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**XX<sup>th</sup> Anniversary Meeting of the Petrology Group of  
the Mineralogical Society of Poland**

*From the deep Earth to the human's environment*

Abstracts and field trips guide



Niemcza, Poland, 17-20 October 2013

***Mineralogia - Special Papers* formerly *Mineralogia Polonica - Special Papers***

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# **XX<sup>th</sup> Anniversary Meeting of the Petrology Group of the Mineralogical Society of Poland**

*From the deep Earth to the human's environment*

organized by

**Mineralogical Society of Poland**



together with

**Institute of Geological Sciences of the University of  
Wrocław**

**Niemcza, 17-20 October 2013**

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## **XX<sup>th</sup> Meeting of the Petrology Group of the Mineralogical Society of Poland**

*Welcome to the XX<sup>th</sup> Session of the Petrology Group of the Mineralogical Society of Poland!*

Over 20 years ago, at the end of 1992, group of our professors, led by Alfred Majerowicz from the University of Wrocław, established the Petrology Group of the Mineralogical Society of Poland. In October 1993, the first meeting of the Group was organised in Wrocław; Jacek Puziewicz was elected to be the chair, presenting the program of organisation of annual meetings which should bring together the petrologists working in Poland and enable youngest researchers to show the results of their studies to the broader audience.

The first Session of the Petrology, organised by the Wrocław team, was hold in Trzebieszowice with ca. 30 participants. The next sessions were also organised by Jacek Puziewicz and his students and co-workers, and gradually they started to gain the broad whole-country audience. The third weekend of October proved to be the very good term for the Sessions. These were the “hard times” for Polish science, with low funding in the period of political and economical transformation and with the Earth sciences entering gradually the international research and cooperation schemes. The Sessions were thus the low-budget ones, with some unexpected events, like total collapse of heating in Kowary (20-22 October 1995) during the second Session, which forced all the participants to impregnate themselves intensely each evening. In spite of budget restrictions, the Sessions were always full of joy of both scientific and not-scientific nature, and the gathering of all participants during intense evening discussions became also the tradition after the Kowary one.

Two important things happened at the turn of XX<sup>th</sup> and XXI<sup>st</sup> century. The first Session of the Petrology Group hold in English took place in 1999 in Sobótka-Górka. The change of Sessions language was important for making them visible to the international audience and to enable the non-Polish petrologists to participate. I remember well the strange feeling when the group consisting of more than 90% of Polish started to communicate in English... The Session in Sobótka-Górka was the last one from the series organized by the Wrocław team. The next Session – in Osieczany in 2000 was the first one organised by the group from another research centre and the first one organised outside the Sudetes. In the following years all the petrology research groups from Poland organised the Sessions.

Now we are used that the annual Sessions of the Petrology Group simply are. We are used to their mixed local/international character and to their individual style. We feel that they are the joint venture of us, Polish petrologists, and we enjoy participating. Let's enjoy!

*Jacek Puziewicz  
Head of the Organising Committee*

## MEETINGS OF THE PETROLOGY GROUP OF THE MINERALOGICAL SOCIETY OF POLAND

- 1994** Session in Trzebieszowice (14 – 16.10); topic: "Problemy petrologii skał zdeformowanych niekoaksjalnie", organizer: University of Wrocław
- 1995** Session in Kowary (20 – 22.10); topic: "Nomenklatura skał metamorficznych" (Prace Specjalne, Zeszyt 6), organizer: University of Wrocław
- 1996** Session in Lubawka (18 – 20.10); topic: "Zastosowanie metod geochemicznych do rozwiązywania problemów petrologicznych i geologicznych" (Prace Specjalne, Zeszyt 8), organizer: University of Wrocław
- 1997** Session in Pokrzywna (17 – 19.10); topic: "Integracja badań petrologicznych i tektonicznych w celu zrekonstruowania historii kompleksów metamorficznych granicy Sudetów Zachodnich i Wschodnich na Bloku Przedśudeckim" (Prace Specjalne, Zeszyt 9), Organizer: University of Wrocław
- 1998** Session in Karpacz (16 – 18.10); topic: "Strukturalna i metamorficzna ewolucja bloku Karkonosko-Izerskiego" (Prace Specjalne, Zeszyt 11), Organizer: University of Wrocław, Institute of Geological Sciences-Polish Academy of Sciences
- 1999** Session in Sobótka-Górka (15 – 17.10); topic: "Metamorphic evolution, igneous activity and structural development of the Strzelin Crystalline Massif" (Prace Specjalne, Zeszyt 14), Organizer: University of Wrocław
- 2000** Session in Osieczany (13 – 15.10); topic: "Geology and petrology of the Upper Silesia and the Małopolska Terranes Boundary Zone" (Prace Specjalne, Zeszyt 17), Organizer: Jagiellonian University, Kraków
- 2001** Session in Łądek Zdrój (18 – 21.10); topic: "Metamorphism in the Śnieżnik area, organized on occasion of Centennial anniversary of Kazimierz Skulikowski's birth and 300 years of the Wrocław University, (Prace Specjalne, Zeszyt 19), Organizer: Institute of

