## **MINERALOGIA – SPECIAL PAPERS**

## Volume 47, 2017

Abstracts and field trip guide

XXIV<sup>th</sup> Meeting of the Petrology Group of the Mineralogical Society of Poland

Sessions: "Isotopes as tools to understand the Earth and Environment"

Organized by the Mineralogical Society of Poland and the Soil Science Society of Poland

## "Petrogenetical records in phosphates – insights into their formation/transformation processes"

## Organized by the Committee of Mineralogical Sciences: Polish Academy of Sciences

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# INTERTECH POLAND

The XXIV Session of the Petrology Group of the Mineralogical Society of Poland organized jointly with the Subcomission of Micromorphology and Soil Mineralogy of the Soil Science Society of Poland and the Committee of Mineralogical Sciences: Polish Academy of Sciences

The Conference aims to bring together petrologists, geochemists, mineralogists and soil scientists using/interpreting/modeling isotope analyses in their respective fields of studies. The leading theme **"Isotopes as tools to understand the Earth and Environment"** should be a platform to exchange ideas and approaches to solving scientific problems. We hope that this meeting will start new perspective collaborations in the realm of interdisciplinary sciences.

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## General programme of the Conference

#### Day 1: Thursday 19.10.2017

16:00Registration, Icebreaker Welcome Reception17:00-19:00Marzena OLIWKIEWICZ-MIKLASIŃSKA (National<br/>Science Centre),

**Workshop:** "How to successfully apply for NCN grants ?" (in Polish)

#### Day 2: Friday 20.10.2017

8:45 Welcome and Opening of the Conference Session I: "Isotopes as tools to understand the Earth and Environment" 9:00 – 16.00 Oral Session

Keynote presentations:

Ana-Voica BOJAR: Isotopic and mineralogical investigations of hydrated sulfates

Bruno DHUIME, Chris HAWKESWORTH, Hélène DELAVAULT, Peter CAWOOD: New insights on continental growth, the start of plate tectonics and the emergence of the continents

Vojtěch ETTLER, Martin MIHALJEVIČ: Using metal isotopes for tracing the environmental pollution in soils and geochemical archives

Markus EGLI: Dates and rates – cosmogenic nuclides as a tool for soil and landscape processes

 16:30 – 18:00
 Poster Session

 19:00 - ???
 Social Event

### Day 3: Saturday 21.10.2017

Session II: "Petrogenetical records in phosphates – insights into their formation/transformation processes" 9:00 – 11.00 Oral Session Keynote presentation:

Romain TARTESE: Apatite: A fingerprint for the origin of volatiles in the Solar System

#### **Session III: General session**

11.00 – 16.00	<b>Oral Session</b>
16 <b>.</b> 30 – 18 <b>:</b> 30	Poster Session
19:00 - ???	Social Event

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

# **Invited Speakers**

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



#### Isotopic and mineralogical investigations of hydrated sulfates

Ana-Voica BOJAR

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The investigated hydrated sulfates (gypsum, polyhalite) are of Permian-Triassic age and occur in the evaporitic deposits of the Northern Calcareous Alps, Central Alpine Mesozoic, New Mexico as well as the Zechstein facies of Europe.

The present study investigate the isotopic composition of elements as sulfur, oxygen and hydrogen of the sulfate anionic group as well as of water of crystallization. Using appropriate fractionation factors, the isotopic composition of brines was calculated.

Gypsum and polyhalite have different dehydration temperatures. Polyhalite loses crystallisation water at 285°C (Fisher et al., 1996), its structure being more stable than that of gypsum, which loses crystallisation water at 200°C (Kemp, 1999).

Gypsum and polyhalite experienced a complicated thermal history in the Eastern Alps, their isotopic composition reflecting thermal history and different dehydration temperatures. Polyhalites were not thermally overprinted over 285°C, preserved their water of crystallisation and rather (re)crystallized at temperatures between 100°C to 200°C. On the other hand, secondary growth features were described for polyhalite of the Eastern Alps showing recrystallisation younger than Permian. We may assume that during this process reequilibration and /or incorporation of low amount of meteoric fluid took place.

Alpine overprint temperatures were high enough in order to drive dehydration of gypsum to anhydrite. Rehydration to gypsum is possible if fluids are available and temperature decreases under the dehydration limit of the mineral. The calculated isotopic compositions of brine (using the oxygen and hydrogen isotopic compositions of gypsum crystallisation water), indicate that during rehydration/recrystallization calcium sulfate (gypsum, anhydrite) incorporated meteoric water. Those meteoric waters were more depleted in heavy isotopes of oxygen and hydrogen than the present day meteoric water, suggesting cooler conditions and/or higher altitudes.

#### Acknowledgments

We acknowledge CEEPUS mobility grant for Ana-Voica Bojar making possible cooperation with Mass Spectrometry Laboratory, Institute of Physics, Maria Curie-Skłodowska University.

#### References

Bojar, A.-V., Hałas, S., Bojar, H.-P. and Trembaczowski, A., 2017. Late Permian to Triassic isotope composition of sulfates in the Eastern Alps: palaeogeographic implications. Geological Magazine, DOI: 10.1017/S0016756816000996

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



## New insights on continental growth, the start of plate tectonics and the emergence of the continents

Bruno DHUIME<sup>1,2</sup>, Chris HAWKESWORTH<sup>2</sup>, Hélène DELAVAULT<sup>2</sup>, Peter CAWOOD<sup>3</sup>

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The continental crust has evolved over billions of years, helping to create the environment we live in and the resources we depend on. Less than 5% of the geological record consists of juvenile rocks older than 3 Ga and there are no known rocks older than 4.03 Ga. In contrast recent models of continental growth suggest that at least ~60-75% of the present volume of the continental crust had been generated by 3 Ga. Such models imply that large volumes of pre-3 Ga crust were destroyed and replaced by younger crust since the late Archaean.

Our modelling suggests that new continental crust was generated continuously, but with a marked decrease in the growth rate at  $\sim$ 3 Ga. Destruction rates increased markedly at  $\sim$ 3.0 Ga, which we ascribe to the onset of plate tectonics. Over 100% of the present volume of continental crust has been destroyed and recycled back into the mantle since that time, and during the mid/late Proterozoic the volume of continental crust may have exceed its present value.

There is increasing evidence that  $\sim 3$  Ga marked the transition between two different types of continental crust. Continental crust generated before this time was on average mafic, dense and relatively thin (< 20 km). In contrast, continental crust that formed after 3 Ga gradually became more intermediate in composition, buoyant and thicker. The increase in crustal thickness is accompanied by increasing rates of crustal reworking and increasing input of sediment to the ocean. These changes may have been accommodated by a change in the lithosphere strength at around 3 Ga, as the latter became strong enough to support high relief crust. This time period therefore indicates when significant volumes of continental crust started to become emergent and was available for erosion and weathering, thus impacting on the composition of the atmosphere and oceans.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



# Dates and rates – cosmogenic nuclides as a tool for soil and landscape processes

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In the last decades surface exposure dating using cosmogenic nuclides has emerged as a powerful tool in Quaternary geochronology and landscape evolution studies (Ivy-Ochs and Kober, 2008). Cosmogenic nuclides are produced by cosmic rays and accumulate in rocks, sediments and soils. These nuclides can be used as tracers and are widely used to quantify rates of geomorphic processes, such as total denudation and erosion, and to fingerprint sediment sources and sinks. However, unlike many other dating or tracer techniques, methodological assumptions limit their usefulness in geomorphology and soil science.

In this presentation, typical examples from dating, glacier history reconstruction and glacial erosion using in situ produced <sup>10</sup>Be to soil redistribution rates using meteoric <sup>10</sup>Be are presented. Assumptions and related problems are discussed. Cosmogenic isotopes, such as <sup>10</sup>Be, are used to determine rates of soil production, denudation, erosion and chemical weathering. In this context, often steady-state conditions are assumed: the soil or the weathering mantle maintains a constant depth or a constant mass per unit area over time – an approach that has been criticised by Phillips (2010) and Zollinger et al. (2017). Erosion rates, soil thickness and in general weathering vary over time. Using a non-steady-state-approach, additional approaches to determine physical erosion and chemical weathering surface erosion over time and ii) meteoric <sup>10</sup>Be in soils or sediments. Cosmogenic nuclides are a powerful tool to derive dates and rates. However, the limitations and assumptions behind still need to be tested and there is room for further development.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



#### Using metal isotopes for tracing the environmental pollution in soils and geochemical archives

Vojtěch ETTLER<sup>1</sup>, Martin MIHALJEVIČ<sup>2</sup>

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Ore mining and smelting constitutes an important source of the environmental pollution and especially soils represent a sink for metal(loid)s emitted into the environment by these anthropogenic activities (Ettler, 2016). Topsoils are particularly suitable indicators of the extent of contamination near mines and smelters and indicate the key role of prevailing wind direction on the spatial distribution of metal(loid). Dust particles from mining and smelting operations emitted by the smelters are often composed of relatively soluble phases (sulfates, chlorides), which are dispersed by the wind and are deposited into the soils, where they dissolve and released contaminants can be transported downward the soil profiles (Ettler et al., 2011). Contrasting behaviors of different contaminants released from smelter dusts are demonstrated on laboratory and field experiments in soils and indicate that soils from (sub)tropical and semi-arid areas are significantly more vulnerable to this kind of contamination. With a special emphasis on mining and smelting districts in Africa we will demonstrate, how we can trace the sources, the extent and biogeochemical processes in highly polluted soil systems using combination of metal (Pb, Cu) isotopes and concentration patterns of metal(loid) contaminants. Moreover, the application of metal isotopes for the determination of historical patterns of pollution will be demonstrated on geochemical archives in tree rings (pine and marula trees) (Mihaljevič et al., 2011, 2015).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



#### Apatite: A fingerprint for the origin of volatiles in the Solar System

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Apatite  $[Ca_5(PO_4)_3(F,Cl,OH)]$  forms in a wide range of geologic and biologic settings on the Earth. Apatite is also ubiquitous in meteorites sampling undifferentiated chondritic asteroids and differentiated planetary bodies (e.g., McCubbin and Jones, 2015). Therefore, measurements of OH, F and Cl contents in extra-terrestrial apatite have been used to infer the volatile abundances in planetary bodies such as the Moon (e.g., McCubbin *et al.*, 2015), Mars (e.g., McCubbin *et al.*, 2012) and asteroid 4-Vesta (Sarafian *et al.*, 2013), although complex volatile partitioning between silicate melt and apatite may complicate calculations of magmatic volatile budgets (Boyce *et al.*, 2014). In addition, apatite analysis has proved crucial to characterize the H and Cl isotope compositions of bodies such as 4-Vesta (Barrett *et al.*, 2016; Sarafian *et al.*, 2017), Mars (Hallis *et al.*, 2012; Sharp *et al.*, 2016) and the Moon (McCubbin *et al.*, 2015; Barnes *et al.*, 2016). We will review this wealth of recent data in this presentation, and the implications for volatile transport in the Solar System.

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

# Session

# "Isotopes as tools to understand the Earth and Environment"

Organized by the Petrology Group of the Mineralogical Society of Poland and the Subcomission of Micromorphology and Soil Mineralogy of the Soil Science Society of Poland

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



## Exhumation of the (U)HP Seve Nappe Complex, Scandinavian Caledonides - constrained by <sup>40</sup>Ar/<sup>39</sup>Ar white mica geochronology

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Ultra-high pressure (UHP) metamorphic lithologies in the Seve Nappe Complex (SNC) of the Scandinavian Caledonides provide a basis for investigating subductionexhumation dynamics of the Caledonian Orogeny. Exhumation of SNC UHP complexes has recently been hypothesized by the 'vacuum-cleaner' model. Testing of this model requires strategic geochronological studies. Eclogite-bearing metasedimentary rocks of the SNC Vaimok Lens (c. 482 Ma peak metamorphism) are an ideal natural laboratory for such task as they exhibit an exhumation-related foliation, defined by alignment of white mica.

To constrain the timing of exhumation-related deformation, we employed in-situ and single-grain fusion <sup>40</sup>Ar/<sup>39</sup>Ar white mica geochronology on metasedimentary rocks of the Vaimok Lens, targeting the S2 foliation. Six key samples were chosen for dating to encompass a spectrum of deformed rocks across the field area. In-situ results (mean  $\pm 1$ s.d.) demonstrate a strong link between <sup>40</sup>Ar/<sup>39</sup>Ar dates and deformation: relatively undeformed samples with coarse micas yield  $470 \pm 6.3$  Ma; moderately deformed lithologies with 'bent' micas yield  $458 \pm 10.4$  Ma; and highly deformed rocks exhibiting mica-fish structures yield  $447 \pm 7.9$  Ma. These rocks contain retrogressive metamorphic mineral phases, aligned with the S2 foliation, which reflect retrogressive temperature conditions >450-500°C. Thus, we interpret the oldest in-situ dates from the undeformed samples to represent a cooling during exhumation of the Vaimok Lens. In contrast, the relationship between younger <sup>40</sup>Ar/<sup>39</sup>Ar dates and increased strain recorded in the micas indicates <sup>40</sup>Ar/<sup>39</sup>Ar dates were (partially) reset via recrystallization during subsequent deformation. Compared to in-situ results, single-grain fusion provided younger dates for non- to moderately-deformed micas ( $452 \pm 7.8$  Ma,  $443 \pm 5.7$  Ma, respectively) and indistinguishable dates for highly-deformed micas ( $450 \pm 10.1$  Ma). Electron microprobe geochemical maps revealed patchy zoning of elemental Al, Mg, and Ti, resulting from a Bt-after-Ms decompression reaction affecting all mica phases and recrystallization for the deformed mica. We interpret the younger single-grain dates for non- and moderatelydeformed grains to reflect mixing of discrete <sup>40</sup>Ar domains, highlighting the lack of spatial control for the technique.

These results demonstrate the power of in-situ  ${}^{40}\text{Ar}/{}^{39}\text{Ar}$  white mica geochronology and illustrates that the Vaimok Lens of the SNC experienced long-lived ( $\geq 30$  m.y.) exhumation. Such results will provide crucial constraints for testing the 'vacuum-cleaner' model and contribute to our understanding of subduction zone dynamics.

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# U-Pb age constraints on re-equilibration processes in high-U,Th zircon in pegmatite from Piława Górna (the Góry Sowie Block, SW Poland)

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The zircon intergrown with xenotime in pegmatite from Piława Górna (the Góry Sowie Block) was studied with respect to complex texture, and geochronological record in zircon. The zircon (ca. 2000 µm in size) demonstrates ca. 1100 µm wide, patchy zoned core and porous rim. The porosity also developed in the intergrown xenotime and mimics continuity along the zircon rim. The zircon core reflects homogeneous patches or patches with numerous up to several microns-sized inclusions of U, Th-rich phases and up to ca. 50 µmsized inclusions of uraninite. The micro-Raman analyzes revealed increasing broadening of the  $v_3(SiO_4)$  band at ca. 1000 cm<sup>-1</sup> that suggests increasing metamictization from little disordered outermost rim towards amorphous core. The EPMA results indicate high variations of UO<sub>2</sub> (0.28-0.95 wt.% in rim; 2.84-9.62 wt.% in core) and ThO<sub>2</sub> (<0.22 wt.% in rim; 0.33-0.84 wt.% in core) in the zircon. All these results indicate that the zircon domains were affected by a diffusion-reaction process in the core and coupled dissolutionreprecipitation process in the rim. The U-Pb LA-ICP-MS dating of zircon yielded discordant data with upper intercept age of 2086±35 Ma and lower intercept age of 373±18 Ma (n=65; MSWD=5.2). Concerning the youngest ages characterized by <10% discordance, three ages (0.1-2.9% discordant) in the rim yielded concordia age of 382±14 Ma (MSWD=1.4) interpreted as reflecting the timing of complete re-equilibration of the isotopic system due to fluid-mediated coupled dissolution-reprecipitation within the rim. The high radioactivity related to high U-Th concentration resulted in further Pb-loss in the core. The geochronological results strongly contrast with field observations. Although anatectic pegmatite dikes generally discordantly cut the tectonized migmatites and amphibolites related to ca. 380 Ma HT/MT-MP metamorphic event, the morphology, textural features and high-Th,U composition of the zircon suggest its origin related to crystallization in pegmatite at 2086±35 Ma, whereas 373±18 Ma age is related to reequilibration of the whole system (i.e. Pb-loss and annealing).

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# Sulfur isotopes record chalcophile metal transport through the lower oceanic crust: IODP Hole U1473A, Atlantis Bank, Southwest Indian Ridge.

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Primary and secondary transport of chalcophile metals through the oceanic lithosphere control the formation of seafloor massive sulfide deposits. Although, chalcophile elements have been investigated in the upper oceanic crust, little work has thoroughly examined their migration through the lower oceanic crust due to the scarcity of drilled material. In 2016, IODP Expedition 360 drilled the 810-m-deep U1473A hole into the gabbroic lower crust of the Atlantis Bank ocean core complex at the Southwest Indian Ridge (32°42'S, 57°17'E; Ciążela et al., 2016). We selected 100 evenly distributed samples representing the range of lithologies in the drill hole to analyze their metal and sulfur contents and sulfur isotopes.

Sulfur isotopes allow distinguishing between the mantle- and seawater-derived sulfur. While mantle  $\delta^{34}$ S is ~0‰, seawater  $\delta^{34}$ S is ~21‰, which elevates  $\delta^{34}$ S in hydrothermal sulfides to higher values (typically 2 to 9‰). We have so far observed mantle  $\delta^{34}$ S, between -1‰ and 1 ‰, in 37 of 38 samples. These samples contain pyrrhotite-chalcopyrite-pentlandite grains and show low variations in sulfur and metal contents. The only sample with higher  $\delta^{34}$ S (3.8 ‰) is located at 75 mbsf and contains pyrite.

The consistent mineral, trace element, and S isotope composition throughout the hole indicates the predominant role of magmatic processes in the transport of chalcophile metals through the lower oceanic crust. This contrasts with the upper oceanic crust, where hydrothermal fluids play an important role. In Atlantis Bank, the upper crust was removed during detachment faulting, subsequent tectonic uplift and erosion. The pre-erosional high-temperature seawater circulation was likely limited to the upper crust, and later low-temperature fluids did not significantly affect the sulfur and metal distribution.

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#### Lead isotopes and element concentrations as proxy of anthropogenic origin of air pollution in the Sudeten holiday area

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The Sudeten is an important holiday destination for Polish and foreign tourists. In the same time, the vicinity of developing industrial centres put the Sudeten to the risk of air pollution. The presented study is a reconstruction of the changes in air quality during the last 150 years and an assessment of sources (distal vs. local) using two peat cores: from 'Na Równi pod Śnieżka' and from 'Jagniecy Potok' respectively.

We measured concentrations of Pb, Zn, Cu, Cd, Al using ICP-MS. The chronology of the cores was obtained using <sup>210</sup>Pb age-depth modeling. Stable lead isotopes values were obtained by TIMS after ion chromatographic separation. Isotope composition obtained for the peat profile was compared with measurements of local bedrock samples as well as with literature data. The mineralogical composition of the core was also studied using X-ray diffraction of ashed peat and scanning electron microscopy of dry samples.

Total concentrations of Pb, Zn, Cu and Al vary from 1 to 131 mg kg<sup>-1</sup>, 5-104 mg kg<sup>-1</sup>, 0.3-21 mg kg<sup>-1</sup>and 300 – 15 000 mg kg<sup>-1</sup>, respectively (comp. Fiałkiewicz-Kozieł et al. 2015). In 'Na Równi pod Śnieżką' maximum values are reached at ca. AD 1970, together with a maximum of mullite  $(3Al_2O_3 \cdot 2SiO_2)$ , an anthropogenic marker originating from high-temperature coal combustion, which is found starting from the 40 cm in 'Na Równi pod Śnieżką' and from 22 cm in 'Jagnięcy Potok', upwards. The observations conducted by SEM confirm the occurrence of spheroidal aluminosilicate particles (SAP) from 1930', which suggests a supply of lead mainly from coal.

The highest concentrations in the Izery correspond with suggested ecological catastrophe caused by power plants of the Black Triangle. The overall <sup>206</sup>Pb/<sup>207</sup>Pb signature ranged from 1.160 to 1.173 in both peatlands, indicating a main contribution of lead from anthropogenic sources while a contribution of the local rocks seems negligible.

