibe.ch

The complexity of zeolite poses a problem in their classification. According to IMA guidelines, zeolites with the same framework type, showing a wide range of chemical compositions, belong to one series (Coombs et al. 1997). Authors highlighted that the different Si:Al ratios and hydration levels are insufficient parameters to describe a zeolite as a new mineral. Recently, garronite-Na with a **GIS**-type structure has been found (Grice et al. 2016). However, known gobbinsite is also Na-dominant zeolite with the **GIS** framework. Both species slightly differ in hydration degrees and Si:Al ratios reflected in Na content (Table 1). Recently, Si-rich garronite-Na has been found (Hirahata et al. 2022), corroborating a solid solution between garronite-Na and gobbinsite. The differences between them seem insufficient to distinguish separate mineral species.

Table 1. Comparison of garronite-Na and gobbinsite

	Garronite-Na	Gobbinsite
end-member formula	Na ₆ [Al ₆ Si ₁₀ O ₃₂] ·8.5H ₂ O	Na ₅ [Al ₅ Si ₁₁ O ₃₂] ·11H ₂ O
space group	<i>I</i> 2	<i>Pmn</i> 2 ₁
Unit cell	<i>a</i> (Å)	9.990
parameters	<i>b</i> (Å)	10.104
	<i>c</i> (Å)	10.032
	β (°)	10.036
		90.11
References	Grice et al. 2016	Gatta et al. 2010

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To modify or not to modify? Eco-designed biofunctional NaP1 zeolite as an efficient U scavenger

Maciej SOBCZYK¹, Chau NGUYEN DINH¹, Tomasz BAJDA¹

¹Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology al. A. Mickiewicza 30, 30-059 Krakow, Poland, msobczyk@agh.edu.pl

In 2023, we are halfway through achieving the objectives of Sustainable Development Goals (SDGs) set by the European Commission (EC) to shape clean, affordable, and long-lasting synergy between humans, the economy, and the environment. In order to comply with SDGs No. 6 (Clean Water and Sanitation), 7 (Affordable and Clean Energy), and 12 (Responsible Production and Consumption) a novel design of efficient, stable, and reliable materials are of primary concern to treat polluted water streams as an effect of constantly increasing urbanization and industrialization.

Furthermore, the transition to a clean energy system, requires the deployment of nuclear reactors, possessing a massive threat of radioactive elements discharge, particularly U to water and soil. Taking into account all of the abovementioned objectives, here, we propose a novel approach to eco-design bio-functional synthetic NaP1 zeolite via surface decoration employing a biodegradable surfactant molecule (coconut betaine - CB) in order to fabricate an effective adsorbent aimed at removing U from water. (Biswas et al., 2019)

NaP1's surface decoration was studied under varying CB load expressed as the % of zeolite's External Cation Exchange Capacity (ECEC) probed by the hexamine cobalt (III) chloride. The combined FT-IR spectroscopy coupled with elemental CHN analysis revealed the successful introduction of the biosurfactant molecule to the zeolite, simultaneously incorporating into the material O and N heteroatoms present in the CB molecule, being able to strongly attract aqueous uranyl species via the creation of the coordination bond.

The impact of pH on U removal onto studied biofunctional organo-NaP1 zeolite showed the highest U uptake at near-neutral conditions ($\text{pH}_{\text{eq}} \sim 6$), while the adsorption isotherm studies showed superior removal U performance in the amount of 137.37 mg/g, 139.51 mg/g and 142.26 mg/g for 0.44ECEC CB/NaP1, 0.89ECEC CB/NaP1 and 1.66ECEC CB/NaP1 respectively, compared to only 44.48 mg/g for raw NaP1 zeolite.

Near future research objectives would also be discussed in regards to the application of advanced spectroscopies to reveal the local U coordination and its oxidation state after removal on biofunctional NaP1 zeolite, applying lab-scale X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS) available at synchrotron light sources.

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Tectonic mélange of continental and oceanic crustal slices in the Western Alps subduction complex a reinterpretation of tectonic units in the Piemonte Zone

Maria Iole SPALLA¹, Marco FILIPPI¹, Guido GOSSO¹, Thomas GUSMEO², Gisella REBAY³, Manuel RODA¹, Davide ZANONI¹, Michele ZUCALI¹

¹*Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano, Milano, Italy*

²*Dipartimento di Scienze Biologiche, Geologiche ed Ambientali, Università degli Studi di Bologna, Bologna, Italy*

³*Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia, Pavia, Italy, Italy*

A tectonic mixing of thin slivers of calcschist, fine-grained gneisses (metasediments and metagranitoids), quartzite, metabasites and serpentinites occurs all along the western margin of central and southern Sesia-Lanzo Zone (SLZ - Austroalpine Domain – Western Alps) at the boundary with Piemonte Zone (PZ) metaophiolites, and extends from Santanel klippe to Lanzo Massif, over a distance of 50 km. All the rocks belonging to SLZ and PZ together underwent four episodes of deformation, giving rise to a complex regional tectono-stratigraphy. The metamorphic mineral assemblages marking successive foliations, detected from the central to the southern part of the SLZ western margin, indicate that various metamorphic conditions dominate in different portions of this tectonic mixing. In the southern sector of this “mixing zone” parageneses marking superposed foliations indicate that rocks experienced an early eclogite facies imprint, followed by re-equilibration under blueschist facies conditions, and that they were finally widely retrogressed under greenschist facies, during the last two deformational stages. The strong syn-metamorphic deformation of this rock assemblage leaves, at the moment, the interpretation on its origin open: i) the present day configuration could be entirely due to transposition that occurred in a mantle wedge at the early stages of deformation, up to eclogite facies conditions, during active subduction; ii) a detrital origin of these alternating layers of terrigenous and carbonaceous rocks may correspond to a primary sequence of an extensionally-thinned continental margin reworked in the Alpine subduction system.



Major recrystallization events in the Tatra Mts: insights from palaeotemperature and rock magnetic studies

Dorota STANECZEK¹, Rafał JUNOSZA-SZANIAWSKI², Martin CHADIMA^{3,4}, Leszek MARYNOWSKI⁵

¹*Institute of Earth Sciences, University of Silesia in Katowice, Sosnowiec, Poland; dorota.staneczek@us.edu.pl*

²*Department of Magnetism, Institute of Geophysics, Polish Academy of Sciences; Warszawa, Poland; rafsz@igf.edu.pl*

³*AGICO Ltd., Brno, Czech Republic; chadima@agico.cz*

⁴*Institute of Geology, Academy of Sciences of Czech Republic, Prague, Czech Republic;*

⁵*Institute of Earth Sciences, University of Silesia in Katowice, Sosnowiec, Poland; leszek.marynowski@us.edu.pl*

The tectonic evolution of the Tatra Mts involves several different events that lead to the formation of the current geological setting of these mountains. Among the most important processes are the Cretaceous nappe thrusting and Oligocene burial of the Mesozoic units. Such events are generally linked with an accumulation/stacking of sediments which as a result increases the temperatures affecting the underlying rocks. Studying the palaeotemperature rates and their spatial distribution may provide some compelling data not only for tectonic reconstructions but also for palaeomagnetic research since it is well-known, that increased temperatures have an impact on the magnetic mineralogy of rocks (Aubourg & Pozzi, 2010). In this study, we focused on two units: Cretaceous marly limestones (Mraznica Fm.) from the nappe units and Oligocene siltstones (Huty Fm.) from the post-thrusting cover. The magnetic mineralogy of the sampled rocks was identified by measuring the in-phase and out-of-phase magnetic susceptibility, hysteresis curve, and the Isothermal Remanent Magnetization (IRM). In order to assess the palaeotemperatures, vitrinite reflectance was measured and, additionally, its value was calculated based on the distribution of methylphenanthrenes (methylphenanthrene index) obtained from gas chromatography-mass spectrometry analyses. The data along with other parameters, such as total organic carbon and carbonate content was later compared to the obtained rock magnetic results. Generally, phyllosilicates control the magnetic susceptibility in both units. In the case of ferromagnetics, single-domain, and pseudo-single-domain magnetite was determined to be the most common/important mineral. Changes in vitrinite reflectance of Cretaceous samples are related to those reported in Oligocene rocks, and in both units increase towards the SE. Additionally, larger amounts of small-sized magnetite grains are found in sites with the highest vitrinite reflectance values. Such data confirms the impact of one major recrystallization event, which affected both studied units.

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Sills or lava flows? Lava flows or pyroclastic rocks? New data on the eruption and emplacement of problematic volcanic rocks from Masca (the Miocene Teno shield volcano, Tenerife)

Kornelia STOLARCZYK¹, Marek AWDANKIEWICZ¹

¹*Institute of Geological Sciences, University of Wrocław, Poland, e-mail: kornelia.stolarczyk@uwr.edu.pl*

In the vicinity of Masca village in Tenerife, Miocene volcanic rocks of the older formations of the Teno shield volcano are exposed. These volcanics formed during a period of dynamic evolution of the volcano, characterized by large-scale landslides and changes in petrological characteristics of eruption products, such as magma chemistry and the amount and type of phenocrysts, linked to the depth of magma origin (Longpré et al., 2009).

The studied small section of the Teno shield volcano, c. 20 meters thick, has previously been interpreted as a succession of basaltic lavas with ankaramites in the lower part, all cut by younger basaltic dykes. The ankaramites, with up to 65% of phenocrysts, were tentatively interpreted as specific lava flows enriched in phenocrysts due to magma stagnation at mantle depths (Longpré et al., 2009) or in effect of crystal accumulation in a flowing, deflating lava (Gill & Thirlwall, 2003). However, new data suggest a need to reconsider these views and point to a more complex sequence of volcanic events.

The ankaramites show planar structures interpreted as bedding, as well as clastic textures and good sorting visible in specimens and thin sections - all features being typical of pyroclastic deposits. These observations suggest the emplacement of the ankaramites not as lava flows but during explosive eruption(s), by pyroclastic fall processes, with related aeolian fractionation resulting in enrichment in crystals. The overlying basaltic lavas provide a record of subsequent effusive activity. Cross-cutting basaltic dykes, as well as previously unrecognized but abundant sills between lava flows, document the final subvolcanic activity. Altogether, this relatively thin volcanic sequence reveals a complex development during explosive, followed by effusive and then by subvolcanic activity.