Geological Sciences-Polish Academy of Sciences, University of Warsaw, University of Wrocław, Adam Mickiewicz University, Poznań

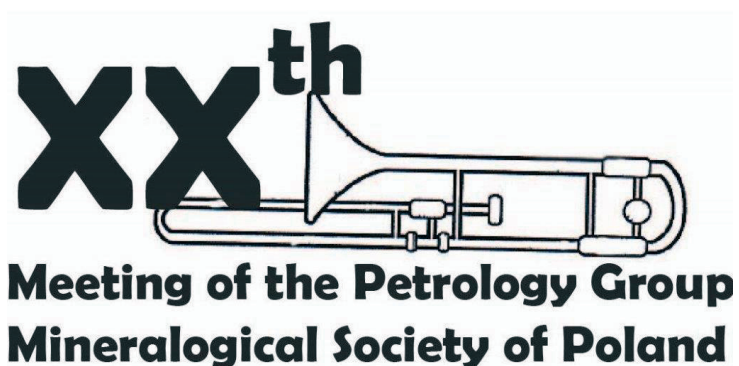
- 2002** Session in Szklarska Poręba (17 – 20.10); topic: "Granitoid massifs and evolution of their cover", organized on occasion of 50<sup>th</sup> anniversary of the Faculty of Geology of the Warsaw University, (Prace Specjalne 20), Organizer: Warsaw University
- 2003** Session in Głucholazy (17 – 19.10); topic: "Eastern cover of the Zuloa pluton" organized on occasion of 30 years of the Petrography direction in teaching at the University of Wrocław, (Prace Specjalne 23), Organizer: University of Wrocław
- 2004** Session in Ustronie (14 – 17.10); topic: Hypabyssal magmatism and petrology of the flysch in the Western Carpathians. (Prace Specjalne 24), Organizer: University of Silesia, Katowice
- 2005** Session in Stary Folwark (13 – 16.10); topic: Crystalline rocks of the East-European craton. (Prace Specjalne 26), Organizer: Warsaw University, Polish Geological Institute
- 2006** Session in Złotniki Lubąskie (19 – 22.10); topic: Mantle beneath SW Poland and some occurrences of related Tertiary volcanism. (Prace Specjalne 29), Organizer: University of Wrocław
- 2007** Session in Bukowina Tatrzańska (18 – 21.10); topic: Orogenic and platform granitoids. (Mineralogia Polonica – Special Papers 31), Organizer: University of Silesia, Katowice
- 2008** Session in Szklarska Poręba (10-14.9). (Mineralogia - Special Papers 32), Organizer: Jagiellonian University, Kraków
- 2009** Session in Święty Krzyż (24 – 27.9); topic: Magmatism and metamorphism in the Holy Cross Mts. (Mineralogia - Special Papers 34), Organizer: University of Silesia, Katowice.
- 2010** Session in Różanka (14 – 17.10); topic: Lamprophyres and related mafic hypabyssal rocks: current petrological issues (Mineralogia – Special Papers 37), Organizer: University of Wrocław

- 2011** Session in Bukowina Tatrzańska (21 – 23.10): topic: Migmatites: Contemporary Views and Examples (Mineralogia – Special Papers 38), Organizer: University of Science and Technology, Kraków
- 2012** Session in Obrzycko (19 – 21.10): topic: Meteorites: insights into planetary compositions (Mineralogia – Special Papers 40), Organizer: Adam Mickiewicz University, Poznań