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# Greenhouse gases (CO<sub>2</sub>/CH<sub>4</sub>) as potential indicators of pollutants in local atmosphere: Karpacz city (SW Poland) case study

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The main goal of this study was to investigate the temporal changes of  $CO_2/CH_4$  concentrations and their carbon isotopic composition in the atmosphere of the touristic town of *Karpacz* city (population c.a. 5000 citizens, may increase to 18000 in touristic season). Many authors investigate the atmospheric greenhouse gases as indicators of climate change, but they are also useful tools to assess input of pollutants.

The analyzed area is typical Polish touristic mountainous resort which is characterized by a serious atmospheric pollution problem, especially during the cold season, due to the extensive use of solid fuels. For the purpose of the study two measurement campaigns were carried out in *Karpacz* city: (I) 23-25 February 2017 and (II) 13-15 March 2017. The campaigns were characterized by different synoptic conditions: I campaign – rain, snow and strong gusts of wind, whereas II campaign - lower wind speed, no precipitation, and atmospheric stability during the nights.

Air samples were gathered using personal air samplers and SKC 11 Tedlar bags in 4h intervals. CO<sub>2</sub> and CH<sub>4</sub> concentrations, as well as  $\delta^{13}C(CO_2)$  and  $\delta^{13}C(CH_4)$  were analyzed using G-2201i Picarro CRDS analyzer. During I campaign CO<sub>2</sub> concentrations are avg. 485.3±43 ppm with  $\delta^{13}C$  of avg. -11.4±1.0‰ and CH<sub>4</sub> concentrations are avg. 1906±23ppb with  $\delta^{13}C$  of avg. -37.8±1.5‰. During II campaign CO<sub>2</sub> concentrations are avg. 444.9±13ppm with  $\delta^{13}C$  of avg. -14.0±0.5‰ and CH<sub>4</sub> concentrations are avg. 1965±21ppb with  $\delta^{13}C$  of avg. -48.8±1.8‰. Besides statistical analysis that was conducted for all measured parameters (Spearman's rank correlation coefficient made in Statistica 12.0 software) the binary mixing model (Keeling plots) was constructed for CO<sub>2</sub> and CH<sub>4</sub> for both campaigns.

To sum up, different meteorological conditions in both campaigns are reflected in pollutants character and their temporal fluctuations. The first campaign with dynamic meteorological parameters and lowest air temperature is dominated by fluxes of anthropogenic origin for both analyzed greenhouse gases (mainly derived from coal and wood burning). During the second campaign, despite unfavorable meteorological conditions, carbon dioxide and methane gases had higher concentrations and their isotope composition reflect more natural character (soil  $CO_2$  and bio-origin  $CH_4$ ). Moreover, it should be noted in geochemical/isotope data interpretation, that the air quality depends on local hotspot of atmospheric pollutant, but also on both regional meteorological conditions as well as local scale circulations e.g. inversion layers or gravitational flow-down of air in ventilating the valley and shaping air quality in *Karpacz* city area.

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#### Diachronous metamorphism and exhumation of the Sudety Mts: evidence from monazite geochronology and thermodynamic modeling

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The Sudetes comprise several geological units assigned to Variscan terranes/lithotectonic in Central Europe: Saxothuringia, Bohemia (Teplá-Barrandia) and Moldanubia of Gondwana descent and Brunovistulia that represents a complex borderland of Laurussia. Our new P-T thermodynamic modeling and electron microprobe in-situ Th-U-total Pb monazite dating of metamorphic rocks in the Sudetes and Fore-Sudetic Block were confronted with the published data to provide more details on the diachrony of tectonothermal events related to prolonged and complex development of the Variscan belt.

The monazite geochronology applied to granulites and para- and orthogneisses of the Góry Sowie Massif confirmed a Middle Devonian (~400-380 Ma) age of tectonometamorphic events and justified the assignment to the Bohemian terrane. The comparable dates obtained for distinct, respectively Y-rich and Y-poor monazite zones confirmed furthermore that cooling and exhumation of the Sudetic part of Bohemia occurred by the Late Devonian, ~40-30 Ma earlier than in all other Sudetic units. The monazite ages of adjacent units cluster around ~360 and ~340 Ma. Such two age clusters were found in the Chałupki paragneisses that probably belong to Brunovistulia and in the Stara Kamienica mica schists in the Izera-Karkonosze Massif that belongs to Saxothuringia. Interestingly, polymetamorphosed metapelitic hornfelses in the Szklarska-Poręba Belt in the same massif yielded only single age cluster at ~360 Ma. On the other hand, distinctly younger monazite ages of ~305 Ma were found in metapelites of the Keprník Dome in the Brunovistulian basement. Further study is in progress to clarify the geological meaning of these dates.

Some sheeted granitoid plutons intruded along the terrane boundaries during the Visean and recorded the final displacements between the terranes that converge in the area of the Sudetes. The mineral assemblages and P-T thermodynamic modeling performed on metapelites intruded by 340 Ma Niemcza granodiorites and those adjacent to the  $\sim$ 310 Ma Karkonosze granite indicate that in both units the granitic magmas, while stitching the terrane boundaries, influenced thermally the country rocks at shallow depths corresponding to  $\sim$ 1-2 kbar. All the data concur the polyphase tectonothermal evolution of the Sudetes, which was related to complex, Mid-Devonian to Early Carboniferous terrane juxtapositions in the Bohemian Massif, yet demand further testing and refining the proposed scenarios.

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#### Pb mobilization through annealing in zircon

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Zircon (ZrSiO<sub>4</sub>) has a robust crystal structure and U-Pb dating of zircon is arguably the most versatile technique in identifying multiple episodes of geological activity. However, recent studies have shown that heterogeneous Pb distribution in zircon can compromise U-Pb isotope systematics on the micro- and nano-scale (utilizing secondary ion mass spectrometry, SIMS / nanoSIMS; transmission electron microscopy, TEM; and atom probe tomography, APT). Ancient radiogenic Pb mobility in zircon has been documented in areas around the world, and the nature of retention of radiogenic Pb in zircon affected by metamorphism is not completely understood.

There are two examples where annealing in radiation-damaged zircon produced nanoinclusions of metallic Pb, in the Napier Complex of East Antarctica and the Kerala Khondalite Belt of southern India. In both cases, documented by TEM observations, hosting rocks experienced ultra-high temperature (UHT) conditions (>950C) Both also have yielded zircon ages that suggest growth at high temperatures over periods possibly as long as 100 m.y.

Recent APT studies on zircons from the Jack Hills of Western Australia and Rhodope Metamorphic Complex in Greece have revealed clustering of Pb atoms in metamorphosed zircon, rather than Pb nanospheres. It have been argued that the formation of Pb clusters need not occur under UHT conditions. Various mechanisms of Pb mobilization during annealing, through concentration into radiation-damaged domains or migration of crystal defects, have been proposed.

It is not yet clear how the various types of clustering of Pb atoms in a matrix of damaged zircon relate to the formation of Pb nanoinclusions. However, it is possible that Pb clustering is a precursor of nanoinclusion formation that progresses through extended and/or higher T metamorphic episodes.

Further work is now being conducted by the authors to shed more light on the processes of Pb mobilization in zircon.

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# Meteoric <sup>10</sup>Be in soils – different approaches for understanding erosion and layering

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The meteoric <sup>10</sup>Be is produced in the atmosphere, adheres to ice crystals and deposited at the Earth's surface primarily by rainfall and dry deposition Secondary (or recycled) meteoric <sup>10</sup>Be deposition is associated with dustfall that has previously accumulated <sup>10</sup>Be. Also, meteoric <sup>10</sup>Be can be involved in soil processes as illuviation - adsorbs to fine particles such as clay and relocate with depth. Moreover, <sup>10</sup>Be might be used to asses occurrence of mixing processes (Wyshnytzky et al., 2015) in soils as well as track slope sediments transport (Waroszewski et al., 2017, in press). Knowing concentration of <sup>10</sup>Be and using proper equation it is possible to calculate erosion rates (Zollinger et al., 2015). However, in heterogeneous materials data about meteoric <sup>10</sup>Be concentrations are hard to interpreted. For instance, Waroszewski et al., 2017 (in press) estimated erosion rates in the mountainous soils on 640 – 1020 t km<sup>-2</sup> a<sup>-1</sup>. However, due to different origin of particular soil horizons, rates were recalculated (200 – 410 t km<sup>-2</sup> a<sup>-1</sup>) after excluding surface layers, to better represents reality. Therefore, 10Be should be treated as a perspective tool in soil science but with caution and some certain limitations. This study deals with such examples in a review manner.

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#### Asthenospheric Signature in Mantle Xenoliths from Enmelen, Chukotka, NE Russia

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The late Cenozoic intra-plate Bering Sea Basalt Province (BSBP) comprise 17 volcanic fields that occur on islands in the Bering Sea, on the west coast of Alaska and on the northeast cost of Russia. The lavas are mainly tholeiitic and alkaline olivine basalts with subordinate basanites and nephelinites. The Enmelen volcanic field in east Chukotka, NE Russia, differs from the other volcanic fields in that the majority of the lavas are strongly undersaturated (nephelinites, olivine melanephelinites and basanites) and carry abundant mantle xenoliths.

The xenoliths are mainly fertile spinel lherzolites but few depleted spinel lherzolites occur as well. Based on the bulk rock and clinopyroxene trace element chemistry, the Enmelen spinel lherzolites can be divided into three groups. Group A represents nonmetasomatized xenoliths that have experienced 3-4% fractional melting. Group B is represented by spinel lherzolites that have whole-rock chondrite normalized REE patterns with strongly enriched LREE relative to HREE [(La/Yb)<sub>N</sub>=9]. Their clinopyroxene is also enriched in LREE and plot sub-parallel to the whole-rock REE patterns [(La/Yb)<sub>N</sub>=7]. The lack of hydrous phases suggests that group B has experienced cryptic metasomatism. Group C is characterized by the presence of amphibole. In this group, the clinopyroxene is characterized by the zonation of the LREE. While the chondrite-normalized REE from the core have patterns with depleted LREE, (La/Sm)<sub>N</sub>=0.21, similar to those of group A, the (La/Sm)<sub>N</sub> ratio increases continuously from 0.21in the core to 2.44 in the rim. The introduction of fluids, rich in H2O, LREE, and LILE as well the formation of amphibole must have taken place shortly prior to the transportation of the xenoliths by the host lavas to the surface, since trace element re-equilibration has not been achieved. The clinopyroxene Sr, Nd, and Hf isotope systematics generally overlap the range of MORBs  $({}^{86}\text{Sr}/{}^{87}\text{Sr}=0.70222-0.73100, {}^{143}\text{Nd}/{}^{144}\text{Nd}=0.51303-0.51333 {}^{176}\text{Hf}/{}^{177}\text{Hf}=0.28303-0.28363).$ Consequently, the depleted isotopic compositions coupled with the trace element enrichments suggests that any metasomatc overprint must have been relatively recent. These data collectively suggest that the Enmelen peridotite xenoliths most likely originated from the convective asthenosphere.

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#### U-Pb age of young zircons from a Roxolany tephra (S Ukraine)

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The Pleistocene loess-soil sequence from the Roxolany profile (46°10'N, 30°27'E) forms the Pleistocene subaerial cover of the VII terrace of the Dniester River. It is unique due to the occurrence of a thin layer of volcanic ash, the "Roxolany Tephra", within the upper bed of loess.

The first results of SHRIMP U-Pb analysis performed in the Micro-Area Laboratory (PGI-NRI, Warsaw) of zircons from the tuff indicated ages of less than 1 Ma. Thus, the analyses were repeated for selected, pyroclastic originated zircons with special analytical conditions: 7 scan for each analytical point and longer counting time for <sup>206</sup>Pb (20 s). The ages were calculated separately for each spot using correction for U-series disequilibrium and initial <sup>230</sup>Th. We applied calculation procedure described by Williams et al. (2016) and Li et al. (2017), by which the effects of U-series disequilibrium were calculated from first principles using the equations of Bateman (1910).

The age spectrum obtained for young zircon grains separated from the "Roxolany Tephra" fits very well to the history of the Ciomadul volcano in the Romanian Eastern Carpathians postulated by Wulf et al. (2016).

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# Nickel isotope fractionation during weathering of ultrabasic rocks and Ni lateritic ores smelting

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Weathering of ultrabasic rocks under temperate climate leads to incomplete hydrolysis of silicates. On the contrary, complete hydrolysis observed under tropical conditions leads to the formation of lateritic profile with high Ni content. Therefore, laterites are extensively mined for Ni and used in metallurgical processes. The aim of our study is to determine Ni isotope fractionation during weathering of ultrabasic rocks under temperate climate and Ni

The studied serpentine soils (Leptosol, Cambisol) formed under temperate climate are derived from serpentinized peridotite (the Szklary Massif) and serpentinite (Jordanów). The serpentinized peridotite has a lighter isotopic composition ( $\delta^{60}$ Ni) compared to serpentinite (0.13 ± 0.06‰ and 0.20 ± 0.06‰ respectively). Soil horizons in the Szklary Massif are isotopically lighter compared to the parent rock ( $\Delta^{60}$ Ni<sub>soil-rock</sub> up to -0.22‰). Similar trend is observed in Bw and BwC horizons in Jordanów except to the surface horizon ( $\Delta^{60}$ Ni<sub>soil-rock</sub> = 0.12‰). Nickel extracted by DTPA-CaCl<sub>2</sub> in the Szklary Massif presents heavy isotopic composition compared to the soil ( $\Delta^{60}$ Ni<sub>DTPA/CaCl2-soil</sub> up to 0.74‰), while in Jordanów, the  $\Delta^{60}$ Ni<sub>DTPA/CaCl2-soil</sub> is more variable. The Ni isotope signature ( $\delta^{60}$ Ni) for Ni-bearing silicate ores from the Szklary Massif is 0.46 ± 0.05‰. Furthermore,  $\delta^{60}$ Ni for pyrometallurgical slags, a by-product of Ni laterites smelting ranges from – 0.22 ± 0.05‰ to 0.55 ± 0.06‰.

Our results demonstrate that weathering of ultrabasic rocks could lead to the removal isotopically heavy pool of Ni (at least in the Szklary Massif) confirming previous results in other ultramafic areas. Furthermore, one may consider that decomposition of organic matter could be responsible for heavy isotope signature of soil from surface horizon in Jordanów. Moreover, other factors such as pedogenesis or types of Ni-containing secondary minerals may affect the biogeochemical cycle of Ni. The variability in  $\delta^{60}$ Ni in slags could reflect changes in smelting techniques and yields or stages of Ni smelting (Kierczak et al., 2009).

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#### Layer boundaries attract sulfides throughout the igneous layering of the lower oceanic crust: IODP Hole U1473A, Atlantis Bank, Southwest Indian Ridge

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IODP expedition 360 drilled 810-m-long Hole U1473A into the gabbroic lower crust of the Atlantis Bank oceanic core complex at the Southwest Indian Ridge (SWIR, 32°42'S, 57°17'E; Ciążela et al., 2016). Coarse-grained (5-30 mm) olivine gabbro prevails throughout the hole, ranging locally from fine- (<1 mm) to very coarse-grained (>30 mm). Several zones of a distinct grain size and modal igneous layering were found within the hole. Notably, the layer boundaries seem to be enriched in sulfides as observed during shipboard core description. To verify these observations, we studied the bulk-rock Cu and S contents, S isotopes and minerals of three zones around layer boundaries.

Bulk rocks enclosing coarse- and fine-grained gabbro within 5 cm from the layer boundaries contain on average 1010 ppm S. In contrast, fine- and coarse-grained gabbro located ~10 cm away from the layer boundaries contain only 720 and 585 ppm S, respectively. The average S content across the entire hole is 673 ppm. The transitional zones between the layers are also enriched in Cu (265 ppm) with respect to the fine- and coarse-grained gabbro away from the layer boundaries (119 and 72 ppm Cu, respectively). The average Cu content across the hole is 84 ppm. As revealed by optical microscopy and image analysis, thin sections crosscutting the layer boundaries show more sulfides (~0.75 vol.% for fine- and ~0.37 vol.% for coarse-grained gabbro) than those non-cross-cutting the layer boundaries (~0.57 vol.% for fine- and ~0.27 vol.% for coarse-grained gabbro).

All the investigated samples contain pyrrhotite-chalcopyrite-pentlandite grains exsolved from former monosulfides and show mantle-derived  $\delta^{34}$ S signature of ~0‰. Although both features indicate igneous origin of sulfide enrichment, its exact mechanism is yet difficult to understand. This Autumn, we plan to investigate the major and trace element, and S isotope composition of the inherent sulfides *in situ* to better constrain their formation.

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# The Wilkow syenite – the unique remnant of the 380-360 Ma magmatic event at the Gondwana north-eastern margin

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Ultrapotassic magmatism is widespread in Variscan Europe and marks the post-collisional episode during the major stage of Gondwana and Laurasia collision. The ultrapotassic rocks are dated at 330-350 Ma (U-Pb and Pb-Pb in zircon), which contrasts with the Wilkow syenite dated in this study at ca. 370-380 Ma. The syenite is, therefore, a remnant of an early variscan subduction at the Gondwana north-eastern margin. As such, it provides information on crustal and mantle sources at the age that is rarely preserved in the Variscan record. Detailed study of chemical and isotope composition of accessory minerals from the syenite shows that it represents magma composition (not cumulate) and that the magma source was predominately enriched mantle. Similarities between mantle enrichment processes at 370-380 Ma and those at 340 Ma suggest a general process of mantle enrichment by melting of the subducted granulite protolith. As such, the Wilkow svenite can be related to the Gory Sowie granulites, which also yield older ages (360 - 400 Ma)than the granulite metamorphism in other parts of Bohemian Massif. Despite the age difference, the chemical and isotope characteristic of the protholith was similar during both episodes of deep subduction and in both cases the protholith was a part of Gondwana continental crust. However, distinct chemical composition of the studied syenite compared to younger ultrapotassic rocks (high Rb and K as well as low Th/La ratios) distinguish the mantle source form other sources found not only in Variscan Europe, but also in Alpine/Himalaya orogeny. In detail, the reconstructed mantle source for Wilkow syenite has been modified during relatively cold subduction with the overlying ultradepelted mantle modified mostly by fluids. In contrast to Bohemian Massif ultrapotassic rocks, the Wilkow syenite chemical and isotope composition was not modified by later crustal contamination.

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### Sediment dating in artificial acidic lakes – how to overcome disadvantages of lead-210 method

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Lead-210 method is often used to date lacustrine sediment sequences of age up to 120-150 yrs. The method based on direct or indirect (via <sup>210</sup>Po, assuming its isotopic equilibrium with <sup>210</sup>Pb) measurements of <sup>210</sup>Pb activity in sediment column. Then, several models of lead deposition can be applied and age of every sample can be calculated. The most popular models are constant rate of <sup>210</sup>Pb supply model (CRS) and constant initial concentration model (CIC). The age of sediment horizons for which <sup>210</sup>Pb activity was not measured the age can be calculated using non-parametric models and curve fitting functions, eg. MOD-AGE algorithm (Hercman et al. 2014). The models work usually well in 'standard' sediment sequences.

However, in some unusually cases, the dating meets several problems. One of them is lead migration along sediment column in extremely acidic lakes. The process manifests with equal lead activity along entire sediment sequence or concentration of lead in deeper horizon, for example on the border of oxygen-anoxic conditions. The process can be identified with independent dating methods, e.g. radiocarbon or cesium-137 stratigraphy.

The other problem with dating of some artificial lake sediments is their too young age. The models of age calculation, applied in <sup>210</sup>Pb method, refer to activity of 'old' sediments (supported or autigenic <sup>210</sup>Pb) origins from radiogenic disintegration of U-series isotopes. In very young lakes (younger than 100-120 yrs.) this activity can not be measured. In such a case, *a priori* information on lake age can be used. Without such data, the level of supported <sup>210</sup>Pb activity can be extrapolate from the total activity of <sup>210</sup>Pb in upper part of sediment sequence. However, this is possible only in sediments with ideal (or close to ideal) exponential decrease in lead activity with depth in sequence.

The third problem is a wrong calculation of supported <sup>210</sup>Pb activity. It is possible when sediment of lake basement (eg. ceramic clays) are consider as a lake sediments and their <sup>210</sup>Pb activity is applied to dating models. This problem can be resolved with carefully examination of sediment lithology and additional analyses, e.g. elemental analysis or biological examination (Sienkiewicz and Gąsiorowski 2016).

