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Abstracts and field trip guide

XXVth Meeting of the Petrology Group of the Mineralogical Society of Poland

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Session:

"Petrology in narrow and wide perspective:25 years of sessions of the Petrology Group of the Mineralogical Society of Poland"

Organised by University of Wrocław, Adam Mickiewicz University and Legnica Copper Museum

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The XXV Session of Petrology Group of the Mineralogical Society of Poland

Welcome to the 25th Session of the Petrology Group of the Mineralogical Society of Poland! Petrological research comprises geologically directed studies of rock provenance and evolution, which are essential for understanding of Earth's dynamics, but also the applied studies of mineral chemistry and physics, necessary for new deposits prospection and exploitation, and many side applications in archaeology, soil science, inorganic waste management, and others. The Sessions of the Petrology Group always gathered researchers working in broad spectrum of problems and made a platform for highly specialized discussions. We hope that the 25th Session will follow that tradition. Thus, enjoy science and remember that after-science social life was always the admirable part of our meetings!

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Table of Contents

Invited Speakers

Justyna BARON Archaeological objects as a subject of multifaceted analysis. Some examples of archaeological and geological co-operation	17
Hilary DOWNES, Aidan J. ROSS Meteorites as witnesses to Solar System Evolution	19
Marek GRAD Podolian, Saxonian and Baltic plates — from Teisseyre-Tornquist Line to TESZ	23
Károly HIDAS, Carlos J. GARRIDO, Nicole DILISSEN, Wolf-Achim KAHL, Vicente LÓPEZ-SÁNCHEZ VIZCAINO, Manuel J. ROMÁN-ALPISTE Reading rocks: microstructure visualization in the service of	
petrology	25

Abstracts

Abigal BARKER, Karolina GOŁUCHOWSKA, Maciej MANECKI, Jarosław MAJKA, Jerzy CZERNY, Robert ELLAM Unzipping the Iapetus ocean through SW Svalbard	9
Christopher BARNES, Jarosław MAJKA, David SCHNEIDER,	
Katarzyna WALCZAK, Michał BUKAŁA, Karolina KOŚMIŃSKA	
Small Scales, Large Implications: investigation of µm-scale zircon and	
monazite domains documents Cambrian subduction in the Seve Nappe	
Complex, Scandinavian Caledonides	0
Wojciech BARTZ, Piotr CHACHLIKOWSKI, Anna KUKUŁA,	
Magdalena MATUSIAK-MAŁEK	
Mineralogy and provenance of lithic artifacts from the settlements in	
Kuyavia (north-central Poland)	1

Jakub BAZARNIK, Jarosław MAJKA, William C. MCCLELLAND, Karolina KOŚMIŃSKA, Synnøve ELVEVOLD, Karsten PIEPJOHN, Zbigniew CZUPYT U-Pb SHRIMP zircon dating of metaigneous rocks from West Ny- Friesland, northern Svalbard: Improved connections between Svalbard and Greenland
Łukasz BIRSKI, Ewa SŁABY, Alicja WUDARSKA, Katarzyna GROS Secondary transformation processes of primary Archaean phosphates from Barberton greenstone belt
Michał BUCHA, Anna DETMAN, Bernd R.T. SIMONEIT, Damian MIELECKI, Cezary PIWOWARCZYK, Aleksandra CHOJNACKA, Mieczysław K. BŁASZCZYK, Mariusz O. JĘDRYSEK, Leszek MARYNOWSKI, Anna SIKORA Anaerobic decomposition of lignite by autochtonous microflora
Daniel BUCZKO, Magdalena MATUSIAK-MAŁEK, Brian J.G. UPTON, Theodoros NTAFLOS, Michel GRÉGOIRE, Jacek PUZIEWICZ Non-peridotitic xenoliths and megacrysts from Loch Roag monchiquite (Outer Hebrides, UK): messengers from lower crust or echoes of mantle processes?
Michał BUKAŁA, Christopher BARNES, Jarosław MAJKA, Stanisław MAZUR Shaken not stirred: seismo-metamorphic evolution of subducting slab recorded by Tsäkkok eclogites, Swedish Caledonides
Małgorzata CEGIEŁKA, Bogusław BAGIŃSKI, Ray MACDONALD The complex accessory mineral assemblage of the "Green Granite", Ilímaussaq Complex, Greenland
Małgorzata CEGIEŁKA, Katarzyna MAZUR, Witold MATYSZCZAK Accessory mineral assemblage of the granite from Kopki hills in the vicinity of Jelenia Góra (the Karkonosze pluton, West Sudetes)
Andrzej CHMIELEWSKI, Sławomir OSZCZEPALSKI, Andrzej GŁUSZYŃSKI, Artur KUCZAK Variability of ore mineralization in the vicinity of fault zones in the "Radwanice-Gaworzyce" copper-silver deposit

 Jakub CIĄŻELA, Bartosz PIETEREK, Magdalena PAŃCZYK, Zbigniew CZUPYT, Adrian FIEGE, Juergen KOEPKE, Andrzej MUSZYŃSKI, Marina LAZAROV Pioneer SHRIMP measurements of S isotopes in pyrrhotite and chalcopyrite: details of the method and first insight into S isotope fractionation during cooling of sulfide liquid40
Jakub CIĄŻELA, Daniel MEGE, Marta CIĄŻELA, Joanna GURGUREWICZ, Pierre-Antoine TESSON, Bartosz PIETEREK, Andrzej MUSZYNSKI Volcano heights reveal prolonged magmatic and hydrothermal activity in the Tharsis province on Mars41
Marta CIĄŻELA, Daniel MEGE, Jakub CIĄŻELA, Ioanna GURGUREWICZ, Pierre-Antoine TESSON Lithology of the Martian surface from thermal remote sensing data42
 Justyna CIESIELCZUK, Maciej GÓRKA, Dominik JURA, Monika J. FABIAŃSKA, Magdalena MISZ-KENNAN Stable carbon isotopes of bituminous coals from Upper Silesian Coal Basin (Poland) in comparison with their geochemistry and organic petrography
Justyna CIESIELCZUK, Roman WŁODYKA, Andrzej PAULO, Magdalena SIKORSKA, Grzegorz RACKI, Jerzy ŻABA, Krzysztof GAIDZIK The origin of feldspars in Cretaceous Ashua limestones, southern Peru44
Andrew DOBRZAŃSKI, Rachel WALCOTT, Linda KIRSTEIN, Christian SCHRÖDER, Ian BUTLER, Bryne NGWENYA, Laetitia PICHEVIN Using Petrological Trends to Understand the Volatile Evolution within the Norra Kärr Lanthanoid (REE) Deposit
Haochen DUAN, Changqian MA, Abigail K. BARKER Petrogenesis of hornblende gabbro in the East Kunlun, China: signatures of a mid-ocean ridge46
Agata DUCZMAL-CZERNIKIEWICZ, Natalia HOSKA, Daniel ZIMNY, Marcin ZIMNY Minerals of copper, lead, and zinc and distribution of metals in soil profiles from the area of the exploitation of copper deposits (Lower Silesia)

Magdalena MATUSIAK-MAŁEK, Brian J.G. UPTON, Jacek PUZIEWICZ, Theodoros NTAFLOS, Michel GRÉGOIRE Petrology of mafic and ultramafic xenoliths from Fife, Scotland
Jakub MIKRUT, Magdalena MATUSIAK-MAŁEK, Leif JOHANSSON, Theodoros NTAFLOS, Jacek PUZIEWICZ, Michel GRÉGOIRE Ultramafic xenoliths from Scania (SW Sweden) – preliminary results
Kamil NOWAK, Justyna BARON, Jacek PUZIEWICZ, Małgorzata ZIOBRO Research on the production traces and microstructure of the bronze objects. Symbolic meaning of manufacturing or results of production technology?
Monika NOWAK, Monika KOWAL-LINKA, Zoltán PÉCSKAY Brunovistulian lithospheric mantle xenoliths from a newly recognized nephelinite dyke at the Folwark quarry, Opolian Silesia (SW Poland)71
Levente PATKÓ, Jakub CIĄŻELA, László Előd ARADI, Nóra LIPTAI, István János KOVÁCS, François HOLTZ, Csaba SZABÓ Fe and Cu isotope signatures in sulfide blebs from various upper mantle xenoliths from the Nógrád-Gömör Volcanic Field (Northern Pannonian Basin)
Bartosz PIETEREK, Jakub CIĄŻELA, Henry DICK, Andrzej MUSZYŃSKI Local example of sulfide differentiation through melt-rock reaction at the lower oceanic crust (U1473A, Atlantis Bank, Southwest Indian Ridge)
Anna PIETRANIK, Angelika TOMANKIEWICZ, Jakub KIERCZAK, Arkadiusz PRZYBYŁO Chemically variable zircon populations in rhyolites: implications for dating and reconstruction of magma processes
Arkadiusz PRZYBYŁO, Anna PIETRANIK, Grzegorz ZIELIŃSKI Monzodioritic magma differentiation processes recorded in apatite from the Niemcza Zone: Insights from <i>in-situ</i> analyses by electron microprobe
······································

Jacek PUZIEWICZ, Magdalena MATUSIAK-MAŁEK, Theodoros NTAFLOS, Michel GRÉGOIRE, Anna KUKUŁA, Mateusz ĆWIEK The origin of mantle roots of Variscan Orogen in Central Europe
Bartosz PUZIO, Maciej MANECKI Prediction of the solubility stable for Pb – As – bearing apatites with different halides substitutions
Maciej RYBICKI, Leszek MARYNOWSKI Anhydrosaccharide emissions from detritic lignites and xylites
Zbigniew SAWŁOWICZ Pyritization of organic remains
Magdalena SĘK, Elżbieta HYCNAR Mg-rich carbonates as sorbents in dry methods of desulphurization 80
Mateusz P. SĘK Polymetamorphic tourmaline vein from Wołowa Góra, SW Poland81
Ewa SŁABY, Robert ANCZKIEWICZ, Łukasz BIRSKI, Katarzyna GROS, Gabriela KOZUB-BUDZYŃ, Hervé MARTIN, Jean-François MOYEN, Mudlappa JAYANANDA Accessory minerals as indicators of the crystallization / recrystallization of a granitic pluton – a multi-tools research approach
Piotr SŁOMSKI, Jacek SZCZEPAŃSKI Paleoredox conditions changes across the Ordovician and Silurian boundary: evidence from trace metals
Julia SORDYL, Bartosz PUZIO, Maciej MANECKI Phases analysis of the synthetic Pb – As – bearing apatites with various substitutions of halides
Małgorzata SZCZEPANIAK, Marta ŻURAKOWSKA, Danuta MICHALSKA Stone from cultural heritage in different environmental conditions - petrography and SEM-EDS analysis
Jacek SZCZEPAŃSKI, Dariusz MARCINIAK PT history preserved in mica schists from the Doboszowice Metamorphic Complex (Bohemian Massif, Fore-Sudetic Block)

Dorota ŚRODEK, Mateusz DULSKI, Irina GAŁUSKINA,	
Evgeny GAŁUSKIN Raman imaging as a tool for interpretation of structural cages occupation in the mayenite group minerals	. 87
Magdalena TUCHOWSKA, Tomasz BAJDA, Grzegorz RZEPA, Klaudia DĘBIEC, Łukasz DREWNIAK Batch and column sorption of As(V) onto bog iron ores	. 88
Diana TWARDAK, Adam PIECZKA Extremely fractionated phosphates in the Julianna pegmatitic system at Piława Górna, Góry Sowie Block	. 89
Katarzyna WALCZAK, Jarosław MAJKA, Simon CUTHBERT, Ellen KOOIJMAN, Matthijs A. SMIT U-Pb zircon dating of the diamond-bearing gneiss from Fjørtoft supports the "dunk tectonics" model for the Scandinavian Caledonides	. 90
Edyta WALUŚ, Maciej MANECKI Crystal structure of Mn-substituted synthetic stannite from the isomorphic series Cu ₂ (Fe _{x-1} Mn _x)SnS ₄	.91
Magdalena WOŁOWIEC, Tomasz BAJDA, Małgorzata KOMOROWSKA-KAUFMAN, Alina PRUSS, Grzegorz RZEPA Effectiveness of water treatment residuals in removing heavy metals and metalloids from aqueous solutions	.92
Alicja WUDARSKA, Ewa SŁABY, Michael WIEDENBECK, Łukasz BIRSKI, Katarzyna GROS, Aivo LEPLAND, Richard WIRTH, Jens GÖTZE Secondary processes in the Eoarchean Isua supracrustal belt – clues from chlorine isotopes, TEM and CL studies of apatite	.93
Katarzyna ZBOIŃSKA, Wojciech BARTZ Petrography and provenance of sandstones from architectural details from south-western Poland – preliminary results	.94
Grzegorz ZIEMNIAK, Karolina KOŚMIŃSKA, Maciej MANECKI, Jarosław MAJKA Interpretation of discordant detrital zircon ages from the Southwestern Basement Province of Svalbard	.95

Małgorzata ZIOBRO, Jacek PUZIEWICZ, Theodoros NTAFLOS,	
Michel GRÉGOIRE, Magdalena MATUSIAK-MAŁEK,	
Mateusz ĆWIEK	
Lithospheric mantle underlying Northern Phyllite Zone of Variscan	
orogen in Europe: Nidda (Vogelsberg) case study	. 96

Field trip guide

XXVth Meeting of the Petrology Group of the Mineralogical Society of Poland

Invited Speakers

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Archaeological objects as a subject of multifaceted analysis. Some examples of archaeological and geological co-operation

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Introduction

Archaeology, from its very beginning, is focused on objects and their relations and/or influence on human beings. Our knowledge about past is shaped by data derived from various types of archaeological evidences. Over the ages, people manufactured, modified, used, discarded and re-used various things involved in all aspects of their biological, cultural and social lives. Gosden (2005) says "Objects produced within a recognizable set of forms and styles have influences on the ways in which people make and use them". These objects are both portable artefacts and monumental structures analysed for their shape and decoration, standardisation or uniqueness. Their context and possible social and cultural impact is studied as well. The interests in provenance of the raw materials used in manufacturing archaeological objects demonstrate a long history of cooperation between archaeology and Earth sciences including petrography (for more about history of petroarchaeological studies in SW Poland see Majerowicz et al. 1999).

My presentation concerns several examples of a successful co-operation of archaeologist and petrologists basing on studies run in SW Poland for last several decades with the particular focus on Bronze and Iron Age studies. I argue that the successful co-operation means rising and discussing new questions and sometimes even answering them to improve our knowledge about the past.

Petrology in archaeology

The traditional division of the prehistory refers to raw materials – Ch. J. Thomsen in his fundamental the work from 1827 on prehistoric collection of the Royal Museum of Nordic Antiquities in Copenhagen introduced three periods of the human prehistory: Stone, Bronze and Iron age. Next generations of archaeologists developed sophisticated tools to distinguish and sub-divide the periods, but on the other hand criticised inaccuracy and relativeness of the system. Although criticized, the system is still the base of everyday archaeological practice and ordering mass of evidence.

The Bronze and Iron ages are fascinating periods of human prehistory demonstrating use of various raw materials. Most of them – probably excluding only wood and animal hard tissues – are the field of both archaeological and geological studies. Stone tools, pottery, pigments, glass objects and metal artefacts made of copper and its alloys, gold, silver, lead and iron are made of rocks and have been analysed by specialists in geology.

The main area of the co-operation are of course stone objects. In archaeology of so called metal periods, the main research is focused on metal tools which were believed to replace tools made of other materials. That turned out not to be true as the use of stone objects was

crucial in everyday activities both in prehistoric and early historic societies (e.g. Lisowska 2013). In studying the stone artefacts the petrology is involved in traditional analysis like identification of rock types and establishing their possible provenance (Skoczylas 2014).

The petrographic identification is also a basic analytical tool in study on prehistoric ceramics. Both composition and possible provenance of ceramic paste with the particular focus on temper made of crushed/powdered/sewed/selected rocks have been the subjects of numerous studies. Also thermal analysis brings important data on firing conditions. In case of metal objects, although the main focus refers to the provenance studies i.e. possible locations of copper/tin/gold ores deposits, recent results of co-operation between archaeologists and geologists demonstrated local traditions and different skills of metal working in early Bronze Age communities in SW Poland.

Another type of substances analysed with the petrographic methods are pigments. At Bronze and Iron age sites, many examples of sophisticated decoration made on the vessels walls with mineral pigments of various colours occur. Local production of glass beads also required good knowledge on available minerals.

The successful interdisciplinary co-operation means we learn about past communities – how people improved their skills in processing local/non local/exotic materials. Were they more traditional or rather open to new technologies? Did they travel to search for the desired raw materials? How did they learn to cast metal objects and how long did it take in various areas of SW Poland? Therefore, the co-operation between petrologists and archaeologists gives much more information than simple rock identification and provenance data.

The research is realized under the project " Community, identity, ritual. Interdisciplinary research pattern in studies on cremation cemeteries of the Lusatian culture communities" supported by the The National Science Centre, Poland (NCN 2016/23/B/HS3/00450).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Meteorites as witnesses to Solar System Evolution

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Introduction

Among the many different varieties of meteorites, the achondrites yield most information about the evolution of asteroids and planets. A suite of achondrite meteorites derived from asteroid Vesta represent different parts of the crust of this body; other meteorites are known to have come from the crust of Mars and the Moon. In contrast, a suite of meteorites known as ureilites is derived mainly from the mantle of an unknown asteroid. In October 2008, an asteroid called 2008 TC₃ hit the Earth and more than 600 fragments of the body landed in northern Sudan (Goodrich et al. 2014). These fragments, collectively known as the Almahata Sitta meteorites, were found to be mostly ureilites, but with many different textures and compositions, as well as many foreign fragments such as carbonaceous, ordinary and enstatite chondrites. This is good evidence that ureilites come from a "rubble pile" asteroidal body, in which pieces of the mantle of a pre-existing body have been jumbled up in a random fashion, with non-ureilite fragments added (Herrin et al. 2010). Therefore, reconstructing the pre-existing ureilite body is like trying to complete a jigsaw puzzle with most of the pieces missing and with some pieces that do not belong to the same puzzle!

Mineralogy and geochemistry of ureilite meteorites

Ureilite meteorites mostly consist of silicate minerals, mainly olivine (with core compositions in individual meteorites ranging from Fo_{75} to Fo_{97}) and lesser amounts of low-Ca pyroxene (usually pigeonite but sometimes enstatite). Augite is rare and only occurs in a few ureilites. From the mineralogy, we can deduce that we are dealing with fragments of a depleted mantle of an ancient planetesimal. Geothermometry indicates that the silicate minerals reached temperatures of 1190-1320 °C, hot enough for both core formation and silicate partial melting to have begun (Warren 2012).

Rare Earth Element (REE) patterns for the silicate minerals are LREE-depleted, indicating that a silicate melt has been removed from the planetesimal mantle. As witnesses to the missing silicate melt, glass inclusions, basaltic melt clasts in breccias, and even a LREE-enriched ureilite-related trachyandesite clast have been found (Bischoff et al. 2014). Some unusual ureilite meteorites contain more pyroxene than olivine, which may be the result of melt impregnation within the depleted mantle.

The silicate minerals show evidence of shock metamorphism and of reduction which took place at high temperatures. This evidence suggests that the original planetesimal was destroyed by impact which it was still hot. Only a part of this body re-accreted to form the present-day asteroid from which ureilite meteorites were derived.

In addition to the silicate minerals, up to 6 wt% carbon is generally present in ureilites and is considered to be part of the original mineralogy of the parent planetesimal. This carbon occurs as amorphous carbon, graphite and as diamonds. The occurrence of diamonds is probably related to shock metamorphism. When the planetesimal was destroyed by impact, the carbon reacted with the olivines to form Fo₉₉ rims decorated with tiny inclusions of native iron. Pyroxenes can also show reduced rims. Carbon is absent in those ureilites which have been melt-impregnated, as C does not dissolve in silicate melts.

Sulphides and metals are also found in ureilites, mainly along grain boundaries. The grain boundary metals show depletion in highly siderophile elements, suggesting that they are left over from formation of a small Fe-FeS core within the original planetesimal. There are no known iron meteorites that represent the ureilitic core.

Oxygen and carbon isotope geochemistry of ureilite meteorites

One of the most curious observations about ureilites is that, unlike meteorites from the Moon, Mars or Vesta, they show a wide variation in their oxygen isotope ratios (Figure 1) which also correlates with Fo content (mg#) of their constituent olivines (Clayton, Mayeda 1988). This strongly suggests that the ureilite planetesimal did not reach a temperature high enough for its mantle to become molten. Thus, it did not experience a "magma ocean" stage which would have homogenized the olivine compositions and oxygen isotopes, as is generally seen in mantle rocks from Earth. Figure 1 implies that there were two components involved in the accretion of the original ureilite planetesimal, one of which had high Δ^{17} O and low mg#, and the other had lower Δ^{17} O and higher mg#. The precise nature of these two components is a matter for discussion, but one possibility is that they could be Mg-rich and Fe-rich chondrules, which also show a similar range of oxygen isotopes.



Figure 1. Oxygen isotope compositions versus mg# (Fo content) in olivine in ureilite meteorites. Data from Clayton and Mayeda (1988) and Downes et al (2008).

Recent work (Barrat et al. 2017) has shown that carbon isotopes also vary systematically within ureilite meteorites, such that those with low mg#s have $\delta^{13}C = 0 \%$ and those with high mg#s have more negative $\delta^{13}C$ values. Thus, the carbon isotope

compositions also differed between the two components that mixed to form the original planetesimal.

Space weathering of ureilite regolith?

The rubble pile asteroid from which ureilites meteorites are derived has been exposed to space for billions of years. Some ureilites are brecciated samples which contain the same variety of compositions of silicate minerals in a single sample as seen in across all the individual unbrecciated meteorites, as well as carbon phases, sulphides and metals (Goodrich et al. 2004; Downes et al. 2008). Among the effects which exposure to the Solar Wind has had is the formation of a group of unusual iron silicide minerals. Figure 2 shows the range of compositions found, including minerals such as suessite (Fe₃Si) and xifengite (Fe₃Si₃). Such minerals must have formed in an extremely reducing environment on the surface of the asteroid, perhaps in the presence of the carbon native to ureilites. A similar mineral hapkeite (Fe₂Si) has been found in the regolith of the Moon (Anand et al. 2014).



Figure 2. Fe versus Si (wt %) in metals and silicides from ureilitic regolith breccia meteorites Data from Downes, Ross et al (unpublished) analysed at Johnson Space Center, Houston, Texas

Regolith as a "meteorite capture mechanism"

The regolith of the asteroid from which ureilites are derived also acted as a "capture mechanism" for many different fragments of other solar system bodies. Among the examples, we have found a small fragment of granite derived from a volatile-rich parent body which is at present unknown in the solar system (Beard et al. 2015). Other clasts have been found which are meteorites that differ from meteorite types presently found in our collections. Thus, they give us an opportunity to expand our investigations into regions of the solar system which do not presently yield meteorites.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Podolian, Saxonian and Baltic plates – from Teisseyre-Tornquist Line to TESZ

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Abstract

In the area of the Central Europe three large continental scale tectonic units meet together, namely Precambrian East European Craton (EEC) to the northeast, Variscan West European Platform (WEP) terranes to the southwest, and younger Alpine Carpathian arc in the south. The reference structure of the Central Europe is a sharp edge of the East European Craton. In the area of Poland the south-western margin of EEC is marked as Teisseyre-Tornquist Zone (TTZ), which continues to the north as Sorgenfrei-Tornquist Zone (STZ).