**XX<sup>th</sup> Anniversary Meeting of the Petrology Group of  
the Mineralogical Society of Poland**

*From the deep Earth to the human's environment*

***Invited lectures***







## **Solid speciation studies a tool to assess potential release of « Heavy Metals » from mining and industrial contaminated sites**

Hubert BRIL

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Usually, metallic pollution is assessed only in chemical ways: the administrations in charge of environmental questions take waste sample(s), water sample(s) and/or a plant sample(s). After collection, the samples are crushed, analysed and the results represent the maximum expected (or the maximum possible) pollutants release. Potential risks are assessed by chemical extractions operating for one day, one month etc. more or less aggressive chemicals which are supposed to act as given environmental conditions (e.g. reductive, acidic etc.). Afterwards the results are compared to environmental quality standards, for example the Water Framework Directive (Directive 2000/60/EC) of the European Union. In conclusion, the polluted site is notified as more or less dangerous and remediation works are expected before the beginning of such and such a year.

These chemical methods have the advantage of being practical, rapid (several days are sufficient to test a site), precise (encoded) and (the most important) cheap. However they present important imprecisions because they are based on the hypothesis of similar behaviours between chemicals and alteration processes, they also give incorrect estimates of potential risks, they only give a mean diagnosis for a bulk sample, and finally, the time factor is not correctly taken into account. On the other side, mineralogical approaches are perceived as too difficult to implement, too time consuming, too expansive and too vague in the conclusions they allow. Moreover the results seem to be too complex to be understood by all the actors, scientists and non scientists.

Nevertheless, mineralogical studies which are based on classical microscopies and spectroscopies but also on more recently developed tools such as synchrotron facilities include very different aspects and can give answers to numerous questions and are really predictive. Indeed, the observation of mineral assemblages (primary, secondary and even “tertiary”) and their relationships constitutes a good qualitative introduction to the historical evolution of the site. The knowledge of the solid speciation of the main pollutants allows a reconstruction of the physico-chemical conditions, of their formation whereas the stability of all the phases can be estimated by the observation of the damages really affecting the different metal-bearing phases.

Based on examples concerning mining and industrial waste, the presentation will draw the contribution of mineralogy and petrology to the understanding of surface processes involved in metallic pollutions.



## Geochemical and petrological constraints on the origin of the Lithospheric Earth Mantle underneath the back arc environment along the North and Far East Russia

Theodoros NTAFLS

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### Introduction

The Pacific East and Northeast Russia is part of the circum-Pacific orogenic system, which formation is attributed to the subduction of the Paleo-Pacific plate and the eastern Eurasian continent. Along this orogenic system the Okhotsk-Chukotka volcanic belt, the Kamchatka and the Sikhote-Alin fold belts are the dominating tectonic structures (Parfenov & Natal'in, 1985). Within these structures Neogene alkali basalts brought to the surface mantle xenoliths of variable composition and their study enable us the possibility to infer the petrological and geochemical nature of the lithospheric mantle as well as the melting and metasomatic processes taking place in the upper mantle.

### The Okhotsk-Chukotka Volcanic Belt

In the northernmost volcanic province Enmelen in Chukotka the lavas comprising nephelinites, olivine melanephelinites and basanites brought to the surface mantle xenoliths and an unusual large amount of pyroxene, ilmenite and phlogopite megacrysts. A striking feature of the basaltic lavas is their enrichments in LILE and Ti suggesting the presence of phlogopite in the source. Radiogenic Sr, Nd, Hf and Pb isotopic ratios approach MORB-values indicating that enrichments of a long lived depleted source in LILE was a recent event. The basaltic lavas have been generated in the asthenosphere and the calculated T and P of the melt segregation vary around 1400°C and 3.5 GPa respectively precluding plume activity in the area and supporting lithospheric extension.

The sampled xenoliths hosted by the lavas, besides the megacrysts, are mainly fertile spinel lherzolites but few depleted spinel lherzolites occur as well.