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### Dating metamorphic rims using LA-ICP-MS depth profiling technique on zircon from the Snasahögarna diamond-bearing gneiss, Scandinavian Caledonides

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The Scandinavian Caledonides provide a comprehensive record of a Himalaya-type orogen. Of particular interest is the Middle Allochthon, including the Seve Nappe Complex (SNC) that represents the Baltoscandian rifted distal margin zone. Previous age determinations of the SNC (ultra)high-pressure metamorphic rocks yielded ages from c. 500 Ma (Norrbotten) to c. 450 Ma (Jämtland). Ordovician UHPM is recorded in eclogites, peridotites and gneisses of the SNC rocks in northern and central Jämtland. Details about studied here Snasahögarna diamond-bearing gneiss are given by Majka et al. (2014).

Separated zircon grains were relatively small, ranging in length from 50 to 150  $\mu$ m, and mostly subhedral. After mounting in indium, every grain was imaged via SE and BSE in order to avoid crystals regions with apparent fractures or other outgrowths phases. Prepared zircon grains were analyzed with use of the LA-ICP-MS depth profiling technique at the University of New Brunswick, Fredericton, Canada. U-Th-Pb isotopic analyses were conducted simultaneously with trace elements concentration measurements.

Out of the obtained results, we distinguished a group of 11 concordant ages for zircon rims with a mean age of  $458.6 \pm 8.0$  Ma. High Th/U ratios (0.2 - 0.9) of studied zircon rims suggest their crystallization prior to the Th-bearing phases (monazite and allanite). Steep HREE pattern (with an average Lu/Gd ratios of 18) of zircon rims, as well as subhedral external shape of studied zircon grains suggest overgrowths crystallization in the high temperature regime (Rubatto 2017). Therefore we interpret obtained age as reflecting zircon crystallizations under high-grade metamorphic conditions.

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### Peraluminous vein granites from the Suwałki Anorthosite Massif and their tectonic significance – evidence from zircon age study by SHRIMP IIe/MC

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#### Introduction

Suwałki Anorthosite massif (SAM) with associated Fe-Ti-V deposits is a most significant component of anorthosite-mangerite-charnockite-granite AMCG suite widespread within the Mesoproterozoic crust of the Mazury Complex, in the East European Craton (EEC). SAM contains a massive core of anorthosite surrounded by zones of norite, gabbronorite, diorite and "ferrolite" AMCG suite including also ferroan metaluminous A-type granite emplaced between 1.53-1.50 Ga, was there after tectonically overstretched. Much of the fissures that cut the massif were filled by red aplite, fine grained granite and pegmatite intruded after the final stage of SAM formation and its tectonic activation. In this study, zircon grains extracted from granite veins were analysed using ion microprobe (SHRIMPIIe/MC) to determine the age of their crystallization to constrain petrogenesis of the SAM including veins assemblage and to understand their tectonic significance.

#### Results

The aplite and pegmatite from a central part of SAM (Boksze, Udryn, Krzemianka, Jeleniewo drilling) yielded a crystallization age in the range of 1495 ±11 Ma -1488.7 ±4 Ma, that is almost immediately after the last pulses of successive generation of SAM with its associated AMCG suite at 1498 Ma (Filipów). Moreover, most of granite veins have an unusually high proportion of inherited zircon grains. Some of them come directly from AMCG yielding age of cores at 1518 ±9 Ma (Boksze) known from the intrusion of the A-type granitoids, but most of the peraluminous aplites contain inherited zircon cores in the range from 2019±26 Ma to 1815 ±10 Ma and minor group in the range 1774±12 Ma to 1617 ±9 Ma. It evidences directly that magma generation processes included a melting of the proximal Svecofennian host rocks. The emplacement of the widespread granite veins postdating the main ca. 1.53-1.50 Ga tectono-thermal activity in the SAM by ca. 20-25 Myr but pre predating at least by 20 Ma granite magmatism and high-grade metamorphism in southern Fennoscandia (EEC) of Hallandian or Danopolonian event (1.47–1.42 Ga).

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# *In situ* analysis of chlorine and oxygen isotopes in apatite by secondary ion mass spectrometry

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The isotopic analysis of apatite  $Ca_{10}(PO_4)_6(F,Cl,OH)_2$  is a very useful tool for studying geochemical processes on Earth and other solar system bodies. Apatite is not only the most common phosphate mineral in rocks, but it is also an essential constituent of bones and teeth. Therefore, oxygen and chlorine isotopes in apatite have been recently used for investigation of both biological and abiotic processes. Measurements of the <sup>18</sup>O/<sup>16</sup>O ratio in conodonts have allowed for reconstructing palaeotemperatures, reef evolution, and glacioeustatic sea-level fluctuations (e.g., Joachimski *et al.* 2006). Analyses of <sup>37</sup>Cl/<sup>35</sup>Cl ratios have proved valuable in tracing metasomatic processes and fluid-rock interactions (e.g., Kusebauch *et al.* 2015).

Secondary ion mass spectrometry (SIMS) has a major advantage over gas source methods as it provides a means for targeted *in situ* measurements at the microscale, which is an important fact in the case of very small samples. However, SIMS' requirement of homogeneous reference materials (RMs) for quantitative measurements is one of the limitations of this method. Due to the complicated crystal chemistry of apatite, matching chemical composition of reference materials is paramount. Therefore, the aim of our research is to develop a suite of well-characterized reference materials with  $\pm 0.2\%$  repeatability of <sup>37</sup>Cl/<sup>35</sup>Cl and <sup>18</sup>O/<sup>16</sup>O measurements. We have tested 32 samples, provided by mineral collections, using both isotopic (SIMS) and chemical (EPMA) methods. With further determination of absolute  $\delta^{37}$ Cl and  $\delta^{18}$ O values we would like to provide apatite RMs to all interested SIMS laboratories, making the data they generate traceable.

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### Tungsten (W) and its isotopes as geochemical process tracer

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#### Introduction

Stable isotopic fractionation of non-traditional elements (Fe, Zn, Cu, Mo, Hg, U) is well suited to trace particular processes such as metal-silicate differentiation, paleo environment, geochemical processes (alteration, adsorption and co/precipitation). Stable tungsten (W) isotopes have been explored following the recent analytical development, in addition to wide application of radiogenic W isotopes in cosmochemistry. This study is aimed to better understand the W mobility and its isotope fractionation during alteration of silicate minerals, adsorption and co-precipitation with other minerals, thereby, to establish W stable isotopes as a new tracer of geochemical processes.

#### **Materials and Methods**

Anorthite and diopside were chosen for dissolution experiments as plagioclase and pyroxene end-members of silicates. The first set involved the dissolution as a function of pHs (1, 3, 5, 7, 9, 11) under agitation (50 rpm) for 24 hours, whereas the second set involved continuous dissolution with pH drift. Both experiments were performed at a constant liquid to solid ratio (L/S =10), at ambient temperature ( $21 \pm 2$  °C) and pressure (1 atm). In parallel, co-precipitation of carbonates (aragonite, calcite), oxides (scheelite) and adsorption onto goethite have been performed to understand the fate of W as post-alteration conditions.

Element concentrations were measured with a quadrupole ICP-MS, while isotope compositions were determined using a MC-ICPMS. In parallel, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDS), and Raman analyses were used to characterize and compare fresh and altered samples in order to give insights regarding the surface morphology, the mechanisms of alteration, and the formation of secondary mineral phases.

#### Results

Preliminary results show that W being very mobile during alteration with preferential leaching of lighter W isotopes into the solution. Similarly, lighter W adsorbed onto the surface of goethite (FeOOH). On the other hand, heavier W precipitated with CaCO<sub>3</sub> (calcite) and CaWO<sub>4</sub> (scheelite). As W is a heavy mass element, it could alter the nucleation and crystal orientation of carbonate, meaning the crystal structure of aragonite is destabilized, resulting in the formation of rhombohedral calcite crystals.

### XXIVth Meeting of the Petrology Group of the Mineralogical Society of Poland

# Session

### "Petrogenetical records in phosphates – insights into their formation/transformation processes"

Organized by the Committee of Mineralogical Sciences: Polish Academy of Sciences

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



### CL studies of the apatite from Archean Barberton Greenstone Belt

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Apatite is a common accessory phase in many environments. Sedimentary apatite forms from a Ca-phosphate precursors, while magmatic apatite crystallizes from the melt. Therefore characteristics of both types should differ and reflect the signature of the environment of its origin. Moreover, later alteration can also be recorded by apatite crystals. Calcium phosphate crystals found in the rocks of Archean Barberton Greenstone Belt (GB) (3.5-3.2 Ga) might be useful to understand the Early Earth environments. Furthermore, it might help to explain how Life arose on the Earth. It is crucial to point out which apatite crystals preserved original, primordial signature of their origin and which recorded signature of subsequent alterations. Cathodoluminescence (CL) microscopy combined with spatially-resolved CL spectroscopy is suitable to achieve that goal.

Analyzed apatite crystals, at least partially underwent secondary alterations. Furthermore, no clear correlations between environment of origin and the gradation of alterations were observed. Apatite crystals from single rock type can show either advance or initial grade of alterations. Strongly transformed apatite crystals illuminate in yellow, which is associated with lack of emission bands of REE<sup>3+</sup> and therefore dominant role of  $Mn^{2+}$  as the activator. On the other hand, partially altered apatite crystals shows wide range of CL colors; pinkish, violet and green. Locally, crystal edges are yellow which indicates that fluids were altering these crystals, yet to a limited extent. Furthermore, their CL spectra have revealed presence of very sharp emission bands of REE, i.e.  $Eu^{2+}$ ,  $Tb^{3+}$ ,  $Dy^{3+}$ ,  $Sm^{3+}$  and  $Nd^{3+}$ .

Future research of apatite crystals, that underwent alteration to a limited extent, can provide information about the environment of Archean, the time in which Life arose and developed.

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### Two Madagascar monazite crystals as potential reference materials for U-Pb microanalysis

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Two monazite crystals from Madagascar, TS-Mnz (Tsaratanana) and ANK-Mnz (Ankazobe) supplied by a mineral dealer, were evaluated in terms of their potential as reference materials for U-Pb isotope and Th-U-total Pb EPMA dating. These monazites were analyzed for the element and isotope homogeneity utilizing Electron (EPMA) and Ion (SHRIMP) Microprobes combined with micro-Raman.

Monazite TS-Mnz is reddish brown with initial weight of 11.77 g. The TS-Mnz in highcontrast BSE-imaging demonstrates homogeneous, clear domains, and domains including numerous inclusions. The TS-Mnz contains 4.80-9.04 wt.% ThO<sub>2</sub> (average 6.89 wt.%; n = 74), 0.16-0.27 wt.% UO<sub>2</sub> (average 0.21 wt.%) and 0.21-0.38 wt.% PbO (average 0.29 wt.%). Two sessions of the SHRIMP analyses provided concordant  $^{206}$ Pb/ $^{238}$ U ages 894.8±5.3 Ma (n = 25, MSWD = 0.69) and 894.1±5.0 Ma (n = 15, MSWD = 0.76).

Monazite ANK-Mnz is significantly larger, with an initial weight of 278 g. The crystal reveals gem quality, crystal-clear domains (up to several hundred microns-sized), homogeneous in high contrast BSE-imaging; and domains with inclusions. The rim is porous, easy to be recognized and neglected for the standard. The ANK-Mnz contains 5.72-7.62 wt.% ThO<sub>2</sub> (average 6.97 wt.%; n = 40), 0.20-0.34 wt.% UO<sub>2</sub> (average 0.26 wt.%) and 0.14-0.19 wt.% PbO (average 0.17 wt.%). The SHRIMP analyses provided concordant  $^{206}$ Pb/ $^{238}$ U age 517.8±4.4 Ma (n = 22, MSWD = 3.8).

Monazite in nature is compositionally heterogeneous and commonly registers multiple geological processes that occasionally may affect its Th-U-Pb system. Consequently, natural monazite is a difficult material for age standard. Our preliminary results demonstrate that the selected monazite crystals, despite their compositional variations, reveal homogeneous concordant ages and may be considered as new potential age reference materials for U-Pb age microanalysis. Further characterization by LA-ICP-MS and TIMS is going to be conducted for better characterization of these monazite crystals.

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## Stability relations between monazite and allanite during metamorphic processes – new experimental data

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The relative stabilities of monazite and allanite during metamorphism depend on P-T conditions, bulk rock composition and fluids. These relations were recognized in nature and replicated using thermodynamic modeling (Spear 2010) and laboratory experiments (see Budzyń et al. 2017 and references therein). The current study explores relative stabilities of monazite and allanite in the presence of silicate minerals assemblage, approximately replicating metapelitic geochemical environment, and 2M Ca(OH)<sub>2</sub> or Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O fluid, under P-T conditions 200 or 400 MPa and 450, 550, 650, 750°C.

Monazite was altered and allanite/REE-rich epidote formed on the starting monazite and allanite in runs with 2M Ca(OH)<sub>2</sub>. These results partially confirm thermodynamic modeling of Spear (2010) that increased bulk Ca content expands allanite stability field towards higher temperatures. In runs with  $Na_2Si_2O_5 + H_2O$ , monazite was partially altered with formation of REE-rich fluorapatite-fluorcalciobritholite, while allanite alterations resulted in partial- to complete breakdown and replacement by secondary phases, including REE-rich fluorapatite-fluorcalciobritholite. Although high bulk CaO content, the high Na activity in the fluid resulted in allanite breakdown demonstrating that relative stabilities of monazite and allanite strongly depend on bulk CaO/Na<sub>2</sub>O ratio. In opposite to previous similar experiments (e.g. Budzyń et al. 2017), no compositional alteration of monazite with disturbance of Th-U-Pb system occurred in the presence of allanite, which alterations and breakdown utilized aggressive fluid.

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# A phosphate-bearing pegmatite from Michałkowa, Góry Sowie Block, southwestern Poland

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The studied pegmatite is hosted in migmatites and amphibolites of Michałkowa in the central part of the Góry Sowie Block (GSB), the northeastern part of the Bohemian Massif. It crystallized from anatectic granitic magmas, intruded in the younger stage of the GSB metamorphism at ~370-380 Ma. The Michałkowa pegmatite has special significance for mineralogists as the type locality for sarcopside (Websky 1868), maneckiite (Pieczka et al. 2017) and graftonite-(Ca) (Hawthorne and Pieczka, under review). The pegmatite represents the LCT (Lithium-Cesium-Tantalum) phosphate subtype of the rare-element pegmatite class (classification after Nowak 2005). A Another phosphate-bearing pegmatite occurring directly in the GSB is a pegmatite at Lutomia (Włodek et al. 2015). However, besides the same origin of these pegmatites, the phosphates from Michałkowa show lower Mn-Fe fractionation, more advanced metasomatic processes and less advanced hydrothermal alteration in relation to the Lutomia pegmatite. The secondary processes manifest in extensive areas of fine-grained textures after the lamellar and granular textures typical for the primary, magmatic phosphates. At Michałkowa the primary phosphates are represented by monazite-(Ce), xenotime-(Y), fluorapatite, sarcopside, graftonite-(Mn) and graftonite-(Ca), triphylite, hagendorfite group minerals, arrojadite-group minerals, wyllieite-group minerals, johnsomervillieite + sometimes wolfeite. The metasomatic phosphates are represented by alluaudite and ferroalluaudite, wolfeite, wicksite-group minerals, whitlockite-group minerals and lazulite, whereas the hydrothermal and weathering phosphates by ferrisicklerite and heterosite as products of topotactic oxidation of triphilite, members of the phosphoferrite-kryzhanovskite series, ludlamite, jahnsitegroup minerals, beraunite, mitridatite, gormanite, souzalite, childrenite, eosphorite, earlshannonite, phosphosiderite, fairfieldite, dufrénite and Fe-bearthite. The magmatic phosphate assemblage crystallized from hydroxysaline melt separated during cooling from the parental P-bearing anatectic melt; the metasomatic phosphates formed in alteration of the magmatic phosphates under action of HT fluids separated from the hydrosaline melt, and the hydrothermal and weathering phosphates crystallized from hydrothermal solutions or formed by alteration of the primary magmatic and secondary metasomatic phosphates under action of the hydrothermal solutions and meteoric water.

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# Chemical variation of apatite in the igneous rocks of the Niemcza Zone

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Apatite has chemical formula Ca<sub>5</sub>[(F,Cl,OH)/(PO<sub>4</sub>)<sub>3</sub>], but a number of trace elements can be substituted in Ca and P structural sites. The trace element composition can be used to construct discrimination diagrams for apatites from different rock types (Belousova et al. 2002). Also tracing variations in trace element concentration in apatite from core to rim can be used to reconstruct magma conditions (Bruand et al. 2016). The most important trace elements to reconstruct magma conditions are Y, Sr, SREE and these were measured in studied apatite by electron microprobe. The apatite from different granitoid rocks in the Niemcza Zone was analysed to (1) reconstruct magma conditions and magma sources during dioritic and granodioritic magma crystallization and (2) provide general information on factors controlling trace element variability in apatite from different granodioritic to dioritic rocks. The latter problem was dictated by the high compositional variability of granitic sensu lato apatite compared to apatite from other rock types, which can be partly related to different degrees of fractional crystallization and mixing in granitic magmas (Lisowiec et al. 2015). In this study, we focus on three samples (Kośmin granodiorite, Kośmin monzodioritic enclave and Brodziszów monzodiorite). The structural position of apatite is different between the samples. In the Kośmin granodiorite, apatites are contained mostly in amphiboles (70% of apatite population). In contrast, in Kośmin enclave apatites occur mostly in K-feldspar and plagioclase (both about 30%), but not in amphiboles. In the monzodiorite from Brodziszów apatites occur mostly in pyroxenes and at contacts between pyroxenes and amphiboles (30% and 28%). Also, trace element concentrations vary between samples and between individual grains in one sample. In Kośmin granodiorite apatite is enriched in Y, whereas Ce and Sr contents are the highest in Kośmin enclave. Preliminary results show that the composition is not related to whole rock composition but rather is affected by the timing of apatite crystallization.

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### Do the properties of the substrate affect nucleation and crystallization on the surface of iron oxyhydroxides?

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In situ immobilization of toxic metal(loid)s by the formation of virtually insoluble minerals like phosphates and arsenates is a widely-discussed method for remediation of polluted soils and sediments. This process usually takes place in the presence of various iron oxyhydroxide phases which are widespread constituents of polluted media. Synthetic goethite is often used in the model experiments (Manecki et al., 2006). However, the goethite applied in the majority of the studies was relatively well-crystalline whereas natural soil goethites are usually poorly-crystalline. Moreover, in many soils, goethite cooccurs with other iron oxyhydroxides like ferrihydrite, lepidocrocite, akaganeite and so on. In this work, we have verified a hypothesis that mineralogy and crystallinity of iron oxyhydroxide affect nucleation and growth of pyromorphite Pb5(PO4)3Cl (virtually insoluble lead apatite used in remediation procedures) and hence alter the effectiveness of in-situ lead immobilization. For this purpose, batch experiments were carried out using various substrates: synthetic Fe oxyhydroxides (well- and poorly-crystalline goethite, Algoethite, ferrihydrite, Si-ferrihydrite and akaganéite) and Fe oxyhydroxide-rich sediments (bog iron ore and water treatment plant sludge). Two experimental setups were applied: 1) phosphate-loaded minerals were reacted with aqueous Pb(II) or 2) lead-loaded minerals were reacted with aqueous phosphate. The efficiency of lead and phosphate immobilization was assessed by the analysis of the solution (AAS and UV-Vis spectroscopies) whereas the solids were characterized using XRD and SEM-EDS.

The results revealed that the mineralogy and surface chemistry of Fe phases and Fe-rich sediments highly affect the effectiveness and the mechanism of Pb removal, the amount of pyromorphite formed as well as its habit and size. In the case of goethites, more pyromorphite formed when P-goethite reacted with aqueous Pb. In contrast to the previous works, relatively low amount of large pyromorphite crystals emerged indicating precipitation from only slightly oversaturated solution. On the other hand, strongly adsorbed phosphate on ferrihydrite surface appeared to be virtually unavailable for pyromorphite formation and in this case surface ternary adsorption was the most important mechanism of lead immobilization rather than surface precipitation of lead phosphate. **Acknowledgements:** This work was supported by AGH-UST grant no. 11.11.140.319.