Fig. 1. Podolian plate and Berdo-Narol line (Teisseyre, 1893, 1903)

Teisseyre–Tornquist Zone (TTZ) — earlier Teisseyre Line or Tornquist Line, is a term created in commemoration of Polish geologist Wawrzyniec Teisseyre and German geologist and paleontologist Alexander Tornquist (Fig. 1, Fig. 2). At the turn of XIX and XX century, they noticed a fundamental difference in the geology of platform cover between the rigid East European Platform and its more mobile southwestern forefield (Teisseyre 1893, Tornquist 1908, Dadlez et al. 2005). From the very beginning the TTL

was conceived as a linear feature (fault or fault zone) marking the southwestern boundary of the EEC (Fig. 1, Fig. 2). Contrarily, the Trans-European Suture Zone (TESZ) is a term coined by Asger Berthelsen for an assemblage of suspect terranes boarded by the East European Craton and the Variscan orogeny. It is not a linear structure, but a terrane accretion zone, 100–200 km wide. Both terms, TTL and TESZ, should not be mistaken, as is the case on many maps concerning the problem (Dadlez et al. 2005).



Fig. 2. Saxonian and Baltic plates (Tornquist, 1908)

The TTZ/STZ is a major lithospheric structure, which appears to be a deep-seated boundary reaching at least down to a depth of about 200 km as shown by tomographic analysis of shear wave velocity structure of the mantle under Europe. Another indication of the deep-seated nature of this zone was obtained from observations of earthquakes and explosions located in Europe. To explain the observed blockage of energy from regional seismic events by TTZ, the structural anomaly between eastern and western Europe must reach at least down to a depth of about 200 km.

Continental scale tectonic units of the Central Europe are clearly visible in the crustal structure, Moho depth map, and also gravity, magnetic and heat flow maps.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Reading rocks: microstructure visualization in the service of petrology

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Imaging and quantitative analysis of representative 3-D microstructure of large geological samples composed of mm to cm-sized grains is limited by currently available analytical techniques. X-ray micro computed tomography (μ -CT) is a powerful tool for imaging relatively large sample volumes with sufficient resolution but it does not allow for crystal orientation information, whereas electron backscatter diffraction (EBSD) from 2-D sections of the samples provides quantitative microstructural data that is often difficult to translate into 3-D. Serial sectioning techniques combined with EBSD produce real 3-D microstructural data but they are destructive methods with very restricted available sample volume (max. 10^{-6} cm³).



In this contribution, we explore the potential of combining µ-CT and EBSD (Fig. 1) in a semi-destructive way in order to decipher the reaction history of a metaperidotite sequence formed by the high-pressure dehydration of antigorite serpentinite in a subduction zone. With the help of 3-D microstructural data combined with geochemistry, we demonstrate that growth and nucleation rates of reaction products are strongly controlled by the composition of interstitial fluids. These results show that, besides reaction affinity, surfaceactive molecules may play an important role in shaping the morphology of growing crystals during metamorphism.

Fig. 1. Result of correlative μ -CT and EBSD analyses. A: Olivine grain network with rounded (blue) and tabular (yellow) crystal morphologies. The cylindrical core is ca. 28 mm in diameter. B: Crystal orientation data assigned to a crystal aggregate.

XXVth Meeting of the Petrology Group of the Mineralogical Society of Poland

Abstracts

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Unzipping the lapetus ocean through SW Svalbard

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This study investigates late Neoproterozoic metavolcanics from southwestern Svalbard to determine the evolution of rifting and opening of the Iapetus Ocean as well as the relationship with continental breakup. The aims have been achieved by employing trace element geochemistry combined with Pb isotope geochemistry. Metavolcanic rocks in the South are more enriched in LREE and depleted in HREE in comparison to metavolcanics from the North. Therefore the La/Sm ratio is higher for rocks from the South; La/Sm 3.1-8.6 than for metavolcanics from the North; La/Sm of 1.5-2.4. Similarly, the Sm/Yb ratio is also enriched in rocks from the South; Sm/Yb of 3.4-8.7 and decreases towards the North; Sm/Yb of 1.2-2.0. Pb isotopes also decrease from the South ²⁰⁶Pb/²⁰⁴Pb(i) 18.85-19.33 to the North ²⁰⁶Pb/²⁰⁴Pb(i) 17.49-18.31. The metavolcanics from SW Svalbard indicate an increasingly depleted character from South to North. In the south garnet was present during melting suggesting that melting occurred relatively deep under a thick lithosphere. Whereas the North is characterised by melting a garnet free source under a thinner lithosphere. We also observe that the enrichment of the source decreases northwards likely due to diminishing influence from the older, metasomatised sub-continental lithospheric mantle. Therefore, we propose that the metavolcanics from SW Svalbard carry the footprint of continental breakup and rifting. The estimated age of these rocks, as well as a number of coeval exposures in the Arctic Caledonides are potentially connected with Rodinia breakup and Iapetus Ocean opening.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Small Scales, Large Implications: investigation of µm-scale zircon and monazite domains documents Cambrian subduction in the Seve Nappe Complex, Scandinavian Caledonides

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The eclogite-bearing Vaimok Lens of the Seve Nappe Complex (SNC), Scandinavian Caledonides, predominantly consists of metasedimentary rocks that are highly deformed and contain retrogressive mineral assemblages, both developed during exhumation. In order to see through the exhumation overprint of the metasedimentary rocks and examine the prograde metamorphic evolution of the Vaimok Lens, LA-ICP-MS depth-profiling and Th-U-total Pb dating was applied to zircon and monazite, respectively. Results obtained from the zircon depth-profiling revealed zircon cores with igneous REE patterns and crystallization ages predominantly spanning from the Neoproterozoic to the Paleoproterozoic with minor Archean input. Almost half of the zircon grains exhibited rims with significant enrichment of LREE with minor HREE and U enrichment, coupled with Th depletion. These rims also exhibit subdued Eu anomalies (0.6-1.2). Discordance regressions for three samples calculated the age of the rims: 488 ± 22 Ma, 474 ± 32 Ma, 499 ± 25 Ma. These results indicate that detrital zircon experienced recrystallization during Caledonian orogenesis under high-pressure conditions. The LREE-rich nature of the rims indicates the presence of an LREE-rich fluid catalyzing recrystallization. In this same package of rocks, electron microprobe chemical mapping revealed a core-rim structure of monazite grains defined by an irregular, lobate boundary. Results of Th-U-total Pb analysis for the cores yielded an average content of 0.88 wt% for Y_2O_3 and 2.61 wt% for total HREE (Gd₂O₃ to Lu₂O₃). In contrast, monazite rims show depletion of Y₂O₃ (0.18 wt%) and total HREE (1.69 wt%) with Eu anomalies of 0.4-0.6. The age of cores were calculated to c. 597 ± 15 Ma whereas the rims were calculated to c. 493 ± 4 Ma. Collectively, these results likely indicate dissolution-reprecipitation of Neoproterozoic monazite during Caledonian orogenesis. This process recorded garnet growth near high-pressure conditions thereby providing a fluid source that triggered both dissolution-reprecipitation of monazite and the recrystallization of the zircon rims. This would allow for LREE liberation from monazite, providing the enrichment source for the zircon rims. This study demonstrates the efficiency of utilizing high-resolution techniques to extract critical information from µm-scale domains of zircon and monazite. These results document Cambrian subduction in the SNC that poses significant implications for the geodynamic evolution of the Scandinavian Caledonides as a whole.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Mineralogy and provenance of lithic artifacts from the settlements in Kuyavia (North-central Poland)

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Lithic (non-flint) artifacts collected from archaeological sites located in the Kujawy region are of late Neolithic (4,000-3,000 BC) and early Bronze Age (2,000 BC). Communities in prehistoric times used not-only locally available glacial erratics but also imported, stone material. The main purpose of our research was to: 1) determine the lithology of studied artifacts, and 2) attempt to determine the provenance of the stone material. As a result, obtained data will allow to draw some conclusions on activities, social interaction of aforementioned societies in the Kujawy region, and outline some prehistoric exchange networks. The total of six samples were studied by 1) polarizing microscopy, 2) powder X-ray diffraction (XRD) and 3) scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectrometer (EDS).

XRD studies point to plagioclase and pyroxene as major phases, opaques (magnetite/ilmenite) and secondary minerals (smectites, chlorite) occur subordinately. The rocks have aphyric or occasionally porphyritic texture (plagioclase porphyrocrysts prevails over pyroxene ones). The matrix is composed of fine laths of plagioclase (andesine-labrador) sometimes with albitic rims, pyroxene (augite to diopside) and scarce alkali feldspar (single crystals and rims formed on plagioclase), opaques, apatite and Fe-Mg- rich glass. Uncommon relics of olivine occur in some of the samples, but are partly replaced by secondary iddingsite-bowlingite. The opaques have composition from magnetite to ilmenite, and frequently contain some amounts of copper. Secondary silica phases (quartz, opal, chalcedony) fill pores in the rock.

Potential sources of basaltic rocks used in prehistoric ages in Kujawy region are: glacial erratic from Scandinavia, basaltic rock transported from Lower Silesia (Poland) or Volhynia (Ukraine). Scandinavian and Polish basaltic rocks are silica unsaturated, alkali basalts comprising mostly of porphyrocrysts of olivine and pyroxene, feldspathoids occurs abundantly in matrix. The Volhynia basaltic rocks are formed of pyroxene, while olivine is scarce and feldspathoids do not occur at all. Moreover, those rocks underwent strong albitization, contain secondary silica phases (quartz, opal, chalcedony), and meaningful amounts of copper-bearing phases. These diagnostic features allowed us to establish the provenance of the lithic artefacts as Volhynia basaltic rocks. The proposed research methodology is a good tool to determine prehistoric lithic artifacts provenance.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



U-Pb SHRIMP zircon dating of metaigneous rocks from West Ny-Friesland, northern Svalbard: Improved connections between Svalbard and Greenland

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Precambrian basement rocks of the Atomfjella Complex in West Ny-Friesland, northern Svalbard (Witt-Nilsson et al. 1998) include felsic metaigneous rocks that were previously established to be c. 1750 Ma using conventional U-Pb zircon dating techniques (e.g. Hellman et al. 1997). These felsic rocks are cut by numerous mafic dykes of unknown age.

We performed U-Pb zircon dating of metagranitic rocks that yielded ages ranging from 1760 Ma to 1740 Ma. A metagabbro dyke cutting the felsic metaigneous rocks yielded an age of 1373±4 Ma (Bazarnik et al. 2018). In contrast, another metagabbro and a metatrondhjemite occurring in a postulated tectonic window in the lowermost thrust sheet of the Atmofjella Complex (Witt-Nilsson et al. 1998) yielded c. 2000-1980Ma ages. The new ages are not known from other Svalbard's basement provinces, but they have been reported from North East Greenland. Hence, a close link between the latter and West Ny-Friesland is postulated here.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Secondary transformation processes of primary Archaean phosphates from Barberton greenstone belt

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The studies of Archean abiotic environments and possible preservation of volatile isotopic signature of the early Earth primary signature are crucial for understanding the origin of Life. Phosphates that precipitated in Palaeoarchaean may provide new data on H and Cl isotopic composition of the oldest geological record. However, due to long history of secondary alterations and transformations, and high grade of metamorphism primordial isotopic signature of volatiles could be obliterated. Located in the Kaapvaal craton of SE Africa Barberton greenstone belt (BGB) (3.5-3.2 Ga) have experienced low grade, greenschist facies metamorphism. Therefore, rocks of BGB could, at least to some extent, preserved primordial signature of the environment of their origin. This unique features make rocks of BGB perfect to trace the characteristic of primary early Archaean phosphates and their transformation processes. Multi-tool analyzes have been used in the research of phosphates from sedimentary (BIFs and metacherts) and ultramafic units of BGB.

Multi-tool analysis of apatite confirmed that assumptions. Analyzed apatite crystals, at least partially experienced transformation processes. Furthermore, apatite crystals from single rock type can show either advance or initial grade of alterations. Collected data allowed to distinguish three group of phosphates. First group is represented by unaltered apatite of ultramafic origin. Predominantly these are Cl-enriched OH-apatites with REE distribution patterns that show slightly increasing concentrations of LREE. Moreover, primordial magmatic zonation have been observed. Second group is represented by apatite crystals of sedimentary origin. EMP analyses revealed that these crystals are Cl-depleted, REE-rich hydroxy-fluorapatie with variable F:OH ratio. Their REE profiles are flat with positive Eu anomaly. Their CL spectra have revealed presence of very sharp emission bands of REE, whereas TEM observations display sponge-like structure, most likely due to precipitation from seawater, and presence of highly elongated pyrrhotite and iron oxide inclusions. Last group is represented by both, sedimentary and volcanic samples, yet their features point out to advanced metasomatic alterations. The assumption of the secondary origin of these apatites is based on REE content, yellow luminescence in CL spectra that is caused by dominant role of Mn²⁺ as the activator, absence of water in halogen site, TEM structures and the presence of mineral inclusions. Furthermore, these data can indicate the composition of fluids that altered Archaean phosphates.

Multi-tool studies are crucial for future δD and $\delta^{37}Cl$ investigations of apatite crystals of Archaean age and can provide information about the environment of early Earth.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Anaerobic decomposition of lignite by autochtonous microflora

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Lignite is a organic-rich rock containing complex biopolymers – lignin and cellulose, which are relatively difficult for decay by bacteria. In this work autochthonous microflora from the lignite deposit in the Konin area (Central Poland) was stimulated by the molassescontaining medium in packed-bed reactors. During incubation lignite was decomposed to a mixture of various compounds after depolymerisation and partial fermentation of monomers. Our results show decomposition of lipids during anareobic incubation under laboratory conditions. The concentrations of compound classes including: n-alkanes, nalkanols, *n*-alkanoic acids, diterpenoids, triterpenoids and steroids significantly decreased in biodegraded lignite due to activity of autochthonous microflora. Concentration of some compound classes and individual organic compounds (e.g. saccharides) increased in biodegraded lignite. The ratio lignin:cellulose increased from 11 to 13 in lignite after its decay, which indicates more intense cellulose biodegradation. The products of cellulose degradation were mainly α - and β -glucose. Typical products of lignin degradation were pcoumaric acid, ferulic acid and acetophenone. Other degradation products were phenylpropanoic and phloretic acids, tyrosol and 2-phenylethanol. We interpret the presence of this compounds as the anareobic decomposition of polymers including main lignite constituents: lignin and cellulose.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Non-peridotitic xenoliths and megacrysts from Loch Roag monchiquite (Outer Hebrides, UK): messengers from lower crust or echoes of mantle processes?

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The xenolith suite of Eocene (Faithfull et al. 2012) monchiquite dyke from Loch Roag (Lewis Island, Scotland) comprises ultramafic, mafic and felsic rocks as well as clinopyroxene and feldspar megacrysts. The peridotitic xenoliths represent samples of Archean mantle underlying marginal parts of North Atlantic Craton, while the origin of non-peridotitic xenoliths and the megacrysts is uncertain.

The studied xenoliths are diorites, orthoclasite and biotite-bearing clinopyroxenites. Feldspar forming diorites typically has composition of An_{30-40} , but single K-rich (Or_{95-100}) grains occur as well. Feldspar in orthoclasite and megacrysts has composition of Or_{83-84} and Or_{55-100} , respectively Clinopyroxene in diorites is Al-augite or Al,Fe-diopside with Mg# ranging from 56 to 75. The clinopyroxene (Al-Fe diopside) in orthoclasite and that forming intergrowths in megacrysts of alkali feldspar has Mg#~55 and from 40 to 73, respectively. Clinopyroxenites consists of Al-Fe diopside with Mg# varying from 85 to 64. Feldspars are typically LREE-enriched and have negative Zr-Hf anomalies. Clinopyroxene is also LREE enriched with slight negative anomalies in Zr-Hf and well-marked negative Ti and Sr anomalies. Alkali feldspar and clinopyroxene forming orthoclasite are always lower in trace elements than those from other xenoliths and megacrysts.

We suggest that dioritic and clinopyroxenitic xenoliths originated due to fractionation of mafic magmas. Alkali feldspar-rich rocks are supposedly of different origin. Similar feldspar-bearing samples from Betic Cordilliera in Spain are interpreted as effect of mantle metasomatism by crustal felsic magmas in subduction zones (Avanzinelli et al. 2018).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Shaken not stirred: seismo-metamorphic evolution of subducting slab recorded by Tsäkkok eclogites, Swedish Caledonides

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The Tsäkkok tectonic lens in the Swedish Caledonides consists of sediments and pillow basalts metamorphosed at eclogite-facies conditions. This volcano-sedimentary succession represents distal part of the Baltica passive margin, which was buried at a cold subduction regime and subsequently emplaced onto the Baltica platform at the late stage of the Caledonian orogeny (e.g. Kullerud et al., 1990).

Garnet in the Tsäkkok eclogites records a two-stage growth along a prograde P-T path and contains abundant glaucophane and paragonite (among other) inclusions within a core and omphacite inclusions within a rim. The garnet core shows a prograde zoning marked by rimward increase of X_{Prp} (10-23 mol.%) and decrease of X_{Alm} (61-55) and X_{Sps} (5-1). The garnet rim has a constant $Alm_{50}Prp_{30}Grs_{19}Sps_1$ composition. Chemical mapping of garnet revealed a network of healed micro-fractures and vermicular channels propagating outward from the polyphase inclusions of clinozoisite + kyanite + quartz + amphibole, interpreted as lawsonite pseudomorphs. Additionally, some garnets record a massive fracturing coupled with fluid-assisted omphacite \pm phengite crystallization in the newly formed cracks. Matching shapes of the separated garnet fragments, suggests splitting apart with no additional displacement. Disjointed grains do not record any offset, which implies a lack of simple shear component during deformation. A network of sub-parallel fractures is also preserved in the matrix, cutting through garnet and omphacite grains among the others.

Therefore, we suggest that the Tsäkkok eclogites show the first documentation of *internal* fluid generation due to lawsonite, glaucophane and mica(?) breakdown at the blueschist to eclogite facies transition. Overpressured fluids reduced the magnitude of normal stress at overall lithostatic pressure conditions and triggered seismic event(s) recorded as a brittle failure at high-pressure conditions.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



The complex accessory mineral assemblage of the "Green Granite", llímaussaq Complex, Greenland

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The Ilímaussaq complex, Greenland, is a multistage alkaline to peralkaline intrusion whose emplacement took place around 1160±5 Ma (Krumrei et al. 2006) and was structurally controlled by subsidence and stoping (Marks, Markl, 2015). The complex was formed by at least three principal intrusions, with the Green Granite during second intrusive phase alongside quartz syenite.

The main goal of this research is a detailed description of complex mineralogical assemblage comprising the Green Granite. To characterize it thoroughly, multiple analytical methods such as optical microscopy, scanning microscopy (SEM/EDS), electron microprobe analysis (EPMA), mass spectrometry (ICP-MS) and X-ray diffraction (XRD), were used. The main focus was the determination of empirical formulas of the mineral phases present in the rock, as well as the textural relationships between them. Over 25 phases where identified, with chevkinite-(Ce) being described for the first time at Ilímaussaq.

On the QAP-diagram the Green Granite plots in the alkali feldspar granite field. It is a holocrystalline, porphyritic, massive granite characterized by bulky perthitic alkali feldspars accompanied by well-developed quartz with undulose extinction. The granite has a very high content of incompatible elements reaching 5.07%. The amphibole group is represented by arfvedsonite, ferro-richterite and ferro-ferri-katophorite, which implies that crystallization took place under rather reducing conditions. Clinopyroxene forms radial rims surrounding amphibole and aenigmatite and isolated crystals. The zonation recognized in some of them suggests that the melt was evolving with enrichment of Fe and Na and depletion of Mg, Ca, Ti and Al. There is also a wide range of accessory minerals, most of which incorporate Ti (titanite, ilmenite, neptunite, narsarsukite, leucosphenite, pyrochlore and chevkinite), Nb (pyrochlores, narsarsukite, leucosphenite, titanite, ilmenite) or REE (monazite, britholite, pyrochlore, chevkinite, zircon, fluorite) into their structure. Some of them (e.g. pyrochlore, britholite and zircon) exhibit alteration, which went in the direction of silica and hydroxyl enrichment and depletion of fluorine and REE.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Accessory mineral assemblage of the granite from Kopki hills in the vicinity of Jelenia Góra (the Karkonosze pluton, West Sudetes)

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Samples of fine-grained granite with single K-feldspar porphyritic variety sensu Berg (1923) from Kopki hills near Jelenia Góra were investigated by means of SEM-EDS and electron probe microanaliser (EPMA). Based on the obtained data primary and secondary mineral assemblages were distinguished. The primary minerals include allanite-(Ce), fergusonite-(Y), xenotime-(Y), thorite, scheelite and uraninite. Bastnäsite-(Ce), parisite-(Ce) and cerianite-(Ce) are secondary phases, possibly accompanied by monazite-(Ce).



Fig. 1. BSE images; a – bastnäsite-(Ce) replacing allanite-(Ce); b – parasite-(Ce) with cerianite-(Ce) surrounded by unidentified silicate.

Bastnäsite-(Ce) and the phase with chemical composition similar to parisite-(Ce) occur as anhedral inclusions within silicates. Two types of uraninite can be distinguished (i) frequently mutually intergrown euhedral cubic crystals with dimensions $\leq 15 \mu$ m; (ii) anhedral inclusions up to 20 μ m in allanite-(Ce) and fergusonite-(Y). Fergusonite-(Y) appears as inclusions in other phases (e.g. biotite, quartz, plagioclase, titanite) or as discrete grains. The monazite-(Ce) crystals reach ca. 20 μ m and occur as inclusions in allanite-(Ce). The allanite-(Ce) is abundant, reaching up to 0.5 cm. The grains frequently show zonation as well as signs of alteration typical for hydrothermal modification (Poitrasson 2002).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Variability of ore mineralization in the vicinity of fault zones in the Radwanice-Gaworzyce copper-silver deposit

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During the petrographic research the variability of ore mineralization in the fault zones (normal, reserve and strike-slip faults) in the area of the copper and silver deposit Radwanice-Gaworzyce has been studied. Detailed microscopic and electron microprobe examination were made. In the all analyzed profiles, the presence of oxidized geochemical facies (Rote Fäule) barren with ore mineralization but significantly enriched with hematite was confirmed. Rote Fäule facies occurs at a different level of the Zechstein copper-bearing series from the lower part of the Weisliegend up to several meters in the Zechsteinkalk. Over the series of oxidized rocks the reduced sediments with highly elevated concentration of ore minerals were recognized. In the area of research, the reduced profiles are characterized by the predominance of copper sulphides from Cu-S group, where chalcocite dominates. The most intensive mineralization occurs in the Kupferschiefer above the oxidized bottom part of the Weisliegend, and above the oxidized shale and/or oxidized lower part of the Zechsteinkalk. The dominant form of ore mineral occurrences is very finegrained dissemination. Ore minerals usually feature hypidiomorphic and idiomorphic structure. Veinlets, replacements of carbonate minerals and fillings of fractures are less common. Microprobe examination has shown elevated concentrations of silver in copper sulphides (up to 4% by weight). A decrease in the concentration of silver in copper ore minerals towards the top of the mineralized horizon was distinguished. Chalcopyritebornite association in the form of tiny veins and irregular nests as well as aggregations of chalcopyrite and pyrite are found, both within the reduced and oxidized rocks. Besides, on the fault planes crossing different geochemical zones, increased amounts of chalcopyrite, bornite, pyrite, tetrahedrite and tennantite are commonly encountered. The presence of this type of mineralization indicates their secondary origin with respect to disseminated primary Cu-S-type sulphides and that secondary mineralization phase such as chalcopyrite and pyrite aggregates superimposed on the primary Cu-S-type mineralization. The distribution of oxidized zones determines the location of the ore body both vertically and laterally and the hematite mineralization occurring as high as in the Zechsteinkalk indicates the most intense upward activity of oxidizing solutions. In places where the front of oxidation exceeded significantly the horizon of the Kupferschiefer, the ore mineralization is more impoverished than in the case when the oxidation front stopped on the border of the Kupferschiefer with the Weisliegend. Tectonic deformations have not influenced the distribution of primary ore mineralization, nevertheless the ore body was subsequently disrupted as a result of formation of extensional and compressional features that host secondary mineralization.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Pioneer SHRIMP measurements of S isotopes in pyrrhotite and chalcopyrite: details of the method and first insight into S isotope fractionation during cooling of sulfide liquid

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IODP Expedition 360 drilled the 810-m-deep U1473A hole into the lower crust of the Atlantis Bank ocean core complex at the Southwest Indian Ridge (33.7°S, 57.3°E). Gabbro from a depth of 615-730 mbsf contain up to 8 mm large igneous sulfides (Ciążela et al., 2016). Igneous sulfides of this size are unusual in the lower oceanic crust and rare elsewhere. The sulfide grains are composed of pyrrhotite (75-85 vol.%), chalcopyrite (5-20 vol.%), and pentlandite (1-5 vol.%). Textural observations indicate that pentlandite and pyrrhotite exsolved from monosulfide solid solution (mss), and chalcopyrite is formed after intermediate solid solution (iss). Mss and iss form upon cooling of sulfide liquid (Holwell and McDonald, 2010).