According to the trace element analyses of whole-rock and clinopyroxenes the Enmelen spinel lherzolites can be divided into three groups. Group A represents non-metasomatized 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 intermediate and HREE ( $La_N = 9 \times C1$ ). Their clinopyroxenes are also enriched in LREE and plot sub-parallel to the whole-rock REE patterns ( $La_N \sim 70 \times C1$ ). The lack of hydrous phases suggests that group B has experienced cryptic metasomatism in previous stage(s) of their evolution before re-equilibration. Group C is characterized by the presence of amphibole. Chondrite-normalized REE from the core of clinopyroxenes have patterns with depleted LREE similar to those of group A. However, their rims show, relative to the core, an increase of the LREE ( $La_N/Sm_N = 0.21$  and 2.44 for core and rim



respectively). The introduction of fluids, rich in OH, LREE, Sr and Ti and the formation of amphibole must have taken place shortly prior to the incorporation of the rocks into the host lavas and before re-equilibration could be achieved.

The clinopyroxene Sr, Nd, and Hf isotope systematics ( $^{86}\text{Sr}/^{87}\text{Sr}= 0.70222\text{--}0.7310$ ,  $^{143}\text{Nd}/^{144}\text{Nd}=0.51303\text{--}0.51333$ ,  $\epsilon\text{Hf}=9.03\text{--}30.33$ ) indicate long term parent daughter depletion. In contrast to the radiogenic isotopes, whole-rock and trace elements represent fertile mantle that might have its origin in the asthenosphere (Ntaflos et al. 2008).

Further to the south in the area north of Magadan the mantle xenoliths are mainly anhydrous spinel lherzolites that are strongly to weakly foliated. The REE in clinopyroxenes have typical concave upwards mantle normalized patterns precluding metasomatic processes. In addition, the low  $^{87}\text{Sr}/^{86}\text{Sr}$  and the high, partly higher than MORB,  $^{143}\text{Nd}/^{144}\text{Nd}$  point to an asthenospheric origin. A possible model explaining the origin of the Viliga peridotites is a 'piecemeal' breakup of the subducted palaeo-Pacific plate, which allowed an upwelling asthenospheric mantle to intrude in the evolved window(s) between the slab pieces. Subsequently, olivine melanephelinites that were generated at deeper levels sampled the spinel lherzolites from the asthenospheric mantle on their way to the surface.

### **The Shikhote-Alin fold belt**

In the back-arc environment of Far East Russia, mantle xenoliths from Sikhote-Alin(KO) and Primorie (SV), Far East Russia are fertile spinel lherzolites with amphibole, phlogopite armalcolite, fassaite and röhrite in some of the studied samples. Though samples from both localities are fertile there is a systematic difference in their fertility. The KO samples have mg# varying from 0.891 to 0.899 and are slightly more fertile than the SV samples that have mg# ranging from 0.898 to 0.904. The cpx REE confirm this trend as the (La/Yb)<sub>N</sub> in KO samples range from 0.10 to 1.00 and in SV samples from 0.15 to 1.73.

The clinopyroxene Sr and Nd isotopic ratios range from 0.702599 to 0.703567 and 0.512915 to 0.513153, respectively, resembling Pacific MORB isotopic ratios.

En route breakdown of disseminated amphibole produces second generation of cpx and olivine and traces of glass as well fassaite and röhrite indicating crystallization at very shallow depths. Melt pockets consisting of Ca-rich glass plagioclase rutile, ilmenite and armalcolite suggest introduction of small amount of an unusual Ti-Ca-rich anhydrous silicate melt at mantle depths.

The lithospheric mantle beneath the studied area represents the residue after partial melting of up to 5% of a primitive mantle. Despite the fact that the studied area experienced several subducting episodes, the lithospheric mantle appears to be unaffected from the upwelling fluids/melts of the subducted slab(s). Since there is no indication for plume activity, and/or evidence for refertilization, it is likely that the lithospheric mantle has been delaminated as the result of tectonic events (lithospheric attenuation, inverse tectonic) associated with the subduction processes and that the studied spinel lherzolites represent upwelling asthenosphere.

### **Conclusions**

It is evident that the subducted palaeo-Pacific oceanic plate did not affect the back-arc lithospheric mantle along the Pacific East and Northeast Russia. While in the Okhotsk-Chukotka Volcanic Belt the study of the mantle xenoliths reveals processes related to the fact that the downwards moving slab experienced a piecemeal breakup which allowed an upwelling asthenospheric mantle through the window between the slab pieces, the studied mantle xenoliths from Sikhote-Alin and Primorie show that the lithospheric mantle has

been delaminated as the result of multiple tectonic events related to several subduction events in the area.