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# Apatite as a source of information about the content of volatiles in melts – facts and myths.

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Apatite commonly occurs as an accessory phase in magmatic, metamorphic and sedimentary environments. Its interaction with fluids can trigger its transformation into a set of alteration minerals. Because of the diversity of apatite crystallization/recrystallization paths it can be considered as an indicator of the environment in which it originated. Magmatic apatite is commonly used to obtain insights into the source and differentiation path of the magma. However, it might be a deceptive tool if its origin is not accurately recognized. Such detailed study on the origin of multiply populations of apatite has been done on phosphates crystallized from mafic, shergottite (Martian) magma. Two generations of fluorapatite (F>Cl~OH and F-rich), chlorapatite and merrillite were recognized with the use of TEM (Transmission Electron Microscopy) and mineral chemical analyses. Contrary to the fact that chlorapatite is most often found in Martian mafic rocks, it was fluorapatite that we proved as the magmatic phase. Indeed, the research results indicated that the documented volatile budget of the two generations of fluorapatite was related to their magmatic origin. The apatite grains crystallized from an evolved magma during its final differentiation and degassing stage. In turn, chlorapatite replaced merrillite and does not record the volatile budget of the mantle-derived shergottite magma. The relationship between merrillite and apatite indicates that apatite is most probably a product of merrillite reacting with fluids. REE pattern of Cl-apatite point to an origin associated with exogenous fluids mixed with fluids exsolved from evolved magma. The study shows that, among the three types of apatite, only the fluorapatite (F>Cl~OH) is a reliable source for assessing the degree of Martian-mantle hydration. Consequently, the uncritical use of apatite to assess the water content and source of magmas can lead to false assumptions if the genesis of the apatite is not precisely determined. For the shergottite, the water content and the relative volatile ratio for parental magma has been calculated from fluorapatite. Comparing the environment of Martian parental magma generation to the terrestrial mantle in term of water content, the former has a characteristics intermediate between enriched and depleted MORB.

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#### Quantitative determination of Ostwald ripening of mimetite

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The objective of this research was quantification of Ostwald ripening process of mimetite crystals. Mimetite  $Pb_5(AsO_4)_3Cl$  is a member of apatite group, isostructural with pyromorphite and hydroxylapatite. To date, the ripening process of these minerals has only been examined qualitatively, and almost no results have been recorded regarding the absolute time when precipitation ceased. Mimetite was synthesized by precipitation from aqueous solution. The precipitate was sampled periodically, identified with powder X-ray diffraction and examined with electron microscopy SEM/EDS. The image analysis software *ImageJ* was used for quantitative characteristics of aging process.

Based on 2D analysis of SEM photomicrographs the evolution of mimetite from nearly amorphous precipitate to fully grown crystals indicates systematic growth of larger crystals and dissolution of those which are smaller than 1  $\mu$ m. The average crystal size evolves as follow: after 0.5h of aging – 1.4 $\mu$ m, after 1h – 2.7 $\mu$ m, after 3.5h – 4.3 $\mu$ m, after 24h – 7.5 $\mu$ m, after 100h – 8.8 $\mu$ m. This evolution represents logarithmic trend with R<sup>2</sup> = 0.99 (Fig. 1). After 100 hours of aging the process has been still proceeding. Ostwald ripening time of mimetite differs from pyromorphite despite that they are isostructural lead apatites (Rakovan, 2002; Flis et al., 2011). Funding is provided by the AGH University of Science and Technology in Kraków through statutory research project No 11.11.140.319.



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### A combined EPMA - Raman spectroscopy characterization of '*Quensel–Mason's sequence*' minerals from granitic pegmatite at Lutomia.

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The 'Quensel-Mason's sequence' minerals are represented by six different phosphates occurring in phosphate-bearing pegmatites. This sequence shows gradual transformation of Li-bearing phosphates: triphylite  $\text{LiFe}^{2+}\text{PO}_4$  and lithiophilite  $\text{LiMn}^{2+}\text{PO}_4$  into partly-oxidized phases: ferrisicklerite  $\text{Li}_{1-x}\text{Fe}^{3+}_x\text{Fe}^{2}_{1-x}\text{PO}_4$  and sicklerite  $\text{Li}_{1-x}\text{Mn}^{2+}_{1-x}\text{Fe}^{3+}_x\text{PO}_4$  and finally to fully-oxidized phases: heterosite  $\text{Fe}^{3+}\text{PO}_4$  and purpurite  $\text{Mn}^{3+}\text{PO}_4$  (Quensel 1937, Mason 1941). Determination of the specific phase without knowledge about  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio or Li content is very difficult and is always based on optical properties of individual phosphate crystals. All colorless crystals of '*Quensel-Mason's sequence*' are considered to be members of triphylite-lithiophylite series, yellow to dark brown crystals are considered to be sicklerite or ferrisicklerite and the opaque crystals are considered as heterosite or purpurite. Crystals of triphylite-group minerals are almost always partially inhomogeneous and data obtained by Mössbauer spectroscopy could be difficult in interpretation.

In granitic pegmatite at Lutomia triphylite is one of the main constituents of phosphate nodules, overgrown with graftonite and sarcopside. Many of the primary phosphate nodules are partially or almost completely altered by hydrothermal fluids, what results in crystallization of many different hydrothermal phosphates, including alluaudite-group minerals, whitlockite-group minerals, kryzhanovskite, triplite-group minerals and also ferrisicklerite and heterosite.

In this work we present complex interpretation of mineralogical data based on chemical electron microprobe analysis and data from micro-Raman spectroscopy. On the basis of several parameters obtained from chemical analyses, including (1)  $P_2O_5$  wt. %, (2) sum of all components concentrations and (3) ( $\Sigma Me^{2+}/P$ )<sub>atomic ratio</sub>, we propose a new scheme of the chemical formula calculations. All of the chemical calculations are in good agreement with in-situ Raman spectra of individual crystals.

Acknowledgements. This work was financially supported by AGH University of Science and Technology grant no 11.11.140.319 and National Science Centre of Poland grant no 2015/17/N/ST10/02666.

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# Stable isotopes in apatite – a case study from the >3.7 Ga Isua Supracrustal belt, SW Greenland

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Geochemical studies of apatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(F,Cl,OH)<sub>2</sub>, a volatiles-rich mineral, provide valuable information about the environment of its formation, e.g. composition of the host magma (Boyce and Hervig 2008), as well as give us an insight into volatile evolution in lunar rocks and meteorites (e.g., Sarafian *et al.* 2017). Environmental conditions and abiotic processes on Early Earth are a still poorly understood chapter of Earth's history. Therefore, we have undertaken a study of the origin and evolution of volatiles in Archean by studying the isotopic ( $\delta D$  and  $\delta^{37}$ Cl) composition of apatite crystals from the >3.7 Ga Isua Supracrustal belt, a unique geological succession containing the oldest banded iron formations (BIF).

Isotopic analysis by secondary ion mass spectrometry (SIMS) is a very useful tool for the investigation of samples available in small quantities, such as Archean apatite crystals, but it is also a challenging task due to the complicated crystal chemistry of apatite and strict requirements of SIMS method for reference materials for quantitative measurements. Our investigation of D/H ratios in Isua samples shows that the hydrogen isotopic composition of apatite has been reset during its long and multi-phase geologic history, and therefore hydrogen cannot be used for assessing a true primary signature of the Archean hydrosphere. Isua rocks preserved clear traces of at least one amphibolite-facies metamorphism which was overprinted by further metasomatism of local importance. A variety of types and intensity of these secondary processes is reflected by a broad range of halogen compositions, rare earth elements abundances, small variations in chlorine isotope ratios (<sup>37</sup>Cl/<sup>35</sup>Cl), and cathodoluminescence properties of apatite crystals.

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### Influence of liquid nitrogen freezing of shale rocks on their compressive strength

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The aim of this study is to check the efficiency of freezing of shale rocks in the stage prior to hydraulic fracturing to optimize the results of fracturing process. Results of laboratory tests simulation and effects of experiments conducted on shale rocks to determine permanent change their compressive strength are presented.

To achieve above-mentioned change, freezing process was first simulated with the use of finite element method (FEM) using the Fluent ANSYS Software, to predict possible results in order to choose the freezing method and optimize the time of freezing.

Nine samples of shale rocks from the same core were divided into three groups of different height. In each group one sample was tested in room temperature, one directly after being freezed and one after returning to room temperature. Tests were conducted on the shale rocks samples with the use of an auto-measuring hydraulic press.



Fig. 1. Compressive strength factor (Rs) for samples group 1 (*upper left*), 2 (*upper right*) and 3 (*lower right*) each before freezing, after freezing, and after returning to room temperature.



Both freezed rocks and rocks after returning to room temperature, represent diminished compressive strength (Fig. 1). It suggests that prior freezing of rocks can increase the efficiency of fracturing.

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# Thermal history of the Wełnowiec dump told by means of mineralogical, geochemical and geophysical methods

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The Wełnowiec dump is located one kilometer from the center of the Katowice town in Upper Silesia Coal Basin, Poland. It operated from 1991 as a rubbish dump collecting in total about 1.6 million tonnes of urban wastes to June 1996. The residents living next to the dump complained about unpleasant odour. This is why it was decided to reclaim the municipal waste landfill with coal wastes which were huge volume by-products of operated coal mines. It was planned to form a multi-barrier system composed of 0.3 m of compacted coal mine wastes, 0.5 m of clays, 0.1 m of sand, 0.3 m of gravel, 0.6 m of uncompacted coal mine waste mixed with soil, and 0.4 m of humus on the top.

We proved geophysically, that properly planned reclamation has never been performed, much more coal wastes with much higher coal content were deposited on the dump without any packing and fire-preventing measures what caused self-ignition and self-heating of the overamounted coal wastes. The most intensive fire expanded at the northern slope and appeared as hot spots at the South. The areas affected by the thermal activity are visible on the surface as exhalating minerals encrusted vents and fissures which emit hot exhalations containing water vapour, carbon mono- and dioxide, methane and other light hydrocarbons. There the dump surface is permeated with water and bitumen formed in pyrolytical conditions in a self-heating zone located deeper within the dump. Temperature is high < 80°C in these places. The highest measured temperature at 0.3 m subsurface reached 770°C.

Geophysical methods easily distinguish municipal (<26 m) and coal wastes (1-10 m), documenting the real thickness of coal wastes used for reclamation of the municipal Wehowiec dump. There is absence of the planned multi-barrier system 2.2 m thick in the recultivation layer within the whole Wehowiec dump. Its thickness is changeable, its composition heterogeneous and internally diversified. At the southern slopes of the dump the "recultivation" layer does not exceed 2 m. It is enough for unpacked coal wastes with much more organic matter than was acceptable, to start the processes of self-heating and self-ignition and emanate harmful components to the soil, air, and groundwater.

Unburned and overburned wastes reveal huge differences detected by petrographical, geochemical and mineralogical methods. Self-heating significantly alters the chemistry of wastes, causing changes in mineral composition and elements migration. Minerals which are stable at low temperature rebuilt their structures, usually release moisture and some elements or disintegrate. Mineral composition of the overburned wastes are totally different from the initial one. However, there is lack of the possibility of detection of the changes of coal-wastes caused by self-heating by geophysical methods.

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# Petrology of mantle peridotite xenoliths from Hirzstein and Baunsberg in Hessian Depression (Germany)

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The northern part of the Hessian Depression (central part of Germany) comprises alkali olivine basalt occurrences in Hirzstein and Baunsberg (suburbs of Kassel), which contain abundant peridotite xenoliths. The region is situated in Rheno-Hercynian Zone of the European Variscan orogen, close to its contact with (located to the south) Mid German Crystalline Rise.

The xenoliths have 5-10 cm in diameter. Their textures (sensu Mercier and Nicolas 1975) are protogranular to porphyroclastic. Olivine forms 1-6 mm subhedral crystals with deformation lamellae. Orthopyroxene (with parallel lamellae of clinopyroxene) and clinopyroxene grains are usually subhedral, up to 4 mm long. Large grains of spinel occur in intergranular aggregates and interstitially between primary minerals.

The content of forsterite in olivine divides xenoliths into two groups: A (Fo=89.9-91.4%) and B (Fo=87.6-89.3%). Xenoliths from group A plot into OSMA field by Arai (1994). They contain high-Mg orthopyroxene and clinopyroxene (Mg#=0.90-0.92 in both phases; Al 0.09-0.22 a pfu in opx and 0.13-0.25 a pfu in cpx). Baunsberg orthopyroxene is depleted in Ca (0.01-0.02 apfu) compared to the Hirzstein one (0.02-0.05). Group B orthopyroxene has Mg# 0.88-0.89 and contains 0.11-0.22 atoms of Al pfu. Clinopyroxene has Mg# 0.87-0.89 and contains 0.17-0.31 atoms of Al pfu. Spinel exhibits significant variation in Cr# (0.12-0.52) and is Mg-rich (Mg#=0.66-0.76).

The studied xenoliths are mostly lherzolites with low content of clinopyroxene. They differ from the Lower Silesian (SW Poland) ones (Puziewicz et al. 2015) by higher content of Al in pyroxenes. The REE and trace element contents in the latter suggest both silicate and carbonatite metasomatism, while Baunsberg xenoliths show evidence only for carbonatitic metasomatism (La-Ce enrichment, Th-U, Sr positive and Nb-Ta negative anomalies). The xenoliths form Hirzstein and Baunsberg show strong heterogeneity of upper mantle beneath Hessian Depression.

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### Fluid-induced alteration of chevkinite-(Ce): an experimental approach

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The chevkinite-group of minerals (CGM) are being increasingly recognized as important carriers of REE, HFSE and actinides. In common with other REE-bearing accessory minerals, such as monazite, apatite, allanite and xenotime, the behaviour of CGM during fluid-aided alteration has profound significance for the mobility of REE, Th and U. Recent studies at Warsaw of the hydrothermal alteration of the chevkinite-group of minerals (CGM) have revealed several replacement sequences, related mainly to the composition of the fluids, particularly the proportions of such ligands as  $(OH)^-$ ,  $CO_3^{2-}$ ,  $F^-$ ,  $CI^-$  and  $SO_3^{2-}$ , although temperature and oxygen fugacity ( $fO_2$ ) can also play important roles (Bagiński et al., 2016; Macdonald et al., 2015 a, b). In order to quantify the effects of some of these parameters, an exploratory series of experiments has been undertaken at the Deutsches GeoForschungsZentrum Potsdam where natural chevkinite-(Ce) from Haramosh, Pakistan, plus natural albite and quartz, were reacted with Ca(OH)<sub>2</sub>-, CaCl<sub>2</sub>- and NaFbearing fluids at 600° and 400 MPa.

The preliminary results are very promising. The chevkinite-(Ce) has been notably altered in the presence of the hydroxyl- and F-bearing fluids but not by the Cl-bearing fluids. This is in accord with our empirical conclusions from the natural assemblages. Here we report on the results of two experiments.



Fig.1. BSE HDR images of experimental products. Chv, chevkinite-(Ce); Ttn, titanite; Hd, hedenbergite; Qtz, quartz; Ab, albite; Ggr, gagarinite-(Ce). BSE+Ti+Ca+Na+Al- the image is a result of combining data from BSE and x-ray mapping of given elements to obtain a clearer picture.

(1) Experiment A. Chev + Ab + Qtz + Ca(OH)<sub>2</sub> + H<sub>2</sub>O, 600°C, pressure 400 MPa, time 21 days. The chevkinite-(Ce) shown in Fig. 1A is being replaced around its rims by britholite; the dark patches are pore space. The mode of replacement is consistent with coupled dissolution-reprecipitation (Putnis, 2009). Note also how alteration has proceeded up the small fractures in the crystal to the right. Titanium and Ca released during alteration have formed titanite and some Ca and Fe have gone into minor hedenbergite. The albite was part of the original mineral mix. Several of the natural alteration sequences studied by us have formed titanite-bearing assemblages, with the REE being incorporated into other accessory minerals, in this case britholite (e.g. Macdonald et al., 2015a, b).

(2) Experiment B. Chev + Ab + Qtz + NaF + H<sub>2</sub>O, 600°C, 400 MPa, 21 days. Here (Fig. 1B) the chevkinite is being replaced by euhedral to subhedral crystals of gagarinite-(Ce),  $(Na_x(Ca_xCe_{2-x})F_6)$  embedded in a matrix of quenched glass and albite. The formation of gagarinite-(Ce) (formerly zajacite-(Ce)) is a totally unexpected result. The mineral is known from only one locality, the Strange Lake pluton, Canada, where it occurs in a hypersolvus granite (Jambor et al., 1996), and has never been recorded in association with CGM. Whilst not directly relevant to CGM alteration, a happy by-product of the experiment is the first determination of the conditions of formation of gagarinite-(Ce).

The overall results from this research will be major advances in our understanding of how REE-HFSE-actinide-bearing accessory minerals are altered by fluid-aided processes and the implications for element redistribution. These, and upcoming, results will give insight into the specific physical-chemical mechanisms in the metasomatic alteration of minerals in general as a function of mineral-fluid chemistry and P-T.

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# Coal seam 505 thinning and disappearance in the Jas-Mos mine (SW part of the Upper Silesian Coal Basin, Poland)

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The coal seams in the Upper Silesian Sandstone Series of Namurian C, exploited among others in the Jas-Mos coal mine in SW part of the Upper Silesian Coal Basin, Poland, reveal partly reduced thickness and disappearance within thick red beds located below unconformity in the Carboniferous top surface. Thinned coal seams occur also beneath thin red siltstones and within intra-Namurian nonconformities. The spread of coal seam 505, its regular ca 3.2 m (mined) and reduced thickness together with differences in a coal type (increasing values from coking coal type 35.2 to antracite type 42 adjacent to the reduced part) are presented in Fig. 1.



Preliminary mineralogical, petrological and geochemical results exclude weathering as a cause of the coal seams reduction and the presence of overlying varicoloured siltstones. It can be interpreted as the result of combustion of the peat seams in areas up to 3 km<sup>2</sup>. Funds from the project 2016/21/B/ST10/02293, National Science Centre, Poland.

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# Mineralogical and petrographical characteristics of historical copper slags from Kondratów and Leszczyna in Lower Silesia

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Studied metallurgical copper slags represent a remnant of historical metallurgical activity in the area of Old Copper Basin, Lower Silesia, Poland. Exploitation and smelting of copper ore related with the Zechstein Kupferschiefer formation was conducted at this site since Middle Ages. The aim of this study was to verify whether historical slags present an environmental hazard as large quantities of such material can still be found in the area.

Slags consist mainly of SiO<sub>2</sub> (approx. 46 wt %), CaO (17 wt %), Al<sub>2</sub>O<sub>3</sub> (15 wt %) and Fe<sub>2</sub>O<sub>3</sub> (3 wt % in Leszczyna and 14 wt % in Kondratów) with minor amounts of K<sub>2</sub>O (5 wt %). Furthermore, elevated concentrations of metallic elements – up to 4.5 wt % of Cu are observed. On the basis of textural and phase characteristics three phase assemblages are distinguished in the studied slags. First consists of glass and Cu droplets, second and most abundant, is fully crystalline and contains leucite, diopside, wollastonite, anorthite, metallic phases (mostly sulfides) and quartz. The third assemblage is uncommon and composed of augite and fayalite. The most important constituents of the slags are metallic phases reaching up to 0.5 mm due to their high content of metals and high susceptibility to weathering. These phases are widespread in all the assemblages and therefore represent a potential hazard for the environment.

Field observations coupled with mineralogical analyses reveal that the slags present signs of weathering such as oxidation of metallic phases and crystallization of the secondary minerals (e.g., brochantite occurring on the slag surface and cuprite replacing Cu sulfides). Leaching test carried out under varying pH conditions reveals that the highest release of metals occurs under acidic conditions (pH 2-3) whereas at pH 11-13 moderate leaching is noted. Among analyzed metals, Cu and Fe present the highest mobility (>10 000 mg kg<sup>-1</sup> at pH 2) whereas Pb and Cr are the least mobile. It is noteworthy that Cu, Fe and Zn are easily leached from crystalline compared to glassy slags.

Our research reveals that the analyzed historical slags constitute a potential source of contamination to the surrounding area. Its susceptibility to weathering, high metal content and metal ability to migrate from slags, especially in acidic conditions suggest probable soil and water pollution at the studied site.