Large sizes of pyrrhotites and chalcopyrites allowed us to measure their $\delta^{34}S$ signature using a Sensitive High Resolution Ion MicroProbe (SHRIMP) in order to better understand S isotope fractionation during cooling of sulfide liquid. To monitor the accuracy and precision of measurements, we used the Sudbury pyrrhotite and the CPY-1 chalcopyrite reference materials with known $\delta^{34}S$ signatures of $\pm 2.4 \pm 0.2\%$ (1 σ), and $\pm 1.4 \pm 0.2\%$, respectively. In our measurements, we obtained $\delta^{34}S$ values of $\pm 2.39 \pm 0.06$ (1SE, Standard Error of the mean, n=21) for the Sudbury pyrrhotite and $\pm 1.42 \pm 0.09$ (n=14) for the CPY-1 chalcopyrite indicating high accuracy and precision. The high precision reflects excellent isotope homogeneity of the used reference materials.

Average $\delta^{34}S$ signatures for 12 measured samples range from $+0.2 \pm 0.4\%$ to $+2.2 \pm 0.2\%$ in pyrrhotites, and from $-2.0 \pm 0.6\%$ to $-0.5 \pm 0.2\%$ in chalcopyrites. Neglecting minor pentlandite (1-5 vol.%), bulk sulfide $\delta^{34}S$ signatures can be estimated and range from -0.1 to +1.5% (Table 1). These $\delta^{34}S$ values are consistent with the $\delta^{34}S$ values obtained for the whole-rocks (-0.1 to +0.3%; Ciazela, 2018) and within a typical range of -2 to +2% observed for primitive mantle S sources (e.g.; Peters et al., 2010). The higher $\delta^{34}S$ values obtained for pyrrhotite when compared to chalcopyrite are generally consistent with thermodynamic calculations. However, the predicted S isotope equilibrium fractionation between pyrrhotite and chalcopyrite ($\Delta^{34}S_{po-ccp}$) is only +0.2% at 800 °C (Li and Liu, 2006; Ohmoto and Goldhaber, 1997) and contrasts to high (+1.9 to +4.1%) $\delta^{34}S$ differences between pyrrhotites and chalcopyrites in our 12 samples. As sulfides are of magmatic origin our results likely indicate important role of kinetic fractionation effects during sulfide cooling, which may be related to sulfur diffusion.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Volcano heights reveal prolonged magmatic and hydrothermal activity in the Tharsis province on Mars

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Although Martian minerals and rocks match those on Earth, geological processes on Mars differ by lack of plate tectonics and negligible erosion in the rare atmosphere. Both allow us a better than on Earth insight into the earliest planet history. We take advantage of limited erosion and lack of plate tectonics on Mars to track down the intensity of volcanism in the Tharsis province from Early Noachian (~4 Ga) to Late Amazonian (~0.1 Ga).

Tharsis is the largest volcanic province of Mars with well-known 21-km-high Olympus Mons and hundreds of other large, medium, and small volcanoes. We catalogued the large and medium (>3 km high) volcanoes and collected information on their height and age as estimated through crater counting. Our results indicate a distinct inverse correlation (R = -0.50) between volcano heights and their summit caldera ages. Importantly, we do not see such an inverse correlation in other volcanic provinces. For example, three large volcanoes of the Elysium province do not show any dependence on age. The Elysium province is, however, characterized by relatively thin crust (40-50 km; Tenzer et al., 2015) and shortlasting volcanism mostly limited to Noachian and Hesperian (Platz and Michael, 2011). Tharsis, on the other hand, is featured by thick crust (70-90 km; Tenzer et al., 2015) and prolonged tectonic activity of nearly constant intensity throughout the Martian history (Bouley et al., 2018). Our new results support this indicating prolonged magmatic activity in Tharsis. After a coeval beginning of volcanic activity in the entire Tharsis province in Early Noachian, small magma reservoirs stopped working and yielded smaller volcanoes, whereas larger magma reservoirs were and perhaps are still active, and are marked by the largest volcanoes.

In this light, Olympus Mons calderas may be the best candidate to search for CH_4 , H_2S , SO_2 , and HCl emissions associated with hydrothermal venting and metallogenesis. The CH_4 emission on Mars was detected by the Curiosity rover (Webster et al., 2018), Mars-based orbiters (Formisano et al., 2004; Fonti and Marzo, 2010), and Earth-based telescopes (Mumma et al., 2009). However, only Fonti and Marzo (2010) have noted enhanced CH_4 emission related to active volcanism. The ongoing ExoMars mission of the European Space Agency (ESA) may support their preliminary results thanks to currently operating Trace Gas Orbiter (TGO). Two TGO instruments, Atmospheric Chemistry Suite (ACS) and Nadir and Occultation for MArs Discovery (NOMAD), can detect atmospheric CH_4 down to a low level of 0.25 ppt with a good spatial resolution of 15 km. ESA invited eight guest investigator groups in Europe to participate in the ExoMars mission. Our group is one of the eight, and aims at searching for CH_4 , SO_2 , H_2S , HCl, and associated sulfide deposits in the volcanic provinces of Mars.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Lithology of the Martian surface from thermal remote sensing data

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Thermal inertia shows the ability of subsurface (few upper cm) to store heat. Helping to understand the surficial geology and recent processes, thermal inertia is one of the key parameters estimated through remote sensing. On Mars, thermal inertia cannot be measured directly and is most often modelled. Thermal inertia models are complex and difficult to apply by broader community of scientists. We therefore present a new method based on Apparent Thermal Inertia (ATI), which approximates thermal inertia, and can be directly calculated from surface albedo, diurnal temperature difference, digital elevation model, and solar geometry.

Our method is entirely based on available data and does not require additional modelling. The method is suitable for flat and sloping terrains. We demonstrate this in a test area in Valles Marineris. The method is especially useful for three petrological applications. Firstly, exposures of harder rocks (ATI > 520 Jm⁻²K⁻¹s^{-1/2} called also tiu) can be distinguished from loose sedimentary material (ATI < 400 tiu). Secondly, sediment grain size can be estimated. For example, dusts (silt fraction) show an ATI < ~200 tiu, and sands an ATI of 260-400. Thirdly, major types of Martian hard rocks such as basalts (1630-2200 tiu) and serpentinites (~2500 tiu) may be distinguished between each other.

Comparison with results obtained by other approaches using modeled data shows similarity in flat areas. However, the significant influence of slope and aspect on albedo and diurnal temperature differences are illustrated by our method. Importantly, the presented approach enables to calculate ATI values almost automatically for most of the Martian surface based on a set of publicly available input data such as temperature, albedo, solar geometry parameters, visible dust opacity, and a digital elevation model.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Stable carbon isotopes of bituminous coals from Upper Silesian Coal Basin (Poland) in comparison with their geochemistry and organic petrography

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Raw seam bituminous coals of different rank and petrographic properties were investigated. The coals are representative of all stratigraphic coal-bearing sequences of Carboniferous age, i.e., from the latest Mississippian mudstone paralic series and Pennsylvanian limnic sandstone- and mudstone series of the Upper Silesian Coal Basin. Coalification increases with depth (the vitrinite random reflectance R_r ranges from 0.56 to 2% with the gradient 0.2%/km) and towards the western part of the basin.

Fifteen samples of bituminous coal were collected from five underground coal mines, namely, Jankowice, Marcel, Ziemowit, Wujek, Piekary and core Gołkowice IV. As their propensity for self-heating can be different they were heated in the laboratory to 400°C in an open system for 24 hours and in a closed system for 2 hours. The heating rate in the closed system was 20°C/min whereas, in the open system, the samples were placed into an oven pre-heated to 400°C. The petrographic and geochemical properties, and the isotope compositions, were determined for both raw- and heated samples. The aim of the study was to identify any trends in the petrography, and in the isotope- and organic geochemistry in open- and closed experimental environments.

The general trend of ¹³C content tends to increase with increasing rank in the raw coals, however the influence of other factors are also noticed. The heating experiments revealed almost the same isotope composition of the raw coals and the samples heated in the closed system; differences range from 0.01-0.45‰, as it is known for natural coals. Significant differences ranging from 0.18-9.79‰ were demonstrated for samples heated in the open system. In these cases, some extracted/desorbed carbon species (methane/carbon dioxide/hydrocarbons) depleted in ¹³C in comparison to raw coal material probably escaped during the heating procedure and ended up enriching residual thermally changed coals in ¹³C. Such compositional changes are shown by depletion of bituminous fraction in lighter *n*-alkanes in the range of *n*-C₁₁-*n*-C₁₈ ca in 15-20% rel. When the system is closed, there are no changes in the final total isotopic composition as no components are carried away despite the changes in petrographic and geochemical forms. In the open system, the final total isotopic compositions of all samples significantly shifted towards isotopically heavier values; in the case of four samples, the shift was ten times greater than in the others.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



The origin of feldspars in Cretaceous Ashua limestones, Southern Peru

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The presence of numerous alkali feldspars in Cretaceous carbonate-evaporitic Ashua Formation, southern Peru, was announced by Ciesielczuk et al. (2016). They occur most frequently in the Ashua limestones of Coniacian – early Santonian age, representing middle to inner carbonate ramp facies. Their frequency depends, however, on the distance from a dacite stock of Late Cretaceous-Paleogene age. They were suspected to be authigenic in the carbonate sedimentary basin, primary in magmatic rock fragments delivered as pyroclasts, or metasomatically altered within carbonate rock of certain stage of diagenesis. The aim of the work is to prove the way of authomorphic feldspars formation. Limestone samples containing feldspars were studied using optical and scanning microscopes, Raman spectroscopy, XRD, EPMA and cathodoluminescence methods.

In the vicinity of partly lithified limestone containing pyroclastic debris, dacitic body intruded, providing heat and driving hydrothermal fluids. Previously deposited pyroclastic material underwent transformations. Detrital components were albitized, adularized, sericitized, and chloritized. Altered plagioclases of albitic composition constituted the nuclei for crystallization of automorphic rims of albitic composition. They did not inherit the optical orientation of albites in core, but the degree of aluminium arrangement in the albite structure was the same. Simultaneously authigenic albite grains crystallised in pores around another nuclei forming crystals up to 500 μ m. This phenomenon was followed by oligoclase crystallization. Some albite crystals are partly overgrown by feldspar containing up to 13% of anorthitic particle. There were two ways of oligoclase rim formation. The first one consists of simultaneous processes of dissolution of feldspars in core and crystallization of oligoclase in rims. The border between core and rim is blurry and diffusive and is caused by lack of space. The second way suggests crystallization of oligoclase rim in open space because the border is sharp and straight.

The oligoclase formation consumes less silica that is necessary to the albite formation. The excess of SiO_2 supported by hydrothermal fluid composition caused the authigenic quartz crystals formation of the size up to 10 μ m and silicification of authigenic albite. Amorphic silica was also found in metasomatised limestone.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Using Petrological Trends to Understand the Volatile Evolution within the Norra Kärr Lanthanoid (REE) Deposit

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Lanthanoids or 'Rare Earths' are critical to a range of advanced technologies; however, the formation processes that result in concentrated economic deposits of lanthanoids remain enigmatic. This research has focused on the evolution of the Norra Kärr syenite which has measured ore grades up to 0.61% TREO (of which 52.6% are HREO) and an indicated resource of 31.1 Mt at 0.4% TREO cut-off grade (Saxon et al. 2015) making it mainland Europe's largest lanthanoid resource. Core samples and analytical data kindly supplied by Tasman Metals Ltd. has provided an unrivalled opportunity to further investigate the evolution of this complex and to build on the previous studies of Sjöqvist et al. (2013) and Atanasova et al. (2017).

A detailed petrographic study of the intrusion combined with electronprobe (EPMA), Mössbauer and LA-ICP-MS analyses have shown that Norra Kärr comprises two separate intrusive events which both display an overall crystallisation sequence of aegirines followed by zirconosilicate phases and finally feldspars. Both intrusive phases also contain separate trends in volatile and lanthanoid evolution. These trends can be picked out using data from amphiboles, biotites and zirconosilicates. Previous modelling work on the Oslo Rift intrusions by Andersen et al. (2013) has shown that the order in which these phases form in an alkaline magma is controlled by the relative activity of a given volatile (F-, Cl-, OH-) in the magma. Future work will involve modelling the volatile and crystallisation trends to see if they affect the location of lanthanoid mineralisation within the intrusion and synthesising the available data into a holistic ore-deposit model for general exploration purposes.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Petrogenesis of hornblende gabbro in the East Kunlun, China: signatures of a mid-ocean ridge

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The eastern Kunlun orogenic belt is an important area to understand the northern part of the Qinghai-Tibet Plateau evolution. We study a hornblende gabbro, from the Kunlun ophiolite, embedded in the Proterozoic basement granitic gneiss by tectonic emplacement. We aim to investigate the source of hornblende gabbro and compare it with other basic rocks in the Kunlun orogenic belt to better understand the early Paleozoic tectonic setting of the Kunlun orogenic belt.

The hornblende gabbro has a large proportion of amphibole (40-45%) and albitic plagioclase. Two populations of amphibole can be identified: the first is calcic amphibole, with high Mg# = 56-70; the second is sodic calcic amphibole, with low Mg# = 38-49. The whole rocks are characterized by MgO 7.7-8.6 wt%, Dy/Yb 1.6-1.8, La/Sm 1.32-1.42, Th/Yb 0.14-0.36, Nd/Yb 3.1-3.4 and high Ni 71-112 ppm, Cr 78-272 ppm as well as Sc >48 ppm. In addition, the hornblende gabbro has ϵ Nd_(i) = +2.26 to +3.43 similar to midocean ridge basalts, with high 87 Sr/ 86 Sr_(i) = 0.7058-0.7070. Calculated by the basic rock magmatic thermobarometer, the hornblende gabbro formed at 1382-1420°C and 1.8-2.7 GPa.

The study of the geochemical properties of the hornblende gabbro indicates that it is MORB type ocean crust. Modelling of trace elements in amphibole constrains partial melting to 10-15% of spinel peridotite to form the hornblende gabbro.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Minerals of copper, lead, and zinc and distribution of metals in soil profiles from the area of the exploitation of copper deposits (Lower Silesia)

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The metals distribution in areas of the exploitation of deposits are very important issue having influence on the protection and usefulness of the soil. Therefore, soil research, as the subject of interest of many scientific fields are very important. In this work were studied mineralogy and chemical composition of sediments in soil profiles located in area of exploitation of copper deposits in Lower Silesia, in the vicinity of tailings storage facilities.

The sediments were examined by sieve method for granulation, and by optical microscopy and X-ray method for mineralogy. Moreover carbonate content, the organic matter and C_{org} content, pH, and metal content using ASA and ICP-MS (Actlab, Canada) methods were determined.

The surface of the soil layers were usually coarse-grained and the lower parts of the profiles were fine- grained, forming the following types of sediments: silts, clayey-silts, and fine-grained sands. The grain size of the sediments from the facilities was higher (over 50% of sediments was coarse-grained). In mineralogy predominantly rock-forming minerals were observed: quartz and feldspar, calcite (in different proportions) and clay minerals: illite, kaolinite and the mixed-layered phases. The malachite, covellite (very rare), cerusite, and sporadically sulphides (galena, sphalerite and pyrite) in the coarse fractions of sediments was observed. The content of metals in soils ranges from 35 ppm to 1667 ppm Cu, Pb from 21 to 1791 and Zn from 18 to 1129 ppm. In soils from facilities the metals reaches to 11000 ppm (Cu), 1786 ppm (Pb), and 869 ppm (Zn).

In soils, decreasing in the concentration of metals is observed down the profiles, while in the area of waste facilities the metals content varied depending on the depth, but the highest content are observed near the surface. The increasing values are correlated with the increase in carbonate and sulphides content, while the increase of the content of metals in soils located outside facilities are correlated with increasing of frequency of the clay fraction or/and organic matter in fine fractions of sediments.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



One-pot synthesis of magnetic composites based on synthetic hydrotalcite

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Synthetic hydrotalcite structures, known as LDH (Layered Double Hydroxides) are materials widely used as catalysts and adsorbents (Miyata, 1975). They are rare in nature, however their synthesis can be easily carried out in the laboratory. Their structure consists of positively charged brucite–like layers with the charge–balancing hydrated anions (A^z) between them. The separation of LDH from the solution is problematic, therefore in recent years, the separation methods, eg. including magnetic properties of materials, are developed (Sulistyaningsih et. al., 2007). So far, magnetic particles of Fe_xO_y were precipitated on the material sufrace as products of separate syntheses. The aim of this work was to design experimental conditions for obtaining LDH-Fe_xO_y materials in one-pot synthesis.

In this work, the simple co-precipitation method was used (Miyata, 1975). For the synthesis, $MgCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ were used as sources of Mg, Al, Fe(II) and Fe(III), respectively. The molar ratio of Mg/Al was set to 2:1 and the Fe_xO_y to LDH ratio were 25wt% and 50wt%. The pH was constantly maintained in the range of 9-10 by aqueous NaOH. Two reference materials were prepared by the precipitation of LDH on earlier synthesized Fe_xO_y powder and by mechanical mixing of LDH and Fe_xO_y.

Obtained materials were characterized by XRD, FTIR and SEM. Results were compared with the reference materials which confirmed the successful synthesis of magnetic composites based on LDH. The XRD showed characteristic peaks for both hydrotalcite and Fe_xO_y phases. FTIR confirmed the presence of M-O bonds typical for LDH. SEM enabled to observe the characteristic stacked layers and the plate-like morphology of LDH.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Metasomatic evolution of basic and ultrabasic rocks from the Central Sudetes (SW Poland) on the basis of volatile elements contents and stable isotopes – preliminary results

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The ultrabasic-basic rock suites from the Central-Sudetic Ophiolite, as well as, the Góry Sowie and Śnieżnik Massifs, were analysed for F and Cl contents, and O and H isotopic composition. To better understand fluid history, metasomatic derivatives were also studied.

The most primitive serpentinites - isotopic composition similar to the modern sea-floor serpentinites - are common in the Ślęża Ophiolite and Góry Sowie Massif. These are characterized by δ^{18} O 7.0 to 7.1‰, δ D -55 to -46‰ and 15-40 ppm F. Serpentinites, which interacted with Variscan granite-derived fluids, are characterized by slightly depletion in heavy isotopes (δ^{18} O 5.7‰, δ D -64‰) and F-enrichment (99 ppm). Serpentinites, affected by the low-T fluids (e.g. weathering), common in the Ślęża and Szklary Ophiolites, are more depleted in heavy isotopes (δ^{18} O 4.3 to 5.1‰, δ D -104 to -80‰), although its F content (20-25 ppm) is similar to the most primitive group. Exceptional serpentinites and its derivatives are limited to the Śnieżnik Massif, where probably interacted with ore-forming fluids, causing its enrichment in F and ¹⁸O, and slighly depletion in D (δ^{18} O 9.3 to 9.8‰, δD -71 to -54‰, 30-146 ppm F). Serpentinite-associated metasomatites from the Variscan granites margins (tremolitite, nephrite, chlorite schist), are isotopically more heterogeneous $(\delta^{18}O 5.9 \text{ to } 7.8\%, \delta D - 71 \text{ to } -39\%)$ and F-enriched (42-647 ppm). Heterogeneity probably reflects granite composition and P-T conditions. Another serpentinite derivative talc schist is also F-enriched (197-337 ppm), irrespective of occurrence (Góry Sowie or Śnieżnik Massifs). Surprisingly, studied rocks are Cl-depleted (metagabbros <100 ppm, serpentinites and talc schists <50 ppm, nephrites <10 ppm). In contrast, ophiolites and modern sea-floor serpentinites contain ~100-2000 ppm structurally bound Cl (Barnes et al. 2006, 2009).

As can be seen in the above, O and H isotopic composition, combined with F content, is an useful tool for tracking the fluid history of basic-ultrabasic rock suites in the continental environment. Furthermore, extreme Cl-depletion of the studied rocks deserves attention.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Sources of pollution and distribution of Pb, Hg and Cd in Wrocław soils

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Urban soils are not the new phenomenon. Human activities in cities often change physical, biological and chemical properties of soils. In particular, urbanization affects the availability of water, the activity of soil organisms and causes the alteration of soil profile. Also the pollution in the cities is more severe and results in elevated concentrations of metals like Pb, Hg, Cd and others (Pavao-Zuckerman, 2008). Metals as Pb, Hg and Cd are considered to be particularly toxic for humans, because they are non-essential components for human life. Overstepping their concentration in organisms results in dangerous diseases including: respiratory insufficiency, nephrolithiasis, cancer, mercury poisoning.

The study was carried out in Wrocław, the capital city of Lower Silesia, Poland $(51^{\circ}07^{\circ}N 17^{\circ}02^{\circ})$. Because of its function, Wrocław is exposed to anthropogenic influence – coal burning, waste incineration, road traffic, metal smelting and others – which is the source of trace elements harmful for human beings. In order to better understand the complexity of urban soils, we analysed the content of metals in soil profiles in the city of Wrocław and for comparison for the city of Byków, Pb isotopes were analysed to better constrain metal sources and their diversity.

Research shows noticeable differences for the soil profiles in Wrocław (urban soils) and for Byków (non-urban soils). First, profiles from Byków are characterized by much lower metal content. Second, the metal content, for Byków, decreases asymptotically with depth, whereas for Wrocław soils, the metal content is diverse and does not depend on the depth. Each of the four analysed localities have different metal contents and there is no common pattern for all the soils as is typical for e.g. soils contaminated by a point pollution source (Tyszka et al., 2016). Similarly ²⁰⁶Pb/²⁰⁷Pb ratios do not correlate with depth or Pb contents suggesting numerous pollution sources in Wrocław including old petrol pollution and coal burning, but also solid admixtures such as slags and bricks with characteristic metal contents and Pb isotope signals.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Biological configuration of hopanes in Ediacaran sedimentary rocks of the East European Craton

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Hopanes are pentacyclic biomarkers originating from a wide range of prokaryotic organisms. Their precursors are bacteriohopanepolyols (BHPs), compounds present in the lipid cell membranes of diverse bacteria. During diagenesis, BHPs undergo geochemical changes leading to the formation of hopanoid acids and hydrocarbons with hopane skeletons. Sedimentary (geological) hopanes exist as three series of compounds: $17\beta(H),21\beta(H)$ -hopanes ($\beta\beta$ hopanes), whose structure configuration is similar to biological hopanes, and its two diagenetic products, i.e. the more thermodynamically stable $17\alpha(H),21\beta(H)$ -hopanes and the less stable $17\beta(H),21\alpha(H)$ -hopanes (moretanes).