The obtained results indicate that the eruption processes, emplacement, and the development of the volcanic sequence in Masca occurred differently than previously assumed and provide a good starting point for further petrological research.

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Hematite formation and growth seen by X-ray diffraction in samples from Earth and Mars

Marek SZCZERBA¹, Jan ŚRODOŃ¹, Elizabeth B. RAMPE², Tanya S. PERETYAZHKO³
Katarzyna LUBERDA-DURNAS¹, Barbara BARYLSKA¹, and CheMin team

¹Institute of Geological Sciences, Polish Academy of Science, Cracow, Poland

²NASA Johnson Space Center, Houston, TX, USA

³Jacobs at NASA Johnson Space Center, Houston, TX, USA

Hematite is a common component of sedimentary rocks deposited under oxidizing conditions. During burial diagenesis, significant changes in the powder diffraction patterns of this mineral have been observed. Hematite is also the most prevalent iron-bearing oxide mineral found in Gale Crater (Mars). It has been detected in 34 of the 36 drill targets studied by the Mars Science Laboratory (MSL) *Curiosity* rover. The main aim of this study was to investigate the reorganization mechanism of hematite, which is reflected in the sizes of crystallites for all four major hematite peaks in the X-ray powder diffraction patterns.

A series of 83 samples from the Ediacaran redbeds, palaeosols, and hydrothermally altered basalt and tuffs of the East European Craton, representing a wide range of origins and diagenetic conditions, were analyzed using X-ray powder diffraction. A series of 10 non-Ediacaran sedimentary rocks of different ages, diagenetic conditions, and localities were analyzed for verification of the received trends. From all of the drilled samples by the MSL *Curiosity* rover, 20 samples were selected for detailed peak analysis of hematite reflections.

Comparison of diffractograms of the smallest hematite crystallites from Gale crater to typical hematite formed on Earth due to weathering (no contribution of diagenesis) shows significant differences between the broadening of (104) and (110) peaks. For terrestrial hematite, the peak (104) is 2-3 times broader than the peak (110), while for hematite samples from Gale crater, both peaks are much broader and have near equal FWHMs.

The results of the whole powder pattern modelling indicate that hematite formed during weathering on Earth has a platy crystallite shape, and the main direction of growth is (001), accompanied by the decrease of micro-strain broadening in (100) and (010) directions. Larger sizes in the a-b plane of terrestrial hematite can be related to slow precipitation or recrystallization from ferrihydrite or goethite precursors.

Calculated crystallite sizes for the Martian hematites are substantially smaller compared to the terrestrial ones, especially in the a-b crystallographic directions, and are typically equant: ca. 2-5 nm in every direction. Such size and shape can be related to the direct precipitation of Martian hematite by dehydration after Fe³⁺ hydrolysis, and the shorter crystallization time compared to terrestrial hematite.



Lichens – bioindicators of atmospheric air pollution. Case study from the Upper Silesia region

Ewa SZRAM¹, Leszek MARYNOWSKI¹

¹*Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia in Katowice, Będzińska 60, 41-200 Sosnowiec: ewa.szram@us.edu.pl, leszek.marynowski@us.edu.pl*

The Upper Silesian primary source of air pollution are anthropogenic emissions, including municipal, domestic and traffic emissions. Significant challenges include increasing public awareness of low emissions in the Silesian province and reducing or eliminating them.

As the lichens are highly sensitive to the presence of even a small amount of anthropogenic organic compounds in the air makes them useful as bioindicators of environmental pollution.

The studied lichen samples provide data on the air contamination with polycyclic aromatic hydrocarbons (PAHs), which are a product of fuel combustion and are both carcinogenic and mutagenic. Identified PAHs include phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, triphenyl, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*j*]fluoranthene, benzo[*a*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene. Phenyl derivatives of polycyclic aromatic hydrocarbons including phenylnaphthalenes (2-phenylnaphthalene and

1-phenylnaphthalene), phenylphenanthrenes (2-phenylphenanthrene) and triphenyls (*m*-triphenyl, *p*-triphenyl and traces of *o*-triphenyl) were also found. Among phenols, *o*-cresol, *m*-cresol, *p*-cresol and 2-nitrophenol were present. The 2-phenyl-dibenzofuran was also detected in lichen samples.

Moreover, the lichens selectively absorb organic compounds like dehydroabietane and simonellite, characteristic of immature organic matter and may indicate low-quality coal combustion (Marynowski et al., 2007). Heavy metals like lead, strontium, nickel, and vanadium were determined among the elements toxic to human health.

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Potentially new mineral, $(\text{Ca}_{0.5}\text{Ce}^{4+}_{0.5})\text{VO}_4$, from a coprolite of Gara Samani, Algeria

Dorota ŚRODEK¹, Georgia CAMETTI², Madani BENYOUCEF³, Rafał JUROSZEK¹, Tomasz KRZYKAWSKI¹, Imad BOUCHEMLA³, Mariusz SALAMON¹

¹Faculty of Natural Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland; dorota.srodek@us.edu.pl, rafal.juroszek@us.edu.pl, tomasz.krzykowski@us.edu.pl, mariusz.salamon@us.edu.pl

²Institute of Geological Sciences, University of Bern, Baltzerstrasse 1+3, 3012 Bern, Switzerland; georgia.cametti@unibe.ch

³Faculty of Natural and Life Sciences, University Mustapha Stambouli of Mascara, Mascara, Algeria; benyoucefmada@gmail.com, bouchemlaimad@gmail.com

A potentially new mineral with an ideal formula $(\text{Ca}_{0.5}\text{Ce}^{4+}_{0.5})\text{VO}_4$ belonging to the xenotime group was found in a coprolite from sand-dominated sediments of the Gara Samani Formation (Algeria). It forms dark green aggregates up to 100 μm in diameter in the pores of the fossil fluorapatite matrix. Phase with composition $(\text{Ca}_{0.5}\text{Ce}^{4+}_{0.5})\text{VO}_4$ is associated with fluorapatite, calcite, barite, goethite, and unidentified Ce-bearing phase forming small up to 3 μm in diameter spherules. The empirical crystal chemical formula of the potentially new mineral is as follows: $(\text{Ca}_{0.53}\text{Ce}^{4+}_{0.47})[(\text{VO}_4)_{0.84}(\text{SO}_4)_{0.08}(\text{PO}_3)_{0.06}(\text{SiO}_4)_{0.02}]$. This mineral has a zircon archetype structure: $I4_1/amd$, $a = 7.15 \text{ \AA}$, $c = 6.33 \text{ \AA}$, $Z = 2$, and $V = 323.83 \text{ \AA}^3$. It is related to the other xenotime group mineral – wakefieldite-(Ce) with the $\text{Ce}^{3+}\text{VO}_4$ end-member formula [1]. In the new phase, the Ce^{3+} is replaced by Ca^{2+} and Ce^{4+} by the schemes: $\text{Ce}^{3+} = 0.5\text{Ca}^{2+} + 0.5\text{Ce}^{4+}$ and $\text{Ce}^{3+} + (\text{VO}_4)^{3-} = \text{Ca}^{2+} + (\text{SO}_4)^{2-}$. The composition, structure, and Raman spectrum of the potentially new mineral are close to those of synthetic Ce^{4+} -bearing orthovanadate $(\text{Ca}_{0.4}\text{Ce}^{4+}_{0.4}\text{Ce}^{3+}_{0.2})\text{VO}_4$ [2]. The following main modes of the Raman spectrum are characteristic of the studied mineral: 956, 877, 740, 474, 361, 256, 147 cm^{-1} . Coprolites played the role of a geochemical barrier for the crystallization of the potentially new Ce^{4+} -containing mineral from solution under oxidizing conditions at low temperatures.

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Regional to prospective exploration – survey program for seafloor massive sulphides deposits within the Polish contracted area on the Mid-Atlantic Ridge

Michał TOMCZAK¹, Agata KOZŁOWSKA-ROMAN¹, Jakub CIAŻELA², Łukasz SMAJDOR¹, Mateusz DAMRAT¹

¹Polish Geological Institute – National Research Institute, ul. Rakowiecka 4, 00-975 Warsaw, Poland; michal.tomczak@pgi.gov.pl, agata.kozłowska@pgi.gov.pl

²Institute of Geological Sciences, Polish Academy of Sciences, ul. Podwale 75, 50-449 Wrocław, Poland

One of the elements strengthening Poland's raw material supply and independence is the Contract between the Government of the Republic of Poland and the International Seabed Authority (ISA) on the exploration of polymetallic seafloor massive sulphides (SMS). This contract, signed in 2018, established a framework for 15-year environmental studies and technology development, which will enhance national capabilities for deep-sea operations. The Polish Contracted area consists of 100 exploration blocks (each 10x10 km in size) divided into five clusters (A-E) with a total area of 10,000 km² located in the Mid-Atlantic Ridge (MAR). The regional exploration of the entire Polish area along MAR started in 2022 with comprehensive shipborne methods aiming at a general understanding of the geological settings of the research area. Acquired high-resolution bathymetric data (50 m cell grid size) allowed for the identification of key seabed structures and sites favourable for hydrothermal activity and associated potential SMS deposits. Additional environmental sensors (pH, ORP, turbidity, CH₄, oxygen, CTD) were deployed in tow-yo mode to identify hydrothermal venting occurrences. The detailed analysis of the obtained data from exploration blocks served for defining twenty potentially prospective (PP) areas, which will be consequently subjected to detailed studies. In 2023, three PP areas with a total area of 230 km² represented by the Oceanic Core Complex (OCC), Axial Volcanic Ridge (AVR), and mid-ocean ridge flank located within cluster A were selected for detailed near-seafloor geophysical and environmental data acquisition. The advances of an autonomous underwater vehicle (AUV) were used to identify and characterize hydrothermal systems and SMS deposits along with environmental parameters. An AUV mission provided a unique and comprehensive data set including e.g. ultra-high bathymetric data (25 cm – 1 m) or Synthetic Aperture Sonar (SAS) images of the seabed structures (3 – 5 cm resolution). These data coupled with geophysical and environmental information such as spontaneous potential or magnetic anomalies and water column data (WCD) allowed for the identification of seabed features associated with hydrothermal activity and deposition of SMS, e.g. inactive hydrothermal field, sulphide mounds cluster, and active venting chimneys. Discovered sites will be targeted for detailed analysis and observation, as well as subsampling during the missions of remotely operated vehicles (ROV). This work will be supplemented by additional environmental (baseline) studies of the entire area, which will contribute to the international community's need to enhance knowledge about deep-sea ecosystems.