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## **Numerical simulation of magma mixing – from macro to micro scale**

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Magma mixing is a process commonly considered to trigger extreme geochemical heterogeneities on a micro and macro scale. On the macro-scale, the process is registered in rock geochemistry and textures. It is commonly accepted that if mixing is the only process occurring in the system, linear correlations between the concentrations of any two elements should result. The process has been simulated using a linear equation combining the composition of the two end-member magmas, that of the hybrid and the progress of the mixing process (Langmuir et al. 1978) – an equation that has been used in many publications (Słaby and Martin, 2008). An important new step in understanding the nature of magma mixing and its description was the application of fractal theory by Perugini and others (Perugini et al. 2003). Fractals are a geometric property of a set of points (each representing element concentration in the magmatic flow field) in n-dimensional space having the quality of self-similarity. The statistical distribution of such a set of points requires use of a non-linear equation.

The micro scale can be clearly recognized in mineral compositions and growth morphologies. Induced by mixing, crystal growth progresses in an environment where the dispersion of magmas proceeds by chaotic stretching and folding. As a result, magma domains with differing characteristics may occur simultaneously and/or sequentially close to the growing mineral surface and elements from all incorporated due to their advection and diffusive fractionation (Perugini et al., 2006; Słaby et al., 2011). The binary diagrams exhibit linear correlation for some elements in the crystal investigated and deviation from such for others, questioning the adequacy of the linear equation for describing the ongoing process on a micro-scale.

The mixing process has been simulated experimentally. A recent simulation by Perugini et al. (2008) is of particular importance for studies of single phase heterogeneity. It opens new perspectives for these studies and, in demonstrating that mixing does not show linear trace-element behavior during exchange on a short time span and allows for in-depth interpretation of trace element distributions in minerals formed during mixing.

Assuming the mixing process and associated chemical exchange to be time dependent, the dynamic of the advection-diffusion process should differ for elements with clearly different rates of diffusion. Indeed the long-range dependence of trace element behavior during mixing, reflected in element distribution in a single mineral, in its micro-domains is described by a non-linear equation (Słaby et al., 2011).

The mathematical description of mixing process depends on a scale, we investigate it. Macro and micro scale may acquire different mathematical models basing on linear or non-linear equations. The choice of the proper attempt of the model preparation should result from detailed recognition of the system geochemistry.

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## Mesoproterozoic Continental Rifting, Alkaline Magmatism, long-term Lithospheric Memories and Mantle Plumes

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South Greenland was part of the Columbia supercontinent in the Mesoproterozoic, consisting of Archaean craton, >2.9 Ga, and Palaeoproterozoic (Ketilidian) ~1.8 Ga. After *ca.* 500 Ma tectonic quiescence two principal episodes of continental rifting occurred at *ca.* 1.3 Ga and 1.16 Ga. Concomitant alkaline igneous activity created the Gardar Igneous Province. Close affinity of the magmatism in both the Older and Younger Gardar episodes points to control by lithospheric rather than asthenospheric mantle processes.

Both episodes involved large-scale basaltic magmatism. The transitional olivine basalt magmas were relatively evolved (MgO <7.5 wt%) with high LILE and F contents. Although enriched in K they were not typical alkali olivine basalts. High Al<sub>2</sub>O<sub>3</sub>/CaO ratios conferred a cpx-poor, troctolitic character. They are principally represented by dyke swarms although thick sequences of subaerial lavas of Older Gardar age are preserved.

Xenolith evidence indicates that a large coeval and comagmatic anorthosite complex underlies the Province, mainly composed of plagioclase flotation cumulates, that crystallised from hawaiitic magmas in the deep crust. Fractional crystallisation of the Gardar basaltic magmas beneath a capping of the anorthosite followed an iron-enrichment trend that led to ferro-mugearite and thence to benmoreite. At this latter stage magma densities were low enough to permit ascent by stoping, forming central-type (probably sub-volcanic) complexes at high crustal levels.