Here we report exceptionally well preserved biomarkers, including $\beta\beta$ hopanes and hopene compounds from the Ediacaran sedimentary rocks (Petersburg region, Belarus and Wolyn). Hopanols and hopanoid acids identified as TMS derivatives were also found in samples from the all investigated regions. The estimated equivalent of vitrinite reflectance for samples of lower thermal maturity is in the range 0.28–0.49% Rr, while for those of higher maturity 0.41–0.57% Rr. Based on recent reports, the possible source of abundant hopanoids present in Ediacaran rocks from the East European Craton are cyanobacterial mats (Bobrovskiy et al. 2018; Kremer et al. 2018). The alternative source of hopanes are planktonic bacteria and their associated dissolved organic matter degradation products (Pehr et al. 2018).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Jotunites - new data from the Suwałki Anorthosite Massif

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Jotunites (hyperstene monzodiorites) are rocks which are related to the magmatic AMCG (anorthosite-mangerite-charnockite-rapakivi granite) suite and occur only (as far as we know) within the Proterozoic massif-type anorthosites. Experiments which were held in the 90. of the XX century proved that jotunitic magma can be treated as parental for anorthosite rocks (Auwera, Longhi 1994).

Jotunites are characterized by a very fine-grained structure made of plagioclase (andesine or labradore), pyroxene (mainly Opx) and secondary biotite. Porphyritic crystals of plagioclase are also present. Jotunitic rocks can be recognize also by high amount of Fe (up to 20,71 wt % Fe₂O_{3t}), Ti (up to 4,18 wt % TiO₂) and P (up to 1,26 wt % P₂O₅) content, which is caused by occurrence of Fe-Ti oxides and apatite (Grabarczyk 2018). The REE distribution in jotunites is low to moderately differenciated (La_N/Yb_N = 6-14). On the spider diagrams jotunites do not show significant Eu anomaly.

Jotunites as rocks related to AMCG suite ought to be present commonly occur within the anorthosite massifs in Mazury Complex, NE Poland. Until now they were recognized only in the Sejny Intrusion and Udryń IG-11 borehole in central part of the Suwałki Massif (Wisznieska et al. 2002).

The newest observation and geochemical research revealed their presence in other boreholes of the Suwałki Massif (SAM): Bilwinowo in south part of SAM (Grabarczyk 2018) Łopuchowo (west past of SAM) and Jezioro Szklinokiemskie (east past of SAM).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Primary vs. secondary origin of apatite from two greenstone belts – Isua and Barberton – insights from the Polytopic Vector Analysis

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The possibility of primary signature preservation in Archean rocks is exceptionally crucial in terms of volatile isotopic signature of the Early Earth. Apatite may provide new data on hydrogen and chlorine isotopic composition of the oldest geological record, however, discrimination between primary and secondary origin is essential. We propose the application of Polytopic Vector Analysis (PVA) to chemical composition of apatites from various Archean rocks from two greenstone belts - Isua (Greenland) and Barberton (South Africa) in order to distinguish different origins of apatites and the extent of alteration processes. The analysis of apatites from five BIF samples from the Isua Supracrustal Belt yielded three different apatite end-members: one unaltered apatite and two significantly altered apatites. The unaltered apatite is REE- and volatile-rich, indicating no involvement of metasomatic fluids. The altered apatite end-members are both REE-depleted, pointing to remobilization of REEs by metasomatism. However, they differ in chemical composition, thus, may represent separate metasomatic events. One event resulted mostly in REE removal, whereas the second affected mainly volatiles. The distribution of the studied samples between unaltered and altered end-members demonstrates in detail the extent to which the samples were metasomatized. Previous studies considered three of the five BIF samples as mostly unaltered (Wudarska et al. 2018), whereas PVA results confirm such hypothesis only for one sample. PVA results of eleven sedimentary and volcanic samples from Barberton Greenstone Belt also provided three apatite end-members: one unaltered REE-rich, F-OH apatite and two altered fluoroapatites. Apatites from three of the studied samples are identical with the unaltered end-member, confirming their primary origin. The remaining sedimentary samples contain variable amounts of the altered end-members pointing to advanced metasomatic alteration. This confirms the assumption of the secondary origin of these apatites based on low REE content, CL spectra, TEM structures and the presence of mineral inclusions (Birski et al. 2018).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



How to Quantify Asbestos combining Point Counting and combined X-ray Diffraction, Infrared Spectroscopy and Thermal Analysis

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Asbestos minerals are known worldwide as a component in construction material due to their exceptional crystal- and chemical properties, even more known for the widely discussed cancerogenic effect on humans who were exposed to asbestos-bearing materials. Nowadays, still about 40 years after the peak in the construction material industry, the regulations guiding people how to analyze and physically deal with asbestos-bearing materials is still mainly directed and restricted to construction materials and associated work. These regulations are therefore not applicable in environments, where asbestos occurs naturally in the bedrock. These include for example tunneling works within infrastructure or mining projects. To quantify the amount of natural asbestos present in such environments is challenging, primarily due to the vast volume of rock, which must be analyzed.

We have applied Point Counting (PC) under light microscope on extensive amount of asbestos-bearing samples. The advantages of PC are the relatively fast analysis time and the sample coverage, i.e. large amount of samples can be analyzed within a favorable time- and economic frame. However, PC as single method encounters problems to secure acceptable quality results due to its detection limit of about 5 μ m and also the petrographic knowledge and subjective interpretation of the analyst.

This study aims to compliment PC with X-ray Diffraction, Infrared Spectroscopy and Thermal Analysis to validate the results and reduce the margin of error from PC, and thereby improve the quality of the results. The choice of diffraction, spectroscopic, and thermal methods are based on the detection limit that reaches down to about 2 μ m and that these are the suitable analytical tools that allow for deciphering the crystal structure differences between a mineral and its fibrous asbestos form from bulk samples.

This joined methodological approach, if successful, could be an important step in the development of a high quality and effective method to analyze and quantify vast amounts of asbestos bearing rocks from vulnerable environments.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



The prograde segment of the P-T metamorphic path for the Kamieniec Ząbkowicki eclogites: first results of phase equilibria modelling

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Eclogites of the Kamieniec Metamorphic Belt (KMB) outcrop as small, isolated lenses embedded in the volcano-sedimentary succession dominated by mica schists with minor metavolcanics, paragneisses, quartz-graphite schists and marbles. The eclogites are composed predominantly of clinopyroxene of omphacitic composition partly replaced by fine grained symplectites (plagioclase and diopside). The clinopyroxene matrix comprises aggregates of euhedral garnet porphyroblast, epidote prisms, white mica and subordinate rutile and quartz. Accessory ilmenite, sphene, biotite, zircon and apatite are present. Amphibole commonly occurs as continuous layers around garnet crystals and also grows at the expense of symplectitic diopside. Due to various degree of amphibolitization, the least retrogressed specimen was chosen for the detailed study.

Garnet crystals have developed strong compositional zoning indicative of prograde growth, i.e. spesartine-rich cores surrounded by rims considerably depleted in Mn and enriched in pyrope and almandine. In contrast, chemical composition of omphacite and white mica is more homogeneous, with X_{jd} in omphacite up to 0.49 and Si⁴⁺ in mica up to 3.48 a.p.f.u. The prograde section of metamorphic path of the eclogites has been constrained by phase equilibrium modelling in the system MnNCFMASTHO with Perple_X software. The calculations for the whole rock composition obtained by XRF analysis aimed at reconstruction of conditions of the earliest metamorphic stage preserved in garnet cores only. The position of the calculated isopleths for garnet shows that rock was subjected to pressures of 1.5–1.6 GPa at temperatures of 340-350°C. Assuming that omphacite, phengite and garnet rims belonged to metamorphic baric peak assemblage and taking into account the fractionation of bulk rock composition during prograde growth of garnet, the second pseudosection was calculated. The position and cross-cutting of compositional isopleths of minerals indicate pressures of 2.4-2.8 GPa at temperatures of 550-570°C.

The reconstructed section of the P–T path for the KMB eclogite is corollary to the substantially cold conditions of subduction as the path follows a 5-7 °C/km geotherm. This geothermal gradient is consistent with the similar value recently obtained for the KMB mica schists with further conclusion of plausible relationships of the studied area with the Saxothuringian domain.

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Reconstructing smelting temperature in the furnace on the base of pyrometallurgical Cu slags from Kondratów and Leszczyna

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Within features important for the metal smelting process, the temperature is one of the highest importance. It is strictly associated with the quality of the process and the type of the furnace. Temperature also influences metal separation from the ore as well as controls the type of crystalline phases appearing in a slag. This in turn is associated with leaching efficiency of metals from slag (Potysz et al. 2018). The aim of this study was to find more suitable method for reconstruction of the smelting temperature than these currently used. We also verify whether glass composition in crystalline slags is caused by disequilibrium crystallization or if with changing conditions, various equilibrium compositions are reached.

The studied material is a waste product of historical metal smelting in the vicinity of Leszczyna in the Old Copper Basin. The area is dominated by the lime-rich sedimentary rocks, mostly shales and marls created in Permian (for more details check the field trip chapter in this book "Old Copper Basin – Polish Copper before the age of KGHM").

The studied slags (29 slag samples) consist mainly of SiO2 (42-49 wt %), CaO (15-27 wt %), Al2O3 (9-19 wt %) and Fe2O3 (3-6 wt % in Leszczyna and 3-21 wt % in Kondratów) with a noticeable amount of K2O (approx. 5 wt %). In particular, low amounts of silica and high of potassium are specific for the analyzed samples. Crystalline phases include leucite, Ca-rich pyroxenes and anorthite.

In this study we reviewed possible approaches to temperature estimates of slag smelting including geothermometers and phase diagrams. Geothermometers are difficult to use because (1) slags lack appropriate assemblages and (2) reliable estimates of phase composition are restricted by their skeletal habits. Phase diagrams were so far not providing believable results, however, it was because they were not chosen appropriately to slag composition. Silica-poor and potassium-rich rock-intended diagram allowed to specify the smelting temperature for the studied slag. Based on CIPW calculations, two groups were distinguished - pyroxene-rich samples with estimated temperature around 1300°C and main group plotting close to the eutectic point with estimated temperature 1249±5°C.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Soils naturally-enriched in metallic elements: should we consider them polluted?

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Elevated concentrations of metallic elements in soils are mainly of anthropogenic origin and related to the extraction and processing of mineral resources, agriculture and transport. As a result of these activities, metallic elements are introduced to the environment, and may end up in food chain posing a threat to the health and life of living organisms. However, another source of metallic elements in the environment, often forgotten in the total assessment of environmental risk, is natural and associated with the occurrence of metal ore deposits or rocks containing elevated concentrations of certain elements. An example of natural materials being an important source of metals are ultramafic rocks and soils that contain up to 2000 mg kg⁻¹ Ni and Cr in the topsoil horizons. It should be noted that the concentrations of metals in these soils often exceed the recommended maximum permissible levels determined by relevant legal acts.

The purpose of this abstract is to draw attention to the mobility of metallic elements naturally present in ultramafic rocks and associated soils. Previous studies of Ni mobility in ultramafic soils and polluted Technosols have shown that Ni of natural origin is more mobile than Ni of anthropogenic origin (Kierczak et al. 2008). It is because naturally occurring Ni is the component of olivine and serpentine group minerals and anthropogenic Ni is predominantly bounded with metallic phases more resistant to weathering. This clearly indicates that it is the mineralogical and geochemical form of a metallic element that affects its potential mobility. Furthermore, it is shown that natural metallic elements can accumulate in plants. Therefore, altogether, areas naturally enriched with metals should also be treated as contaminated. Of course, because of the geogenic origin of pollution, these areas cannot be rehabilitated, however, the cultivation of plants for food purposes should be discontinued. It is also important to point out that the peculiar geochemistry of ultramafic areas causes development of a specific type of vegetation, which is interesting for ecologists and should be protected.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Mantle xenoliths from Alleyras (Devès volcanic field, French Massif Central)

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The Cenozoic Devès volcanic field is located in the area of southern mantle domain of French Massif Central (Lenoir et al., 2000). Analcime basanite lavas from Alleyras (20 km south-east of Le Puy-en-Velay) contain abundant peridotite xenoliths. The xenoliths (up to 10 cm in size) have the composition of spinel lherzolites with porphyroclastic textures, except sample 3763, which is a protogranular spinel harzburgite.

Forsterite content in lherzolitic olivine is 89.5 - 90.5 %, while in harzburgitic one it is 90.6 - 91.0%. Orthopyroxene in lherzolites (Mg# 0.90 - 0.91) has 0.07 - 0.19 atoms of Al pfu (per formula unit), whereas that in harzburgite is Al-poor (0.08-0.10 atoms pfu). Clinopyroxene (Mg# 0.90-0.92) contains 0.24-0.30 atoms of Al pfu in lherzolites and 0.11-0.14 a pfu of Al in harzburgite. Lherzolitic spinel is aluminous (Cr# 0.10-0.12), while the harzburgitic one is more chromian (Cr# 0.46). The lherzolitic clinopyroxene REE contents are slightly (1-10x) enriched relative to primitive mantle. The REE patterns are LREE-depleted. Clinopyroxene in harzburgite is LREE enriched and has well-defined negative HFSE anomalies. The temperatures of cpx-opx equilibration (Brey and Köhler 1990) typically range from 750 to 880 °C in lherzolitic suite and 880 - 920 °C in harzburgite.

Lherzolites exhibit 1-3% of melt extraction, whereas harzburgite 4-6%. Harzburgite exhibits geochemical characteristics, which are rather similar to xenoliths from northern, more depleted mantle domain of Massif Central. The xenoliths from Alleyras show relationships between lherzolites and harzburgite which resemble those occurring e.g. in Lherz peridotitic massif (e.g. Le Roux et al., 2007), where the strongly depleted harzburgites are replaced by the fertile lherzolites.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Geochemical Mapping in Sweden – natural background element concentrations in till and their applications

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Introduction

Geochemical mapping is an established method for studying the spatial distribution of chemical elements in different sample media, e.g., rock, soil, water, sediment and plants, and to document changes in their chemical composition occurring in different compartments of the ecosystem. The geochemical data can be used in various applications: mineral exploration, environmental, medical and forensic sciences, agriculture, forestry, land use planning, etc. The results of geochemical mapping allow understanding of natural processes operating at the continental to regional scale, such as weathering, climate, tectonic evolution, but also to understand the consequences of contamination on the surface environment, which is no longer pristine and undergoes changes caused by human activities. Modern geochemical mapping relies on building databases and providing digital data services to the society.

At the Geological Survey of Sweden, a regional geochemical mapping has been carried out for more than 40 years with the main sample type being glacial till. Overall, chemical analyses of till samples are available from more than 40 000 sites. The currently used analytical methods are nitric acid digestion and aqua regia digestion subsequently measured by ICP MS. More than 60 elements can be obtained with the in-house-developed method at the SGU laboratory. The method was originally developed to serve mineral exploration but in high latitudes it turned out to be an effective method for studying natural background element concentrations. When the last ice sheet melted about 10 000 years ago, large parts of the bedrock in Fennoscandia were covered by several generations of glacial deposits with till as most important. Till reflects best the underlying bedrock with its billion years old history and records soil-formation processes such as weathering style during variable climate conditions. Apart from regional geochemical mapping with sample density 7km², in 2014, the countrywide Geochemical Atlas of Sweden was published with sample density 1 sample per 150 km². The Geochemical Atlas of Sweden provides a harmonized national database with modern baseline geochemical data and it is freely available to the public.

The interpretation of SGUs geochemical maps and statistics reveal several groups of factors influencing the observed spatial trends in the geochemical patterns with the most important being bedrock geology, the presence of ore deposits, the soil type and its properties, and climate controlled by the latitude and altitude. Apart from its main application to identification of mineralisations and bedrock types, the geochemistry of till in northern European countries is an excellent proxy for groundwater quality assessments and risk evaluations.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



The occurrences of Se-bearing minerals in Holy Cross Mountains

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The Se-bearing minerals haven't been noticed in the Holy Cross Mountains (HCM) so far. The first occurrences of these minerals in HCM have been found in the hydrothermal veins in Devonian dolomite in the Laskowa Quarry near Miedziana Góra (Kielce Region) as well as in phyllites in Podmachocice near Górno (Łysogóry Region; Salwa, 2006).

The chemical analyses were performed using Cameca SX100 electron microprobe at Micro-Area Laboratory of the Polish Geological Institute – NRI in Warszawa.

Se-bearing minerals form small anhedral crystals with size upto 20µm within the hydrothermal parageneses in the Laskowa Quarry containing mostly pyrite, chalcopyrite, covellite, galena, fahlore, iron oxides as well as calcite and dolomite. Usually they occur in small cracks in calcite, sometimes Se-minerals replace copper sulphides. Two main types of Se-bearing minerals were found in the Laskowa Quarry: I) Cu-Se phase with S and minor amounts of Pb, Fe, and Ca, and II) Cu-Pb-Se phase with lower amounts of S and Fe and higher of Ca then first one. According the chemical analysis these minerals seem to be selenates.

Se-bearing sulphides from Podmąchocice form very small (up to 5 um) and anhedral crystals in the inner parts of the quartz-chlorite-apatite veins. Selenium occurs mainly in galena in association with Zn and Cu sulphides.

The occurrences of Se-bearing minerals in Poland were noticed by several authors from various geological units (e.g. Szełęg et al. 2013, Kucha 1982). According to these authors Se-bearing phases are commonly concentrated in the oxidation zone. The Se-bearing minerals from the Laskowa Quarry also seem to be formed in oxidation zone from primary copper and lead sulphides, while in Podmąchocice the presence of selenium can be still observe in primary suphides.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Diversification of pottery production in Lusatian culture in the light of pottery surface analysis

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Archaeometric analyses of prehistoric pottery, relying on laboratory techniques routinely used in the Earth sciences (namely: mineralogy, petrography, and geochemistry), usually focus on the identification of components of ceramic pastes used in the past. However, extensive petrographic studies, which are costly and time-consuming, may prove ineffective when dealing with large monotonous assemblages. Less attention has been paid to the identification of various mineral phases intentionally applied onto ceramic surfaces (e.g. graphite, red ochre, thermally treated bone apatite). It should be pointed out that some of the raw materials used at this stage of the pottery production process are not readily available and are consequently supposed to have been traded over large distances. The sophisticated surface treatments served aesthetic purposes but also expressed symbolical, religious or magical meanings, which are now elusive to archaeologists. These efforts may have also significantly influenced some utilitarian parameters, such as permeability. Therefore, the examination of mineral coatings covering ceramic surfaces may allow us for an interesting insight into prehistoric technologies.

The ceramic ware of the Lusatian Culture (dated to the later Bronze Age and early Iron Age 1300 BC - 400 BC) represent a particularly attractive research subject for this branch of archaeometric pottery studies. There is a huge amount of technologically and stylistically diverse ceramics yielded by multi-phase archaeological sites. Archaeological and archeometric studies in recent years indicate a change in the perception of pottery production at this stage of human history.

In our recent investigation we focused on ceramic materials from the Wicina cemetery. This is a unique site, as it belongs to a settlement micro-region which central location is a famous fortified settlement (mid. 8-mid. 6th c. BC), located ca. 800 m from the cemetery (13-6th c. BC). Several research methods have been applied including: thin section studies, SEM-EDS, EPMA and XRD. The results have been compared with data derived from our previous studies of pottery from other Lusatian culture sites in western Poland.

Preliminary results indicate many various ways of surface treatment on a wide range of ceramic assemblages in different parts of Poland. In particular, the following surface treatments have been examined: blackening, application of white inlay, covering with red pigment or engobe.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Alkali tourmalines from the Strzegom – Grabina II quarry (Strzegom-Sobótka granitic massif, Poland)

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The Strzegom-Sobótka (SS) granitic massif is famous for several pegmatite occurrences, showing exceptionally rich amount of chemically interesting and collectible minerals. Accessory minerals are represented in here, i.a. by tourmaline group, usually dominated by schörl specimens, being often associated with quartz and feldspars. Some mineralogical and geochemical data of SS tourmalines are known from few literature sources (Janeczek 1985; Pieczka, Kraczka 1988; Körber, Szuszkiewicz 2005).

The tourmaline samples were collected in 2004 in the Grabina Śląska 15/27 quarry (Grabinex), Strzegom, Poland. Small crystals were found in the pegmatite pocket composed of epitaxial smoky quartz, albite (cleavelandite), microcline, minor stilbite and muscovite, all partially covered with chlorite. Analyzed crystals were recognized as a solid inclusions and overgrowths on quartz and albite. Tourmalines were thin (4-150 nm), showing length up to 5-6 mm. Specimens were mostly opaque, black-brownish, but also green to light-green and pink-blueish.

Loose crystals were investigated using SEM Hitachi SU 8020 with EDX Thermo Scientific

Fisher NORAN 7 at the Faculty of Chemical Fig. 1. Diagram of the XY sites occupancy Technology and Engineering, ZUT, Szczecin, Poland.



of tourmalines from the Strzegom-Grabina II quarry.

The analyzed tourmalines were mostly alkali Fe²⁺ rich schörls, with minor foitite and elbaite. The X sites were dominated by Na^{1+} with insignificant R^{2+} and vacancy. The Y octahedra were occupied by Fe^{2+} and Al^{3+} , with minor Ti^{4+} and Mn^{2+} , being completely depleted with Mg^{2+} ions (Fig. 1).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Oxide and sulphide mineralization of the piribolite from Bystrzyca Górna and some remarks on the P-T forming conditions (Góry Sowie block, Sudetes, Poland)

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The area of Bystrzyca Górna is located within the Góry Sowie block (GS), Sudetes, SW Poland. Several gneisses and amphibolite with small ultramafic bodies has been discovered here and widely described since 18th century. Regional metamorphic complexes of GS developed during several tectonic movements and few-stage crust exhumation are valuable evidence of P-T metamorphism conditions (Żelaźniewicz 1985; Budzyń et al. 2004).

The piribolite samples, collected in 2007, were composed mainly of pyroxene, amphibole, garnet, plagioclase and quartz, with accessory ilmenite, chalcopyrite and pyrite. The samples were showing granoblastic texture, with large garnet phenocrysts up to 2.5 cm diameter. Flat and polished rock samples were investigated using the SEM Hitachi SU 8020 with EDX Thermo Scientific Fisher NORAN 7, at the Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology, Szczecin, Poland.

The Andersen and Lindsey (1985) geothermobarometer was used to calculate the equilibrium temperature and (fO_2) .

In the oxide group minerals domination of ilmenite was found, showing in the planar microscopic analysis contents up to 10 %/cm². Several xenomorphic grains of ilmenite, in some cases with kelyfite texture, were associated mostly with quartz. The small rounded grains of pyrite and chalcopyrite (with chalcopyrite often covered by pyrite) were showing significant Ni and Cu admixtures, up to 2-3 %.