Raman microspectroscopic characteristics of monazite and xenotime: examples from experiments and nature

Fabian TRAMM^{1*}, Grzegorz RZEPA², Bartosz BUDZYŃ¹, Gabriela A. KOZUB-BUDZYŃ², Jakub DYBAŚ³, Jiří SLÁMA⁴

¹*Institute of Geological Sciences, Polish Academy of Sciences, Kraków Research Centre, Kraków, Poland*

²*AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Kraków, Poland*

³*Jagiellonian University, Jagiellonian Centre for Experimental Therapeutics (JCET), Kraków, Poland*

⁴*The Czech Academy of Sciences, Institute of Geology, Prague, Czech Republic*

*corresponding author, e-mail: ndtramm@cyf-kr.edu.pl

Monazite and xenotime are accessory minerals that occur in a wide range of igneous and metamorphic rocks. Both are used in geochronology, geothermometry or provenance studies. However, fluid-induced alteration can significantly disturb the geochemical record in monazite and xenotime, disturb or completely reset U-Th-Pb ages, or replace primary mineral with secondary phase(s). Alteration commonly results in significant changes of the internal structure. Therefore, evaluation of structural changes using Raman microspectroscopy, in combination with compositional analysis, provide structural, textural and compositional information to expand our understanding of the processes involved in fluid-induced alteration.

Monazite and xenotime from the products of laboratory experiments, monazite from Ankazobe (Madagascar) and xenotime from a pegmatite from Piława Górna (Góry Sowie Block) were evaluated with EPMA, LA-ICPMS and Raman microspectroscopy. Raman spectra were collected in unaltered and altered domains of monazite and xenotime with 488 nm, 532 nm and 633 nm excitation lasers, using two instruments, a Thermo Scientific DXR Raman Microscope and a WITec confocal CRM alpha 300 Raman microscope.

In altered domains of monazite, spectral changes include band-narrowing of $\nu_1(\text{PO}_4)$ symmetric stretching band, shift of peak position of Raman bands and distinct increase of intensity and broadening of bands caused by fluorescence effects (ca. $1500\text{--}2500\text{ cm}^{-1}$). In xenotime, spectral changes include broadening of bands caused by fluorescence effects in the range of ca. $100\text{--}900\text{ cm}^{-1}$ and significant increase of intensity and broadening of fluorescence effects at ca. $2500\text{--}3000\text{ cm}^{-1}$. Spectral changes emphasize close similarity to spectra of secondary fluorcalciobriholite. The commonly used 532 nm laser, and the 633 nm laser proved to be very useful for Raman microspectroscopic investigation of monazite and xenotime. The distinct spectral changes demonstrate the usefulness of Raman microspectroscopy to recognize altered domains and presence of secondary phases in monazite and xenotime, which is emphasized in 2D-hyperspectral mapping.

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P-T path of a garnet-bearing mica schist from the Kongsvegen Group, Svalbard

Olga TUREK¹, Karolina KOŚMIŃSKA¹, Jarosław MAJKA², Jakub BAZARNIK³, Grzegorz ZIEMNIAK⁴

¹Faculty of Geology, Geophysics and Environmental Protection, AGH UST, Address al. Mickiewicza 30, 30-059 Kraków; e-mail: olgaturek@student.agh.edu.pl; karolina.kosminska@agh.edu.pl

²Department of Earth Sciences, Uppsala University, Sweden, e-mail: jaroslaw.majka@geo.uu.se

³Polish Geological Institute – NRI, Carpathian Branch, Kraków, e-mail: jakub.bazarnik@pgi.gov.pl

⁴Institute of Geological Sciences, University of Wrocław, e-mail: grzegorz.ziemniak@uwr.edu.pl

The Kongsvegen Group including its highest unit the Bogegga Formation is located in Oscar II Land and belongs to the Southwestern Basement Province of Svalbard. The Bogegga Formation consists of garnet-bearing mica schists and gneisses, accompanied by pegmatites and amphibolite lenses and is interlayered by calc-schists that underwent medium-grade metamorphism (Hjelle et al., 1999). The pressure-temperature (P-T) path of the highest grade garnet-bearing mica schist from the Kongsvegen Group is presented here.

The garnet porphyroblasts, white mica, biotite, quartz, and plagioclase are the major minerals in the studied schist. Muscovite is the main white mica end-member and its Si content varies from 3.075 to 3.162 a.p.f.u. Albite end-member dominates plagioclase although it is slightly enriched in anorthite in the cores. The composition of plagioclase is $Ab_{77-97}An_{2-22}Or_{1-2}$. Garnet can be divided into two generations. Garnet-I, with the composition of $Alm_{76-81}Grs_{6-9}Prp_{8-14}Sps_{2-4}$, contains voluminous quartz and biotite inclusions, and forms the cores of the porphyroblasts. Garnet-II overgrows garnet-I or fills fractures within garnet-I, and is richer in Ca. Its chemical composition is $Alm_{71-72}Grs_{18-23}Prp_{4-7}Sps_{2-3}$. Biotite in the matrix is more Fe-rich ($X_{Fe} = 0.64$ to 0.68) than the one in the inclusions within garnet-I ($X_{Fe} = 0.36$ to 0.50).

To determine P-T conditions, a combination of conventional geothermobarometry using Ti-in-Bt (Henry et al., 2005) and Grt-Bt-Ms-Pl (Wu, 2015) geothermobarometers with thermodynamic modelling using Perple_X program (Connolly, 2005) was used. Both methods allowed to distinguish two metamorphic stages. Stage M1 related to garnet-I growth is estimated at 4.3 – 6.0 kbar and 550 – 615 °C, while garnet-II and the matrix minerals crystallized at stage M2 at 8.3 – 9.4 kbar and 620 – 675 °C. In terms of P-T conditions, the Bogegga Formation correlates with other amphibolite facies units of SW Svalbard (e.g., the Müllerneset Formation, Isbjørnhamna Group, Pinkie and Berzeliussegene units).

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Trace element composition of zircon from the Central Sudetic Ophiolite

Krzysztof TURNIAK¹, Marek AWDANKIEWICZ¹, Robert ANCZKIEWICZ²

¹University of Wrocław, Institute of Geological Sciences, University of Wrocław, Pl. Maksa Borna 9, 50-204 Wrocław, Poland; e-mail: krzysztof.turniak@uwr.edu.pl; marek.awdankiewicz@uwr.edu.pl

² Polish Academy of Sciences, Institute of Geological Sciences, Kraków Research Centre, Senacka 1, 31-002 Kraków; e-mail: r.anczkiewicz@ingpan.krakow.pl

The Central Sudetic Ophiolite emplaced in Emsian (magmatic zircon ages 402.7 ± 0.3 - 402.6 ± 0.2 Ma; Awdankiewicz et al. 2021) - is represented by the low-grade metamorphosed mafic and ultramafic rocks with subordinate plagiogranites and rodingites outcropping as dismembered bodies around the Góry Sowie Massif. Laser ablation ICP-MS trace element analyses of zircon from leucogabbro of the Ślęza Massif (sample S9), Nowa Ruda plagiogranite (sample NS5) and Braszowice plagiogranite (sample BR8) have been carried out to evaluate their petrogenesis and the geotectonic significance.

Samples S9 and NS5 contain euhedral, transparent zircon crystals of similar morphology dominated by {100} prism, showing sector and/or oscillatory zoning indicative of a magmatic origin. The analyzed grains are poor in U and Th (S9: 6-109 ppm U, 2-34 ppm Th; NS5: 7-116 ppm U, 2-73 ppm Th). On the chondrite-normalized REE pattern they show strong enrichment in HREE, the negative Eu and positive Ce anomalies at levels typical of many plagiogranites. High $(\text{Sm}/\text{La})_N > 10$ values imply magmatic character of the analyzed zircons. The discrimination diagrams of Grimes et al. (2007) confirm their origin in the oceanic crust and Ti-in-zircon thermometry indicates crystallization temperature in the vicinity of 800°C.

The zircon crystals from the BR8 plagiogranite show morphology strongly dominated by {110} form. They are mostly subhedral, translucent, show homogenous internal domains or disturbed oscillatory zonation. The crystals are relatively enriched in LREE with $(\text{Sm}/\text{La})_N < 10$ and thus are classified as hydrothermal. However, some crystals show chondrite-normalized REE patterns typical of magmatic origin. Low Ti content indicates that these zircons crystallized at temperature close to solidus. High U and Th content (358-3010 ppm U, 100-3310 ppm Th) give them geochemical characteristics of zircons linked with continental crust suggesting a scenario where contribution of crustal material in generation of BR8 plagiogranite seems to be plausible.

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Behaviour of the REE in experimentally induced hydrothermal alterations of chevkinite-(Ce) – differences between nature and experiment

Kacper URBANIK¹, Bogusław BAGIŃSKI¹, Ray MACDONALD¹

¹Department of Geology, University of Warsaw, Address ul. Żwirki i Wigury 93, 02-089 Warszawa;
e-mail: k.urbanik2@student.uw.edu.pl, b.bagiński1@uw.edu.pl, raymacdonald186@gmail.com

The behaviour of rare earth elements (REEs) during the hydrothermal transformation processes of alkaline rocks is one of the important topics in recent scientific research. A better and deeper understanding of these processes is of profound importance for understanding the mechanisms of rock formation and the origin of some ore deposits, especially REEs.