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### Influence of Selected External Factors on Olivine Structure: Mössbauer Study

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The aim of the presented research was to investigate an influence of selected external factors like temperature and gamma irradiation on olivine (Fe,Mg)<sub>2</sub>SiO<sub>4</sub> structure. The following methods were applied: X-ray fluorescence (XRF), X-ray diffraction (XRD) and Mössbauer spectroscopy.

The transformation mechanism of  $Fe^{2+}$  cations in two samples of natural olivine  $(Fe,Mg)_2SiO_4$  after heat treatment in air in temperature regions  $(400 - 1180)^{\circ}C$  was studied. Additionally, influence of time of heating (from one to niniety-six hours) on stability  $Fe^{2+}$  ions in olivine structure was investigated. Preliminary results an impact of gamma irradiation (0.3 - 1.0kGy) on the crystal structure of olivine were archieved.

The Fe<sup>3+</sup> ions in iron oxides dominate as a primary product of the thermal treatment in air at 1180°C of the natural samples of olivine. The Mössbauer spectroscopy results show that oxidation of iron-bearing olivines starts already after heating at 600 °C and leads to the formation of reducible iron oxides dispersed in the iron-depleted olivine matrix. After heating at 1000 °C the highest value of abundance of iron oxides was observed (Fig.1). Additionally, the <sup>57</sup>Fe Mössbauer spectroscopy results show that iron cation diffusion in olivine structure, oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> ions and creation of iron oxide phases started after heating for one hour. Maximum of these provess were observed after heating for about twenty-four hours. These processes were not observed after heating longer than forty-eight hours. Gamma irradiation did not change crystal structure but led to changing within elementary cell of olivine.



Fig. 1. The room temperature Mössbauer spectra of olivine obtained for initial samples and after heating at 1180°C. Fitted subspectra are visible on the spectrum; O M1, O M2 –  $Fe^{2+}$  in octahedral sites in olivine,  $Fe^{3+}(Si^{4+})$  - Fe in tetrahedral sites, H – Hematite, Mg - Magnesioferrite.

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## Waste incineration bottom ash as a possible source of valuable elements

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A rational waste management in the EU contributed to the fact that attention is paid to the resource potential of waste materials. Storage of increasing amount of waste which are not recyclable takes up a large surface area and can lead to immobilization of some, economically important or even critical from the economic point of view, elements.

One of the methods to reduce the amount of landfilled waste is incineration. As a result of waste incineration, bottom ash (BA) and fly ash are accumulated in the highest amounts.

The goal of the study was to evaluate the raw material potential of BA and the possibility of recovery of economically important elements by comparison their chemical composition to the chemical composition of typical Earth materials such as: continental crust, various igneous and sedimentary rocks as well as comparison to the lowest concentration in currently exploited ores. BA from three waste incineration plants in Poland were studied (one incineration plant of industrial waste and two of municipal waste).

Based on the chemical composition of the BA we can divide incineration residue between two groups - silica saturated (municipal waste incineration BA) and silica undersaturated (industrial waste incineration BA). This distinction is confirmed in TAS rocks classification (trachydacite, trachyandesite and foidite fields) and in CIPW norms calculations (rocks with normative quartz but also with normative nepheline).

Three main elements (P, Ca and Na) were enriched in all BA in comparison to the average rocks compositions, whereas those which can be considered as valuable (Fe, Ti, Mn) were enriched in BA from industrial waste incineration residues only.

Elements which are considered as valuable (Au, Ag, Sb, Be and Ga) as well as these which are of typical environmental concern (As, Ba, Cd, Cu, Cr, Mo, Ni, Pb, Se, Sn and Zn) were generally enriched in comparison to naturally occurring rocks. The REE content was higher only in comparison to the ultramafic and carbonate rocks, whereas for other geological materials the concentrations were higher than in BA. For almost all measured elements the concentration in BA was much lower than the lowest concentration in ever exploited raw materials except for the Sb, Tl and Ba.

Our results indicate that currently, recovery of valuable elements from BA is not a reasonable option, but the evaluation of the economic importance of raw material is based not only on the content of given element but also on other factors e.g., technical costs (mining, mineral processing), environmental or social costs. Within the years the amount of waste will increase significantly and resources of ores and raw materials will be reduced BA can be considered as an important future source of economically important elements.

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### Valuable and critical elements in waste incinerated fly ash

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Decreasing resources of raw materials caused a necessity of prospection for alternative sources of useful elements. One of the potential source of elements is a waste stream, due to increasing amounts of wastes accumulated annually worldwide. Wastes incineration is a common method of their mass and volume reduction with simultaneous recovery of energy. As a result of waste incineration, bottom ash (BA) and fly ash (FA) are produced.

The goal of the study was to evaluate raw material potential of FA and the possibility of recovery of metallic or others valuable elements by comparison of their chemical composition with chemical composition of the Earth materials such as ultramafic, mafic and felsic igneous rocks and various sedimentary rocks. The content of selected elements in FA was also compared to their lowest content in exploited ores.

Samples were collected from two municipal waste incineration plants and one sewage sludge incineration plant in Poland.

Chemical composition of samples differs strongly what is evidenced by the results CIPW norms calculation. The main normative component in sewage sludge FA were apatite, quartz and hematite whereas in the municipal waste FA larnite and feldspathoids. Due to the fact that FA are characterized by unusual chemical composition (very low  $SiO_2$  content) it is impossible to classify them using TAS. Presence of normative quartz in sewage sludge FA is caused by very low content of Al coupled with high content of P and alkali in FA.

In all studied FA only three main elements (P, Ti and Ca) have significantly higher concentration than in natural rocks used for comparison.

Concentrations of Zn, Sn, Cr and Pb, which are considered as metals and elements of environmental concerns, were significantly higher in comparison to naturally occurring rocks. Au and Ag which are considered as precious metals are enriched in comparison to all natural rocks used for comparison. From the list of critical elements only Sb shows higher concentrations comparing to the natural materials, whereas the REE and other critical elements are depleted in FA.

Almost all measured elements concentrations in FA were much lower than the lowest concentrations in economically profitable ores, only for Sb, and Ba concentrations were higher.

Due to the fact that lower amount of FA is produced annually in comparison to the BA, currently the recovery of elements seems not to be profitable except for P which concentrations are close to low to medium grade ores. However, FA should not be excluded as a future Zn, Sn, Cr, Pb as well as Au and Ag waste-based source.

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## Heavy minerals and micromorphological features of carbonate-rich soils at the area of Pieniny Mts.

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Heavy minerals (HM) and micromorphological characteristics are widely recognized as powerful tools for soil provenance and relative chronology determination (Marcinkowski and Mycielska-Dowgiałło, 2013; Stoops et al., 2010). Different classes of HM stability can be found according to weathering and abrasion conditions (Pettijohn, 1941). In turn, micromorphology helps to recognize which features are the result of inheritance from parent material and which are the result of allochthonous additives (Stoops, et al., 2010). In this study, we evaluate the HM composition as well as micromorphological features of carbonate-rich soils at the area of Pieniny Mts.

Soil samples were collected at the area of Pieniny Mts. The HM were separated by suspending them in sodium polytungstate of density 2.97 g·cm<sup>-3</sup>. Then, extracted heavy fraction was examined, using scanning electron microscopy with energy dispersive spectrometer (SEM-EDS). Microscopic observations of thin sections were conducted in both, plane and cross-polarised light. Each description was elaborated on in accordance with the nomenclature proposed by Stoops (2003).

HM composition in studied soils depends on the interaction between the various factors that contribute to soil formation. Different class of heavy minerals have been found. The most frequent HM include: chlorite, pyroxene, amphibole, pyrite, biotite, epidote, zircon, monazite and  $TiO_2$  polymorphs. Soils differed in micromorphological features. Crumby as well as angular and subangular blocky microstructure were described. A complex or compound packing voids were typical for this type of microstructures. Studied soil were characterized by single, double equal, enaulic or double porphyric related distribution pattern.

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## Influence of processing and ageing of municipal waste incineration bottom ash on its metallic components

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The thermal treatment processes are used in waste management as the method for the reduction of waste volume and mass with its simultaneous sanitization. Non-flammable part of waste is concentrated in the bottom ash (BA) and fine grained ashes removed from the furnace with flue gases. The BA produced in large amount worldwide is an inhomogeneous mixture of amorphous and mineral phases and residual fraction from waste. Because of the content of metallic elements concentrated in the BA during incineration it is worth to investigate the possibilities of their recovery. Because of technical and economic limits of effectiveness of metals segregation from waste, their content in the BA can be high.

Studies were based on the municipal waste incineration BA from the installation located in Poland. Samples were collected in 2012 and between 2015 and 2017. Over the years various methods of BA processing (e.g. by using eddy-current separators or only with simple magnets) and storage were used (e.g. it was stored from few weeks to few months on a heap in the space covered by the roof or exposed to atmospheric conditions).

Scanning electron microscopy with EDS analysis allowed for the characterization of the BA components and its structure. To investigate BA chemical composition the ICP-OES and ICP-MS methods were applied and quantitative XRD for the description of the mineral composition. In the experimental part of the studies few processes of the enrichments in metallic components were tested on the material (without crushing of the BA grains).

The bottom ash contained from 10 to 17wt% of metallic elements. Main metals were Fe and Al. In smaller amounts Ti, Zn, Cu, Pb and Mn were present mostly as polymetallic compounds concentrated in small inclusions entrapped in the BA grains and larger separate metallic grains which were easy to recover (e.g. by using gravity separation four- and five-fold enrichment in Cu, Zn, Pb, Sn and Mn were obtained). Extension of the storage time negatively affect the BA composition (e.g. by oxidation and decomposition of Al-rich fragments) and its structure (e.g. by grains cementation) from the point of its processing.

In the BA still ~5wt% of fragmented metal products are present after simple magnetic separation. By using sieving and eddy-current separation ~95% of that amount was removed. This method was effective for the Fe, Ti, Mo, Cr and Cu separation.

Obtained results indicate that the bottom ash from the thermal treatment of waste can be enriched in metals using various processing methods but their effectiveness might be dependent on technologies used in the incineration plant. (e.g. storing, metals separation).

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# Metallic phases as diversified and valuable components of municipal solid waste incineration bottom ash

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Due to development of multiple techniques of municipal waste processing like RDF production or thermal treatment (e.g. combustion, pyrolysis, gasification) these materials are now more often treated as a potential source of the energy than a waste. After the thermal treatment waste mass and volume is reduced and solid post-process residues are generated - the bottom ash which constitutes the dominant part of the residues and ashes separated from the flue gases. Components of these residues are derived from the waste incombustible fraction. It is possible to consider solid residues as material having its own value as potential raw material or an alternative resource for the recovery.

This study focuses on the metallic phases present in the bottom ash from the thermal treatment of municipal waste to estimate their recovery potential. Samples were obtained from the waste-to-energy plant in Poland. The material was studied using quantitative X-ray diffraction, scanning electron microscopy and spectroscopic methods of chemical analysis (EDS, ICP-MS and ICP-OES).

The bottom ash is weakly consolidated grainy material (larger aggregates mixed with the fine fraction) rich in Si, Ca, Al, Fe and Na composed of post-melting components and residual materials. It is glass based (~50 wt% was an amorphous phase) assemblage of multi-element components formed by short exposure of the waste on high temperature (~1100°C) in the furnace, ended with rapid cooling of the inhomogeneous melt using water.

On average 11 wt% of the bottom ash bulk chemical composition was metallic elements concentrated in metallic fragments and partly dispersed within other non-metallic components. Main forms of metallic fragments were inclusions and separate grains characterised by their multi-element composition and various oxygen content. Fe- and Al-rich fragments prevailed others, nevertheless Ti, Zn, Cu and Pb were present in numerous fragments, mostly as minor elements or components of two or three metals alloy.

Relatively high content of Zn, Cu and other metallic elements in the bottom ash and the multiplicity of forms of metallic occurrences positively influence the possibility of the metallic elements recovery. Physical properties of the bottom ash, metallic elements accumulation in the fine fraction and their presence in the form of separate metallic grains allows to consider the implementation of the methods of the bottom ash processing and extraction of its components.

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# Geochemical characteristics of the Nové Město metasedimentary rocks: preliminary results

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The Nové Město unit rocks constitute the western part of the mantle of the Orlica-Śnieżnik Dome, one of the most important geological structures of the north-eastern Bohemian Massif as a part of the Variscan collisional orogeny. The Nové Město unit is comprised of lower grade metamorphosed volcano-sedimentary series of which the protoliths are most often assumed to be of Neoproterozoic age and are commonly correlated with the Teplá–Barrandian zone.

Samples of fine-grained phyllites and mica schists were collected from the Nové Město unit outcrops located in the Orlickie Mountains on both sides of Poland and Czech Republic border. They consist mainly of quartz and mica minerals with subordinate chlorite, K-feldspar, plagioclase and opaque minerals. Garnet, tourmaline and zircon grains are present as accessories.

In order to decipher the provenance of the Nové Město metasediments whole-rock geochemical analyzes were carried out on 18 rock samples collected throughout the research area. Samples were crushed in the preparatory lab of the Faculty of Geology, University of Warsaw. Chemical analyzes for major, minor and trace elements were carried out by means of X-ray fluorescence method (XRF) and the atomic emission spectroscopy inductively coupled plasma with a mass spectrometer (ICP-MS) in AcmeLabs in Canada. The analyzed elements, particularly REE and high field-strength elements (HFSE) and their ratios, are regarded good indicators of geotectonical setting insensitive to the bulk of postdepositional processes. The analyzed samples show fairly uniform chemical composition with only a few showing slightly different characteristics. The Nové Město rocks follow a normal weathering trend and bear no significant signs of weathering or alteration in their geochemical features providing a consistent picture of the source sediment. Minor and trace element contents indicate a source area(s) dominated by felsic magmatic rocks while major element concentrations plot in a greywacke fields pointing to sediment immaturity. The geochemical discrimination diagrams suggest a continental island arc affinity of studied samples which is indicative of a back-arc basin sedimentation environment.

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#### Record of prograde metamorphism preserved in the Chałupki paragneiss from the Doboszowice Metamorphic Complex (Bohemian Massif, Fore-Sudetic Block)

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The Doboszowice Metamorphic Complex (DMC) is situated in the easternmost part of the Fore-Sudetic Block between Doboszowice in the west and Chałupki in the east. The Massif is composed of a metamorphosed volcano-sedimentary succession comprising the Chałupki paragneiss intercalated with mica schists and amphibolites intruded by the Doboszowice orthogneiss. The protolith of the latter was dated at 488.4±6.2 Ma. The volcano-sedimentary succession bear an imprint of tectonometamorphic reworking previously estimated at maximum approximately 700 - 740 °C and 8-10 kbars. For the purpose of this study we examined one sample of the Chałupki paragneiss collected in the abandoned quarry located in the eastern part of the DMC in the vicinity of Chałupki. The sample is characterized by garnet+muscovite+biotite+plagioclase+ilmenite mineral assemblage. The rock bear clear signs of incipient melting. The investigated sample contain two compositional types of garnet grains: (a) larger and zoned garnets with dominant almandine (74-65%), minor spessartine (5-16%), grossular (4–13%) and pyrope (4–16%) components as well as (b) smaller and almost homogenous garnets with almandine (70%), pyrope (14-10%), spessartine (8-12%) and grossular (8%) components. Core-to-rim profiles of zoned garnet porphyroblaststypically display a remarkable increase in almandine and slight increase in pyropeboth dropping at the outer rim coupled with decrease in grossular and spessartine content which slightly increase at the rim of the grains. We interpret zonation pattern of larger grains as due to bulk-rock depletion caused by fractional garnet crystallization and therefore reflecting prograde metamorphism. However, rims of large garnet grains that are characterized by slight increase of spessartine component were most probably modified by resorption related to retrograde cation exchange. We excluded this part of large garnet grains from further thermodynamic modelling. Results of our calculations performed using Theriak-Domino software show that large garnet crystals in the examined sample started to grow at  $650^{\circ}$ C and 7–8 kbar and their formation ceased at 740 -750°C and 4.5-5.0 kbar. Obtained results indicate prograde PT history of the investigated sample of the Chałupki paragneiss that occurred at constantly dropping pressure in the presence of melt.

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# ALL COWARD IN CO

### New data on mantle and crustal xenoliths from Loch Roag monchiquite, Isle of Lewis, Outer Hebrides

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A mid-Eocene monchiquite dyke near Loch Roag (Outer Hebrides, Scotland) brought up a wide array of xenoliths and megacrysts sampled from the deep lithosphere of the southern margin of the North Atlantic Craton (Faithful et al., 2012). The xenoliths include spinel lherzolites, pyroxenites, gabbros, glimmerites, anorthoclasites and corundum-bearing syenites, The accompanying megacrysts include biotite, clinopyroxene, alkali feldspar, apatite and corundum (Upton et al., 1999). We present new data on some ultramafic xenoliths (sp. lherzolites andbiotite pyroxenites) and on felspathic rocks (diorites, anorthoclasites and granulites).

The peridotite sample investigated contains olivine (Fo<sub>89)</sub>, clinopyroxene (Mg#<sup>Na-Diop</sup><sub>88-89</sub>) and orthopyroxene (Mg#<sup>Na-Ens</sup><sub>89</sub>). The spinel composition differs from those reported by Upton et al., (2011) in containing Cr# 0.25-0.32 and Mg# 0.65-0.67 in contrast to values of 0.35-0.67 Mg#=0.65-0.67 (vs. 0.55-0.64) in the spinel suggesting derivation from a lower degree of melting of lithospheric mantle.

The clinopyroxenites (Mg#<sup>Cpx</sup>=66-71 and 79-81; Mg#<sup>Bt</sup>=61-73) are interpreted as apatite-bearing, lower crustal cumulates that originated from more mafic melts than the feldspar-bearing rocks.

The 2-pyroxene diorite xenolith has a cumulate texture. Mg# values of the Cpx and Opx are 64-71 and 60-61, respectively and the feldspars have compositions of  $An_{38-34}$ . Europium anomalies are positive in the plagioclase and negative in the pyroxenes.

Clinopyroxene in anorthoclasite ( $Or_{83-84}$ ,  $Mg\#^{Cpx}=53-55$ ) has no Eu anomaly and is in disequilibrium with coexisting phases. The composition of the feldspar-bearing xenoliths may point their provenance from an alkaline intrusion, while granulite samples another lithology of lower crust.

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### Zn-rich tennantite in ore-bearing marls from eastern part of the North Sudetic Synclinorium, SW Poland

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Tennantite-tetrahedrite mineral group was recognized in the ore associations in orebearing marls of the North Sudetic Synclinorium, but their distributions along ore profiles were not thoroughly examined. The aim of the presentation is mineralogical characterization of the tennantite-tetrahedrite mineral group identified in the examined samples of the ore-bearing marls that are representative equivalent of the Cu-bearing marls mined in the Konrad and Lena mines.

The Zn-rich tennantite was identified as one of the major ore-forming minerals in the lower parts of ore-bearing marls from eastern part of the North Sudetic Synclinorium. This mineral commonly forms complex intergrowths with chalcocite, chalcopyrite and bornite. Zn-rich tennantite are commonly located on the egde of chalcocite, chalcopyrite and bornite aggregates that clearly indicates its crystallization at the end of the mineralization stage.

The concentration of Zn is extremely high and reach up to 8.62 wt.% (range from 4.68 to 8.62 wt.%). The median Zn contents, calculated for 125 analyzes, is close to 6.51 wt.%. The Fe contents are always lower than Zn and vary from 0.41 to 4.34 wt.%. The concentrations of Ag in the examined tennantite depend on the Zn contents, enhanced concentrations lower than 5 wt.%) were determined only in tennantite with Zn concentrations lower than 5 wt.%, while in tennantites with Zn contents in the range from 5.1 to 8.62 wt.% the amount of Ag are constantly below detection limit. The Sb content is very low (usually below detection limit), in some analyzes the concentrations of Sb reach up to 0.24 wt.%. Slightly enhanced amount of Cd (up to 0.15 wt.%) were also determined. The concentrations of Co, Ni, Au, Pb, Hg, Bi, Sn, In, Se,and Te are below detection limits (< 0.08 wt.%).