AFC processes gave 'liquid lines of descent' via trachyte either to quartz trachyte and comendite or to phonolitic residual products. These salic magmas crystallised to layered cumulate sequences showing evidence of unusual magma fluidity. Low viscosities also facilitated ionic diffusion, allowing crystallisation of very coarse behaviour is exhibited in the Ilímaussaq Complex (1.16 Ga) in which agpaitic magmas with (Na+K)/Al >1.2 and very high contents of HFSE were residual. Ilímaussaq is among the world's largest igneous repositories of U, Th, Be, Li, Be and REE.

The anorthosite evolution at depth was a controlling factor in petrogenesis of the salic alkaline rocks. The very low Sr contents and large -ve Eu anomalies are due to early plagioclase fractionation and the abundance of peralkaline compositions is ascribed to Bowen's 'plagioclase effect', again relating to early crystallisation of the anorthosite.



**XX<sup>th</sup> Anniversary Meeting of the Petrology Group of  
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## Duration and tectonics of prograde metamorphism and inversion of the Barrovian sequence in the Sikkim Himalaya, NE India

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The Lesser Himalaya in Sikkim region of NE India uniquely well preserved complete Barrovian metasedimentary sequence. This offers an inimitable opportunity for studying of timing, duration and rates of metamorphism during an orogenic cycle in a relatively simple tectonic setting of the Himalaya. Very little structural disturbance makes this location ideal for investigating the influence of increasing metamorphic grade on isotopic systematics in various geochronometers. We conducted Lu-Hf garnet dating of each metamorphic zone from the first appearance of garnet until muscovite dehydration melting, including all intermediate zones.

Lu-Hf dating of the Lesser Himalayan rocks revealed a very clear younging trend of ages with decreasing metamorphic grade: from  $16.8 \pm 0.1$  Ma at muscovite out reaction to  $10.6 \pm 0.1$  Ma in the garnet zone. Heavy Rare Earth elements zonation patterns in garnets show clear Rayleigh style distribution, which indicates that garnets from all zones preserved prograde growth. Comparison of isotope dilution and laser ablation ICPMS Lu content shows that the ages are representative of the early prograde growth, probably of early passage through a garnet isograd. Thus, in higher grade rocks, burial and heating was initiated earlier. Despite different timing of the growth initiation, separate core and rim dating of an individual garnet crystal from the kyanite zone suggests, that metamorphic peak was likely attained simultaneously in all zones at about 10-11 Ma. Additionally, high spatial resolution dating points to a rather fast synkinematic garnet crystallization. Hence, high precision of the obtained ages is not severely overestimated, which is commonly the case in the slow evolving settings.

High precision Lu-Hf ages allowed us to put rather tight time constraints on the formation of the inverted Barrovian sequence, which from garnet to sillimanite isograd lasted  $4.0 \pm 0.3$  Ma. This is in good agreement with similar estimates for the classic Barrovian sequence from Scotland determined as  $2.8 \pm 3.7$  Ma (Baxter et al. 2002).

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## Permian post-collisional volcanism in the Intra-Sudetic Basin – new data on eruptive processes and magmatic evolution

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The Intra-Sudetic Basin, a late Palaeozoic intramontane trough situated in the eastern part of European Variscides, provides a record of Carboniferous and Permian volcanism in a late- to post-collisional, intracontinental setting. Permian volcanic succession in the SE part of the basin reflects three stages of volcanic activity: (1) caldera-related rhyolitic stage – Plinian-type eruption of rhyolitic magma (tens of cubic km), formation of a caldera (10 km in diameter), deposition of tuffs (mainly ignimbrites); (2) post-caldera andesitic stage – eruption of andesitic tuffs and lavas (with minor intrusive activity) from small volcanic centres inside the caldera, and effusions or shallow level intrusions of basaltic andesites from small shield-type volcanoes outside the caldera; (3) post-caldera trachyandesitic stage – emplacement of basaltic trachyandesite to trachyandesite sills within sediments and tuffs along the caldera margins. Volcanism probably occurred between 290 and 283 Ma and the successive stages indicate a general shift to less evolved and more alkaline compositions with time. The volcanic rocks represent a bimodal, high-K calc-alkaline suite. Fresh mafic rocks consist mainly of plagioclase (bytownite to andesine), ortho- and clinopyroxenes (enstatite, pigeonite, augite), olivine (Fo55) with minor Fe-Ti oxides and alkali feldspars. Phenocrysts comprise olivine, pyroxenes and plagioclase, the latter often showing various disequilibrium textures (resorption, zonation). The rhyolitic tuffs consist of altered glass shards and quartz and alkali feldspar phenocryst with minor lithic clasts. The mafic rocks represent relatively evolved compositions (MgO=2-5%) characterized by enrichment in the large ion lithophile and light rare earth elements, depletion in Ta, Nb, Ti and Sr, negative  $\epsilon_{\text{Nd}}(283\text{Ma})$  of c. -3 and elevated  $\epsilon_{\text{Sr}}(283\text{Ma})$  of 50-60. The rhyolitic tuffs show relative enrichment in Rb, Th, K, Nb, Ta, La and Ce over Zr and Y, and depletion in Ba, U, Sr, P, Ti and Zr;  $\epsilon_{\text{Nd}}(283\text{Ma})$  ranges from -2 to -4 and  $\epsilon_{\text{Sr}}(283\text{Ma})$  from 82 to 94. Parental magmas of the suite (not erupted) possibly originated from a metasomatized mantle and could have also assimilated some crustal rocks. Differentiation of the andesitic/trachyandesitic melts was dominated by fractional crystallization and magma mixing with rather low influence of crustal contamination. The rhyolitic magmas represented the most evolved product of the above processes.