Chevkinite-(Ce) – rare earth and titanium silicate was chosen as the subject of experiments. They were conducted using a standard cold-sealed autoclave in a high-pressure hydrothermal line, using mineral assemblages typical of alkaline rocks and hydrothermal fluids of various compositions. The temperatures varied from 500 to 600°C, and the pressures from 200 to 400 MPa. The duration of the experiments was from 21 to 63 days.

The experiments resulted in a wide range of mineral phases. The main REE-containing phases synthesized were fluorbritholite-(Ce), monazite-(Ce) and epidote supergroup minerals; other mineral phases with significant LREE content (gagarinite-(Ce), titanite) have also been synthesized.

Experimental results are generally consistent with paragenesis formed in natural environments, where hydrothermal alteration of chevkinite (Ce) was observed. However, there were some exceptions. The most puzzling were:

-the absence of allanite (Ce) in most experiments, the mineral most often formed by hydrothermal alteration of chevkinite (Ce) in nature,

-the overrepresentation of britholite-(Ce), which is known from only two places in the world, giving the experimental results an unprecedented character in this matter.

(Ferri)allanite was eventually formed when fluids had high Ca/Na ratios (rich in Ca(OH)₂ and CaF₂), while fluorite crystallized from fluids with low Ca/Na ratios; the relative scarcity of phase in natural chevkinite transformation systems seems to indicate that such fluids are not common in nature.

Acknowledgements

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Hundred-year emission of metal(loid)s from sludge ponds of Fe-Zn Bibiela mine, Poland

Rafał WARCHULSKI¹, Krzysztof KUPCZAK¹, Vojtěch ETTLER², Martin MIHALJEVIČ², Marcin FARUGA, Tomasz KRZYKAWSKI¹

¹Faculty of Natural Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland; e-mail: rafal.warchulski@us.edu.pl; krzysztof.kupczak@us.edu.pl; tomasz.krzykawski@us.edu.pl

²Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic; e-mail: ettler@natur.cuni.cz; mihal@natur.cuni.cz

The Bibiela mine began operations in 1889. It was established despite unfavourable hydrogeological conditions due to the exceptionally rich iron ore associated with the MVT deposits of the Silesian-Cracow area. The mine's operations depended entirely on constantly pumping water into sludge ponds. Most likely due to errors during mining, the clay layers separating the groundwater reservoir within the Triassic rocks were breached, resulting in the complete flooding of the mine and the end of its operations in 1917.

The study focuses on the profile of former sludge ponds (two Technosol samples, two sludge samples, and a sample from the contact zone between them), which had been subject to natural weathering and soil forming processes. The goal is to determine the long-term impact of the sludge on the forming Technosol and the current potential for metal(loid)s emissions from the sludge more than 100 years after deposition.

Petrographic studies (XRD, SEM-EDS) showed that the sludge consists of clay minerals (av. 52.5%), goethite (av. 35.5%), quartz (7.5%), and cerussite (4%). Technosols formed on their basis contain more quartz (av. 33.5%), fewer clay minerals (av. 29.5%), and similar amounts of goethite. The contact zone has an intermediate composition, increased cerussite amount (10.5%), and was found to contain siderite (7%). Chemical analyses (ICP-MS/OES) showed that the sludge material contains high concentrations of the metal(loid)s: Pb (up to 6.2 wt.%), Zn (up to 1.9 wt.%), Mn (up to 1900 mg/kg), As (up to 1500 mg/kg), Cd (up to 110 mg/kg) and Tl (up to 9 mg/kg). Technosol formed on these sediments contains the same metal(loid)s in similar or higher concentrations. The contact zone has the highest concentrations of Pb (8.1 wt.%), Zn (4 wt.%), Mn (2800 mg/kg), and Cd (210 mg/kg). Although according to the standardized leaching tests using demineralized water (EN12457-2) the sludge is non-hazardous, tests using 0.01 M CaCl₂ documented mobilization of metal(loid)s for the primary sediment, Technosol, and contact zone, respectively: Zn up to 100, 350, and 190 mg/kg, Pb up to 8.5, 278, and 6.5 mg/kg, Cd up to 5.5, 6.5, and 8.5 mg/kg. The stabilized pH of sludge samples during this test ranged from 6.28 to 6.55. pH-static leaching tests for sludge in this range (6-7) showed high emissions of Cd (7.5 mg/kg), Pb (9.5 mg/kg), and Zn (325 mg/kg). As pH decreases, metal(loid)s emissions increase rapidly, reaching 160 mg/kg for Cd, 7.5% for Pb, 2.1% for Zn at pH=2.

This study has documented that the Technosols forming on the surface of former sludge ponds are contaminated with metal(loid)s, which can be further mobilized. Even more than 100 years after their deposition, the sludge is still a significant source of metal(loid)s, especially under conditions leading to decreased pH.



Ore-bearing schists from the Stara Kamienica schist belt as an Earth analog for metal ore exploration on the Moon and Mars

Albert WIECZYSTY¹, BogusławBAGIŃSKI¹, Jakub CIAŻĘLA², Marcin KANIA³

¹Department of Geology, University of Warsaw, Żwirkkii Wigury 53 02-089 Warszawa;
a.wieczysty@student.uw.edu.pl, b.baginski1.uw.edu.pl

²Institute of Geological Sciences, Polish Academy of Sciences, Podwale 75, 50-449 Wrocław;
j.ciazela@twarda.pan.pl

³„Poltegor – Instytut” Instytut Górnictwa Odkrywkowego, Parkowa 25, 51-616 Wrocław;
poltegor@igo.wroc.pl

Colonization of the Moon requires a constant supply of mineral resources. Sulfides and metal oxides are crucial for building and sustaining habitat infrastructure. The MIRORES-far-infrared spectrometer selected as the priority payload for the Polish Lunar Mission to be launched in 2028 (Ciążęła et al., 2023) will enable the detection of specific minerals such as pyrite, chalcopyrite, troilite, and ilmenite. These ore minerals exhibit distinct 20–40 μm absorption spectra. With a resolution of <5 m, it will be possible to identify areas with elevated S, Cu, Ti, and Fe concentrations. The target mass and dimensions for the device are ≤ 10 kg and 32x32x42 cm (Ciążęła et al., 2023). The terrestrial version of the spectrometer is adapted to work on a drone. The mass of this version is <2 kg, and the dimensions are 13x13x21 cm.

One of the analog areas suitable for calibrating the spectrometer is a section of the Stara Kamienica schist belt parallel to the gneisses of the Izera Metamorphic Complex (Małek and Mikulski, 2021). The study area is located in Orłowice quarry. The host rocks are mica schists, some of which exhibit pyrite mineralization associated with veins of quartz. During the summer and early autumn, we identified a suitable test field displaying abundant ore mineralization. We mapped a 15x15m surface on a regular grid of 25 sites (separated by 3m) to estimate macroscopically the content of desired minerals based on four samples collected at each site. The location of the sites was determined by Garmin 62s GPS. Pyrite concentration estimated this way ranges between 2–15wt%. The field observations will be validated by XRD analysis and then measured with far IR during MIRORES flights, allowing us to create two geochemical maps. Comparing these maps will validate the spectrometer's capabilities and detection limits for pyrite and other minerals.

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Sulfides in low-pressure ophiolitic chromitites reveal metal enrichment in the upper mantle of the slow-spreading type Ślęza ophiolite (SW Poland)

Piotr M. WOJTULEK¹, Jakub CIAŻELA², Artur PIRKOŚ¹

¹Institute of Geological Sciences, University of Wrocław, M. Borna 9, 50-204 Wrocław; piotr.wojtulek@uwr.edu.pl

²Institute of Geological Sciences, Polish Academy of Sciences, Podwale 75, 50-449 Wrocław; j.ciazela@twarda.pan.pl

The ultramafic member of the Variscan Ślęza ophiolite (SW Poland) comprises podiform-type chromitite veins. Chromian spinel occurs as high-Al (Cr# 0.50 – 0.52) or high-Cr (Cr# 0.57 – 0.69) chromites. All these grains occur in veins together with chlorite and olivine. Chromitites comprise relatively rare sulfide grains occurring in various contexts. High-Al chromite contains mono- or polyphase inclusions comprising chalcopyrite and pentlandite. In polyphase inclusions, chalcopyrite occurs together with diopside, pargasite, or phlogopite. High-Cr chromite contains mostly Ni sulfides and arsenides: millerite, pentlandite, carrollite and nickeline as well as Pb sulfide – galena. Chlorite groundmass comprises millerite, pentlandite, carrollite and cobaltpentlandite. We also found a 20 μm grain of sperrylite (PtAs₂). As previously stated by Wojtulek et al. (2019), chromitites of the Ślęza ophiolite seem to originate from hybridized basaltic melt enriched in water, supposedly due to interaction with surrounding serpentinite. Low amounts of sulfides and their relatively low variability suggest low sulfur as well as base- and platinum-group metal contents in the parental magma of chromitites. Our data confirms that chromitites from ultramafic rocks of the Ślęza ophiolite are poor in platinum group minerals and base-metal sulfides, which suggests that they developed in a low-fertile setting poor in base- and precious metals. This finding matches previously observed depletion in trace elements displayed by ultramafic and mafic rocks of the Central-Sudetic ophiolites (Wojtulek et al., 2022). The low metal fertility of this magmatic system, which had been supposedly developed in a slow-spreading ridge regime (Wojtulek et al., 2022), is related to a refractory feature of the CSO mantle.