The empirical formula of examined Zn-rich tennantites from the North Sudetic Synclinorium is  $(Cu_{9.2-10.7}Zn_{1.2-2.0}Fe_{0-0.9}Ag_{0-0.1})_{\Sigma=11.2-12.5}(As_{3.2-4.1}Sb_{0-0.2})_{\Sigma=3.2-4.1}S_{13}$ . The examined Zn-rich tennantite crystallized from low temperature, Zn-, and As-rich fluids as documented by high Zn/(Zn+Fe) ratios (0.58-0.95), which composition was controlled by earlier crystallization of Fe bearing pyrite, chalcopyrite and bornite that effectively scavening Fe from the hydrothermal fluids. The silver commonly occurs as structural admixture in the bornite or chalcocite mineral group, rather than in Zn-rich tennantite, or forms Ag-native inclusions that range from submicroscopic to 100  $\Box$ m in size.

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### Dissolution of metallurgical wastes in contact with artificial root exudates solutions

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Metallurgical wastes are currently classified as potentially hazardous because they contain relatively high metal concentrations. That necessitates handling these residues in a cautious manner preventing the release of toxic compounds. In contrast, the former industry did not pay as much consideration to the environmental impact of industrial wastes and historically created disposal sites are present in numerous locations. Furthermore, the absence of suitable barriers isolating the wastes from the environment has caused the need for assessment of environmental risk associated with ongoing weathering processes.

The aim of this study was to evaluate leachability of the elements (Si, Fe, Cu, Zn, and Pb) from sulfide-rich lead matte (LM) and glassy copper slags (GS) exposed to the artificial root exudates (ARE) solution simulating organic-rich rhizosphere conditions. The artificial root exudates solutions having dissolved organic carbon (DOC) concentration in the range of 6 mg/L-600 mg/L were employed. Acidified demineralized water (DW) and non-acidified demineralized water were used as experimental controls. Different waste particle size (0.25-0.5, 0.5-1 and 1-2 mm) were used for evaluating its influence on the dissolution process. The experiments lasted 1 week.

The reduction of particle size from 1-2 mm to 0.25-0.5 mm generally has a negligible impact on dissolution process. Organic-rich (*i.e.* 600 mg/L DOC) ARE solution notably increases dissolution of LM and GS as compared to the effect of less concentrated (<60 mg/L DOC) ARE. The release of the elements from GS under exposure to ARE (6-60 mg/L DOC) enhanced element release relative to organic-free control solutions (*i.e.* acidified demineralized water and non-acidified demineralized water), however to a lower extent than ARE (600 mg/L DOC). The dissolution of LM exposed to artificial root exudates (6-60 mg/L DOC) was similar to the dissolution observed under organic-free conditions.

As the result of this study, we conclude that sulfide-rich lead matte and glassy copper slags are prone to dissolution under organic-rich weathering conditions. Therefore, the contact of the metallurgical wastes with rhizosphere may lead to the contamination of surrounding soils. This work gives the further direction of research towards the evaluation of the impact of natural root exudates.

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#### Preliminary data on petrology of peridotite xenoliths from Rochemonteix in French Massif Central

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Cenozoic lavas of French Massif Central are known for numerous occurrences of mantle rock xenoliths. Two different lithospheric mantle domains were defined on the basis of geochemical characteristics of peridotite xenoliths, located to the north and to the south of 45°30' latitute (Downes 2003). The Rochemonteix locality belongs to the southern domain, and is located in the southern part of Cézallier volcanic field, ca. 12 south-east of Riom-és-Montagnes.

The rounded xenoliths occur in tuffitic basaltic rocks and are mostly 4 cm in size. Coisy (1977) reports maximal size of 8 cm. They are mostly equigranular to porphyroclastic lherzolites, some with foliation defined by alignment of elongated grains of olivine and orthopyroxene. We studied in detail 9 xenoliths. Forsterite contents in olivine reveals 2 groups of xenoliths, one with olivine Fo 89.5 – 90.5 and another with olivine ca. Fo 89, plus one amphibole-bearing xenolith of olivine Fo 88.3. The composition of orthopyroxene defines 3 trends with negative correlation between Al and Mg#, each corresponding to the olivine-defined xenolith groups. Orthopyroxene contains 0.10 - 0.20 atoms of Al pfu, except most magnesian xenolith 3808 (olivine Fo 90.5) with 0.07-0.09 atoms of Al pfu. Clinopyroxene (Mg# 0.89 - 0.93) is aluminous (0.10 - 030 atoms of Al pfu), as is spinel (Cr# 0.05 - 0.15), again with the exception of xenolith 3808, which contains spinel Cr# 0.30 - 0.35. Clinopyroxene occurring in all studied samples is enriched in REE relatively to primitive mantle, the degree of enrichment decreases from HREE down to PM level at La.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



#### Mantle roots of the Variscan orogen in Europe

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When the new orogen is assembled, the mantle part of the subducting plate can be "docked" to the mantle wedge of the overriding plate when the subduction stops. The mantle root of the orogen consists thus of (1) mantle wedge of the overriding plate and (2) mantle part of the subducted plate. If the subducting plate is oceanic, the suture possibly is marked by eclogite screens in the lithospheric mantle, marking the former oceanic crust. At the stage of continent-continent collision, crustal screens are introduced into the mantle beneath the orogen. At the late-orogenic stage, lithospheric mantle delamination and replacement by upwelled asthenosphere modify orogenic root architecture. Their lithologies supposedly are different from those assembled at the collision stage.

The Variscan orogen was subjected to rifting commencing the next Wilson cycle in the Alpine epoch. The volcanic activity during that rifting brought to the surface the mantle xenoliths which are the basis for studies of lithology of its mantle root. The metasomatism, which affected lithospheric mantle during rifting produced changes which must be filtered in order to recognize the primary mantle characteristics

The European Variscan Orogen consists of few major tectonostratigraphic units, which supposedly represent independent subduction-collision systems. Their mantle roots differ in terms of seismic anisotropy (Babuška & Plomerová 2006). Numerous petrological data provided by mantle xenolith case studies reveal the variation in lithology of lithospheric mantle beneath the orogen, and three mantle domains of different lithology and geochemical characteristics have been defined up to now (Downes et al. 2003, Puziewicz et al. 2015). Further case studies with extensive use modern analytical techniques should enable better insight into the Variscan mantle root architecture.

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### Effect of iron (II) upon the microbial mineral phases formation under sulphate-reducing conditions

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The objective of this study was to investigate the role of anaerobic sulphidogenic bacteria in the formation of selected mineral phases (biogenic pyrite). Sulphidogenic microbial communities were isolated from soil contaminated with crude oil and heavy metals. The soil samples were collected from selected areas of crude oil mines in south-eastern Poland.

Modified Postgate C medium with sodium lactate as the sole carbon source were used in the selection of microorganisms from the sulphate-reducing bacteria group (SRB). The tested medium included iron (II) chloride at concentrations ranging from 100 to 800  $\mu$ g ml<sup>-1</sup>.

All isolated microbial communities were characterized by high microbiological activity. There reduction of sulphate (VI) ions at a maximum level of 80% and the appearance of hydrogen sulphide were observed in the tested cultures. Sodium lactate was an optimal source of carbon and it was readily biodegradable, which was manifested by the COD reduction. This process was independent of the iron ions concentration.

A significant decrease in iron (II) ions was observed in all stationary cultures. However, there was no increase in iron (III) concentration. The results of powdered X-ray diffraction of post-cultures sediments showed the presence of carbonates, mainly calcite and syderite, and elemental sulphur. The observed drop in iron (II) concentrations may indicate that iron was enclosed in sparingly soluble carbonates or sulphides, as a result of sulphate-reducing bacteria activity. If iron (II) ions were oxidized, then they must have been reduced by bacterial hydrogen sulphide. No sulphides were noted by X-ray method. This fact did not necessarily showed the absence of sulphides in the tested cultures, but it could indicate their amorphous status.

Carbon isotopic studies of post-cultures sediments confirm that the carbon-containing mineral phases were formed *via* the biological pathways. The average value of  $\delta^{13}$  C was -25 ‰ (the VPDB reference was used). SRB activity in the tested cultures contributed to the formation of various mineral phases as their metabolic products. The presence of elemental sulphur in post-cultures sediments indicated the active reduction of sulphates by the microorganisms. In addition, the biodegradation of organic compounds by sulphidogenic microbial communities results in the release of bicarbonate ion, thus it is related with the first stage of the biological precipitation process of calcium carbonate.

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### Iron speciation in the weathering chronosequence on the forefield of Werenskioldbreen glacier (SW Spitsbergen)

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One of the results of global climate change is the rapid retreat of glaciers. The justexposed regoliths undergo enhanced physical and (bio)chemical weathering, resulting in transformations of rock-forming minerals and formation of initial soils. The mechanisms and the rates of these processes are relatively well understood. On the other hand, the studies dealing with the speciation of the weathering products are relatively sparse. This is an important issue in terms of global climate change because in the case of offshore glaciers the weathering products are partially discharged to the ocean as the suspension in meltwater, participating in the input of nutrients. One of the most important nutrient is iron, which is known to limit primary production of the oceans and therefore to affect the global carbon cycle. In this work, the speciation of Fe in three soil samples collected in the chronosequence on the forefield of Werenskioldbreen glacier in SW Svalbard is presented. The geology of the area and sampling details are described elsewhere (Kwaśniak-Kominek et al., 2016). The samples, divided into four size fractions by sieving, were characterized using light microscopy, XRD, and SEM-EDS. This was combined with sequential chemical extractions allowing distinguishing various speciations extracted by appropriate reagents.

The total Fe content dominates in coarse fraction near the front of the glacier but increases and dominates in the fine fraction in the sediments far from the glacier. The coarser fractions are also enriched in 'residual' Fe whereas finer fractions are enriched in 'reactive' Fe. These trends, supported by identification of Fe-rich phases in various parts of the chronosequence, showed lower proportion of primary minerals and higher proportion of weathering products in older soils. Therefore the results evidenced enhanced chemical weathering in the glacier forefield accompanied with formation of reactive secondary iron carriers, chiefly oxyhydroxides.

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### First insights into mineral and geochemical features of the Bystrzyca Górna hornblendite, Sowie Góry massif

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The gneisses and migmatites of the Sowie Góry massif comprise various rocks including HP granulites and eclogites with post-eclogitic amphibolites, metabasites, metaultramafites and pegmatites. Hornblendites are exceptionally rare in the massif and hitherto were reported only from the Bystrzyca Górna outcrop where a few meters thick body is embedded in granulites and together with serpentinites hosted by gneisses. The studied hornblendite shows random texture, coarse-grained in the central part of the body (amphibole prisms yielding up to 6-7 cm in length), gradationally passing towards its marginal parts into finer, mostly medium-grained varieties. The rock is composed of amphibole (80-90 vol.%), apatite (up to 20 vol. %) and dark mica (4-10 vol.%) with accessory epidote group minerals, titanite and zircon. Anhedral to euhedral amphibole crystals have homogeneous chemical composition, with no zoning and correspond to pargasite (Altot: 2.10-2.28 pfu, [Na+K]A: 0.60-0.80 pfu, X<sub>Mg</sub>: 0.82-0.88). They are accompanied by mica of phlogopite composition (Al<sup>VI</sup> 0.24–0.38 pfu, X<sub>Mg</sub> 0.72–0.75) which is commonly replaced by secondary chlorite and titanite. Apatite forms equigranular, polygonal aggregates of F-rich grains (hydrohylapatite to fluorapatite, F: 0.53-1.24 pfu), whilst epidote group minerals show elevated REE contents and classify as allanite-(Ce)  $(Ce^{3+})$  up to 0.37 pfu). The preliminary geothermobarometric estimations based on amphibole composition indicate that the mineral formed at conditions of 954±56°C and 6.5-7.5 kbar.

The hornblendite is characterized by low SiO<sub>2</sub> (39.7–43.3 wt.%), moderate to high TiO<sub>2</sub> (1.09–1.23 wt.%), Al<sub>2</sub>O<sub>3</sub> (12.32–14.09 wt.%), MgO (13.94–16.69 wt.%, mg#: 70-71) and CaO (11.32–15.00 wt.%) contents. The rock also shows a restricted range of Ni (109-190 ppm), Cr (188–224 ppm), Co (50–63 ppm), V (326–388 ppm) and Sc (56–61 ppm). The chondrite-normalized REE diagrams display variable enrichment in LREE (La/Sm<sub>CN</sub>: 1.1-3.0, La/Yb<sub>CN</sub>: 7.8–30.3) and fractionation of MREE over HREE (Gd/Yb<sub>CN</sub>: 3.6–5.3). On primitive mantle-normalized diagrams the profiles show distinct HFSE negative anomalies (Nb/Nb\*: 0.05–0.39, Ti/Ti\*: 0.15–0.60, Zr/Zr\*: 0.17–0.34).

The observed textural relationships coupled with mineral and geochemical features of the studied hornblendites are consistent with their magmatic origin suggesting a hydrous mantle source metasomatized by fluids or melts released from subducted slab. In turn, the estimated P-T conditions point to crystallization at depths within the lower crust (ca. 24-28 km). *Acknowledgements.* The study was financed by the grant no BSt 176804 from the Faculty of Geology and grant no 6/I/2016 from the Consultative Council of the University of Warsaw.





#### Microstructures of felsic rocks as a tool to reconstruct different magma pulses

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Textural studies of major phases in felsic rocks allow characterizing different aspects of magmatic systems such as saturation temperatures as well as cooling paths (Higgins, 2017). Assuming that these aspects are different within particular magma pulses within subvolcanic bodies, textures should also help to distinguish and recognize the thermal evolution of different magma pulses. Also accessory minerals such zircon are known to fingerprint complex history of magmatic systems. We decided to check whether combined texture analyses (crystal size distribution) and zircon study provide and support our previous study and interpretation of laccolith formation by different magma pulses.

We used 500 m long drill core from Permo- Carboniferous Landsberg Laccolith (Halle Volcanic Complex). Whole rock geochemistry and modal composition of samples from every 25 meters of the core were investigated by Słodczyk et al., 2015. Proportions between plagioclase and K-feldspar phenocrysts combined with the chemical composition of whole rock throughout the drill core allowed to distinguish four sections representing three magma pulses within investigated upper part of the Landsberg laccolith. Based on this division, we chose representative samples from each section (sampling depth: 29m, 155m, 281m, 378m) for further textural and zircon study.

Crystal size distribution (CSD) diagrams for K-feldspar, plagioclase and quartz show variable crystallization conditions for particular sections: kinetic growth and coarsening for two generations of K-feldspar in section 1; equilibrium for section 2 and 4; alternate kinetic and equilibrium growth in section 3. Differences within upper and lower part of the laccolith are also supported by two types of textures in zircon and variable Hf concentration patterns revealed by mapping and traverse measurements.

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#### Porosity of gas bearing shales from the Baltic Basin

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Eighty-nine Ordovician and Silurian gas bearing shale samples representing sediments from the Kopalino, Sasino, Prabuty, Pasłęk (including Jantar Member) and Pelplin Formations were collected from four wells (W1, M1, B1 and O3) located in the Baltic Basin. These samples were studied by means of organic petrology, X-ray diffraction (XRD) along with  $N_2$  and CO<sub>2</sub> low-pressure adsorption (NLPA and CDLPA, respectively), water and kerosene immersion porosimetry (WIP and KIP, respectively) as well as image analysis techniques in order to describe their pore network and its relationship with mineral constituents within each formation.

Analyzed samples represent mainly argillaceous mudstones, however some samples from well O3 and well W1 depart from this picture and represent siliceous-argillaceous, calcareous or calcareous-argillaceous mudstones. Examined samples are characterized by total organic carbon (TOC) content falling in the range from 0.13 to 7.20 wt. % and vitrinite equivalent reflectance (Ro) ranging from 1.02 to 1.22.

Total porosity measured using WIP is in the range from 4.6 % to 10 %, while KIP gave values from 1.5 % to 8.9 %. N<sub>2</sub> adsorption measurements revealed that mesopore specific surface area calculated on the basis of Brunauer-Emmet-Teller theory (BET) is in the range from 11.75 to 34.48 m2/g, while their volume calculated on the basis of Barrett-Joyner-Halenda method (BJH) ranges from 0.024 to 0.062 cm<sup>3</sup>/g. Carbon dioxide adsorption measurements showed that micropore specific surface area calculated on the basis of Dubinin-Radushkevich theory (DR) is in the range from 9.17 to 21.18 m<sup>2</sup>/g, while their volume calculated on the basis of Dubinin-Astchakov method ranges from 0.007 to 0.015 cm<sup>3</sup>/g. Moreover, as indicated by N<sub>2</sub> adsorption data both pores greater than ~30 nm and smaller than ~4 nm are important contributors to total pore surface area.

In general, rather weak correlation between different mudstone constituents (including observed types of organic matter) and porosity measured by means of various techniques (WIP, KIP, NLPA, CDLPA and image analysis) reveal that there is no single factor controlling porosity in the investigated suite of samples. However, as indicated by gas adsorption techniques, in case of mesopores the dominant role is played by organic matter for the Jantar, Prabuty and Sasino Formations, while for the Pelplin Formation performed analyses point to importance of clay minerals.

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#### Seasonal variations in trace metal distribution in degraded peatland in Miasteczko Śl. (S Poland)

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A small, heavily polluted mire was studied to follow seasonal changes in trace metals concentration in pore water and their speciation in the peat soil. The aim was to evaluate the risk associated with meal mobilization and to assess the fate and behavior of the metals in the organic-rich environment, depending on the yearly variations in temperature and precipitation.

The studied mire was degraded through extensive melioration and exploitation in the past. Since the late  $60^{\text{th}}$ , it has also suffered from deposition of pollutants from Zn-Pb smelter, which is located only 700 m from the mire in west direction. Both the high metal load and extensive melioration resulted in very poor vegetation, limited almost solely to one sedge species – *Carex rostrata*.

Electrical conductivity (EC) and pH was measured ca. twice a month in the frost-free season starting during mire rewetting after summer drought in 2015. Zn, Pb and Cd was measured using atomic absorption spectroscopy (AAS) and main cations and anions using ion chromatography (IC) every second month. Mineral inventory was analyzed using scanning electron microscopy (SEM) and x-ray diffraction (XRD). Selected samples of precipitation and lakes' water from the same localization (without peaty substrate) was analyzed accordingly to compare with the mire pore water.

The highest variations in metal and sulfate concentration were observed between low and high water table level conditions. The first measurement conducted after the drought gave values of Zn, Pb and Cd as high as 458, 5.9 and 12.6 mg l<sup>-1</sup>, respectively. It was the only situation during the almost two years study when Cd was over twice times more abundant than Pb. At this time sulfate concentration was 1687 mg l<sup>-1</sup>, EC – 2290  $\mu$ S cm<sup>-1</sup> and pH – 4.08. During water-logged conditions the Zn, Pb and Cd concentrations were relatively low (<6.7, <0.65 and <0.15 mg l<sup>-1</sup>, respectively) with no significant difference between the winter and summer season. EC oscillated between 92-253  $\mu$ S cm<sup>-1</sup> and pH between 4.51 – 6.63. SEM investigations reveal abundant authigenic mineralization composed of Zn and Pb sulfides during waterlogged conditions. During dryness, Pb-rich barite and Zn sulfides occurred in the peat and a crust composed of Pb sulfate and gypsum was additionally observed at the mire surface.

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### Exhumation related quartz fabrics preserved in the Kamieniec Metamorphic Belt (Bohemian Massif, Fore-Sudetic Block)

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Deformation-induced quartz fabrics from mica and quartzo-feldspatic schists exposed in the Kamieniec Metamorphic Belt were used to characterize thermokinematic record preserved in volcano-sedimentary complex defining the eastern fragment of the European Variscan Belt. Documented microstructural record allow to recognize three different quartz fabrics which were ascribed to approximately isothermal exhumation followed by nearly isobaric cooling of the Kamieniec Metamorphic Belt. During the initial phase of exhumation (stage 1) recrystallization of quartz occurred in the field of grain boundary migration at temperatures of ca. 550-650 °C and pressures of 8 kbar. It was characterized by constrictional strain and low differential stress, which we relate to regional-scale folding that initiated exhumation. The latter process is signaled by formation of melt pockets preferentially located within hinge zones of developed folds. Following deformation stages were characterized by non-coaxial shearing with top-to-SW to WSW kinematics. Stage 2 was characterized by grain boundary migration recrystallization and bear a record of nearly isothermal exhumation to ca. 3 kbar. Mentioned pressure drop was deduced from appearance of two types of quartz porphyroclasts displaying subrgrain patterns controlled by occurrence of prismatic and a combination of prismatic and basal subgrain boundaries. Furthermore, stage 2 was associated with emplacement of granitoid veins. Their intrusion most probably led to mechanical weakening of the whole complex and most probably facilitated late orogenic lateral spreading of the volcano-sedimentary sequence. The final stage 3 underwent in the field of subgrain rotation recrystallization suggesting important drop o temperature of deformation to ca. 420 - 470 °C and probably underwent at pressures of ca. 2-3 kbar. This was associated with significant increase in differential stress and evolution of conditions of deformation from ductile to brittle-ductile regime.