The estimated ilmenite P-T crystallization conditions were $630-648^{\circ}$ C; $log10 f(O_2)$ in range of -16 to -17. Ilmenite was showing several eutectic intergrowths with quartz, suggesting crystallization during decompression and silicification. Pyrite and chalcopyrite mineralization is probably result of later events during GS block exhumation.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Secondary minerals of polymetallic deoposit in Kletno in the light of new geochemical data

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Polymetallic deposit in Kletno is located in Lądek-Śnieznik Metamorphic Unit. Local weathering processes have led to formation of numerous secondary minerals. Here we present new results on the local supergene mineralogy obtained using an electron microprobe. It allowed to depict substitutions occurring in minerals and to ascribe them to appropriate isomorphic series.

The minerals are mainly arsenates: clinomimetite-like species, philipsbornite, arseniosiderite, erythrite, metazeunerite and newly identified arsentsumebite and arsenogorceixite. They coexist with secondary Zn minerals (smithsonite, aurichalcite, hemimorphite) and U (uranophane). The first mineral-listed may represent a new mineral of the apatite supergroup - a Cu analogue of vanackerite. Substitution of elements like Co and Ni in some minerals in noteworthy.

Formation of the minerals studied may relate to heavy metal release. The results of research on the supergene zone of the Kletno deposit may be utilized to plan actions preventing the occurrence of possible contamination in the studied area.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Inclusions on duty in high pressure metamorphic rocks

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In this presentation, we are going to review the role of solid and fluid inclusions for deciphering pressure-temperature-time-deformation (P-T-t-D) paths of deeply subducted rocks. Indeed, inclusions entrapped in metamorphic porphyroblasts offer a valuable insight into an evolution of high pressure (HP) lithologies, in which they are found. Thanks to broad stability fields of host porphyroblasts (such as e.g. garnet) and their capability to entrap other solid and fluid phases, nearly a complete history of HP rocks, including prograde, peak and retrograde stages, can be reconciled.

Qualitatively, a thermal regime during subduction can be deciphered based on recognition of such temperature-sensitive mineral indicators as carpholite, lawsonite and glaucophane as well as pseudomorphs after the aforementioned phases. Self-evident ultrahigh pressure indicators like coesite and diamond give a direct insight into peak pressure conditions, whereas late pseudomorphs after the latter as well as other high-pressure phases such as omphacitic clinopyroxene and phengitic mica inform about retrogressive changes.

Recent development in trace elements and elastic geothermobarometric techniques offers direct quantitative tools allowing us to draw detailed pressure-temperature (P-T) paths. A number of recent studies utilizing such trace elements thermometers as Zirconium in Rutile, Titanium in Zircon and Titanium in Quartz coupled with Quartz in Garnet elastic barometer emphasizes the applicability of solid inclusions in quantitative estimates on (especially) prograde parts of P-T paths. The results obtained using these thermobarometers linked to internal zoning of porphyroblasts and inclusion-host based conventional thermobarometry give a comprehensive set of information on an evolutionary path of the studied rock. Also, if experimentally homogenized, fluids and melts can give us well-constrained P-T conditions of their entrapment in porphyroblasts. Especially, in the case of HP-(ultra)high temperature rocks, melt inclusions provide much more precise P-T constrains than those obtained using classical, thermodynamics-based calculations.

Additionally, solid inclusions such as zircon, monazite, rutile and apatite can be used to assess the timing and rates of subduction-exhumation processes. Context-sensitive dating of these entrapped phases provides another extremely valuable insight into porphyroblasts' growth. If coupled with P-T data and careful kinematic analysis of inclusion trails, it can serve as a complete "micropetrological" set of necessary information for reconciling a complete P-T-t-D evolution of investigated lithologies.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Comparison of two techniques for strain rate calculation in naturally deformed polymineralic rocks

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Experimental studies prove that geological strain rates are in the order of 10^{-9} to 10^{-15} s⁻¹. However, determination of strain rate in naturally deformed rocks is a challenge and various techniques have been developed to estimate its value. The main objective of this study is to evaluate the credibility of results provided by two techniques of strain-rate estimation in naturally deformed rocks i.e. using experimentally derived flow laws and fractal analysis. For our tests we chose samples of paragneiss and mica schist from the Doboszowice massif (DM) and Kamieniec metamorphic belt (KMB) cropping out in the eastern part of the Fore-Sudetic Block. Available data suggest that investigated samples from DM were deformed and metamorphosed in a relatively HT conditions reaching up to 670 °C and 8 kbar, whereas mica schists from the KMB were deformed at PT conditions ranging from 550 - 560 °⁶C and 7 - 7.5 kbar.

Fabrics of the examined samples from the DM were shaped by grain boundary migration recrystallization mechanism (GBM) and quartz microstructure of rocks from the KMB are, depending on the sample, typical for transition between subgrain rotation recrystallization (SR) and GBM as well as for SR mechanisms. Median grain diameter of quartz aggregate in the DM samples ranges from 156 - 365 microns and in the KMB mica schists falls in the range of 52 to 77 microns. Calculated flow stress varies from 6.2 to 46.1 MPa. Strain rates of the order of approximately 10^{-13} and 10^{-9} s⁻¹ were obtained using experimentally derived flow laws, which at PT conditions recorded by the analyzed samples from the DM are typical for GBM mechanism and for KMB samples are characteristic for transition between SR and GBM as well as SR mechanisms. On the other hand, utilizing method of fractal analysis of quartz grains calculated strain rates for the whole analyzed suite of samples are considerably higher and range from 10^{-7} to 10^{-6} s⁻¹. Consequently, at PT conditions of deformation resolved for the analyzed rocks, obtained values of strain rates are rather characteristic for transition between SR and bulging mechanisms, which is not observed in the analyzed suite of samples.

Summing up, the method of strain rate estimation based on experimentally derived flaw laws gives reliable results, while strain rate approximation utilizing fractal analysis of quartz grains fails. Importantly, chosen calibrations of experimentally derived flaw laws take into account the presence of water in the rock, which may be the controlling factor for the strength of the crust.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Occurrence and characteristics of saccharides and saccharols in Mesozoic and Cenozoic lignites and their application as fungal biomarkers

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Trehalose, mannitol and arabitol are treated as a main saccharides of extant fungal metabolism (Emygdio et al. 2018), but their occurrence and distribution in sedimentary rocks have rarely been considered (Marynowski et al. 2018). Here, we identify these sugars in Miocene lignites and Late Cretaceous mudstones and brown coals. The co-occurrence of trehalose, mannitol and arabitol in the investigated rocks suggests their fungal origin, because these three saccharides are major compounds present in most modern fungi, including the very common mycorrhizal and wood-rotting groups. Therefore, we conclude that these sugars should be treated as new fungal biomarkers (biomolecules) present in sedimentary organic matter. Trehalose and mannitol are major compounds in total extracts of the samples and a sum of their concentration reaches 4.6 μ g/g of sample. The arabitol concentrations do not exceed 0.5 μ g/g, but in contrast to trehalose, the concentration correlates well with mannitol, suggesting that they have the same role in fungi. Based on the trehalose vs. mannitol and arabitol distributions in Cretaceous samples and their comparison with data for modern fungi, we preliminarily conclude that the coal seams from the Rakowice Małe section were formed during warmer climatic periods than the overlying sediments. Other saccharols and sugar acids like D-pinitol, quinic acid and shikimic acid, were found for the first time in sedimentary rocks, and their source is inferred to be from higher plants, most likely conifers. The preservation of mono- and disaccharides of fungal origins in pre-Palaeogene strata implies that compounds previously thought as unstable can survive without structural changes in immature organic matter.

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Petrology of mafic and ultramafic xenoliths from Fife, Scotland.

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Permo-Carboniferous mafic volcanic rocks occurring in Scotland contain mafic and ultramafic xenoliths which provide information on the composition of the lower crust and lithospheric mantle at the time of volcanism. Here we present data on xenoliths in a late Carboniferous basanite intrusion at Ruddon's Point and Coalyard Hills, Fife, Scotland.

The studied xenolith suite comprises of anhydrous spinel lherzolites, wehrlite, olivine clinopyroxenite, clinopyroxenite and websterite. Peridotites have porphyroclastic texture and consist of Mg-rich olivine (Fo₈₇₋₉₀), Al-rich pyroxenes (0.25-0.31 apfu in Cpx and 0.15-0.19 apfu in Opx) and Cr-poor spinel (Cr#=0.15-0.20, Mg#=0.70). Wehrlite has cumulative texture with cumulus olivine (Fo₈₃₋₈₄) and intercumulus clinopyroxene (Mg#=0.83-0.86, Al=0.23-0.29 apfu). Clinopyroxenites and websterites have adcumulative textures. Olivine in clinopyroxenites and Ol-clinopyroxenites is Fo₇₈₋₈₂, clinopyroxenes have Mg# from 0.75 to 0.85 with Al ranging from 0.17 to 0.30 apfu. Clinopyroxene-orthopyroxene equilibrium in most of peridotites was achieved in temperatures from 960 to 1010°C, in websterite it was 970-990°C (Brey and Köhler geothermometer, 1991).

Clinopyroxene forming peridotites is characterized by flat HREE and is slightly depleted to slightly enriched in LREE ((La/Lu)_N=0.4-2.5). The only significant anomalies in clinopyroxene's multi-trace element patterns occur at Th-U (positive) and Nb-Ta (negative). Clinopyroxene in clinopyroxenites and websterite has concave downward REE pattern ((La/Lu)_N=2.3-8.7) and slight negative Ti anomaly.

The lherzolite xenoliths represent upper mantle rocks. Lherzolite suffered from 1 to 7% of melt extraction. Peridotites have been metasomatised by subduction-related melts enriching pyroxenes in Th and U. Clinopyroxene in wehrlite is texturally later than olivine, but strictly follows the general trace element characteristic of peridotites, thus may represent precipitate from the metasomatic melt. Subduction-related metasomatism seems to be widespread in Scottish lithosphere south from Moine Thrust Zone, but with numerous local variations (Hughes et al., 2015 and references therein). The pyroxenites are considered to have originated by crystal settling from an alkaline silicate melt. Their formation is possibly related with Carboniferous, rifting-controlled volcanism.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Ultramafic xenoliths from Scania (SW Sweden) – preliminary results.

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In Mesozoic S Sweden was affected by rift-related alkali basalt volcanic activity. Some of the basaltoids carried mantle and crustal xenoliths (Rehfeldt et al. 2007). In this study we discuss the composition of ultramafic xenoliths in order to reconstruct the evolution of lithospheric mantle beneath the East European Craton (EEC) underlying the area.

Peridotites (mostly anhydrous harzburgites and lherzolites) are porphyroclastic or protogranular; one harzburgite has unequigranular texture. The xenoliths form two groups varying by bulk-rock chemical composition and textural features: the low-Mg# group (Mg#=0.88-0.89) comprising porphyroclastic lherzolites and the high-Mg# (Mg#=0.90) group comprising protogranular xenoliths. All the peridotites are LREE enriched. Forsterite content in olivine and Mg# in pyroxenes are lower in low-Mg# group (90-91 and 0.90-0.92, respectively) and higher in high-Mg# group (91-92 and 0.91-0.93, respectively).

Clinopyroxene in the high-Mg# peridotites has convex downward REE patterns with bump at Nd, while that in low-Mg# peridotites is characterized by convex upward REE patterns and slight positive Eu anomaly. Scarce clinopyroxene in harzburgite with unequigranular texture is LREE-depleted.

The equilibration temperature of pyroxenes are ~1200°C in the high Mg# peridotites, while in the low-Mg# ones it is 900-1000°C (Brey, Köhler 1991).

The low MgO content and clinopyroxene enrichment in LREE of the low-Mg# samples, suggest that their composition was not shaped by partial melting but by cryptic metasomatism. The high-Mg# samples record $\sim 10\%$ of depletion, but were also metasomatically enriched. The preliminary results suggest that lithospheric mantle beneath S Sweden may be formed of at least two main lithologies varying in melting and metasomatic history. None of the lithologies shows features typical for cratonic mantle (e.g. Fo content in olivine <92.)

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Research on the production traces and microstructure of the bronze objects. Symbolic meaning of manufacturing or results of production technology?

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Archaeological experiments focusing on the reconstruction of metallurgical activities related to the younger parts of the Bronze Age allow us to discuss the issues of casting production in prehistory.

The presented results are related to the experiment, which allowed to answer questions, connected with the production methods and strength of bi-valve clay casting mould. It was investigated the influence of high temperature on the surface of casting moulds as well as the possibility of comparing the mould negative with the cast. One of the main goal of the activities was to observe production traces on the surface of reconstructed objects. These traces could be compare with original prehistoric objects, eg. from cemeteries. Thanks this research it would be possible to analysis, whether objects in graves are produced in "special" way and with symbolic meaning of manufacturing, or these traces are results of production technology.

The second goal of the activities was to perform archaeometallurgical analyses using scanning electron microscopy (SEM). During the experiment two types of sickles were cast. The reconstructed sickles served to make a series of samples that were taken from the part of blade. Samples were collected from as-cast sickles, sickles with forged surface and forged and then annealed.

Obtained observations create a database that contains images of the microstructure of objects at various stages of production. The results can be compared with the analyses made for samples taken from the original items.

The combination of "classical" experimental archaeology with specialized archaeometallurgical methods make it possible to obtain a whole spectrum of new information.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Brunovistulian lithospheric mantle xenoliths from a newly recognized nephelinite dyke at the Folwark guarry, Opolian Silesia (SW Poland)

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Mantle xenoliths contained in Cenozoic basaltoids from Lower Silesia and Upper Lusatia were previously identified and examined in detail. The lithospheric mantle beneath these regions was assigned to the Saxothuringian domain. A newly recognized mantle xenolith-rich dyke from Opolian Silesia offers a rare opportunity to see inside the Brunovistulian lithospheric mantle. We report here on a volcanic body from the easternmost part of the Cenozoic Central European Volcanic Province, which possesses very numerous mantle xenoliths.

The large new dyke has been identified at the Folwark quarry, located ~6 km south of the city of Opole, where Cretaceous marls are exploited. The dyke, which is a subvolcanic body, is over 200 m long (with terminations that do not crop out, but run into the quarry walls) and from 10 to 35 cm wide. The rock is classified as nephelinite, although the presence of numerous secondary calcite-filled round pores (0.3–5 mm in diameter) could affect the whole-rock analysis. The nephelinite consists of clinopyroxene (Ca-rich diopside; mg# 70–78), olivine (Fo ~86), nepheline, and spinel crystals. The preliminary results of the K-Ar dating point to the dyke having Oligocene origin, similar to other volcanic bodies in Opolian Silesia.

Mantle xenoliths (<1-5 cm in diameter) are very frequent. Hitherto, 19 xenoliths have been examined in detail. They mainly represent mantle ultramafic rocks, including harzburgite (47%), dunite (37%), and lherzolite (11%); a mafic rock, clinopyroxenite (5%), was also recognized. Almost all of the xenoliths have a protogranular microstructure, but in the case of five xenoliths, the olivine crystals display the preferred orientation.

Thirteen xenoliths were studied by EPMA and can be subdivided into two types, on the basis of the chemical compositions of their minerals. The first group is more numerous (77%) and contains harzburgites and dunites with Ol (Fo 90–92, Ca mostly below detection limit up to ca. 400 ppm, Ni ca. 3100 ppm), Opx (enstatite, mg# 91–92), Cpx (diopside, mg# 92–94, rarely augite mg# 90–92), and spinel (cr# 35–65). Rare phlogopite and feldspar crystals also occur in these xenoliths. The second group (23%) contains harzburgite, dunite, and lherzolite with Ol (Fo 91, Ca ca. 1300 ppm, Ni ca. 3200 ppm), Opx (enstatite enriched in Ca, mg# 91), Cpx (augite, mg# 90–91), and spinel (cr# 50). Secondary alternations of the minerals are identified, with olivine crystals generally being replaced by calcite, while Opx and Cpx remained unchanged. The investigation continues and is partly financed by NCN grant 2014/13/B/ST10/02102 and UAM funds.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Fe and Cu isotope signatures in sulfide blebs from various upper mantle xenoliths from the Nógrád-Gömör Volcanic Field (Northern Pannonian Basin)

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The Nógrád-Gömör Volcanic Field (NGVF) is located in the northern part of the Pannonian Basin, and is one of the five xenolith-bearing alkali basalt occurrences in the region. In NGVF, a lherzolite and a wehrlite series were distinguished based on petrographic and geochemical investigations. The lherzolites represent precursors for the metasomatic wehrlites.

In this study, we focus on sulfide blebs, which are more abundant in wehrlites compared to the lherzolite xenoliths. Sulfides appear as inclusions within silicates or as interstitial grains with the size of 5-80 μ m and 5-200 μ m, respectively. The sulfide blebs consist mostly of pentlandite, pyrrhotite and chalcopyrite. Pyrrhotite and chalcopyrite are frequent in wehrlites and rare in lherzolites.

We studied the compositional differences between bulk sulfides from the two rock series using electron microprobe (EPMA). The wehrlitic sulfides show higher Fe and Cu contents compared to the lherzolites, which however depict higher Ni and Co amount. In order to understand the wehrlitization better, we applied femtosecond laser ablation-inductively coupled plasma mass spectrometer (fs-LA-ICPMS) to obtain δ^{65} Cu (deviation of 65 Cu/ 63 Cu from NIST SRM 976 expressed in ‰) and δ^{57} Fe (deviation of 57 Fe/ 54 Fe from IRMM-014 expressed in ‰) values.

The distinct chemical compositions between lherzolitic and wehrlitic sulfides suggest their origin related to mantle metasomatism for the wehrlitic sulfides. Melt metasomatism was proven to efficiently enrich the upper oceanic mantle in sulfides and metals. Our current results show that this process may also be effective in the upper continental mantle. In addition, sulfide precipitation from melt percolating through the upper continental mantle seem to trigger isotope fractionation.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Local example of sulfide differentiation through melt-rock reaction at the lower oceanic crust (U1473A, Atlantis Bank, Southwest Indian Ridge)

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IODP expedition 360 drilled 810-m-long Hole U1473A into the lower crust of Atlantis Bank ocean core complex located at the Southwest Indian Ridge (SWIR, 32°42'S, 57°17'E; Dick et al., 2017). Coarse-grained (5-30 mm) olivine gabbro prevails throughout the hole, ranging locally from fine- (<1 mm) to very coarse-grained (>30 mm). We studied two distinct intervals of igneous layering at 110-167 and 577-596 meters below seafloor (mbsf) to understand distribution of sulfides, and found that the layer boundaries are enriched in sulfides and chalcophile elements.

The sulfide grains throughout the layering are on average composed of pyrrhotite (Fe_{1-x}S; 72-82 vol.%), chalcopyrite (CuFeS₂; 11-20 vol.%), pentlandite ([Ni,Fe]₉S₈; 2-10 vol.%), and troilite (FeS) which are typical paragenesis of magmatic origin (Alt and Anderson, 1991). The sulfides are usually associated with Fe-Ti oxides (exsolutions of titanomagnetites and ilmenites), amphiboles and apatites, located at the rims or interstitial positions of olivines and clinopyroxenes. The pentlandite and troilite exsolutions in pyrrhotite indicate high-temperature formation of sulfides, which is most likely after sulfide liquid separated from mafic magma (Craig, Kullerud 1969). In fact, relatively homogenous mineral and chemical composition of sulfides, along with δ^{34} S (+0.1 to +1.0‰) and δ^{65} Cu (-0.7 to -1.0‰) isotope signatures suggest that magmatic processes caused the sulfide enrichment at the layer boundaries.

To further constrain the nature of the sulfide-enriching process at the layer boundaries we determined Platinum Group Element (PGE) contents of the sulfide grains. Experiments predict PGE fractionation during differentiation of sulfide liquid and distinguish the IPGE (Ir, Os, Ru) and PPGE (Pd, Pt, Rh) subgroups based on their contrasting behavior. Our sulfides from the coarse-grained gabbro are IPGE-rich, and from the fine-grained gabbro are PPGE-rich. Notably, the sulfides of the layer boundaries are also enriched in PPGEs. This is most likely the result of focused late-stage magma flow (fine-grained gabbro) through crystal mush (coarse-grained gabbro) and the formation of local chemical disequilibrium between the two. Such chemical disequilibrium may lead to the increased precipitation of sulfides at the layer boundaries, which could be driven for example by FeO drop followed by lowering sulfur concentration at sulfide saturation (SCSS) level of the late-stage melt (e.g., Ciazela et al. 2017; 2018).

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Chemically variable zircon populations in rhyolites: implications for dating and reconstruction of magma processes

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Large eruptions of silicic magmas occur episodically in the Earth history and may have a large impact on the composition and structure of the continental crust. In the late Paleozoic Europe, from 301 to 289 Ma, the episode of volcanic activity produced over 80000 km3 of magma. However, taking into account the relatively low precision of U-Pb zircon dating by ionprobe, as well as specific processes of rhyolite magma formation, this time span is a rough estimation. More precise dating of the rhyolites can be done by zircon dating by CA-ID-TIMS, but so far it has been largely unsuccessful due to either lead loss or presence of antecrystic component in zircon population in a single sample.

Therefore, we suggest that the way forward is a detailed characteristic of diverse zircon population in thin section, which should identify antecrystic and autocrystic components. The proposed approach comprises three-stage analyses of zircon in thin sections in order to choose the grains populations with similar characteristic and in assumption giving the most precise age. The first stage includes SEM-CL analyses of zircon, which should give information on the position of the zircon in the rock structure as well as on the internal zircon morphology. This stage is important because it should identify grains, which are potentially antecrystic. The grains should be then characterized chemically in the second stage in order to define a set of parameters required to recognize the grains in zircon separates and avoid taking them for CA-ID-TIMS analyses.

The detailed characteristic by SEM-EDS was done for rhyolites from Chemnitz Basin, Halle Volcanic Complex, Intra-Sudetic Basin, North Sudetic Basin, Steinwald, Teplice-Altenberg Volcanic Complex and Tharandt Caldera. Usually, two or three zircon populations with different internal structures, sizes, mineral associations and inclusions were identified in each sample. These results indicate the necessity of careful zircon characteristic in thin sections before studies on zircon separates are undertaken. Potentially, much better understanding of rhyolitic ages and magma evolution is obtained, when each of the identified populations is analysed separately and strongly linked to the position of the population in the rock structure.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Monzodioritic magma differentiation processes recorded in apatite from the Niemcza Zone: Insights from *in-situ* analyses by electron microprobe

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Apatite is a common accessory, magmatic mineral that commonly occurs also as a detrital component in sediments. Apatite is a versatile in the way that it has an unique chemical composition often reflecting the magma or fluid composition from which it crystallized. Increasing amount of apatite compositional data from a variety of igneous rocks shows that many factors may control apatite composition making it a promising tool for reconstructing magma evolution. In this study we test factors, which may control apatite chemical variability such as (1) occurrence of apatite as inclusions in a range of major minerals, (2) crystallization of apatite in mineralogically and chemically diverse non-hybrid monzodioritic magmas and (3) magma differentiation processes.

The rock types analysed in this study include granodiorites (Kośmin) and monzodiorites (Kośmin - 2 enclaves, Przedborowa, Brodziszów and Koźmice). As such the samples represent two sets, which can be compared and interpreted separately: the first set includes four monzodioritic samples and the apatite occurrence and composition can be interpreted in terms of diorite magma variability, the second set includes two enclaves and granodiorite representing different stages of magma mixing/mingling and the apatite composition can be interpreted in terms of this open-system magma evolution process. Apatite from each sample was analysed for major (P, Ca, F) and minor (Ce, Y, Si) elements.