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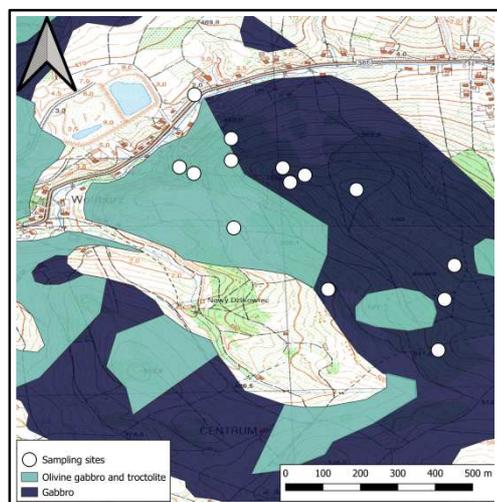
Field study of the Nowa Ruda Massif: insight into fractional crystallization-driven metal differentiation

Wojciech WOŹNIAK¹, Jakub CIAŻELA¹, Eman ELSHERIF¹, Piotr WOJTULEK²

¹Institute of Geological Sciences, Polish Academy of Sciences, ul. Podwale 75, 50-449 Wrocław

²Department of Economic Geology, Institute of Geological Sciences, University of Wrocław, Pl. Maksy Borna 9 50-204 Wrocław

Oceanic studies *in situ*, for instance, along the Atlantis Bank ocean core complex at the Southwest Indian Ridge, suggest that sulfides and oxides typically fractionate early and, therefore, tend to accumulate within lower zones of the crust, which are by ~50% enriched in Cu and other metals compared to the upper zones (Ciążela et al., 2018). In the Central Sudetic Ophiolite, insight into such accumulation is possible in the Nowa Ruda Massif (NRM). NRM is comparable to the Ślęza Massif, but the oldest northern part contains extensive outcrops of the lowermost lower crust with primitive olivine gabbro and troctolite. Layered gabbro consisting of darker and lighter laminae is also present. Further south, various types of gabbro can be observed, which eventually turn into diabase in the southernmost parts of the formation (Wojtulek et al., 2022). This variety will allow for studying progressive change in the crystallization conditions of magma and its impact to form metal-rich horizons.



The field examination has allowed the collection of ~50 appropriate samples from ~14 outcrops (Fig. 1) to examine possible modes of metal migration. The poster will present the field examination results, macroscopic classification of gathered samples, and microscopic insight into associated ore minerals, which will be followed later by a more complex geochemical investigation.

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Fig. 1 Simplified geological map of the northern part

of the Nowa Ruda Massif with indicated sampling sites.

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9th Meeting of the Mineralogical Society of Poland
28th Meeting of the Petrology group
of the Mineralogical Society of Poland

“Oceanic lithosphere: rocks, minerals, and critical resources”

Field trip guide



Śląza Massif in the Central Sudetic Ophiolite: a brief overview

Jakub CIAŻELA¹, Eman ELSHERIF¹, Wojciech STAWIKOWSKI², Piotr WOJTULEK³, Weronika PATALAS¹, Łukasz KRUSZEWSKI⁴, Anna KUKUŁA¹

¹*Institute of Geological Sciences, Polish Academy of Sciences, ul. Podwale 75, 50-449 Wrocław, Poland; e-mail: j.ciazela@twarda.pan.pl*

²*Institute of Geology, Adam Mickiewicz University, ul. Krygowskiego 12, 61-680 Poznań*

³*Institute of Geological Sciences, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław*

⁴*Institute of Geological Sciences, Polish Academy of Sciences, ul. Twarda 51/55, 00-818 Warsaw*

The Central Sudetic Ophiolite (CSO) is located in the Sudetic area, the NE segment of the Bohemian Massif, at the eastern termination of the Variscan orogenic belt (Fig 1). The CSO is the most extensive ophiolitic exposure in the Bohemian Massif, stretching out for over 50 km and reaching up to 35 km in width. The ophiolite is the remnant of the Variscan oceanic lithosphere incorporated into the Continental lithosphere due to the closure of the Rheic Ocean. The CSO represents an ancient supra subduction zone (SSZ)-type oceanic lithosphere formed in a slow- to intermediate spreading regime (Wojtulek et al., 2022).

The CSO consists mostly of ultramafic (STOP 1 of the field trip) and mafic (STOP 2) rocks, interpreted as an ophiolite by Majerowicz (1979) and topped by oceanic sediments (STOP 3). Unlike a typical layered ophiolitic complex, the CSO is heterogeneous, with gabbroic bodies formed due to local magma injections (Wojtulek et al., 2022). The ophiolitic complex consists of at least four units, located both in the Sudetes and at the Fore-Sudetic Block (Fig. 2A): the Śląza Massif (including Kunowska Hill) in the north, Szklary Massif in the east, Nowa Ruda Massif in the southwest, Braszowice-Brzeźnica Massif in the southeast. Four boreholes, Przeclawice IG-1 (606 m deep), Przeclawice IG-2 (605 m), Czarna Góra CZ-1 (980 m), and Borek Strześliński IG-1 (1413 m) show that ophiolitic sequences spread at least 25 km to the east from the Śląza Massif.

This field trip targets the Śląza Massif as the largest body of the CSO; the absolute width of its crystalline part is ~20 km (Fig. 2B). The Śląza Massif displays a complete ophiolite pseudostratigraphic sequence (Kryza and Pin, 2010) and comprises from bottom to top: 1) serpentinized peridotites of the upper mantle with narrow chromite-rich horizons of the Radunia and Czernica hills, 2) an ultramafic-mafic unit of the mantle-crust transition zone with peridotitic, pyroxenitic, and gabbroic rocks of Tąpadła Pass, 3) gabbro of the lower crust with thin ferrogabbro horizons, 4) dike-gabbro transition zone of Kunowska Hill, 5) diabase sheeted dikes of Wieżyca Hill, 6) metabasalts of Gozdnicza Hill, and 7) dark radiolaria-bearing metacherts representing ocean floor sediments (Kryza and Pin, 2010). Most of these layers will be presented during the half-day field trip on 22.10.2023, which will include mantle (Outcrop Tpl1) and crust-mantle transition zone (Outcrop Tpl 2) on **STOP 1** at the Tąpadła Pass (Fig. 2C), gabbro (Outcrop GK1), dikes (Outcrop GK2), and basalts (Outcrop GK 3) on **STOP 2** at Kunowska Hill (Fig. 2D), as well as ocean sediments (Outcrop PK1) on **STOP 3** near Pustków Wilczkowski (Fig. 2E); all described below.

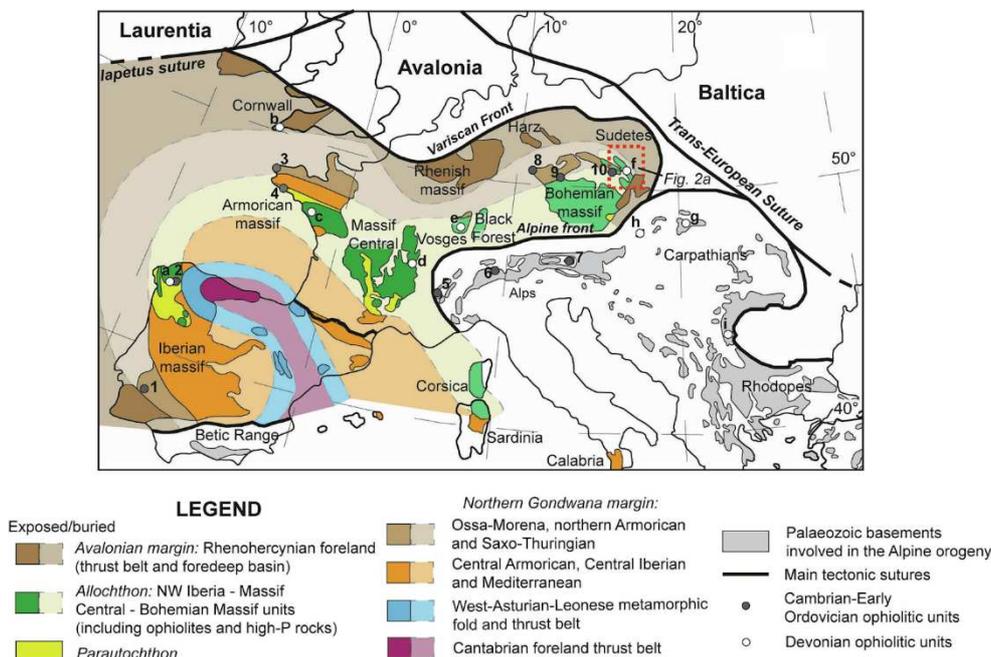


Fig. 1. Ophiolitic massifs in the Variscan belt of Europe (modified from Plissart et al., 2017; Martínez Catalán et al., 2020; Wojtulek et al., 2022). Cambrian-Early Ordovician ophiolites involve (1) Ophiolites of the Ossa-Morena Zone; (2) The Vila de Cruces; (3) The Conquet gabbro; (4) The Audierne gabbro; (5) The Chamrousse ophiolite; (6) The Wildschönau ophiolite complex; (7) The Stubach Complex; (8) The Vesser volcanic sequence with gabbroic intrusions; (9) The Mariánské Lázně Complex and (10) The Leszczyńiec Complex. Late Devonian ophiolitic complexes are represented by: (a) Upper Ophiolitic Units in the NW Iberian Massif: the Careón, Purrido and Moeche ophiolites; (b) the Lizard Complex; (c) the Drain Le Hâvre metagabbro; (d) the Brévenne metavolcanics; (e) ophiolitic rocks in the Vosges; (f) the Central Sudetic ophiolites - see also Figure 2A; (g) the Pernek and (h) the Zlatnik ophiolites and (i) The Balkan-Carpathian Ophiolite.