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## Cadmium concentrations and distribution in primary and weathered slags from Pb-Zn smelting in Swietochłowice site (Upper Silesia, Poland)

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Cadmium is a toxic element, generally highly mobile and easily transferred from Cdbearing ore minerals to the environment as shown by numerous leaching experiments and studies of biota. However, the behaviour of Cd is less understood during smelting activities, when it is transferred from Cd-bearing ore to the smelting by-product. Weathered slag material, with Cd concentrations over 500 mg/kg, occurs at the abandoned slag pile after Pb-Zn metal smelting in Świętochłowice, Upper Silesia. Such material, extremely enriched in Cd (15 mg/kg is a legislative guideline for industrial soils), offers the possibility to study the distribution of Cd within a slag fragment and Cd mobility. Two samples were analysed in detail: "Cd-rich slag" and "Cd-poor slag". Analyses of these samples show different origins of Cd in the slag.

In "Cd-rich slag" Cd was distributed among late crystallizing phases such as rims of Pbhardystonite or Pb silicates and it was strongly incompatible in early crystallizing phases such as Pb hardystonite and Zn-spinel. Trace element analyses of the Pb-hardystonite and Zn-spinel showed similar Cd concentrations in both phases (20-100 mg/kg), which otherwise have different major and trace element composition. This suggests that Cd is not a constituent of crystal lattice, but occurs in another form, probably as Cd-enriched inclusions similar to those identified by electron microprobe. As such, Cd behaviour and distribution are different to that of other potentially toxic elements, which are selectively partitioned in one or more major phases.

On the other hand, our "Cd-poor slag" was a particular sample, initially enriched in sulphides. In that sample, Cd was detected only in secondary Fe(hydro)oxides, which were the product of sulphides weathering, probably original Cd carriers. Cd was also mobilized from this sample in the similar manner as it is mobilized from original ore minerals. The implication is that Cd can be bound to different phases and can be released in different conditions, although most of it is easily accessible during weathering.

General distribution of Cd within slag and particularly its enrichment at rims and in inclusions, as well as in secondary phases, suggests its high potential mobility from the slag to the environment.

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#### Mineral transformations in technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite

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Fly ash and bottom ash from thermal power stations are industrial wastes which are susceptible to weathering in the environment. First manifestations of transformations occur immediately after deposition of ashes in a disposal site and they continue in technogenic soils (Technosols) developing from the ashes on surfaces of such sites. Technosols developed from bituminous coal and lignite ashes in Poland were studied in order to identify the most important mineral transformations during the first several decades of soil development. Mineral transformations can serve as good indicators of pedogenesis in the studied Technosols. Quantitative X-ray diffraction analyses, Fourier transform infrared spectroscopy, optical microscopy, and scanning electron microscope-energy dispersive spectroscopy studies showed that the mineral transformations proceeded more dynamically in Technosols developed from lignite ashes, whereas they were less expressed in soils formed from bituminous coal ashes. Technosols developed from bituminous coal ashes contained mineral phases inherited from ashes (aluminosilicate glass, mullite, quartz, magnetite, hematite, and traces of maghemite and barite) as the major constituents. Small contents of secondary/pedogenic calcite, iron oxyhydroxides, and most likely short-range order Si- and Al-containing phases originated within ~60 years of pedogenesis. Technosols developed from lignite ashes contained aluminosilicate glass, quartz, hematite inherited from fly ash, as well as a variety of secondary minerals (vaterite, calcite, bassanite, gypsum, ettringite, hydrotalcite, and brucite) which were formed as an effect of rapid mineral transformations after ash deposition. After about 40 years, pedogenesis (accelerated by reclamation and a few year intense cultivation) led to the formation of a new mineral assemblage with the predomination of calcite, gypsum, and hydrotalcite.

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### Mixing of loess with different residuum materials recorded in soils – a view from the geochemical and mineralogical perspective

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Loess is a terrestrial wind-blown sediment with the dominance of silt-sized particles. Usually, loess occurs in thick deposits but also can form thin layers. In certain circumstances, especially at the edge of such thick and thin loess deposits, loess can be strongly incorporated to local residuum materials or even imitate them, thus loess can be confused with products of in situ weathering (Waroszewski et al., 2017). As loess has very distinct geochemical and mineralogical composition (Scheib et al., 2014; Újvári et al., 2008), major and trace elements, as well as heavy minerals, can be used as a discriminant of materials provenance and origin. For this study, we chose profiles that represent different cases in terms of underlying residuum strata (e.g. granite, serpentinite, basalt, Permian sandstone), which were covered and mixed with loess. We apply in this study few plots and bivariate plots (eg. Ti/Zr vs. Ti/Nb, Ti/Zr vs. Ce/Y, Zr/Hf, and TiO<sub>2</sub> vs. Ni) of selected elements to: (i) evaluate an aeolian contribution to the soils, (ii) differentiate the soil substrates, and (iii) estimate the thickness of mixed zones of aeolian materials with underlying substrates.

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### Petrographic study of the late Gothic portal and adjacent epitaphs from the St. Elizabeth of Hungary Church (Wrocław, Poland)

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Petrographic study of samples obtained from historic buildings offers an interdisciplinary approach, requiring not only mineralogical and petrographic analyzes, but also architectural or construction insights, as well as a knowledge about the wider historical context in relation to the studied object. This work is dedicated to the one of the greatest monuments in Wrocław, expressing the power of Medieval bourgeois families – St. Elizabeth of Hungary Church. One of its architectural details, the southern portal at the foothills of the Church's tower, is an example of late Gothic Silesian stone art and also illustrates an interesting use of natural and artificial stones throughout the history.

The analyzed portal is the only one within the Basilica's portals, which was made in a Gothic manner (others are Renaissance and Baroque). It was built in 1456 and by the present time was renovated many times. The aim of this study was the detailed petrographic characterization of materials used in this element (both natural rocks and mortars) and an attempt to identify the construction phases of the architectural detail (which elements are original and which are the results of subsequent restoration treatments), as well as an attempt to determine the provenance of the natural rocks.

A total of twelve samples from the portal and four adjacent epitaphs were studied by means of: polarization microscopy, computer image analysis, thermal analysis, X-ray diffraction, cathodoluminescence studies and scanning electron microscope SEM-EDS.

Ten samples represent quartz sandstones with silica-clay binder accompanied with Fehydroxy-oxides. They are differentiated in terms of predominant grain size and matrix content: five samples are medium-grained quartz arenites, three – fine-grained quartzwackes and two - medium-grained quartzwackes. These rocks are mostly similar to upper-Cretaceous sandstones from the North-Sudetic Basin. Samples of clastic rocks show also signs of weathering and the influence of the atmospheric pollutants, confirmed by the presence of the secondary phase - gypsum. Diversity within the samples may be the result of the nineteenth-century restoration treatments.

Among all of the collected samples, one represents modern, cement-lime mortar and one sample is crystalline marble, which provenance is uncertain (probably it may be a marble from Sławniowice).

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### Mineral veins from mélanges in the Magura nappe (Western Outer Carpathians, S Poland)

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Northern part of Carpathian mountain belt in Europe consists of Cretaceous – Early Miocene flysch sequences, thrusted to the north on the Miocene molasse of the Carpathian Foredeep. The flysch occurs in the series of nappes. Tectonic mélanges consisting of fragments of Carpathian sandstones and mudstones embedded in clayey, deformed matrix occur in the Magura nappe in tectonic windows of Sopotnia Mała, Szczawa and Mszana Dolna (Poreba Wielka area).

The studied material from all of the locations is similar. The matrix of mélanges consists mainly of sand to silt-sized grains of quartz and carbonate cement. The matrix is commonly cut by calcite veins of thickness of 0.03-3 mm. The veins over 1 mm are filled mainly with blocky calcite, while veins of thickness under 1 mm are filled with columnar calcite. EDS analyses reveal small contents of Fe (0.77-2.33 wt. %), Mn (up to 2.32 wt. %) and Mg (<0.60 wt. %) in calcite. Locally calcite contains traces of SiO<sub>2</sub> (up to 2 wt. %), supposedly due to micrometric grains of quartz not visible in electron image. The veins contain also a subordinate quartz. It is found between calcite crystals or as euhedral crystals of less than 1 mm size growing on the surface of calcite ("Marmarosh diamonds"). Apatite, strontianite and baryte-celestine are accessories.

Considering quite homogeneous data obtained from calcite chemical analyses and cathodoluminescence studies, we assume that the veins were formed during one episode of carbonate mineralization. Crystallization of calcite was followed by infiltration of silicabearing solutions, from which the euhedral quartz crystallized. The absence of large deformed zones in calcite crystals and the growth of columnar calcite perpendicular to vein walls indicate that the veins were formed after the main tectonic activity that produced the mélanges.

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

Field trip guide

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



### Fieldtrip: Geology in the City: Mineralogical and Isotopic Aspects of Wrocław.

#### STOP 1: Geochemical-isotopic monitoring of the atmospheric natural and anthropogenic components as a quality assessment tool for the environment

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#### Location: Observatory of Department of Climatology and Atmospheric Protection - Kosiby 6/8 Str - 51°06'19,0" N 17°05'20,0" E

#### Introduction

In spite of efforts to improve air quality in Poland in last 30-years, the influence of air pollution sources, on the both animate and inanimate nature, is still significant. Classical air quality monitoring carried out in Poland by the Regional Inspectorates for Environmental Protection (RIEP) provides only quantitative information regarding, among others: concentrations of PM10/PM2.5, benzo(a)pyrene, ozone, carbon monoxide and oxides of nitrogen and sulphur, without providing answers about the pollution origin, so the qualitative information. Currently, it is requested by the global atmospheric research standards to develop such tools in the monitoring of atmospheric pollutants, which yield the widest possible information on the origin of gaseous pollutants and particulate matter (qualitative information), mixing ratio, the direction of pollutants migration and the processes that had induced their characteristics. The large input in helping of understanding of pollutant levels, migrations, mathematical models of the spread of atmospheric pollutants yield scientists from Department of Climatology and Atmospheric Protection, Institute of Geography and Regional Development, University of Wrocław (e.g. Kryza et al., 2015; Malkiewicz et al, 2016; Werner et al., 2016). Moreover, several papers in this area but focused on isotopic analyses were also published by scientists from Institute of Geological Sciences, University of Wrocław.

Isotopic analyses coupled with analysed concentrations of particulate matter (Górka and Jędrysek, 2008; Górka et al., 2009, 2011a, 2012, 2014a; Kosztowniak et al., 2016), atmospheric gases (Zwoździak et al., 2010; Górka et al., 2011b, Górka and Lewicka-Szczebak, 2013; Górka et al., 2014b) and ions dissolved in the precipitation (Jędrysek, 2000; Górka et al., 2008, 2011a, 2017; Ciężka et al., 2016), can provide important information on their origin in the atmosphere. This is due to distinct physicochemical characteristics of substances of the same chemical composition, but different isotopic ratios of elements forming their structures. In most cases, the gaseous compounds, particulates,

and ions dissolved in the atmospheric precipitation may originate from both natural and anthropogenic sources. In practice, these sources often show substantial differences in the isotopic composition, hence the isotopic analysis can be successfully used to assess the origin and to quantitatively calculate the contribution of individual sources using isotopic mass balance. This characteristic "isotopic fingerprint" of each substance was the key to work on these investigations.

The analyses in micro scale, like the analyses of stable isotopes ratios of light elements (H,O,C,N,S) being discussed here, are commonly seen as very complicated and expensive experiments available for a narrow group of specialists only. Such an opinion is not reasonable, since this kind of research has potentially wide practical application possibilities, and its costs are constantly decreasing. Therefore, the primary goal of my research was to develop a simple and reliable tool for the qualitative evaluation of atmospheric pollutants, which, when given to the departments involved in the monitoring of air pollution in Poland/rest World, would significantly enhance their research opportunities.

The proposed enrichment of the classical knowledge by using analyses of the stable isotope ratios of light elements in air pollution studies can be applied for: **both gaseous pollutants** (A), **ions dissolved in atmospheric precipitation** (B), **atmospheric particles** (C) and **bioindicators used in atmospheric studies** (D).

#### (A) Gaseous pollutants

Carbon dioxide, along with water vapour, CH<sub>4</sub> and N<sub>2</sub>O, is responsible for a greenhouse effect which significantly contributes to global climate warming. In common with CH<sub>4</sub> and N<sub>2</sub>O, CO<sub>2</sub> may be derived from natural and anthropogenic sources such as e.g. microbiological production and transport or industrial pollution, respectively. Therefore, the total pool of tropospheric CO<sub>2</sub> and CH<sub>4</sub> has been shown to be a mixture of background CO<sub>2</sub>/CH<sub>4</sub>, originating from the upper layer of the troposphere, and not disturbed by local processes and additional contributions of anthropogenic and/or biogenic CO<sub>2</sub>/CH<sub>4</sub>. However, the concentration and carbon isotopic studies can supplement classical pollutant monitoring and provide useful information on sources and sinks of atmospheric CO<sub>2</sub> and CH<sub>4</sub>.

The main aim of our study (Górka and Lewicka-Szczebak, 2013; Górka et al., 2014b) was to assess the natural and anthropogenic contributions of CO<sub>2</sub> and CH<sub>4</sub> in the urban atmosphere of Wrocław City (SW Poland) using combined quantitative (CO<sub>2</sub>/CH<sub>4</sub> concentrations) and qualitative analysis ( $\delta^{13}$ C of CO<sub>2</sub> and CH<sub>4</sub>). Between 21 January 2011 and 22 December 2011, 17 sampling campaigns were performed at 3-week intervals and in total 255 samples were collected in Wrocław area. The measured  $\delta^{13}$ C(CO<sub>2</sub>) values of major end-members for two winter heating and for one vegetative season suggest soil respiration as the main source of atmospheric CO2 during the vegetative season and a very significant impact of fossil fuels combustion during the winter heating seasons. There were significant increases in CO<sub>2</sub> concentrations at many sampling locations after the opening of a new motorway (A8 highway) on 31<sup>st</sup> August 2011. We hypothesise that the new motorway contributes to the increase of CO<sub>2</sub> across the city.

The dominant  $CH_4$  source was biogenic, namely, the methane produced at sewage irrigation fields (man made biogenic emissions) and local wetlands (natural biogenic input). During the growing season emitted  $CH_4$  spread to considerable distances, depending on the prevailing meteorological conditions. During the cold period, biogenic input was negligible and other anthropogenic sources (biomass burning and city network gas) of methane could be observed.

#### (B) Ions dissolved in atmospheric precipitation

The chemical analysis of ions (anions and cations) from precipitation (rain/snow) are widely used for many years by scientists to answer origin/processes of ions formed in the atmosphere. Moreover, some papers are based on isotopic analysis of ions deposited by atmospheric precipitation. Our isotopic analysis concerned anions dissolved in precipitation e.g.: sulphates (Górka et al., 2008, 2017), bicarbonates (Górka et al., 2011) and ammonium (Ciężka et al., 2016).

Sulphur dioxide is still a major industrial pollutant in the atmosphere. However, its origin is not always easily traceable, particularly at a regional scale where numerous sulphur sources coexist. Geochemical tracers, such as the stable sulphur ( $\delta^{34}$ S) and oxygen  $(\delta^{18}O)$  isotopic compositions of sulphates in precipitation, have been successfully applied for estimation of the S-contribution from multiple sources to the atmosphere (Górka et al., 2008, 2017). Our five-year (2004-2009) monitoring program of precipitation in Wrocław (SW Poland) yield to determine the LMWL (Local Meteoric Water Line) for Wrocław. Moreover, the stable sulphur isotope results confirm that sulphates in precipitation primarily originate from high temperature (minimum mean over-sampling period 680 °C) combustion of fuels with  $\delta^{34}$ S signatures  $\leq 4.4\%$ . The stable oxygen isotope composition of sulphates and precipitation water indicates that the primary sulphate (generated directly by industrial processes) contribution was <49% during the whole study period, with a mean of ~20% during the non-heating and ~40% during the heating periods (Fig.1). The  $\delta^{34}S(SO_4)$ value for precipitation displays multi-seasonal oscillations with an amplitude of about 2‰, which has not been previously reported. The mechanism driving the oscillation needs further investigation in order to reveal possible associations between this phenomenon and climatic patterns or changes in fossil fuel use. This new evidence from 5-year-long records needs to be taken into consideration when analysing trends from shorter-term observations.



Fig. 1 Total concentration of sulphates in precipitation and calculated relative contribution of primary/secondary sulphates in precipitation during the five-year observation period (2004-2009) in Wrocław downtown (Górka et al., 2017 – modified).

As was mentioned in point (A) entitled gaseous pollutant the analysis of both the concentration and isotopic composition of carbon dioxide are performed around the world for many years. Therefore, we started to investigate an additional research question concerning the evaluation of atmospheric anthropopressure (anthropogenic  $CO_2$ ) based on

the isotopic analyses of dissolved inorganic carbon (DIC) in precipitation., because in the literature the values of isotopic composition of (DIC) from atmospheric precipitation was not reported, and only mathematical calculations for it were commonly assumed. Our paper (Górka et al., 2011) describes results of chemical and isotopic analysis of inorganic carbon species in the atmosphere and precipitation for the calendar year 2008 in Wrocław. Surprisingly, no statistical correlation was observed between the concentration and  $\delta^{13}$ C value of atmospheric CO<sub>2</sub> and DIC in precipitation. These observations contradict the commonly held assumption that atmospheric CO<sub>2</sub> controls the DIC in precipitation. We infer that DIC is generated in ambient air temperatures, but from other sources than the measured atmospheric CO<sub>2</sub>. The calculated isotopic composition of a hypothetical CO<sub>2</sub> source for DIC forming ranges from -31.4 to -11.0‰, showing significant seasonal variations accordingly to changing anthropogenic impact and atmospheric mixing processes.

The chemical compositions (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>,  $HCO_3^{-}$ ) of wet precipitation and nitrogen isotope compositions  $\delta^{15}N(NH_4^+)$  were studied (Ciężka et al., 2016) from January to December 2010 in Wrocław. Results of a principle component analysis show that 82 % of the data variability can be explained by three main factors: 1) F1 (40 %) observed during vegetative season (electrical conductivity, HCO<sub>3</sub><sup>-</sup>,  $NO_3$  –,  $NO_2^-$ ,  $NH_4^+$  and  $SO_4^{2-}$ ), mainly controlling rainwater mineralization; 2) F2 (26 %) observed during vegetative and heating seasons (K<sup>+</sup>, Ca<sup>2+</sup> and Mg2+), probably representing a combination of two processes: anthropogenic dust and fertilizers application in agricultural fields, and 3) F3 (16 %) reported mainly during heating season (Na<sup>+</sup> and Cl<sup>-</sup>) probably indicating the influence of marine aerosols. Variations of  $\delta^{15}N(NH_4^+)$  from -11.5 to 18.5‰ identify three main pathways for the formation of NH<sub>4</sub>+: 1) equilibrium fractionation between NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>; 2) kinetic exchange between NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>; 3) NH<sub>4</sub><sup>+</sup> exchange between atmospheric salts particles and precipitation. The coupled chemical/statistical analysis and  $\delta^{15}N(NH_4^+)$  approach shows that while fossil fuels burning is the main source of NH4<sup>+</sup> in precipitation during the heating season, during the vegetative season NH4<sup>+</sup> can originate from local sewage irrigation fields in Osobowice or agricultural fertilizers.

#### (C) Atmospheric particles

Atmospheric particulate matter (PM), a mixture of solid and liquid particles of organic matter, mineral dust, secondary aerosols and trace metals, has been studied extensively due to its potential human health impacts and its visibility impairment. The PM emitted to the atmosphere by fuel combustion processes can have negative effects on human health, due to its content of toxic components (heavy metals, BTX e BenzeneeTolueneeXylenes, PAHs e Polycyclic Aromatic Hydrocarbons). Carbon isotopic analysis of PM in the urban air has been applied to assess the anthropogenic input by many authors. Carbon isotopic  $\delta^{13}C$  data for total PM provides information about the origin of atmospheric particles (e.g. soil OC – organic carbon, OC from bio-sources, OC from fossil and other fuel combustion) and allows the assessment of the magnitude of anthropogenic impacts on the total atmospheric PM haze. Therefore, the major goals of our study were to determine the organic matter sources and anthropogenic impact of atmospheric PM in Wroc1aw (SW Poland) and other Lower Silesia localisation.