We suggest that Ce/Y ratio is particularly useful in apatite studies, especially in dioritic rocks, because: (1) it can be measured by an electron microprobe, for fine-grained dioritic apatite, (2) it can be measured in-situ and directly linked to the host in which apatite occurs and (3) it is strongly controlled by apatite saturation temperature and high Ce/Y are typically observed in igneous rocks with early amphibole crystallizing before apatite and (4) it is relatively constant for a single sample and that can be used as a tracer of a single versus multiply apatite source rocks e.g. in provenance studies. On the other hand Ce/Y is not a good record of magma mixing process, which in apatite from the dioritic enclaves/ granodioritic host seems to be well recorded by variations in Ce and Si concentrations.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



The origin of mantle roots of Variscan Orogen in Central Europe

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Central and eastern parts of the Variscan orogen of Europe consist of two subductioncollision systems (Saxo-Thuringian, ST, and Rheno-Hercynian, RH, Zones) separated by a fossil volcanic arc (Mid-German Crystalline High, MGCH). South of them is located the extensive fossil Gondwana margin - Moldanubian Zone (e.g. Lardeaux et al. 2014). Cenozoic alkaline volcanic rocks, related to rifting in the foreland of Alps, spread over most of the Variscan areas and locally carry peridotitic samples of subcontinental lithospheric mantle (SCLM). Numerous xenolith studies demonstrated that SCLM beneath European Variscan orogen is lithologically variable. After the Cenozoic metasomatic overprint is filtered off, it appears that the eastern part of ST Zone ("Lugian" unit) is underlain by a strongly (up to 35 %) depleted harzburgitic mantle of oceanic affinity, which possibly represents a slice of Rheic Ocean plate attached to the Bruno-Vistulian terrane. Its occurrence shows that slices of oceanic plates could be docked to the margin of growing orogen. Mantle roots of central and western part of the ST Zone are heterogeneous, as well as the mantle underlying RH zone and MGCH. They supposedly consists of slices of continental and oceanic plates assembled during the Variscan orogeny.

The mantle underlying the West Moldanubian (sensu Lardeaux et al. 2014) unit possibly originated due to refertilization of depleted harzburgites (Lenoir et al. 2000) or asthenosphere upwelling and "lithospherization". The large-scale upwelling could have happened during orogen delamination (late Carboniferous-early Permian).

Two different kinds of SCLM occur beneath the Variscan orogen of Europe. The first one consists of mantle fragments assembled during collisional stage of orogen growth. It underlies the majority of orogen. The second one is a new lithosphere which originated during late-orogenic delamination, asthenosphere upwelling and subsequent cooling.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Prediction of the solubility stable for Pb – As – bearing apatites with different halides substitutions

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The structure of apatites, corresponding to the general chemical formula $M_5(TO_4)_3X$, is very flexible and allows for numerous substitutions e.g. F⁻, OH⁻, Cl⁻, Br⁻ and I⁻ at position X. Systematic variations of stability (expressed as ΔG°_f) with anionic X substitutions in the apatite structure are commonly observed. Such variations are used for prediction of the Gibbs free energy of formation ΔG°_f of Pb-As-bearing apatites (for which these values are still sparse) as well as to calculate the Gibbs free energy of dissolution reaction ΔG°_r of apatites:

$$M_5(TO_4)_3X \le 5M^{2+} + 3TO_4^{3-} + X^{-}$$

Based on ΔG°_{r} and thermodynamic data for specific ions the solubility constant (K_{sp}) for selected apatites was predicted.

for selected Pb - As - bearing apatites. logK_{sp} $\Delta G_{f}^{\circ}[kJ/mol] \Delta G_{r}^{\circ}[kJ/mol]$ Phase Pb₅(AsO₄)₃F -2749 401.3 -70.30 Pb₅(AsO₄)₃OH -2659 435.51 -76.30 Pb₅(AsO₄)₃Cl -2634436.53 -76.48 Pb5(AsO4)3Br -2583 413 -72.35 Pb₅(AsO₄)₃I -2535 417.1 -73.07 -70 -78 -76 -74 -72 -68 -2400 logK_{sp} of apatite of apatite -2500 Br [kJ/mol] Cl -2600 бон ΔG°, -2700 $y = -16.381x^2 - 2423.4x - 92161$ $R^2 = 0.9932$ -2800

Table 1. Examples of experimental (bold) and predicted (italic) $\Delta G^{o}{}_{\rm f}$ and $logK_{sp}$

Fig. 1. Parabolic variation of $logK_{sp}$ with the ΔG°_{f} for Pb – As – bearing apatites. Pb₅(AsO₄)₃OH is not included in the trendline.

The novelty of the research stems from the fact that for the first time the K_{sp} values for $Pb_5(AsO_4)_3F$, $Pb_5(AsO_4)_3Br$, $Pb_5(AsO_4)_3I$ have been proposed. Systematic variations of $logK_{sp}$ of apatites and their ΔG°_{f} are observed and will be utilized for correlation, interpolation and extrapolation (Fig. 1.).

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Anhydrosaccharide emissions from detritic lignites and xylites

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Anhydrosaccharides such as levoglucosan, mannosan and galactosan are products of cellulose and hemicellulose thermal decomposition and are widely known as organic tracers of biomass burning. Preliminary analysis of Miocene lignites from Poland and Germany indicate that all types of brown coals contain considerable amounts of cellulose. Thus, it cannot be ruled out that in many regions of the world, where lignites are used as a solid fuel, levoglucosan as well as possibly also mannosan and galactosan are mistakenly considered as derived from biomass burning, while their actual sources are connected with combined biomass and lignite combustion.

Derivatized lignite extracts were analyzed using gas chromatography coupled with mass spectrometry (GC-MS). In all lignite types monosaccharides (including arabinose, xylose, fructose and glucose), and disaccharides (such as sucrose and trehalose) were identified. These compounds are most likely derived from cellulose and hemicellulose decomposition (Marynowski et al. 2018).

The pilot burning tests of Miocene lignites from various Polish mines have shown that levoglucosan is a major polar compound in xylites and important or detectable in detritic coals, whereas mannosan and possibly also galactosan are also present in various concentrations. This indicates that some part of anhydrosugars present in aerosols might originate from brown coal combustion, and not, as commonly believed only from biomass burning. Interestingly, all lignite samples do contain thermodynamically less stable hopanes (such as $17\beta(H)$, $21\beta(H)$ -hopane or $22R-17\alpha(H)$, $21\beta(H)$ -homohopane) as well as alkylated picenes and alkylhydropicenes. These compounds are common in lignite, brown coal or sub-bituminous coal smoke (Oros, Simoneit 2000) and are not known as biomass burning in samples with high concentrations of levoglucosan.

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Pyritization of organic remains

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Pyritized organic remains are common in the sedimentary record. In sediments and the overlying water column, living and decaying organisms supply organic matter which creates anoxia and sulphide production via sulphate reduction. Pyritization is a process of replacement of a hard part of organism and/or infilling it by pyrite and its period of formation varies from days to milions of years. Typical necessary factors are: bacteria (*Desulphovibrio*), sulphates, metabolizable organic matter, and dissolved iron (Fe^{2+}). Pyrite (FeS₂) forms via reaction of sulfur with iron. BSR (bacterial sulphate reduction) produces H₂S and/or HS⁻; H₂S reacts with dissolved Fe forming iron monosulphides (mackinawite and greigite) which finally can transform to pyrite (direct formation of pyrite is rarer). Differentiation of the pyritization is dependent on environmental conditions, place and time of action. Iron sulphides, usually pyrite, occur inside hard remains (replacing soft bodies), replace skeletons and sometimes encrust them. Pyritization is often a multistadial proces as we can observed in one specimen both infilling, replacement and encrustation. In addition to pyrite, its precursors, mackinawite and greigite are present in organic remains, sometimes even in the same compartment. Pyrite polymorph - marcasite is rare. Occurrences and habits of pyrite crystals vary, from framboidal aggregations and framboids to euhedra (cubes, octahedra and their modifications).

Pyritization is observed in remains built of different materials: silica (eg. radiolaria, diatomea, some sponges); carbonates, like calcite, aragonite, or Mg-calcite (eg. foraminifera, gastropods, molluscas, amonites, belemnite rostra); phosphates (rare, excl. bones and teeth); organics (eg. dinocysts, insects). In addition to hard parts pyritized can be ichnofossils (eg. burrows, coprolites, annelides tubes, etc.), "soft-parts" (rare, excl. Trilobites) and plant cells (eg. wood, pollens).

Pyrite can exceptionally preserve organism morphology (eg. "soft parts") but it also can destroy fossils through the pyrite oxidation (eg. in the museum). Pyrite can be oxidized to iron oxy/hydroxides, usually preserving morphology of the primary crystals, or to iron sulphates, commonly loosing the primary shapes. Sometimes it can lead to mistakes, like founding in dinosaurs bones globules of "blood cells" built of iron oxides which were found to be oxidized pyrite framboids. Various kinds of leaching of pyrite crystals are observed in organic remains, both chemical and microbiological.

Use of pyrite framboids as indicators of palaeoenvironmental conditions is limited to sediments and framboids which formed inside skeletons cannot be taken into account.

It is worth noting that apart from iron sulphides also other sulphides can sometimes replace or infill hard parts (eg. ZnS in gastropods).

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Mg-rich carbonates as sorbents in dry methods of desulphurization

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The basic SO_2 sorbents in the fluidized bed combustion are high-quality limestone. The SO_2 binding is possible thanks to the decarbonization process of carbonate. As a result of the process, highly reactive and porous calcium oxides are formed and react with SO_2 to form anhydrite. Research shows that it is also possible to use other carbonate rocks such as dolomite and magnesite (e.g. Kaljuvee 2005, Antony 1995).

Magnesites and dolomites were examined as potential SO_2 sorbents under fluidized bed combustion condition. Series of experiments at laboratory scale were conducted to determine sorption effectiveness. The raw samples, calcined and sulphated ones were examined by physico-chemical and mineralogical methods. The sorption properties of the examined carbonates range from good to excellent in the Ahlstrom Pyropower-Reactivity scale (1995). The results of some dolomites are even higher than for currently used limestone sorbents (Hycnar et al. 2015). The textural parameters were determined by mercury porosimetry and low-temperature nitrogen adsorption method. In the case of very good and excellent sorption properties samples, after calcination the volume of pores (generally) in range 0.01-4 μ m significantly increased and after SO₂ sorption disappeared. It is related to filling of the pores with sulphates. Pores with appropriate diameters allow free flow of SO₂ into the centre of the grain. The sulfates formed on the surface of the sorbent grains also show a porous texture, similar to honeycomb.

It was shown that the high content of $CaCO_3$ and $MgCO_3$ is not only one decisive parameter for the effectiveness of desulfurization. The impact has also porous texture formed during the calcination process. Confirmed participation of MgO in the binding of SO_2 - the magnesium sulphate (MgSO₄) and the double sulfate (CaMg₂(SO₄)₃) were formed as stable phases under experimental conditions.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Polymetamorphic tourmaline vein from Wołowa Góra, SW Poland

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The Wołowa Góra Mt. region near Kowary is a part of the eastern metamorphic cover of Karkonosze granite belonging to the Kowary-Czarnów metamorphic unit. The rocks formed from mixed magmatic-sedimentary protoliths of ~490 Ma age, which underwent regional Variscan metamorphism under MP-MT conditions and were modified by contact metamorphism induced by the Karkonosze granite pluton. Tournalines of the Kowary-Czarnów unit are mainly represented by dravite and fluor-dravite, partially evolving to oxy-dravite, and less frequent by schorl-uvite-type tournalines.

Examined tourmalines occur as zoned crystals (1) in almost monomineral aggregates in quartz veins in the region of pass between the Czoło Mt. and Wołowa Góra Mt., and as syntaxial growing crystals (2) coexisting with K-feldspar and chamosite that fills small cracks in the host granite gneisses. All these tourmalines belong to the alkali tourmaline group (Na+K > Ca > \Box at the X site) with different ocupancies of the anionic W site by OH,F and O. The older generation (1) evolves from oxy-species in the internal parts of the multizoned crystals, to fluor- and hydroxy-species in their external parts. The Y and Z structural sites are mainly occupied by Mg and Al. These tourmalines represent rather high Mg/Mg+Fe ratio up to 0.98 and all of them can be classified as dravite ($^{W}(OH^{1-}+F^{1-}) > ^{W}O^{2-}$ and $^{W}OH^{1-} > ^{W}F^{1-}$). The content of Fe, Ca and Ti increases in external parts of the crystals reaching 1.10 Fe apfu 0.30 apfu and 0.10 Ti apfu. The younger generation (2) is represented only by hydroxy-species, with Fe content reaching 1.6 apfu, Ca 0.26 apfu, and Ti 0.16 apfu. The Mg/(Mg+Fe) ratio fluctuates from 0.23 to 0.58 apfu, indicating a simply solid solution between Fe-rich dravite and Mg-rich schorl species.

Tourmalines of older generation (1) are mainly products of multistage prograde Variscan metamorphism and maybe contact metamorphism stage of \sim 320 Ma. The younger generation (2) could be related to the final stages of contact metamorphism or even magmatic processes. The increase of Fe, Ca and Ti in younger tourmaline varieties of the area is the most likely a result of partial dissolution and recrystallization of amphiboles, plagioclases and Ti-oxides in the contact metamorphism stage. Chamosite replace a former biotite within a cracks, which imply a fluid-assisted recrystallization at lower-T conditions (\sim 250° C based on Jowett 1991).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Accessory minerals as indicators of the crystallization / recrystallization of a granitic pluton – a multi-tools research approach

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Accessory minerals capable of incorporating many trace elements into their structures and sensitive to alteration processes are perceived as good indicators of the geochemical and thermal conditions of their formation and transformation environments. Crystallization and recrystallization processes are fixed in the composition and growth/regrowth textures of mineral domains. The more parameters (P-T conditions of the system, element activity in the magma or fluid, volatile fugacity, melt structure, fluid X_{CO2}, salinity, pH, mineral assemblage buffering effect, etc.) define the course of processes, the greater the possibility of a more accurate description of the system through not only the composition of minerals but also the more difficult identification of the progress of these processes. Using data acquisition and processing with multiple tools for accessory minerals is needed to give detailed insight into granitic pluton magmatic and post-magmatic development. Research on two accessory minerals, apatite and titanite, has been used to decipher their appearance due to magmatic crystallization and changes due to interaction with hydrothermal fluids. The minerals were collected from the Late Archaean Closepet granite (Dharwar craton, India). The origins/compositions of melts and fluids were determined and the materials dated. The magmatic and hydrothermal system can be described as a high-temperature (Zrin-titanite thermometer), multi-source and multi-phase system with clear influence from mantle activity. Titanite preserves high REE concentrations in its pristine domains, whereas REEs are leached together with other trace elements due to hydrothermal interaction. The apatite REE pattern is not changed by hydrothermal interaction, but some volatiles have been exchanged. Titanite pristine and altered domains were dated (using the U-Pb system), and they demonstrate similar ages. Thus, based on apatite-titanite study, reconstructed hybrid melt and fluid compositions (immiscible H2O-CO2 and saline brines) show an Archaean magmatic/hydrothermal system, which may be related to active mantle-crust interaction, probably supported by a hot-spot environment.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Paleoredox conditions changes across the Ordovician and Silurian boundary: evidence from trace metals

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Trace metals were used as paleoredox indicators in order to assess the conditions at the sediment-bottom water interface across the Ordovician and Silurian boundary. Geochemical data were measured for 87 mostly argillaceous mudstones representing Pelplin, Pasłęk (including Jantar Member), Prabuty and Sasino formations. The samples were collected from four wells drilled in the Polish part of the Baltic Basin.

The concentrations of major, minor and trace elements were measured by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS), additionally, the content of total organic carbon (TOC) and total sulphur (TS) was measured by the LECO[®] carbon and sulphur analyser. The seven indices: Mo, DOP (degree of pyritization), authigenic uranium (U_{aut}), V/Cr, U/Mo, Ni/Co, Ni/(V+Ni) have been examined in order to determine paleoredox conditions recorded in each lithostratigraphic unit. We excluded the U/Th ratio due to the highly positive correlation of Th and Al, which is an indicator of the terrigenous provenance of the former and makes Th data useless in studies of paleoredox conditions.

Generally, we observe a good correlation between most of the trace metal indices and TOC concentration. Noticeable peaks occur in the lower part of the Jantar Member as well as several peaks occur throughout the Sasino Formation. This suggests repeating and short-term episodes of dysoxic to euxinic conditions recorded in these lithostratigraphic units. The remaining parts of the analysed section were in general deposited in the more oxygenrich regime.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Phases analysis of the synthetic Pb – As – bearing apatites with various substitutions of halides.

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The apatite-group minerals are tolerant to various chemical substitutions. Their diverse composition results in many geological, technological and environmental occurrences. Here, we identified the systematic relation between structural and spectral properties of Pb-As – bearing apatites with different anionic substitutions. Although some of them may not have natural equivalents, they are highly informative in understanding the crystal chemistry of Pb-As – bearing apatites.

A wet method of synthesis from aqueous solutions was used to precipitate the five phases: $Pb_5(AsO_4)_3X$, where X were: F, OH, Cl, Br or I. The pH was kept above 4.5 during synthesis to avoid precipitation of other phases. All five synthesized phases were characterized using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), powder X-Ray diffraction (XRD), infrared absorption spectroscopy (FTIR) and Raman spectroscopy.

The maximum size of grains is ca. 8μ m (Fig. 1.). Systematic shift of peaks is apparent on the diffraction patterns. The position of an intense reflection (211) moved from 29.62°20 for Pb₅(AsO₄)₃F to 28.83°20 for Pb₅(AsO₄)₃I. The hexagonal system and *P6₃/m* group of symmetry were used for the calculations of unit cell parameters. The cell parameters for Pb₅(AsO₄)₃I were determined for the first time. The results show systematic increase in unit cell parameters with increasing ionic radius (R_i) of specific halide (Table 1). The position of AsO₄ absorption bands in FTIR spectra shifts towards thehigher wavenumber with increasing ionic radius of halides, which is due to the increasing atomic mass.



Fig. 1. Scanning electron micrograph (SEM) of synthetic Pb₅(AsO₄)₃I.



Fig. 2. Linear variation of the cell volume (V) with ionic radius of halides (R_i) for Pb-As bearing apatites (squares). Pb₅(AsO₄)₃OH is not included in the trend (circle).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Stone from cultural heritage in different environmental conditions - petrography and SEM-EDS analysis

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Poland and Scotland have rich architecture heritage and many buildings in the both countries have been constructed or decorated with sandstone that can be subjected to weathering (deterioration) in different ways. Durability of stone material in a building depends on its composition, construction type, façade orientation, climate, human impact (inappropriate conservation or cleaning), and air pollution.

The climate is one the most significant factor that impacts on stone and panel preservation. Aqueous dissolution, frost damage, secondary mineral phase crystallization, and microbiological growth, all related to the climate, lead to the building stone deterioration. The main aim of research was to compare the impact of the climate on the stone deterioration in Scotland and Poland, as these experience different weather condition. Scotland has nearly three times more average rainfalls over year than Poland, thus chemical weathering and biodeterioration process are predominant there. Weather conditions in Poland, especially severe frost in the winters, have huge impact on stone decay through freeze-thaw cycles (physical weathering). Moreover, the human activity on the degradation of building stone was also determined.

The sandstone samples from Poland (University of Economics and Business and National Archives in Poznań) and Scotland (Paisley Town Hall and Scott Monument, Edinburgh) were collected to compare types of stone degradation. The petrographic and experimental analysis were used to compare the types of stone degradation, including the precipitation of secondary mineral phases, the rate of stone weathering, and the influence of mechanical and chemical cleaning. The samples showed different iron-rich cements: in the Polish building sandstones hematite was found, while in the Scottish samples ankerite is abundant. Gypsum (as a common byproduct of the interaction between sulphur dioxide and stone) and other types of salts are present in all samples, regardless their provenance. In the Polish and Scottish samples black crust was also identified (gypsum can trap solid polluting particulates and form common black crusts with Fe, Ni, Pb, Pt, Sn incrustation).

The investigation evidenced different ways of stone degradations depending on the climate type and human impact (smog, acid rains and others).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



PT history preserved in mica schists from the Doboszowice Metamorphic Complex (Bohemian Massif, Fore-Sudetic Block)

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The eastern part of the Fore-Sudetic Block is viewed as formed owing to Variscan collision between two crustal domains represented by the Brunovistulian and the Saxothuringian microplates. However, details of this collision process are still a matter of discussion. In order to determine the metamorphic P–T path and to better understand the metamorphic evolution of this part of the Variscan Belt of Europe we investigated garnet bearing mica schist collected in the Doboszowice Massif in the eastern Fore-Sudetic Block.

Results of our calculations performed using Theriak-Domino software (de Capitani, Petrakakis 2010) and utilizing an automated method for the calculation of P–T paths from garnet zoning proposed by Moynihan and Pattison (2013) show that large garnet crystals reaching 1 cm in diameter in the examined mica schist started to grow at ca. 524 °C and 4.9 kbar and ceased at 668 °C and 8.0 kbar. In the investigated sample garnet grains grew in equilibrium with white mica characterized by low Si⁴⁺ content do not exceeding 3.06 apfu. However, the investigated sample contains relics of white mica with Si⁴⁺ reaching 3.22 to 3.30 apfu indicating high pressures of up to 13 kbar prevailing most probably before garnet growth.

The compositional growth zoning preserved in garnet implies one stage in the P-T history during garnet growth with a dP/dT of ~ 0.011 kbar/°C. Assuming a rock density of 2800 kg/m³, the value of 0.011 kbar/°C corresponds to burial of 29 km, with a temperature increase of 13.0 °C for every km of burial. At the end of garnet growth, conditions of 8.0 kbar, 668 °C indicate an average instantaneous geothermal gradient of 22.9 °C/km for the same rock density. We attribute this phase of rock history to crustal thickening and Barrovian metamorphism recorded by mica schists cropping out in the eastern part of the Doboszowice Massif.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Raman imaging as a tool for interpretation of structural cages occupation in the mayenite group minerals

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A crystal structure of minerals from mayenite group includes zeolite-like cages, which in Nature can be occupied by F^- , CI^- , OH^- or H_2O . The similarity of mayenites to zeolites depends on the mobility of particles located in such structural cages. Therefore, they can incorporate ions and molecules from the environment and can be hydrated easily.

The Raman imaging shows that apparently homogeneous crystals of mayenite group minerals have developed zonation corresponding to different substitutions in the structural cages. The most common zonation in this group is connected to the presence of OH⁻ ions and neutral molecules H₂O in the structure. The theoretical model of water incorporation into mayenite structure consists of four stages corresponding to formation of: 1) typical low - hydrated fluormayenite with OH⁻ in the W site, according to schemes ^WF⁻/^WCl⁻ → ^WOH⁻ or ^W□→^WOH⁻ (band at 3576 cm⁻¹); 2) hydrated fluormayenite with structural defects, according to schemes ^WF⁻ + 2^W□+ ²⁰O²⁻→^{20a}3(OH)⁻+3^W□ or ²⁰O²⁻→2^{O2a}(OH)⁻ (bands at 3610 and 3680 cm⁻¹ respectively); 3) high - hydrated fluormayenite with "kyuygenite water", according to scheme ^W□→H₂O (low-intense bands in 2800-3550 cm⁻¹ range); 4) the fully hydrated fluorkyuygenite (broad bands in 2800-3550 cm⁻¹ range).