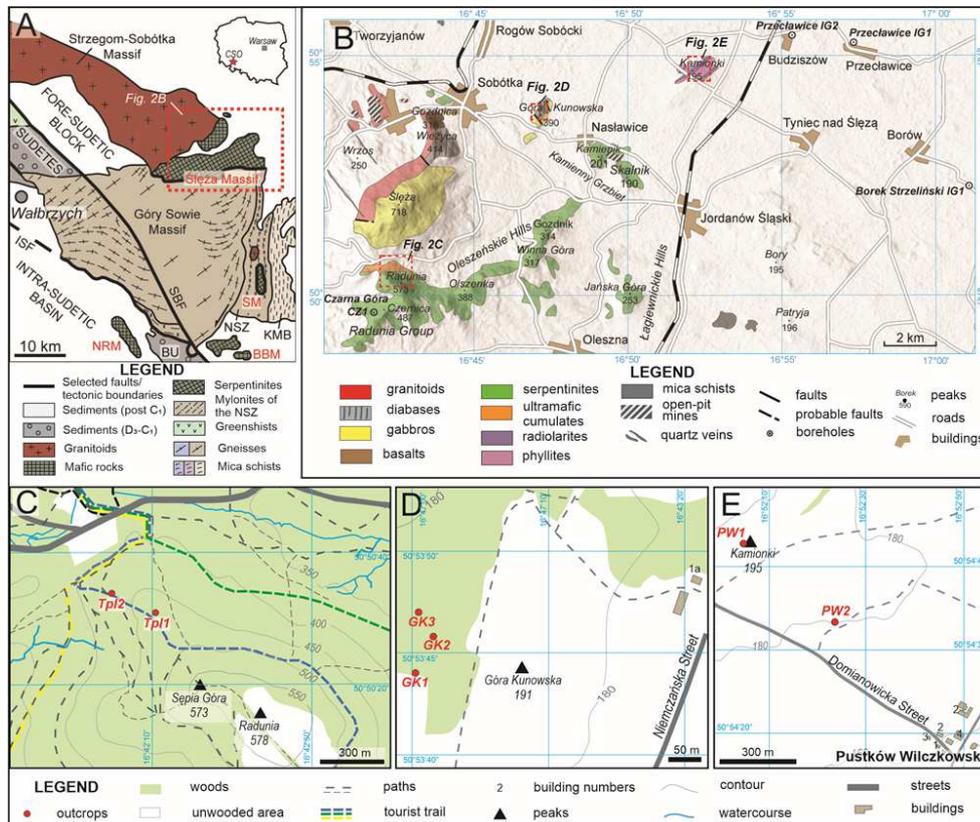


Fig. 2. (A) Context map of the Central Sudetic Ophiolite (CSO) with names of the four massifs written in red. BBM – Braszowice-Brzeźnica Massif, SM – Szklary Massif, NRM – Nowa Ruda Massif. Other abbreviations: ISF – Intrasudetic Fault, SBF – Sudetic Boundary Fault, BU – Bardo Unit, NSZ – Niemcza Shear Zone. **(B)** Detailed map of the main ophiolite massif, Ślęza massif. Adapted from Wojtulek et al. (2022). **(C-E)** Exact locations of outcrops from the field trip: C - STOP 1, D - STOP 2, E - STOP 3. Outcrop PW2 can be explored only individually due to difficult access.

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STOP 1: Tąpadła Pass at the Ślęza Massif: upper mantle and mantle-crust transition

Jakub CIAŻELA¹, Eman ELSHERIF¹, Piotr WOJTULEK², Wojciech STAWIKOWSKI³

¹*Institute of Geological Sciences, Polish Academy of Sciences, ul. Podwale 75, 50-449 Wrocław, Poland; e-mail: j.ciazela@twarda.pan.pl*

²*Institute of Geological Sciences, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław*

³*Institute of Geology, Adam Mickiewicz University, ul. Krygowskiego 12, 61-680 Poznań*

Outcrop locations:

Tpl1: 50°50'30.8"N; 16°42'10.8"E (upper mantle)

Tpl2: 50°50'33.7"N; 16°41'60.0"E (mantle-crust transition)

The Tąpadła Pass provides the critical set of outcrops, giving insight into the upper mantle and crust-mantle transition of the Ślęza Massif. Outcrop Tpl1 (Fig. 2C of introductory section) displays serpentinitized peridotites of the upper mantle (in the past called the Gogołów-Jordanów serpentinite massif), and Outcrop Tpl2 an ultramafic unit composed of serpentinitized peridotite, pyroxene and amphibole-rich ultramafic rocks typical for the crust-mantle transition zone, as well as gabbro of the lower crust (Kryza and Pin, 2010).

The depleted mantle body exposed at best at Outcrop Tpl1 (Fig. 1A) is composed mostly of heavily serpentinitized harzburgites or dunite, mostly with harzburgitic protolith (Gunia, 1992; Dubińska and Gunia, 1997; Gunia, 2000; Wojtulek et al., 2016a; 2017). Fresh dunite occurs only at drill holes, such as Borek Strzeliński borehole BS-1, between 1255–1307 m. These are typically composed of lizardite and chrysotile and show no relics of primary minerals but retain pseudomorphs after pyroxenes (“bastite”) and olivine (mesh textures). Some serpentinites have relics of olivine and pyroxene. Sulfides are mostly nickel sulfides, including pentlandite, heazlewoodite, and millerite (Gil et al., 2020), typical for the abyssal serpentinitized peridotite (Ciążela et al., 2018)

Serpentinites with olivine and clinopyroxene are more common when adjacent to the gabbroic rocks (for example, at Outcrop Tpl2; Fig. 1B) and were formed likely due to basaltic melt percolation through peridotite causing recrystallization (Wojtulek et al., 2022). Melt percolation assemblages are mostly represented by aggregates of anhedral clinopyroxene and amoeboidal chromite occurring interstitially between olivine. These phases are partly replaced by antigorite, which is a higher-temperature phase of serpentine (Ulmer et al., 1995), which is a typical form of contact metamorphism observed along gabbroic veins also in abyssal peridotites (Ciążela et al., 2017) due to contact with late migrating melts (Borisova et al., 2021). The melt-percolation clinopyroxene has very low Ti and REE contents, suggesting a highly refractory mantle source typical of N-MORB-type melts depleted in supra-subduction zone (SSZ) setting but lacking subduction-related enrichment (Wojtulek et al., 2022). The Cr and Mg values of melt-percolation chromite suggest formation from back-arc or fore-arc affinity melts (Wojtulek et al., 2022). These rocks of the CSO are believed to have formed in a mature, intra-oceanic backarc basin. The local gabbroic veins demonstrate sub-crustal crystallization of silicate minerals from migrating melts.

Chromitite layers within the mantle body, typical for oceanic sub-Moho mantle (Dilek, 2014), are located too far from STOP 1 to be included in the field trip, 1 km uphill south from Tpl1 and Tpl2 close to the Czernica summit, but deserve to be mentioned. They are irregularly fractured and have two chromite generations. Primary chromites, poor in iron, occur mostly in the central part of the grains (cores) and are surrounded by secondary Fe-enriched chromite, which also occurs along fractures. Chromitites are also enriched in sulfides compared to depleted mantle peridotites. The sulfides are typically <50 μm but occasionally up to 400 μm (Wojtulek et al., 2016b).

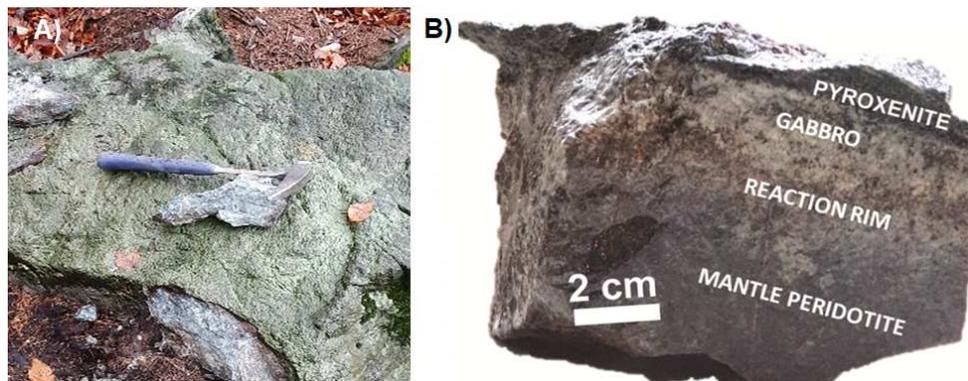


Fig. 1. **A)** Typical serpentinized mantle of Śleża Massif from Outcrop Tpl1. **(B)** Refertilized mantle in contact with a gabbroic vein showing a typical reaction rim between the melt channel and serpentinized mantle collected from the mantle-crust transition zone at Outcrop Tpl2.

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STOP 2: Kunowska Hill at the Ślęza Massif: gabbro, dikes, and basalt

Eman ELSHERIF¹, Jakub CIAŻELA¹, Piotr WOJTULEK²

¹*Institute of Geological Sciences, Polish Academy of Sciences, ul. Podwale 75, 50-449 Wrocław, e-mail: eman-elsherif@twarda.pan.pl*

²*Institute of Geological Sciences, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław*

Outcrop locations:

GK1: 50°53'44.0"N; 16°47'00.1"E (gabbro)

GK2: 50°53'45.7"N; 16°47'01.4"E (dikes)

GK3: 50°53'47.1"N; 16°47'00.5"E (basalt)

Kunowska Hill is an isolated most eastern outcrop of the Ślęza Massif and represents a middle section of its lower oceanic crust with the uppermost gabbro, dykes, and lowermost basalts offering several outcrops showing the transition of plutonic, through subvolcanic to volcanic rocks of the Ślęza ophiolite. Gabbro is isotropic, medium- to coarse-grained rock with ophitic texture, exhibiting a wide range of metamorphic overprint. Primary clinopyroxene and saussuritised plagioclase are accompanied by secondary amphibole, albite, titanite, ilmenite, epidote, and chlorite (Kryza and Pin, 2010; Wojtulek et al., 2019; Floyd et al., 2002). The pyroxenes are often replaced by amphiboles, ranging from actinolite to Mg-hornblende, and epidote-group minerals (mostly clinozoisite and epidote-clinozoisite solid-solution). The saussuritised plagioclase has an anorthite content ranging from 20 to 50% (Wojtulek et al., 2022). The occurrence of metamorphosed mafic rocks displays the most robust evidence for regional metamorphic changes. The rarity of

laminated gabbros and the abundance of isotropic gabbroic bodies in this plutonic part of the ophiolites are well-displayed and argue for a slow spreading process (Nicolas and Boudier, 2003; Wojtulek et al., 2022).

A gabbro-ferrogabbro contact (Fig. 1) is noticeably exposed in Kunowska Hill (Outcrop GK1; Fig. 2D of introductory section) related to a horizon of ferrogabbro enriched in Fe, Ti, and V passing through Góra Kunowska (Wojtulek et al., 2022). The occurrence of those rocks in Kunowska Hill and close to the top of Ślęza Mountain of Ślęza Massif in an elongated zone extending in SW/NE direction helped to distinguish the presence of a probable Strzegomiany-Kunów zone (Wojtulek et al., 2019). This zone extends for nearly 7 km in length and 2 km in width from the NE slope of Ślęza to the Kunów village (Muszer et al., 2015). This kind of evolved gabbro typically appears in the upper parts of plutonic sequences of the oceanic crust (Natland and Dick, 2001; Dick et al., 2008) and may represent a deformation horizon parallel to the detachment fault surface.