We started the studies on the use of isotopic analysis to identify quantitative and qualitative solid atmospheric particles from the deposited atmospheric (passive method) (Górka and Jędrysek, 2008) by TSP (total suspended particulates) (Górka et. al., 2009) finally to smallest fraction  $PM_{10}/PM_{2.5}$  (particles less than 10/2.5 µm) (Górka et al., 2012,

2014. We reject very quickly passive method as a not promising tool for isotopic analysis (Górka and Jędrysek, 2008). Hence, our paper from 2009 describes results of applying the palynological and carbon isotopic analysis of the organic fraction of TSP fraction to discriminate distinct pollution sources and assess the anthropogenic impact for the investigated Czerniawa and Cieplice (two health resorts in Lower Silesia, SW Poland) areas. The samples of atmospheric particles were collected in twice a year in summer and winter season (from July 2006 to February 2008). The palynological spectra represent the vast majority local plant communities without a noticeable contribution of long-transported plant particles. Palynological analysis revealed also differences in the specificity of the two sampling areas, i.e. the higher contribution of identified organic material in Czerniawa stands for the more natural character of this site, but is also responsible for the higher allergic pressure when compared to Cieplice. The increased  $\delta^{13}$ C value in winter (heating period) was most probably caused by the uncontrolled contribution of coal soot. On the basis of isotopic mass balance, the calculated contribution of anthropogenic organic particles in the atmosphere reached in winter season 72% in Czerniawa and 79% in Cieplice.

In 2012 we have applied both palynological and carbon and nitrogen isotopic analyses of  $PM_{10}$  to trace its origin and to assess the anthropogenic impact for the Wrocław area. The usefulness of the palynological observations in the case of  $PM_{10}$  was much lower than that for TSP due to the resolution of absorbed particles but is still helpful for distinguishing C3/C4 plants that indicate long-distance transport of pollutants. The  $\delta^{13}C(PM_{10})$  values varied seasonally whereas the  $\delta^{15}N(PM_{10})$  values showed chaotic fluctuations. Our results indicated that during the heating period, the  $PM_{10}$  particles in Wrocław are derived mainly from local home heaters whereas, in the growing period,  $PM_{10}$  particles are derived from local transport and are partially generated by the industrial application of coal combustion outside the city of Wrocław.

Our most important paper concerning atmospheric particles was published in 2014 (Górka et al., 2014a). We analysed the natural and anthropogenic contributions of hydrocarbon groups (aliphatic and aromatic), as well as total organic carbon, in atmospheric PM<sub>10</sub> collected from Wrocław in 2007 (Fig. 2). The PM<sub>10</sub> samples were taken in the seasonal sampling program in 2007, and represent air pollution from all months of the year. The  $\delta^{13}$ C values of the total carbon varied seasonally and the calculated isotopic mass balance confirmed greater coal burning input, reaching 70.5%, in the heating season and dominant transported sources 47.5% in the vegetative season. The data obtained for the aliphatic fractions: carbon preference index (CPI), carbon number maximum (Cmax), wax n-alkane contents (%WNA), and  $\delta^{13}$ C values of the aliphatic fractions indicated a dominant anthropogenic origin (gasoline/diesel/ coal combustion) and a lesser biogenic input (biomass burning and natural organic matter). Petroleum and coal combustion emissions were confirmed by the presence of hopanes and moretanes. The molecular analysis of the concentrations and diagnostic ratios of the polycyclic aromatic hydrocarbons (PAHs) and the  $\delta^{13}$ C values of the aromatic fractions indicated that the main PAH sources were also collectively from the combustion of liquid fuels and coal. Based on PAH discrimination diagrams it is also clear that the main organic carbon source is derived from coal, biomass and petroleum combustion in both seasons. However, taking into account the PAH concentrations during the vegetative and heating seasons, coal and biomass burning seems to be their major source. Additionally, the polar organic compounds (mainly levoglucosan) confirmed a significant contribution from biomass burning to the total anthropogenic input. The general conclusion derived from the coupling of organic tracer analysis and carbon isotopic data of PM<sub>10</sub> was that the total carbon (including insoluble soot) is likely derived from fossil fuels combustion, while the extractable organic matter is a mixture from different sources with significant inputs of biomass burning. We have also shown that dominant organic tracers do not always represent the major input source in aerosol PM and the unresolved part of the organic matter (soot) is important in the carbon budget.



2007 Year

Fig. 2 Temporal variations of the carbon isotopic composition of total carbon, extract fractions (total extract, aliphatic and aromatic fractions) from  $PM_{10}$  during 2007 in Wrocław (Górka et al., 2014a – modified).

#### (D) Bioindicators used in atmospheric studies

The influence of air pollution on living organisms has been investigated for several decades. The increase of anthropopressure factors and a new quality of pollutants affect the organisms in their physiology and morphology. Species, both plants and animals, which accumulate pollutants in their body and show physiological, morphological or anatomical changes under the pollutants' influence are called bioindicators or biomonitors. One of the most popular and often used bioindicators, playing a very important role in monitoring the air quality, are lichens and mosses. In our studies, we used isotopic analyses of sulphur in mosses (Kosior et al., 2015) as well as carbon and nitrogen isotopes in lichens (Ciężka et al., 2016) to assess air quality in analyzed areas.

Sulphur is the element found in surplus in anthropogenic areas and one of the minerals responsible for the development of acid rains. The analysis of the S stable isotopes provides

a powerful tool for studying various aspects of the biogeochemical circulation of sulphur. In our studies,  $\delta^{34}S$  values and S concentrations were determined in a 90 days experiment carried out with the native moss *Pleurozium schreberi* from rural, urban and industrial sites in Upper Silesia in South part of Poland (Kosior et al., 2015). At the same time, *P. schreberi* from a control site was transplanted to the same rural, urban and industrial sites and the  $\delta^{34}S$  values and S concentrations were determined in the same 90 days experiment. The enrichment in <sup>34</sup>S (up to 4.7‰) of the examined mosses point that these plants answered the environmental pollutant stress. The sulphur isotopic composition in the transplanted *P. schreberi* was related to S concentrations of S were noted in the native than in the transplanted mosses from rural and urban sites while the opposite situation was reported in the industrial sites. The transplanted *P. schreberi* was a better sulphur bioindicator than the native moss in more polluted industrial sites and worse in less polluted rural and urban sites (Kosior et al., 2015).

Our second bioindicators investigation concerning the contribution of C/N/S of atmospheric pollutants, as well as their C and N isotopic compositions, which were reflected in the organic compounds inbuilt into the lichen thallus (Cieżka et al., 2016). The chemical and isotopic analyses were carried out on lichen Hypogymnia physodes gathered from Picea abies and Larix decidua, collected in in Karkonoski National Park and its closest vicinity in 2011. The ranges in isotope composition suggest different sources of C and N for Karpacz city compared to the remaining sampling sites. For Karpacz, the  $\delta^{13}$ C values suggest (in case the fractionation product-substrate does not exist and  $\Delta=0$ ) that the dominant sources are coal combustion processes, whereas, for remaining sampling points, the  $\delta^{13}$ C values are ambiguous and are masked by many mixed natural and anthropogenic processes. With the same assumption that  $\Delta=0$ , the  $\delta^{15}N$  values suggest that transport is not a dominant source of nitrogen within Karpacz city. Moreover, in this study we tested the possible fractionation ( $\Delta$ ) for carbon and nitrogen, assuming that within the investigated area, the source of carbon is probably CO2 and/or DIC (HCO3<sup>-</sup>) dissolved in precipitation, while the source of nitrogen is NOx and/or NO3- ion. The calculated fractionation factors were: (i) for gaseous carbon compounds  $\Delta CO_2$ -Corg value from -13.4 to -11.4‰, whereas for the ions form  $\Delta HCO_3^-$  –C<sub>org</sub> value from -16.6 to -14.6‰, (ii) for nitrogen gaseous compounds  $\Delta NOx-N_{org}$  value between approximately. -17 and -5‰, whereas for the ions form  $\Delta NO_3$  - $N_{org}$  value between -9.9 and -3.7‰ (Ciężka et al., 2016).

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### STOP 2: Sandstone in the historic monuments in Wrocław: pollution impact on weathering rates

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Locations: St. Elizabeth's Church (51°06'41.80"N, 17°01'49.51"E), St. Mary Magdalene Church (51°06'34.00"N, 17°02'06.51"E), National Museum (51°06'39.11"N, 17°02'51.48"E), Museum of Architecture (51°06'35.48"N, 17°02'32.50"E), Wrocław Market Hall (51°06'45.13"N, 17°02'24.13"E), Pomeranian South Bridge (51°06'49.73"N, 17°01'52.55"E).

Sandstone is often used as a building stone and undergoes weathering processes leading to the damage of historic monuments. Six historic buildings located in the city centre of Wrocław were studied (St. Elizabeth's Church, St. Mary Magdalene Church, National Museum, Museum of Architecture, Wrocław Market Hall, Pomeranian South Bridge). The research especially focused on determining and assessing differences of weathered sandstone surfaces exposed to environmental factors in anthropogenic setting conditions (sandstones from the monuments) compared to those in near-natural ones (sandstones from the quarries). An additional objective of the research, in cooperation with biologists, was the determination of the main lichen and moss species living on the analyzed building stones and an attempt to assess their role in weathering processes.

The study of rock materials was carried out by means of methods and equipment used in petrography and mineralogy, such as the polarising microscopy, the environmental scanning electron microscopy, the electron microprobe, the X-ray diffraction and other instrumental methods of determining the chemical composition of rocks.

Approximately 130 rock samples were analysed. Sandstones occurring in the monuments of Wrocław and in the quarries show a great similarity in mineral composition and textures. The main framework component in all samples is quartz, with average contents of approximately 98%. Cement is represented by microcrystalline silica and clay minerals (mainly kaolinite). The rocks studied show also significant textural similarities in terms of grain size, sorting and related parameters.

The analysis of sandstone surface reaction zones showed considerable differences between samples taken in the quarries and those from the centre of the of Wrocław agglomeration. The external surfaces of sandstones sampled in the quarries are mostly characterized by a strong granular disintegration with related flushing and redistribution of the comminuted material and its accumulation on the surface of the samples. On the other hand, the surfaces of the sandstones from the monuments and other buildings at Wrocław are additionally covered with a discontinuous, thin but compact crust which was probably formed as the result of reaction of rock components with environmental components (water with dissolved compounds) and then accumulation of reaction products together with environment - derived particles. The main component of the crust is amorphous / microcrystalline with varied elements' composition (predominantly Si, Al, Ca, Fe, S, P). Within this mass and on its surface, there are abundant particles of spherical shape (spherules), showing a variable chemical composition (mainly aluminosilicate glass and iron oxides). There are several secondary substances occurring on the surface of the crust, such as calcium sulphate, barium sulphate, sodium chloride and calcium phosphate.

Secondary substances of this type and spherules are very rarely observed on the surfaces of sandstones from the quarries.

Clear differences were also visible in the geochemical analysis aimed at comparing the heavy metal contents of the altered surface zones and the interior of sandstone samples. The near-surface zones (especially of the samples taken from the historic monuments) are particularly enriched in Pb, Zn, As and Cu and also in Ba, Co, Cs, Nb, Rb, Sr, U, V, Zr, Y.

All the differences in structure and composition of the surface altered zones on sandstones from the historic monuments and from the quarries are the results of different air pollutant concentrations found within the area of urban agglomeration, and that one distant from the anthropogenic impact. A similar relation is also observed in results of the biological analysis. The species diversity of mosses and lichens occurring on the quarry walls was much richer (48 species of lichens, 3 species of mosses) compared to the architecture objects at Wrocław (36 species of lichens,1 species of moss). One could notice also differences in the form of specimens of the same species depending on the place of occurrence. The mosses from quarries have much more developed colonies compared to those from the city buildings. It was similar in the case of lichens. The lichen thalli from the quarries were bigger and more numerous than the equivalent species found in Wrocław.

The results show that despite a general similarity, the differences in structure and composition of reaction zones of sandstones from the two analysed site groups are significant. The main factor that determined the different course of weathering processes was the greater concentration of pollutants (anthropogenic gases and dust) in the urban environment.



Fig. 1 Secondary Electron Microscope images of weathering products: coatings observed in sandstones from the St. Elizabeth's Church (a,c) St. Mary Magdalene Church (b,d,e,f). Gp – gypsum, Brt – barite, Fe-Ox – spherical Fe oxides, Hl – halite.

### STOP 3: Sandstone in the historic monuments in Wrocław: pollution impact on weathering rates

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#### Location: St. Elizabeth's Church (51°06'41.80"N, 17°01'49.51"E)

Monumental St. Elizabeth of Hungary Church in Wrocław is located in the old town, nearby the north-eastern corner of the market square. The first church in this place was erected in Romanesque style, during the times associated with the first location of the city (1220s-1230s). In its present form, the temple was built in the 14th and 15th centuries, expressing the ambition and power of the Wrocław burghers – the founders of the Basilica. Apart from its undeniable, historic value, a part of the architectural details from the church is also an interesting example of the application of the local stones in architecture and art. One of the rocks used in details is sandstone. For example, the sacrament house in the interior of the church was made of sandstone, as well as the portal at the foothills of the Basilica and three of the four adjacent epitaphs (Fig. 1).



Fig. 1. Epitaph of Georg Althoff Scholtz.

Samples of clastic rocks taken from the sacrament house, the portal and adjacent epitaphs represent quartz sandstones with silica-clay binder accompanied with Fe-hydroxy-oxides:

goethite  $\alpha$ -FeOOH and lepidocrocite  $\gamma$ -FeOOH. Both clay minerals and iron hydroxyoxides are considered as primary binder elements.

Petrographically, the samples are similar to each other, with small differences in binder content and grain size. In case of the sacrament house, we additionally distinguished one petrographic variant – medium-grained quartz arenite. The lithic fragments, feldspars or accessory elements (opaque minerals, muscovite, tourmaline, zircon) are scarce. Sandstone samples from the late Gothic portal and three epitaphs are similar. However, the samples are more differentiated than in the case of fairly uniform quartz arenites from the sacrament house. Greater diversity of the samples may be explained by the restoration, because it is known that in the 19<sup>th</sup> century the portal was renovated (Wandrychowska 2013). The framework of the samples is dominated by quartz; also some lithic fragments, feldspars and accessory elements are present, as in case of the sacrament house. A matrix content of more than 15% (Pettijohn et al., 1987) classifies 5 samples as wackes and the others as arenites. Seven samples of sandstone from the portal can be described as medium-grained and three - as fine-grained.

Quite unusual for the analysed sandstones is the presence of minerals such as gypsum or carbonates (calcite), which should be interpreted as foreign substances. It should be noted that carbonates are very easily mobilized. They can be dissolved by rain water and deposited in the rocks even before they are quarried and used for construction purposes. The carbonates in the samples could be derived from the the lime mortars or other details made of limestone, which occur in close proximity. Likewise, migration of carbonates could be caused by the permeation of subterranean water or an influence of precipitation waters (Michniewicz 1996). The presence of gypsum may be explained as the effect of pollution. The analyzed samples were taken from an object located in the centre of a large city, where sulfur compounds (mostly SO<sub>2</sub>), derived from the combustion of fuels, can affect the rate of weathering of natural rocks and – in combination with carbonates – lead to the formation of gypsum (Michniewicz 1996).

An important issue for clastic rocks taken from the portal, the epitaphs and the sacrament house is their provenance. The probable source of sandstones from the examined architectural details were the Conacian joint sandstones from the North Sudetic Basin, occurring for example in outcrops in Żerkowice, Rakowice Małe, Czaple or Wartowice. It is suggested by the petrographic characterization of the samples, the period when the details were produced and the known period of time of exploitation of the Lower Silesian sandstones. These outcrops occur also in close proximity and the historical records mention using these rocks in the significant part of the monuments in Wrocław (Michniewicz 1996).

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### XXIVth Meeting of the Petrology Group of the Mineralogical Society of Poland

### Appendix

### Session

"Petrogenetical records in phosphates – insights into their formation/transformation processes"

Organized by the Committee of Mineralogical Sciences: Polish Academy of Sciences

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



### Hydrothermal synthesis of phosphate and arsenate copper minerals – libethenithe and olivenite

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Libethenite  $Cu_2(PO_4)OH$  and olivenite  $Cu_2(AsO_4)OH$  are endmembers of solid solution series of secondary minerals present in oxidation zones of copper deposits. We developed a hydrothermal method of their synthesis. This will allow in future for experiments simulating processes of their formation and transformations. Also, this may be useful in technical applications since these phases are manufactured as catalysts.

The precipitation experiments were run by precipitation from aqueous solution. At ambient temperature this process is slow, precipitation of libethenite can take as long as three-four months. Formation of olivenite is faster. Solutions containing  $Cu(NO_3)_2 \cdot 3H_2O$ , and  $(NH_4)H_2PO_4$  or  $Na_2HAsO_4 \cdot 7H_2O$  in stoichiometric molar proportions were mixed in 30 ml teflon beakers at pH = 2.9 and placed in autoclave at 120°C for ca. 17 h.

Synthesis of libethenite resulted in formation of deep green, crystalline precipitates with crystals apparent with naked eye. Synthesis of olivenite resulted in finer, cryptocrystalline light green powder. Products of the synthesis were identified with powder X-ray diffraction, Raman spectroscopy and scanning electron microscopy. Olivenite precipitates directly from the solution while libethenite forms through intermediate blue precursor phases. It is apparent that this synthesis is very sensitive to pH and temperature which affect the effectiveness and kinetics as well as the morphology of the precipitates.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



#### Lead phosphates in the soil: revisited

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The amendments of phosphates into Pb-contaminated soils reduce the bioavailability of lead by conversion of labile Pb species into extremely insoluble lead apatite – pyromorphite Pb<sub>5</sub>(PbO<sub>4</sub>)<sub>3</sub>Cl. The stability of lead apatites provide a potential for low-cost *in situ* remediation methods by neutralization of Pb toxicity without removal.

The literature review indicates that vast majority of research concentrates on the effectiveness of the method or on particular case studies. Our understanding of the processes associated with the formation and transformation of Pb-containing solids in the soil environment is still inadequate. Only full understanding of the mineral-water interaction mechanisms and their limitations would allow for intelligent application, optimization and control of this complicated environmental engineering methods in fragile, unequilibrated environmental systems. It took nearly ten years to resolve (at the end of XX century) the initial controversy on the transformation of Ca- to Pb-apatites: Ca-Pb ion exchange mechanism versus dissolution/precipitation. Current hot topics include competition between precipitation of lead apatites and sorption of Pb or phosphates on the surface of other phases existing in the system (particularly on crystalline and amorphous solids containing Fe or Mn), the effect of ionic substitutions on thermodynamic stability, and the microscopic mechanisms of transformation of Pb-containing solids into phosphates.

The role of microbial presence and activity was recognized from the beginning. However, only recently it was recognized that in the P-deficient environment bacteria and fungi can actively scavenge for phosphate. Microbially induced solubilization of pyromorphite results in re-mobilization of Pb in soil solutions. Therefore, long term effectiveness of the method may require constant monitoring and repeated amendments of phosphates in the field. This issue is still poorly recognized in the remediation practice.

There is no evidence that hydroxylpyromorphite  $Pb_5(PO_4)_3OH$  precipitates as a result of the remediation procedures in the field. The analogy between Ca-apatites and Pb-apatites is abused by many researchers. In aqueous Ca-systems,  $Ca_5(PO_4)_3OH$  is the most stable apatite while in Pb-systems the chlorine variety  $Pb_5(PO_4)_3Cl$  is stable and thermodynamically favored. The reasons for that discrepancy still await explanation.

To date, the legal assessment of soil pollution is based on total Pb content (presented in mg  $Pb_{tot}/kg$  soil). The speciation of lead in the system is not even considered. This archaic practice makes *in situ* immobilization/fixation/neutralization techniques legally useless despite the fact that these procedures are successfully applied worldwide for over 20 years.

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