Recently found S-bearing fluormayenite and fluorkyuygenite shows that not only water can be incorporated in different ways. Sulfur can be located in the structural cages according to three mechanism: 1) $2^{W}F'/^{W}OH^{-}\rightarrow SO_{4}^{2-}$ (band at 1006 cm⁻¹); 2) $^{W}F'/^{W}OH^{-}\rightarrow HS^{-}$ (band at 2585 cm⁻¹); 3) $^{W}\Box\rightarrow H_{2}S$ (band at 2600 cm⁻¹). The sulfur-substitution zonation is highlighted by the OH⁻ and H₂O distribution.

The genesis of inhomogeneity in the mayenite group mineral is connected with subsequent processes caused by gas or fluid flow, which changed the composition of the structural cages. Since different conditions are needed for $OH^{-}/H_2O/SO_4^{-2}/HS^{-}/H_2S$ substitution in the mayenite, it is possible to determine the temperatures of thermal events, which lead to the formation of detected fluormayenite or fluorkyuygenite. The first stage of water incorporation takes place at about 900°C, while the "kyuygenite water" is released from mayenite structure at 400°C. The substitution of HS⁻/H₂S is stable only at temperatures up to the 600°C, and the SO₄⁻² remains in the structure above this temperature (the exact release point for this substitution requires further investigation).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Batch and column sorption of As(V) onto bog iron ores

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Arsenic contamination of potable water is a matter of grave environmental concern worldwide. Constant technological progress caused permanent water pollution with arsenic compounds in many regions of the world. Intake of As(V)-contaminated water poses a great threat to human and animal health as it is extremely toxic and carcinogenic. Among many methods of As removal, ones involving sorbents containing oxides or oxyhydroxides, are the most popular. Both batch and column experiments were carried out to examine and compare the sorption characteristics of As(V) onto bog iron ores.

For this study, four samples of bog iron ores were collected at different sites in the Polish Lowlands: Kolechowice (KOL), Biadaszki (BD), Strzyżew (ST) and Dębe Małe I (DM). In batch experiments, the influence of various factors on adsorption of As(V) were studied, including initial As concentrations (0.01-20 mM, pH 7.5) and initial pH values (5 mM, pH 2-11). Column experiments were conducted to evaluate the performance of selected bog iron ores in fixed-bed columns (40 mM, pH 7.5).

Batch and column experiments demonstrated the high adsorption capacity of the material, with the sorption of As(V). Batch experiments revealed that the highest quantities of As(V) were immobilized on BD and ST samples (ca. 16–19 mg/g), while amounts achieved by KOL and DM samples were significantly lower (ca. 11–12 mg/g). The initial pH value significantly affects the effectiveness of As removal. The efficiency of As(V) adsorption is higher in a low pH environment, clearly decreasing with the increase of pH value. The Langmuir and Freundlich isotherm models were applied to describe the adsorption of As(V) onto bog iron ores. The Langmuir isotherm, which assumes coverage of sorbent with a monolayer over a homogeneous sorbent surface composed of a finite number of identical sites, fits the KOL, DM and ST data fairly well with R^2 over 0.895. However, the Freundlich isotherm, which is often used for describing the chemisorption process, fitted the BD data slightly better. Columns packed with bog iron ores showed good As(V) retention. Results revealed that the highest sorption capacity was obtained for ST sample (2.309 mg/g), then KOL, DM and BD (1.523, 1.189 and 0.776 mg/g respectively).

Experiments revealed that highest sorption occur at medium initial concentrations (0.25-0.5 mM) and slightly acidic pH. These findings indicate that bog iron ores has great potential for use as a low-cost filter material to remove arsenic from aqueous solutions. However, there are no simple correlations between mineralogy and sorption capacity. Due to the variability in chemical and mineral composition among different types of bog iron ores, various levels of arsenic removal can be obtained.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Extremely fractionated phosphates in the Julianna pegmatitic system at Piława Górna, Góry Sowie Block

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The Julianna pegmatitic system is exposed since 2007 in a migmatite-amphibolite quarry at Piława Górna in the Góry Sowie Block, Lower Silesia, SW Poland. It is the largest accumulation of pegmatite in Poland. Up to 2011 parts of the deposit containing numerous pegmatite bodies were unveiled and exploited (Szuszkiewicz et al. 2013). In the following years, until now exploitation covered part of the deposit poor in pegmatite mineralization.

Pegmatites from Piława Górna are of an anatectic origin. Julianna system consists of a series of veins, dikes and pods, all of diverse structure, representing different degrees of fractionation and crossing tectonized amphibolites. Due to the great variety of mineralization (more than 140 different minerals discovered) and the presence of rare elements, the pegmatites of the Julianna system are classified as NYF (Nb-Y-F) or mixed NYF + LCT (Li-Cs-Ta) and to the subtype REL-REE and REL-Li.

Phosphate minerals with the highest fractionation occur in LCT pods. At least 14 such minerals were found there to date. They appear in the form of small nodules occurring on the contacts of the lithium-mica – cleavelandite – quartz unit with the spodumene – lepidolite core. These phosphates are characterized by an extremely low Fe content compared to Mn [Mn/(Mn + Fe)>0.995]. The most common primary phosphates are lithiofyllite and Mn-and/or Sr-bearing fluorapatite. These minerals are a matrix, inside which there are small inclusions of triploidite, triplite, hydroxyl- to chlorapatite and pieczkaite. Lithiofyllite exhibits elevated sodium levels, sometimes high enough to evolve in natrofillit. The main secondary phosphates are purpurite and serrabrancaite (the latter creates very fine veins) which occur in lithiofyllite. Apart of them another secondary phosphates close to lermontovite of vyacheslavite and very rare crystals of dickinsonite emerge. These all above mentioned phosphates are accompanied by spessartine garnet (0.95-0.99) and primary Nb-Ta oxides of the columbite group (0.95-0.99).

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U-Pb zircon dating of the diamond-bearing gneiss from Fjørtoft supports the "dunk tectonics" model for the Scandinavian Caledonides

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The Scandinavian Caledonides are a collisional orogen, which resulted from closure of Iapetus in the Late Cambrian-Early Ordovician, culminating in the Late Silurian-Early Devonian. This ocean closure involved multiple subduction-collision events with outboard terranes and terminated with underthrusting of Baltica beneath Laurentia. It also led to formation of a multitude of (ultra-)high pressure (UHP-HP) lithologies yielding various ages of metamorphism. The most pronounced of late Cambrian-early Ordovician UHP-HP events are those recorded in the Seve-Blåhø Nappe of the Middle Allochthon, the latter being the outermost margin of Baltica. Vestiges of the Middle Allochthon also occur within the largest UHP-HP province of the Scandinavian Caledonides, namely the Western Gneiss Region (WGR), formed during the collision between Baltica and Laurentia. Therefore, the rocks of the Seve-Blåhø Nappe occurring in the WGR, could have been subjected to more than one subduction (via the "dunk tectonics" model *sensu* Brueckner and van Roermund 2004) event during the Caledonian orogenic cycle.

Here, we report U-Pb zircon ages obtained from the garnet-kyanite Seve-Blåhø gneiss from Fjørtoft located in the Nordøyane UHP domain of the WGR. Zircon grains were separated from the same sample in which metamorphic diamond was identified in the Scandinavian Caledonides for the first time. The dated zircons display obvious multi-stage growth features and consist of detrital cores overgrown by metamorphic rims. Metamorphic rims yielded two clusters of ages: (1) defining a peak at 446.6 \pm 2.1, and (2) a population ranging from c. 437 to c. 423 Ma. The obtained age pattern reflects complicated and protracted metamorphic evolution of rocks belonging to the Seve-Blåhø Nappe. hence, we postulate that this complex metamorphic zircon ages pattern results from multiple subduction-eduction cycles, as predicted by the "dunk tectonics" model for the Scandinavian Caledonides.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Crystal structure of Mn-substituted synthetic stannite from the isomorphic series $Cu_2(Fe_{x-1}Mn_x)SnS_4$

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Stannite Cu_2FeSnS_4 is a well-known sulfide mineral which is characterized by its semiconductor properties. Its crystal structure allows for numerous substitutions including replacement of Fe by Mn. Stannite analogues from isomorphic series $Cu_2(Fe_{x-1}Mn_x)SnS_4$ (technical acronym CFMTS) may have attracted interest for applications in solar cells and other optical devices due to the properties similar to the established photovoltaic materials of CGIS type (Cu₂GaInSe₄) but lower manufacturing costs.

The aim of this work is to recognize the effect of Mn^{2+} substitution for Fe²⁺ on the crystal structure, unit cell parameters and morphology of crystals. Six members of CFMTS series have been synthesized using the hydrothermal method in the autoclave at 180°C for seven days. The products were analyzed with electron microscopy SEM/EDS and powder X-ray diffraction.

The aggregates of Cu₂FeSnS₄ nanocrystals display nearly spherical shape. The average size of grains is ca. 1 ± 0.5 µm. In contrast, Cu₂MnSnS₄ nanocrystals show spherical agglomerates with sharp-edged structure of grains which are ca. 0.5 µm in size (fig. 1). The XRD pattern of CFMTS matches well with the tetragonal structure. Unit cell parameters are shown in Table 1.

Table 1. Unit cel	l parameters of
$Cu_2(Fe_{x-1}Mn_x)St$	nS_4 solid solution series

phase	a (Å)	c (Å)	$V(Å^3)$
Cu ₂ FeSnS ₄	5.411	10.707	313.47
Cu ₂ Fe _{0.8} Mn _{0.2} SnS ₄	5.425	10.718	315.44
Cu ₂ Fe _{0.6} Mn _{0.4} SnS ₄	5.437	10.719	317.07
Cu ₂ Fe _{0.4} Mn _{0.6} SnS ₄	5.465	10.789	322.26
Cu ₂ Fe _{0.2} Mn _{0.8} SnS ₄	5.481	10.782	323.91
Cu ₂ MnSnS ₄	5.505	10.796	327.14



Fig. 1. The aggregates of nanocrystals A) Cu2FeSnS4; B) Cu2MnSnS4

The results show clearly that the synthesized solid solutions CFMTS are homogeneous and a slight expansion of the cell volume can be observed. The variation of the lattice volume is in agreement with the increasing ionic radius of the substituting element ($Mn^{2+}=83pm$, $Fe^{2+}=78pm$). The analysis of photoelectric properties is in progress to estimate potential application of these nanocrystals in low-cost production of thin film solar cells. This study may allow for improvement of photoelectric and photocatalytic properties of this alternative photovoltaic material.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Effectiveness of water treatment residuals in removing heavy metals and metalloids from aqueous solutions

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al. A. Mickiewicza 30, 30-059 Kraków, Poland; e-mail: gprzepa@cyf-kr.edu.pl. Heavy metal contamination of aquatic environments is a global problem. Heavy metals have attracted attention due to its persistence, accumulation in the food chain and negative effects on human health. In order to remove those pollutants, many methods have been used, including chemical adsorption, especially using low-cost adsorbents. Among them, water treatment residuals (WTRs), which are inescapable by-product from drinking water treatment processes, could be considered. This study aimed to characterize the effectiveness

of Cd(II), Pb(II), Zn(II), Cu(II), As(V), Cr(III), Cr(VI) and P(V) removal by WTRs. Iron, aluminum and manganese compounds are major components of WTRs. The Fe₂O₃

contents range from 40 – 65%. The results of the X-ray diffraction analyses indicated that amorphous substances prevails over crystalline Fe components. According to SEM analysis WTRs formed heterogeneously mixed particles with irregular shapes. Particles have different pore diameter, which enhance heavy metals and metalloids adsorption. WTRs are mesoporous material with large specific surface area, exceeding 130 m²/g. Therefore, the textural parameters of WTRs make them comparable to common adsorbents.

The maximum sorption effectiveness of Cd(II), Pb(II), Cu(II), Zn(II), As(V), Cr(III), Cr(VI) and P(V) reached 78, 82, 75, 91, 65, 74, 86 and 66%, respectively. The effectiveness of heavy metal adsorption by WTRs in all cases increased with initial metal concentrations. The cations immobilization by WTRs was favored by higher pH (9.0-11.0 pH), whereas anions were preferably adsorbed at lower pH (3.0 - 5.0). The adsorption capacity increased with time, within the first hour, the majority of heavy metals in the solution had been adsorbed.

This study indicates that adsorption onto WTRs could be a viable technology of heavy metal removal from aqueous solutions. The sorption depended on the initial concentration, reaction time and pH values. Additional research is planned to determine sorption mechanisms and desorption efficiency.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Secondary processes in the Eoarchean Isua supracrustal belt – clues from chlorine isotopes, TEM and CL studies of apatite

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The Isua supracrustal belt is a unique Eoarchean geological formation located in SW Greenland. Rocks representing banded iron formations, metacarbonates and mafic intrusions were sampled in these outcrops, allowing us to explore Archean Earth remnants. Many studies have already investigated both primary and secondary processes occurring in this area (e.g. Lepland *et al.* 2002), but further research with innovative approaches and new analytical methods should bring us closer to understanding key facts about the early Earth.

We have undertaken a study of apatite crystals from Isua rocks in order to describe secondary processes influencing Isua's primary abiotic environment, which may have been a home for evolving life. Using isotopic signatures (37 Cl/ 35 Cl ratios measured by secondary ion mass spectrometry) and imaging at the micro- and nano-scale (cathodoluminescence and transmission electron microscopy) we have investigated apatite crystals in great detail. These analytical methods have allowed us to evaluate previous findings on the origin of apatite crystals and their subsequent alteration histories (Wudarska *et al.* 2018). From the comparison of our data set with an earlier study of 37 Cl/ 35 Cl in Proterozoic apatite by Kusebauch *et al.* (2015) we conclude that chlorine isotope data are useful for the assessment of samples originating from the same geological context and should rather not be applied to any intercomparisons of specimens from differing localities.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Petrography and provenance of sandstones from architectural details from south-western Poland – preliminary results

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Petrographic analyses are used not only in widely understood geological sciences. Their application can be more unobvious and serve - among others - for the monument conservation. Mineralogical and petrographic studies allow to determine the possible provenance of natural rocks used in historic buildings, enabling the most accurate selection of material used in the renovation of monuments. Presented researches are preliminary analyses of samples of historic building material, taken from selected architectural details from Western and South-Western Poland (voivodeships: Lower Silesia, Lubusz, Greater Poland). Seventeen samples were obtained from: the Elizabeth of Hungary basilica in Wrocław, the General House of the Ursuline Sisters in Wrocław, the St. John Nepomucene monument in Patnówek, the St. John Nepomucene monument in Słone, the Siecieborzyce palace, the lapidarium in Kożuchów, the castle in Siedlisko and the parish church in Kostrzyn Wielkopolski. All analyzed samples are quite similar to each other and represent fine and medium-grained quartz sandstones with a slight content of lithic fragments and feldspars, with silica-clay binder. Preliminary studies allow to state that these sandstones are petrographically similar to upper-Cretaceous sandstones, occurring and exploited in the North-Sudetic Basin and Intra-Sudetic Basin. Due to the petrographic features, as well as historical data and the proximity of the sources of the raw material, it can be concluded that the samples come from the North-Sudetic Basin. Sandstones from the Intra-Sudetic Basin often contain considerable amounts of feldspar or are characterized by a strongly developed silica binder, while the mixed, silica-clay binder observed in the studied samples is typical for the stones from the North-Sudetic Basin (Labus 2009, Ehling 1999).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Interpretation of discordant detrital zircon ages from the Southwestern Basement Province of Svalbard

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Detrital zircon geochronology based on concordant (or nearly concordant) dates proved to be an important tool in the provenance studies. However, dates that are usually rejected due to their significant discordance may also provide valuable information about the tectonometamorphic evolution of the studied units.

Neoproterozoic metasedimentary units of the Southwestern Basement Province of Svalbard: the Pinkiefjellet unit of Prins Karls Foreland, the Deilegga Group of Wedel Jarlsberg Land and the unnamed unit of Sørkapp Land revealed major late Paleoproterozoic to early Neoproterozoic detrital zircon signatures. Plotting of rejected zircon analyses, forming regression lines with clear upper and lower intercepts, gave following results: the Pinkiefjellet unit - 1310 Ma to 360 Ma; the Deilegga Group - 1730 Ma to 640 Ma; the unnamed unit of Sørkapp Land - 1710 Ma to 370 Ma. Lower intercept of the discordant zircons from the Pinkiefjellet unit is interpreted to be related to the Pb-loss caused by Ellesmerian metamorphic event (Kośmińska et al. 2016). Metamorphic age of the unnamed unit of the Sørkapp Land is not known yet, but the calculated lower intercept is comparable to the one obtained for the Pinkiefjellet unit. Discordant zircon grains of the Deillega Group are characterized by Pb-loss at ca. 640 Ma, which may represent the first geochronological evidence for the Torellian metamorphism recorded in the low grade metasediments of Wedel Jarlsberg Land. This lower intercept is similar to monazite ages (ca. 640 Ma) obtained for the amphibolite facies Isbjørnhamna Group of Wedel Jarlsberg Land (Majka et al. 2008).

The discordant detrital zircon geochronology provides an independent confirmation of the already recognized Ellesmerian metamorphism in the Pinkiefjellet unit. The first evidence of Torellian event in the Deilegga Group, and Ellesmerian event in the unnamed unit of Sørkapp Land should be however treated with caution and requires further verification using other geochronological methods.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Lithospheric mantle underlying Northern Phyllite Zone of Variscan orogen in Europe: Nidda (Vogelsberg) case study

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Vogelsberg (Central Germany) Cenozoic volcanic field is a part of CEVP, situated at the northern prolongation of the Upper Rhine Graben towards the Hessian Depression. NW part of the Vogelsberg is underlain by the Rheno-Hercynian Variscan basement, central part by that of the Northern Phyllite Zone and the SE part by the Mid-German Crystalline High. Peridotite xenoliths from the Nidda basanite provide information about lithospheric mantle beneath the Northern Phyllite Zone.

The Nidda xenoliths (3-8 cm in size) are clinopyroxene-poor spinel lherzolites and spinel harzburgites of protogranular and porphyroclastic textures (sensu Mercier & Nicolas, 1975). Forsterite content in olivine defines two groups of xenoliths: A (Fo 90.4-91.5 %) and B (Fo ~89.5 %). Pyroxenes in both groups display high Mg# (0.894-0.925). Orthopyroxene from group A contains 0.10 to 0.23 atoms of Al pfu (per formula unit), whereas clinopyroxene contains 0.09-0.28 atoms pfu. Spinel Cr# ranges from 0.14 to 0.57. The xenoliths of group B contain Al-rich orthopyroxene (0.15-0.20 atoms pfu) and clinopyroxene (0.20-0.27 atoms pfu). Spinel in group B peridotites has Cr# 0.21-0.22 and Mg# 0.77-0.80. All xenoliths fall in the OSMA field in the olivine Fo - spinel Cr# diagram (Arai 1994). The group A clinopyroxene exhibits two types of REE patterns: (1) flat or slightly LREE-depleted and (2) slightly LREE-enriched. Clinopyroxene of group B xenoliths is enriched in LREE relative to HREE. All orthopyroxene REE patterns show enrichment in HREE relative to LREE.

Group A peridotites include one sample of primitive harzburgite only slightly affected by metasomatism and a set of peridotites exhibiting increasing degree of chromatographicstyle metasomatic alteration, manifested by a gradual change of Al content in pyroxenes and spinel and varying REE characteristics. Group B peridotites are similar to those of group A in terms of Al content in pyroxenes and spinel and REE patterns.

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XXVth Meeting of the Petrology Group of the Mineralogical Society of Poland

Field trip guide

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Cretaceous joint sandstones from the North-Sudetic Basin (quarries in Lwówek Śląski) – their exploitation and history of use

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Lower Silesia is one of the richest regions in Poland in terms of the presence of building stones. Numerous granite and sandstone quarries, as well as marble and basalt quarries have contributed to the development of Silesian stonemasonry over the centuries. One of the most widely used construction materials in the area were Cretaceous joint sandstones (Szczepaniak 2015), occurring in the Intra-Sudetic Basin and the North-Sudetic Basin. The reason for this were their aesthetic values, technical parameters and economic criteria (proximity of the source of the raw material, short transport, easy accessibility). Examples of the use of Cretaceous sandstones in historical buildings can be admired to this day, most of all, in the area of Lower Silesia, Lubusz and Greater Poland voivodeships and in the present territory of Germany.

The upper-Cretaceous sandstones from the North-Sudetic Basin (area located between Bolesławiec and Lwówek Śląski) developed in Cenomanian, lower and middle Turonian and middle Conacian (Milewicz 1961). Traditionally, they are divided into lower-, middle- and upper joint sandstone (Labus 2009).

The lower-Cretaceous sandstones of the Cenomanian age, referred to as Lwówektype sandstones (Ger. Löwenberger Sandstein), occur directly in the vicinity of Lwówek Śląski (Ehling 1999). They are characterized by a bright colour (gray, yellow, almost white). They are usually medium-grained to coarse-grained, with a silica-clay binder, and composed mostly of quartz, with sparse lithic fragments and feldspar (Fig. 1A).

The middle joint sandstone (Płakowice-type, Ger. Plagwitzer Sandstein) are Turonian age (Ehling 1999). They were exploited in Płakowice (now a district of Lwówek Śląski) near Lwówek Śląski and Jerzmanice near Złotoryja. They are medium-grained to coarse-grained or unequally grained, with a silica-clay cement, light gray or light yellow in colour. The mineral composition is dominated by quartz with less common lithic fragments and sparse feldspar (Fig.1B).

The upper joint sandstones of the Conacian age are still exploited in numerous quarries (including Czaple, Rakowiczki, Żerkowice, Wartowice) and referred to as the Rakowice-type (Ger. Rackwitzer Sandstein; Ehling 1999). They are quartz sandstones, fine-grained, equigranular, light-gray, yellowish, sometimes brown in colour, which is associated with the presence of Fe-minerals in the cement. The mineral composition of these sandstones consists mainly of quartz (Fig. 1C).



Fig. 1. Microscopic view (cross-polarized light) of: A) Cenomanian, Lwówek-type sandstone (outcrop Szwajcaria Lwówecka); B) Turonian, Płakowice-type sandstone (abandoned quarry in Płakowice-Skałka); C) Conacian, Rakowice-type (working quarry in Rakowiczki).

An attractive place to admire outcrops of Cenomanian sandstones are the rocks located in the southern part of Lwówek Śląski. A group of sandstone rocks, available for tourist traffic, form interesting rock formations and labyrinths, and were created as a result of former exploitation and selective weathering (Fig. 2). This group of rocks is called the



Fig. 2. The Szwajcaria Lwówecka – a group of sandstone rocks in Lwówek Śląski.

Sandstones from Lwówek Śląski have been used since the 15th century (Ehling 1999). The first report in written sources was given by the Jesuit father Zeplichal in 1773 (Walendowski 2010). Over the next centuries, they were used in numerous monuments of the region, including the construction of city walls and the church in Lwówek Śląski and the church in Bolesławiec (Ehling 1999). Window frames of the Renaissance town hall of Poznań (XVI century) were also made of these rocks (Walendowski 2010). Probably, these rocks were used in the Szwajcaria Lwówecka (Lwówek Switzerland).

The rocks themselves are located within the Bóbr Valley Landscape Park, belonging to the Natura 2000 ecological network. One of the reasons for establishing the park was to preserve the geological and geomorphological diversity of this area, including numerous rock formations and outcrops. Located adjacent to the Szwajcaria Lwówecka the Wzgórze Kombatantów (the Veterans' Hill) is a wall of an old quarry (Fig. 3).