The Kunowska Hill ferrogabbro are medium-grained augites, plagioclase, and amphibole as major phases. The concentration of Fe-Ti oxides in Kunowska Hill ranges between 7–15 vol.% (Majerowicz, 2000). The Fe-Ti oxides are mostly titanomagnetite and ilmenite rimmed by titanite. The ilmenite zone in those rocks is enriched in TiO₂ and V₂O₅ (Muszer et al., 2015). The Kunowska ferrogabbro are enriched in pyrites, pyrrhotite, and chalcopyrite (Wojtulek et al., 2019).

The local dikes (Outcrop GK2; Fig. 2D of introductory section) are weakly deformed and pervasively altered metadolerites. They show well-preserved intergranular or ophitic igneous textures (Wojtulek et al., 2022). Dolerites consist of fine-grained amphibole and are often saussuritized or albitized plagioclase. The amphibole compositions range from actinolite to Mg-hornblende. Albite content in plagioclase ranges between 64–74% (Wojtulek et al., 2022). Veins of chlorite, as well as of carbonate and epidote-group minerals, are present. Magmatic oxides, ilmenite and titanomagnetite, along with titanite, are dispersed throughout the rock independent of veins. Dolerites are locally enriched in sulfides, including pyrrhotite, chalcopyrite, pyrite, and sphalerite (Wojtulek et al., 2022). The inherent sulfides form irregular or globular grains, from tens of micrometres up to 1 cm in size.

Metabasalts (Outcrop GK3; Introduction: Fig. 2D) occur as massive lavas, including xenoliths of subvolcanic dolerites and metagabbros, they are in sharp contact with plutonic and subvolcanic rocks of the Kunowska hill (Majerowicz, 2000). Volcanic rocks are completely altered rocks consisting of amphibole and saussuritized plagioclase. They are petrographically variable and display (1) fine-grained, (2) aphanitic, (3) blasto-porphyritic textures. Locally, these rocks are enriched in epidote (Majerowicz, 2000).

The CSO mafic rocks exhibit geochemical characteristics common in refractory N-MORB basalts, as per the clinopyroxene and bulk-rock trace-element compositions. Their N-MORB-normalized trace-element contents are mostly lower than one (Wojtulek et al., 2022). The isotropic gabbroic rocks mostly reveal depleted LREE relative to HREE and show positive Eu anomalies (Wojtulek et al., 2022), typical for rocks that underwent chemical differentiation (Irvine, 1982; Montanini et al., 2008). Based on the compositional features, it can be concluded that the CSO plutonic rocks are cumulates regardless of lacking the layered-diagnostic texture. (Borkowska, 1985; Dziedzic, 1995; Floyd et al., 2002; Wojtulek et al., 2022). The depleted mantle origin of the parental melts of the CSO plutonic and volcanic rocks is evidenced by the low Nb/Yb ratios. A refractory composition of the mantle source is also corroborated by the high initial ϵ_{Nd} values of the gabbroic

rocks and metabasalts (Pin et al., 1988; Wojtulek et al., 2022). Enrichments in some of LILE reveal the interaction with a (hydrothermal) fluid phase due to alteration of the primary peridotites, very likely during either ocean-floor or regional metamorphism (Wojtulek et al., 2022).

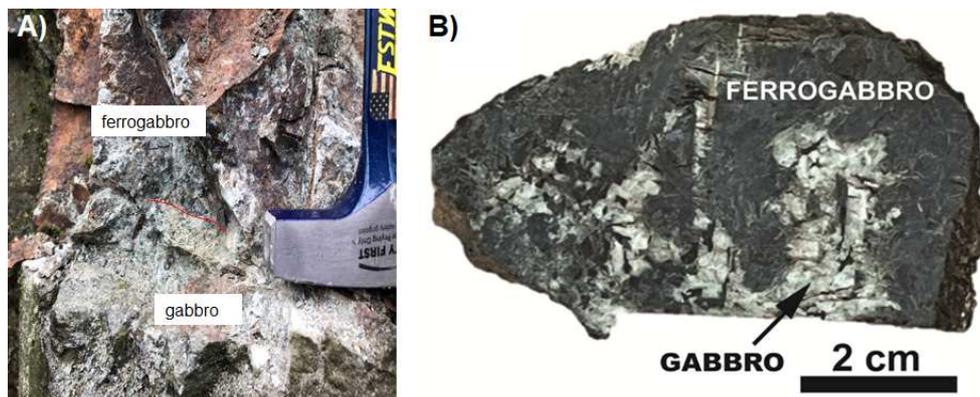


Fig. 1. Ferrogabbro-gabbro contact of Outcrop GK1 at Kunowska Hill in the field (A) and after cutting and polishing a sample from the outcrop (B).

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STOP 3: Kamionki Hill near Pustków Wilczkowski northeast of the Ślęza Massif: oceanic sediments

Łukasz KRUSZEWSKI¹, Piotr WOJTULEK², Jakub CIAŻELA³, Mirosław JASTRZĘBSKI³, Rafał SIUDA⁴, Eman ELSHERIF¹

¹*Institute of Geological Sciences, Polish Academy of Sciences, ul. Twarda 51/55, 00-818 Warsaw; e-mail: lkruszewski@twarda.pan.pl*

²*Institute of Geological Sciences, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław*

³*Institute of Geological Sciences, Polish Academy of Sciences, ul. Podwale 75, 50-449 Wrocław*

⁴*Department of Geochemistry, Mineralogy and Petrology, Faculty of Geology, University of Warsaw, ul. Żwirki i Wigury 93, 02-089 Warsaw*

Outcrop Locations:

PW1: 50°54'43.2"N 16°52'06.3"E (ocean sediments)

PW2: 50°54'33.3"N 16°52'24.7"E (a better outcrop but with difficult access)

Pustków Wilczkowski, located ~30 km S from **Wrocław**, and its surroundings, towards Damianowice and Nasławice are renowned among mineral collectors for probably the best turquoise specimens in Poland. Numerous trenches, after the exploitation of siliceous schists, cut these areas. These rocks appear in the literature also as phyllites and represent open-ocean sedimentation over an ophiolitic sequence (Kryza and Pin, 2010). Idzikowski & Jerzmański (1974) pointed to interesting geochemistry of Silurian formations of the Fore-Sudetic Block, including schists from boreholes at Biskupin and Chocianów; and from Lubań, Jenków, Luboradz, Różana, Złotoryja, Prusice, Bogaczowice, Luboradz, Goczałków Górny, and Pustków. The latter rocks, with elevated V, Mn, Mo, Cu, and Ag. Jamrozik (1979) characterized micropalaeontologically the local “radiolarian metashales” (silica-graphite schists) and suggested a Silurian age. Majerowicz (1984) reported the area to comprise both phyllites and metamorphosed siliceous schists.

Even though the German researchers detected “Mn oxides” in Pustków (Fiedler, 1863; Traube, 1888), the local Mn mineralization remained largely unknown till a very preliminary study by Kruszewski et al. (2021) who identified lithiophorite (Al,Li)₂MnO₂(OH)₂, a cryptomelane-like oxide, ~K(Mn⁴⁺,Mn³⁺)O₁₆, and carpholite, MnAl₂(Si₂O₆)(OH)₄, (a marker of elevated pressure). They occur as usually few-mm-thick,

usually earthy-rich encrustations on the local schists (Outcrop PW 1 depicted in Figure 1A; see also Fig. 2C of introductory section for the exact location) or numerous metallic-black veinlets and veins cutting rounded quartz (quartzite) blocks (sites to the NE and the SW). At one of the sites, a >1-m-large quartzite block with rich, metallic-black encrustation was found. Its Mn phase – currently under study – lacks its metallic luster after some time, thus suggesting some of its Mn to be originally divalent and/or trivalent. Numerous other phase identifications e.g., of bementite, $\text{Mn}_7\text{Si}_6\text{O}_{15}(\text{OH})_8$, birnessite, $(\text{Na,Ca})_{0.5}(\text{Mn}^{4+},\text{Mn}^{2+})_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ (birnessite group), kutnahorite, $\text{CaMn}(\text{CO}_3)_2$, and hisingerite $\text{Fe}_2(\text{Si}_2\text{O}_5)(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, await confirmation. Interestingly, the local Mn oxides/oxyhydroxides are strongly enriched in Co, Ni, and Cu (among others), while the local goethite bears V, As, and Cr. The locally abundant “illite” is strongly enriched in V – the first such record in Poland. Tiny aggregates of plumbogummite, $\text{PbAl}_3(\text{PO}_4)[\text{PO}_3(\text{OH})](\text{OH})_6$, are also relatively frequently observed. The turquoises are associated with crandallite, $\text{CaAl}_3(\text{PO}_4)[\text{PO}_3(\text{OH})](\text{OH})_6$; two generations of this species are recognized: one Ba-rich, slightly strontian, cerian, and yttrian, and another that is purer. Macroscopically distinguishable, white, botryoidal aggregates are sometimes found. Other interesting phosphates are monazite-(La), florencite-(La), $\text{LaAl}_3(\text{PO}_4)_2(\text{OH})_6$, and xenotime-(Y), the latter being occasionally scandian (max. 1.39 wt% Sc). Lanthanum dominance is typical for many (meta)manganolite occurrences worldwide. Alunite (slightly cuprian), $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, and hydroniumjarosite, $(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, are also common (reminding the term “alum shale” once used for some Lower Silesian shales). Another interesting mineral of the site is a potential Al-dominant analog of stilpnomelane. X-ray fluorescence studies of the local metamanganolites also point to Ga and Se enrichment.