Fig. 3. Obelisk on the Veterans' Hill (Buchholz) in Lwówek Śląski - archival photo, 1910 (after: polska-org.pl)

construction of some of the monuments of Wrocław, including architectural details from the St. Mary Magdalene cathedral.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Old Copper Basin – Polish Copper before the age of KGHM

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Introduction

This stop of the trip is dedicated to historical metal smelting and its remnants present in the area of Leszczyna vicinity. A short walk through Dymarki Kaczawskie park, located in Kaczawskie Foothills will allow seeing what is left of historical mining and smelting as well as allow to understand why this was an area of extensive copper production. During lecture, a geological setting will be introduced, together with some of the theories of the copper mineralisation origin. Signs of exploitation are still present in the area's morphology and some of the forms will be presented. Remnants of metal smelting will remain of the main concern. We will shortly introduce the process of metal smelting associated with generation of pyrometallurgical slag and describe the resemblance to natural rocks. In addition, the environmental impact of slag discharge in the area and of its use in local buildings will be explained.

Geological setting

Old Copper Basin is located in south-western Poland in the Sudetes Mountains. Leszczyna and Kondratów are two villages in Kaczawskie Foothills, south-eastern part of the North-Sudetic Basin (Fig. 1) This unit was formed within the metamorphic rocks assigned to the Kaczawa Metamorphic Unit. Distinct structure of the North-Sudetic Basin is a result of deformation of its infill and inversion of the basin. This process led to reactivation of previously existing fault surfaces and creation of new tectonic structures at the end of the Cretaceous (Solecki 2011).

Early Palaeozoic metamorphic rocks appear in the base of the Leszczyna Half-graben. The filling is dominated by Permian and Mesozoic sedimentary rocks. It is a story of repeating transgression and regression of the Zechstein Sea, especially in Early Zechstein, when dolomites, limestones and calcareous mudstones were deposited. This episode was subsequent to Gondwana deglaciation, subsidence of the Zechstein Basin and removal of barriers separating the area from the Arctic Sea (Oszczpalski, Rydzewski 1987). In the Late Zechstein a type of sedimentation changed slightly and besides calcareous mudstones and dolomites, sandstones were deposited too. Various type of the Zechstein Sea-related sedimentation was associated with sea's wide range and its edge present on the surface of the North-Sudetic Basin.

Copper deposits are genetically connected with those of the New Copper Basin (Fore-Sudetic Monocline) in Poland where current copper exploitation is carried out. Deposits of a strata-bound type are one of the oldest in the world and they occur generally within Upper Permian sedimentary rocks, mostly black shales and marls as well as limestones and dolomites. Copper mineralisation is epigenetic and related to the activity of two brines with different chemical and physical parameters (Kucha and Pawlikowski 2006). The mineralisation is related to the Zechstein Kupferschiefer formation.



Fig. 1. Setting of the Zechstein Kupferchiefer Copper ores in Poland (after Stolarczyk et al 2015)

Historical background

There are numerous traces of historical mining and metal smelting in the Sudetes Mountains. One of such areas is the Old Copper Basin. Earliest findings of mining in the area are dated back to the 13th century AD (Stolarczyk et al. 2015). Within this period gold and silver were exploited in the vicinity of Złotoryja. First official attempts of copper mining took

place around the 15th century in Złotoryja area. Soon the exploitation started in the Leszczyna Semi-graben – in Kondratów, Prusice, Leszczyna and Nowy Kościół. Exploitation of Copper ore shales and marls of Zechstein Kupferschiefer formation had been conducted on a small scale for several centuries since the beginning of 16th century. In 1505 first official agreement confirming mining has been released for the lord of the Nowy Kościół to open the first mine in Kondratów. In 1541 Gottes Galbe mine was opened in Kondratów. After 28 years of exploitation, it has been abandoned until the 18th century when numerous mine shafts, as well as a smelter, were re-opened (30's-50's of the 18th century). Mining in Leszczyna has been confirmed since 1661. As the ore was not rich and thick enough, the process was problematical. With new investors, several quarries opened up but failed after a few decades. Within most successful ones Character (17th century), Leszczyńska (17th century) and Stilles Glück (19th century) mines shall be mentioned. Similarly, metal smelting was established a couple times but was most successful with Stilles Glück smelter, working with a mine of the same name.

Post-mining geomorphometry

The recent LIDAR-based geomorphometric analyses distinguishing allowed numerous depressions, sinkholes, quarries as well as dumps and post-flotation tailings (Kowalski et al. 2017). Some mines and mine shafts are still preserved in fairly good condition and most of the forms are well visible using high-resolution models (Fig. 2). With its analysis, it is possible to distinguish changes in the type of mining process. The oldest sinkholes dated possibly even to 13th century result from small-scale vertical exploitation. With technological development, required for exploitation of deeper ores, more advanced mines of marls and limestones were opened.



Fig. 2. Shaft and pits of the Stilles Glück Mine in Leszczyna (Kowalski et al. 2017)

Metal production and smelting wastes

During the pyrometallurgical process of metal smelting, two types of material are produced – metal matte and sulfide-bearing residue called slag. This waste is not as heavy as the matte is, and for this reason, it is removed from the furnace during smelting thus separating two products. The viscosity of hot slag reminds a flowing lava. After cooling and crystallisation it forms hard and stable blocks of various shapes (e.g. Fig. 3). These wastes are important research material as they carry a lot of information regarding the smelting process as well as can create an environmental threat.

The chemical composition of slags from Leszczyna Sami-graben is dominated by silica, lime, alumina and iron with a minor contribution of potassium and magnesia. The composition is rather average but specific for a low amount of silica (less than wt 50%) and relevantly high amount of potassium (about wt 5%). Average Cu concentration exceeds wt 1% and reaches up to wt 4.5%, reminding the amount of Copper in the ore. Major phases are represented by silicate glass and silicates (e.g., leucite, various pyroxenes, melilites, anorthite). The most important constituents are metallic phases such as droplets of metallic Cu, chalcocite, pyrrhotite and bornite, due to their high metals content and susceptibility to weathering.

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Fig. 3. Slag wall in Leszczyna

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Geologic and historic heritage of Grodziec - a castle on a volcano

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The geology

The most recent volcanic activity in Central Europe took place in Cenozoic times. It was related to uplift and rifting of Variscan basement in the foreland of Alpine orogen (Wilson, Downes 1991). Rocks of that age are collectively termed Central European Volcanic Province (CEVP); its eastern limb comprise volcanic rocks related to Eger (Ohře) Rift in the Bohemian Massif and those occurring along the Labe-Odra fault system, located to NE of the Rift (Ulrych et al. 2011). Volcanic activity in SW Poland occurred in three main



Fig. 1. Findings of prehistorical ceramics in Grodziec.

episodes: (1) Oligocene (30–26 Ma), (2) Oligocene- Miocene (22–18 Ma), and (3) Pliocene (5.5–3.8 Ma). Around 3% of the mafic rocks bears xenoliths of mafic and ultramafic rocks and megacrysts of clinopyroxene.

Basanite forming volcanic plug in Grodziec village is 32.16 ± 1.37 Ma (K-Ar ages, Badura et al. 2006) and carries numerous ultramafic and mafic xenoliths and megacrysts. The volcanic rocks are underlain by Triassic sandstones and Permian carbonates of the North Sudetic Basin. Top of the Grodziec plug is crowned by a castle.

The castle

Grodziec hill has a shape of cone with cut top. The flat area was used to build the first, Medieval castle. But primarily the hill might have other shape. The surrounding of the castle is covered by a mixture of basaltic pebbles and clays in which parts of Primeval and Medieval ceramics were found (Fig. 1). Those archaeological findings suggest that Grodziec was a settlement from ancient times and that the uppermost part of the hill might have been aligned before building of the medieval castle, but probably after the existing of castellany stronghold (mentioned for the first time in the year 1155). Pieces of basalt gained during the construction works were used to build (and rebuild in later ages) the castle. Nowadays, the most beautiful examples of mantle xenolith and megacrysts from Grodziec may be observed in walls of the castle and surrounding buildings (Fig.2).



Fig.2. Xenoliths in the wall of Grodziec castle.

The xenoliths

Xenoliths occurring in the Grodziec basanite comprise of samples of upper mantle (peridotites) and of pyroxenitic veins cutting the mantle and lower crust (Matusiak-Małek et al. 2017). Xenoliths from Grodziec may be considered as a typical representatives of ultramafic rocks from SW Poland and Germany.

Due to the content of Fo in olivine, peridotites (mostly harzburgite) are divided into groups: $A - Fo_{89-92}$ and B-Fo₈₄₋₈₉. Peridotites classified as group A

correspond to the characteristics of a typical residual mantle, so-called OSMA (Olivine-Spinel Mantle Array, Arai, 1994; Fig. 3). Pyroxenites were classified as a group C. This compositional variation is typical for xenoliths from Eocene-Miocene basaltoids in SW Poland.

Differences between groups visible in the chemical composition of olivine are followed also by different values of Mg# and the content of major in pyroxenes and Cr# of spinel. In a scale of whole the region of SW Poland and E Germany a strong variability is visible also in the content of trace elements in clinopyroxene; two main REE patterns were described in group A clinopyroxene: U-shaped (enrichment in LREE, impoverishment in MREE) and S-shaped (enrichment in LREE, with deflection at Pr or Nd), in group B all clinopyroxene is characterized by the S-shaped pattern. The Mg# values in clinopyroxene with the U-shaped REE diagram are always elevated (above 0.92).

Lithospheric mantle beneath SW Poland suffered from significant (15- 30%) depletion in basaltic component. The mantle was subsequently affected by chromatographic



Fig. 3. Chemical composition of olivine and spinel forming xenoliths from SW Poland. Olivine-Spinel Mantle Array (OSMA) field after Arai 1994.

metasomatism by CO₂-bearing alkaline silicate melt related to Cenozoic volcanic activity. In this model, pyroxenites represent direct precipitates from the metasomatic melt, while groups B and A record composition of mantle rocks metasomatised at decreasing melt/rock ratios (Fig. 4). During metasomatism a secondary clinopyroxene was crystallized into the peridotites. Locally, reaction metasomatic agent triggered with formation of replacive dunites. Despite numerous local modifications, this model seems to be applicable to the entire lithospheric mantle beneath northern margin of Bohemian Massif.



The limestones

Grodziec is known not only for basalts. The village is a historic locality for excavation of Permian limestones of the North Sudetic Basin. The limestones in this area were calcinated from at least XVII century till (probably) the beginning of XX century. The exact purpose of production of lime is not known, but no trace of metal smelting have been found so

Fig. 4. General model of evolution of lithospheric mantle beneath SW Poland.

far. Therefore, the lime was probably used for construction works of nearby grange. The lime might have also been used as a soil fertilizer in cropping white beetroot (Malec, 2004) during Napoleon's time when embargo was imposed to cane sugar.

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Authors' Index

Α

ANCZKIEWICZ Robert, 82 ARADI László Előd, 72

В

BAGIŃSKI Bogusław, 37, 49 BAJDA Tomasz, 54, 88, 92 BAŁAGA Karolina, 48 BARKER Abigail K., 29, 46 BARNES Christopher, 30, 36 BARNES Jaime D., 49 BARON Justyna, 17, 70 BARTZ Wojciech, 31, 94, 99 BAZARNIK Jakub, 32, 60 BIRSKI Łukasz, 33, 53, 82, 93 BŁASZCZYK Mieczysław K., 34 BOROWSKI Michał P., 49, 61 BUCHA Michał, 34, 67 **BUCZKO Daniel**, 35 BUKAŁA Michał, 30, 36 BUTLER lan, 45

С

CEGIEŁKA Małgorzata, 37, 38 CHACHLIKOWSKI Piotr, 31 CHMIELEWSKI Andrzej, 39 CHOJNACKA Aleksandra, 34 CIĄŻELA Jakub, 40, 41, 72, 73 CIĄŻELA Marta, 41, 42 CIESIELCZUK Justyna, 43, 44 CUTHBERT Simon, 90 CZERNY Jerzy, 29 CZUPRYT Zbigniew, 32, 40 ĆWIEK Mateusz, 76, 96

D

DETMAN Anna, 34 DĘBIEC Klaudia, 88 DICK Henry, 73 DILISSEN Nicole, 25 DOBRZAŃŚKI Andrew, 45 DOWNES Hilary, 19 DREWNIAK Łukasz, 88 DUAN Haochen, 46 DUCZMAL-CZERNIKIEWICZ Agata, 47 DULSKI Mateusz, 87

Е

ELLAM Robert, 29 ELVEVOLD Synnøve, 32

F

FABIAŃSKA Monika J., 43 FERRERO Silvio, 65 FIEGE Adrian, 40

G

GAIDZIK Krzysztof, 44 GAJEWSKA Katarzyna, 48 GAŁSKIN Evgeny, 87 GAŁSKINA Irina, 87 GARRIDO Carlos J., 25 GIL Grzegorz, 49 GŁUSZYŃSKI Andrzej, 39 GMOCHOWSKA Wiktoria, 50 GOLEN Marcin, 66 GOŁUCHOWSKA Karolina, 29 GORYL Magdalena, 51, 67 GÖTZE Jens, 93 GÓRKA Maciej, 43 GRABARCZYK Anna, 52 GRAD Marek, 23 GRÉGOIRE Michel, 35, 58, 68, 69, 76,96 GROS Katarzyna, 33, 53, 82, 93 GUNIA Piotr, 49 GURGUREWICZ Joanna, 41, 42

Н

HANTLER Aaron, 54 HIDAS Károly, 25 HOLMBERG Johanna, 54 HOLTZ François, 72 HOSKA Natalia, 47 HYCNAR Elżbieta, 80

I

ILNICKI Sławomir, 55

J

JAYANANDA Mudlappa, 82 JĘDRYSEK Mariusz O., 34 JOHANSSON Leif, 69 JURA Dominik, 43

Κ

KAHL Wolf-Achim, 25 KĄDZIOŁKA Katarzyna, 56, 102 KIERCZAK Jakub, 56, 57, 74 **KIRSTEIN Linda**, 45 KLONOWSKA Iwona, 65 KOEPKE Juergen, 40 KOMOROWSKA-KAUFMAN Małgorzata, 92 KOOIJMAN Ellen, 90 KOŚMIŃSKA Karolina, 30, 32, 95 KOWAL-LINKA Monika, 71 KOVÁCS István János, 72 KOWALSKI Aleksander, 102 KOZUB-BUDZYŃ Gabriela, 82 KRUSZEWSKI Łukasz, 64 KUCZAK Artur, 39 KUĆ Paweł, 60 KUKUŁA Anna, 31, 58, 76

L

LADENBERGER Anna, 59 LAZAROV Marina, 40 LENIK Piotr, 60 LEPLAND Aivo, 93 LIPTAI Nóra, 72 LÓPEZ-SÁNCHEZ VIZCAINO Vincente, 25 ŁACIAK Dagmara, 61 ŁESIUK Mariusz, 105

Μ

MA Changqian, 46 MACDONALD Ray, 37 MACIAG Łukasz, 62, 63 MACIOCH Anna, 64 MADEJ Stanisław, 49 MAJKA Jarosław, 29. 30, 32, 36, 65, 90, 95 MANECKI Maciej, 29, 77, 84, 91, 95 MARCINIAK Dariusz, 66, 86 MARTIN Hervé, 82 MARYNOWSKI Leszek, 34, 51, 67, 78 MATUSIAK-MAŁEK Magdalena, 31, 35, 58, 68, 69, 76, 96, 105 MATYSZCZAK Witold, 38 MAZIARZ Paulina, 48 MAZUR Katarzyna, 38 MAZUR Stanisław, 36 MCCLELLAND William C., 32 MEGE Daniel, 41, 42 MICHALSKA Danuta, 85 **MIELECKI** Damian, 34 MIKRUT Jakub, 69 MISZ-KENNAN Magdalena, 43 MORRIS George, 59 MOYEN Jean-François, 82 MUSZYŃSKI Andrzej, 40, 41, 73

Ν

NGWENYA Bryne, 45 NOWAK Kamil, 70 NOWAK Monika, 71 NTAFLOS Theodoros, 35, 58, 68, 69, 76, 96

0

OSZCZEPALSKI Sławomir, 39

Ρ

PAŃCZYK Magdalena, 40 PATKÓ Levente, 72 PAULO Andrzej, 44 PÉCSKAY Zoltán, 71 PĘDZIWIATR Artur, 57 PICHEVIN Laetitia, 45 PIECZKA Adam, 89 PIEPJOHN Karsten, 32 PIETEREK Bartosz, 40, 41, 73 PIETRANIK Anna, 50, 56, 74, 75 PIWOWARCZYK Cezary, 34 POTYSZ Anna, 56 PRUSS Alina, 92 PRZYBYŁO Arkadiusz, 74, 75 PUZIEWICZ Jacek, 35, 58, 68, 69, 70, 76, 96 PUZIO Bartosz, 77, 84

R

RACKI Grzegorz, 44 ROMÁN-ALPISTE Manuel J., 25 ROSS Aidan J., 19 RYBICKI Maciej, 78 RZEPA Grzegorz, 88, 92

S

SACHANBIŃSKI Michał, 49 SALWA Sylwester, 60 SAWŁOWICZ Zbigniew, 79 SCHNEIDER David, 30 SCHRÖDER Christian, 45 SEK Magdalena, 80 SEK Mateusz P., 81 SIKORA Anna, 34 SIKORSKA Magdalena, 44 SIMONEIT Bernd R. T., 34, 67 SIUDA Rafał, 64 SŁABY Ewa, 33, 53, 82, 93 SŁOMSKI Piotr, 83 SMIT Matthijs A., 90 SMOLAREK-ŁACH Justyna, 67 SORDYL Julia, 84 STOLARCZYK Tomasz, 56, 102 SZABÓ Csaba, 72 SZUSZKIEWICZ Adam, 49 SZCZEPANIAK Małgorzata, 85

SZCZEPAŃSKI Jacek, 55, 66, 83, 86 ŚRODEK Dorota, 87

Т

TESSON Pierre-Antoine, 41, 42 TOMANKIEWICZ Angelika, 74 TUCHOWSKA Magdalena, 88 TWARDAK Diana, 89 TYSZKA Rafał, 50

U

UPTON Brian J. G., 35, 68

W

WALCOTT Rachel, 45 WALCZAK Katarzyna, 30, 90 WALUŚ Edyta, 91 WIEDENBECK Michael, 93 WIRTH Richard, 93 WŁODYKA Roman, 44 WOŁOWIEC Magdalena, 92 WUDARSKA Alicja, 33, 53, 93

Ζ

ZBOIŃSKA Katarzyna, 94, 99 ZIELIŃSKI Grzegorz, 60, 75 ZIEMNIAK Grzegorz, 95 ZIMNY Daniel, 47 ZIMNY Marcin, 47 ZIOBRO Małgorzata, 70, 96 ŻABA Jerzy, 44 ŻURAKOWSKA Marta, 85



Zmiana wykończe-nia powierzchni posadzki z groszko-wanej na szlifowaną oraz impregnacja, ranit strzegomski. Jurowiec Postępu 4 (HB Reavis), Warszawa

Renowacja i konserwacja powierzchni z naturalnego kamienia, konglomeratów kwarcowych, szlachetnej cegły, ceramiki i lastrika to istota działalności nowoczesnej firmy Marmor-Glanz.

Jeśli poszukujesz idealnych rozwiązań w kwestii zabezpieczenia kamienia przed wsiąkaniem wody czy też plam, potrzebujesz dokonać ostatnich "szlifów" przed oddaniem pracy – wyrównać powierzchnię, naprawić jakiekolwiek uszczerbki, przeszlifować, przepolerować czy też wyczyścić kamień możesz liczyć na innowacyjne podejście Marmor-Glanz, działającej na niemieckiej licencji.



SZLIFOWANIE DIAMENTAMI

Dlaczego technologie, których Marmor-Glanz używa w procesie odnawiania powierzchni kamienia, sa bardziej efektywne od zwykłego czyszczenia?

W większości przypadków podczas usuwania brudu z kamienia zanieczyszczenia wcierane sa w jego strukture, dajac jedynie pozorny efekt czystej powierzchni.

Marmor-Glanz traktuje kamień za pomocą metody szlifowania diamentami na mokro, bezpyłowo, używając środków opartych na nanotechnologii. Po skutecznym odnowieniu powierzchni zostaje ona zaimpregnowana, co zabezpiecza ja przed wnikaniem brudu, a więc ogranicza konieczność częstego "doczyszczania" (względy ekonomiczne).

Marmor-Glanz z powodzeniem usuwa też graffiti, a powierzchnia zostaje zabezpieczona przed ponowną dewastacją





Indywidualne podejście

Wykonanie każdego zlecenia zaczyna się od wizyty u klienta i sprawdzenia stanu powierzchni, która ma być przedmiotem renowacji. Marmor-Glanz rekomenduje rozwiązanie, które najlepiej sprawdzi się w danym obiekcie i na danej powierzchni. Każdy kamień jest inny i wymaga indywidualnego podejścia, stąd ważny jest dobór odpowiedniej technologii. Zlecenia są wykonywane z zachowaniem porządku w miejscu pracy, tak aby realizacja nie kolidowała z funkcjonowaniem obiektu. Z niemal stuprocentową pewnością można powiedzieć, że Marmor-Glanz wyczyści kamień naturalny i jego sztuczny odpowiednik z każdego zabrudzenia.



Marmor-Glanz Polska WARSZAWA · POZNAŃ ·WROCŁAW · GDYNIA · BĘDZIN biuro@marmor-glanz.pl +48 608 559 399 www.marmor-glanz.pl NEW JXA -8530F PLUS

JEOL Ltd. (President Gon-emon Kurihara) announces the release of the JXA-8530FPlus Electron Probe Microanalyzer (EPMA) equipped with the In-Lens Schottky Plus FEG (field emission gun), to be distributed in January 5, 2017.

Product development background

JEOL commercialized the world's first FE-EPMA, the JXA-8500F in 2003. This highly regarded FE-EPMA has long been used in various fields, such as: metals, materials and geology in both industry and academia.

The JXA-8530FPlus is a third-generation FE-EPMA that comes with enhanced analytical and imaging capabilities, delivered by an improved electron optical system. The In-Lens Schottky FEG combined with new software provides higher throughput. This new cutting-edge FE-EPMA also adopts a highly-expandable multipurpose chamber. Incorporating various functions, the JXA-8530FPlus meets a variety of demands of users while maintaining high stability, thus allowing a wider range of EPMA applications to be achieved with higher resolution.

Main Features

- 1. In-lens Schottky Plus FEG EPMA version.
- 2. Advanced software Flexible WDS configuration
- 3. Combined WDS/EDS system
- 4. Multipurpose chamber
- 5. Powerful clean vacuum system.
- 6. Soft X-ray Emission Spectrometer (SXES).
- 7. miXcroscopy (Correlative microscope)



JEOL

At low kV (5-7kV) with WDS (wavelength dispersive X-ray spectrometer), high probe current, and small probe diameter, the JXA-8530F is capable of extreme elemental analysis of sub-micron areas (approaching 100nm)

This new microprobe will include: 1) Trace Element Analysis Program for simpler, optimized analysis of trace elements including adding data collected from up to 5 spectrometers, 2) Phase Map Maker for automatic creation of phase maps based on principal components, 3) Non-Flat Surface Analysis Program for automated WDS analysis of specimens with surface irregularities and plenty of other new and very attractive feature.



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