At Outcrop PW 2 (Fig. 1B; see also Fig. 2C of introductory section for the exact location) a few-cm-thick, hard, black veins occur in the clayey walls of a post-mining trench. Here, the geochemical character of the local ferri-manganese crusts changes to iron dominance. Goethite is a major phase, while Mn occurs exclusively in chalcophanite-group species. Outcrop PW 1 strongly resembles classical Belgian metamanganolite sites, especially the Blaton area (Mont-des-Grosseillers site). This fact sheds new light on Kennan’s ideas on syngenetic and syndepositional character of the Pustków area and the S Belgium sites (as well as S Ireland and Harz), although the Belgian rocks are reported as of Upper Carboniferous, the “classical” outcrops at the Stavelot massif are discussed as part of Cambrian-Ordovician-Silurian Caledonian basement inliers (e.g., Verniers et al., 2001). Within these considerations, one should also mention the occurrence of (phosphate-mineral-bearing) Silurian “shales” in the Świerzawa (Gozdno-Wielisław) area and similar rocks just S to Strzegom.

Some mineral species studied using powder X-ray diffraction (PXRD) and electron microprobe (EPMA) may be seen in Figure 2. Their complex geochemical character is most likely related to black-smokers-like submarine emanations of the nearby Śląza ophiolitic complex. The rocks studied are known as metamanganolites. They are (volcano)sedimentary Mn-rich rocks, and their metamorphic counterparts are often associated with deposits of Au, Co, Ni, Sn, W, Cu, and Ag ores. Indeed, Mn oxides are known for their capability to sequester numerous elements – a process that may be biomediated (e.g., Tani et al., 2022). Thus, manganese may be treated as an “ambassador” of some ore deposits of other metals, as seemingly confirmed, e.g., by Bobos et al. (2018), who noticed links between generations of chlorite-group minerals with particular types of W-Cu-Mo mineralization. This matter is, in particular, related to the fact of Fe

(oxy)hydroxide minerals – also known as elemental scavengers – to precipitate (in the vicinity of a submarine hydrothermal vent) much faster than in the case of their more mobile Mn counterparts that tend to reside in the oceanic water for a much longer time (Glasby, 2006). The source of at least some of the metamanganolite-hosted elements, in the ocean-deposited formations is often ascribed to submarine hydrothermal system, as in the case of P, V, As, Cu, Pb, and Ba in the world-class, though geochemically unique Långban deposit in Sweden (e.g., Chukanov et al., 2015). This may be true for Pustków Wilczkowski.

As noticed by Kennan (2004), at least some metamanganolites – namely *coticules* (whetstones, known, e.g., as spessartine quartzites, and still mined in the Belgian Ardennes – an area that, as suggested by this author, might be regionally correlated with that around the Central Sudetic Ophiolite), are potential lithostratigraphic markers due to their occurrences at craton margins. First *coticules* in Poland were seemingly found coexisting with eclogites at Kamieniec Żąbkowicki (Achramowicz, 2005), a site to which Kennan (2004) also pointed. Metamanganolites are variably addressed in petrology (terms like *gondite*, *quelusite*, and *kodurite* intertwine with *coticules* and manganiferous phyllites, etc. (e.g., Hártopanu & Hártopanu, 1996), leading to some confusion. It might, possibly, be clarified by studying such rocks – as yet undiscovered in the Lower Silesia. This matter is interesting in the case of the Moldanubicum Zone; indeed, Vrána (2011) lists some Czech occurrences of Mn(Fe)-rich quartz-garnet rocks and mentions these rocks as lithostratigraphic markers. A uniquely interesting site of yet another type of metamanganolite, somewhat resembling Belgian occurrences of *kanonaite* (Mn-analogue of *andalusite*) is known from Kojetice (Třebíč area), and both the authors of the description of this occurrence (Novák & Škoda, 2007) and Vrána (2011) conclude that such rocks are “sneaky” as they are often overlooked during field studies. To make the image even more complex, metamanganolite occurrences unrelated to oceanic crusts are known, with a prominent and recent example of granitoid-related ones (thus, possibly, linking metamanganolites, pegmatites, and Li metasomatism; Tombros et al., 2023; Kennan, 2004).

An interesting geophysical feature that occurs in the vicinity of Pustków Wilczkowski (Nasławice-Kunów-Pustków area) is a positive gravimetric anomaly associated with *metagabbro* (Wiszniewska & Petecki, 2016). This feature may be important in the context

of some/potential ore deposits. More:<https://www.mindat.org/loc-259574.html>.

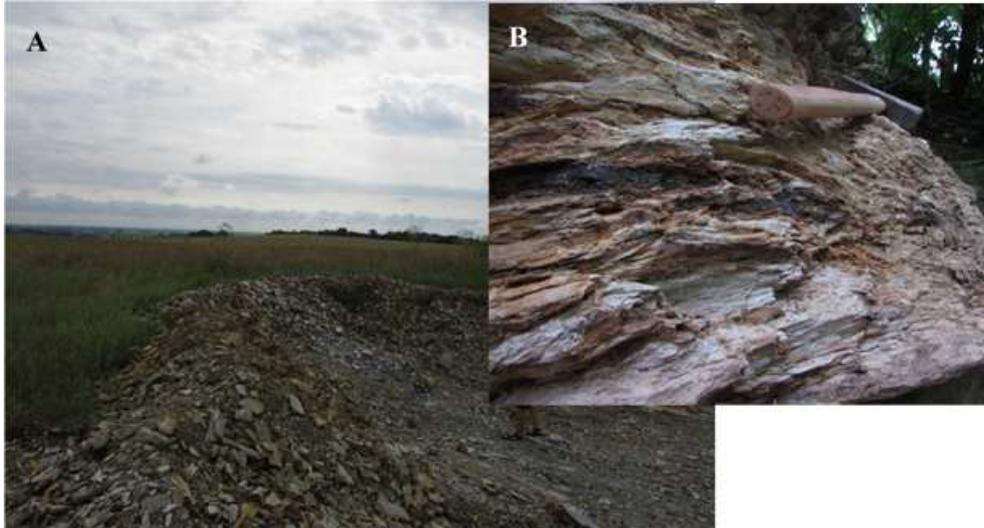


Fig. 1. A) Metamanganolite at outcrop PW1 with Mn > Fe in black encrustations, and B) outcrop PW 2 with Fe > Mn (in black, hard, intra-clay, goethite-rich veins).

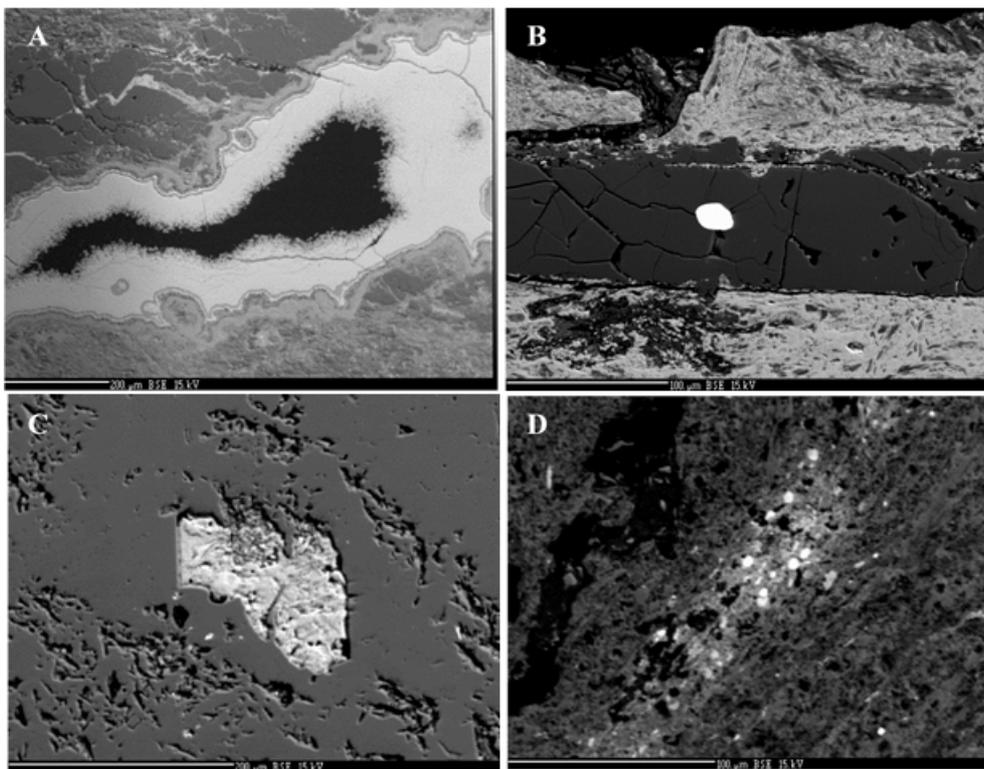


Fig. 2. A set of Backscattered-electron (BSE) images of various minerals from representative thin sections of the Pustków Wilczkowski metamanganolites (Electron Microprobe studies); A) a

pseudomorph-forming (Co,Cu)-enriched lithiophorite in a void of a siliceous matrix; **B–C**) bright chalcopyrite (pure) in quartz surrounded by chaotic fibrous aggregates of Mn silicates (mostly carpholite); **C**) a likely birnessite overgrowing a void in a siliceous matrix; **D**) Scandium-enriched xenotime-(Y) (BSE-brighter; pretulite component substitution) over a veinlet of a complex, yet REE-rich composition.

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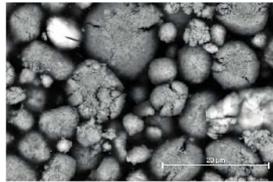
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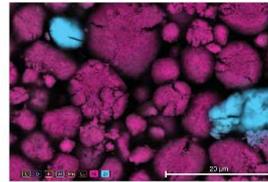
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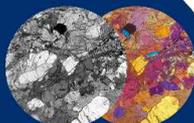
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- tribometry
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- twardościomierze



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AP 207

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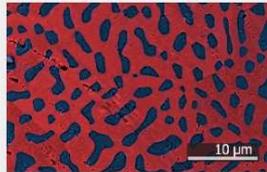
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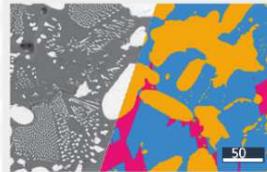


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