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## Mineralogical characterization of Baroque magnesian mortars from the Cistercian church in Kamieniec Żąbkowicki (SW Poland)

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This study presents mineralogical characterization of original (Baroque) mortars and plasters from the church of the Holy Virgin Mary and St. Jacob the Elder located in Kamieniec Żąbkowicki. The church belongs to the post-Cistercian monastery complex, formerly the Augustinian, in 1249 taken over by the Cistercians, who remained here until secularization in 1810. The monastery complex devastated by the Hussite War, was rebuilt in a Baroque style. All of the samples taken for analysis are dated to this period of time.

The samples were analyzed with optical microscopy followed by powder X-ray diffraction (XRD), simultaneous thermal analysis (DSC-TG), sieve analysis, and by scanning electron microscopy (SEM-EDX). All mortars comprise a carbonate binder and a fine to medium-grained inert aggregate, dominated by a quartz, with less common lithic fragments (granitoids and mica schists), plus accessory: garnet, biotite, muscovite, amphibole, staurolite, opaques. Red ceramic fragments and charcoal are very sparse and represent remnants of the burning process (fuel and clay from interior of the kiln).

The carbonate binder is strongly heterogeneous, rich in lime-lumps (binder-related particles), extensively weathered and cracked from secondary salt crystallization (gypsum). The presence of lime lump implies the mortars were poorly homogenized and the lime was dry-slaked during a short time, rich in underburnt carbonate rocks.

Thermal analyses in conjunction with X-ray diffraction allowed to distinguish three main constituents of the binder (fraction <63µm): (a) calcite (b) hydromagnesite and (c) dolomite. The hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) is well identified in the DSC curve showing the peaks corresponding to the three-step endothermal decomposition: at about 253 °C (the release of the four molecules of water of crystallization), followed at about 391 °C (the decomposition of the hydroxide ion to a further molecule of water) and finally, at about 441 °C (release of carbon dioxide). Also the presence of hydromagnesite was confirmed by XRD (peaks: 9.200 Å, 6.400 Å, 5.790 Å, 2.899 Å). The hydromagnesite resulted from the hydration and carbonation of MgO in the lime paste in a moist CO<sub>2</sub> rich atmosphere. This is the first case that magnesian mortars were detected as construction materials in Lower Silesia. Since the deposits of dolomitic marbles have been located in the vicinity of the Kamieniec (i.e. Krowiarki Mts), it seems reasonable that this rock have been included as prime material for the production of lime.

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## Polish vs. Czech moldavites – preliminary SEM investigation

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In Lower Silesia, the first Polish moldavites were discovered (Brachaniec et al. 2013). It is the fourth area, where tektites formed after impact in Ries, Germany may be found. Polish, Czech, Austrian and German tektites belong to Central European tektite strewnfields. Nowadays, only four tektite strewnfields are recognized (Koeberl 2007): Central European, North American, Australasian as well as Ivory Coast.

The investigation material has been collected in Pannonian sediments near Strzegom. Seven pieces of transparent, green tektites with their total weight 0.3 g were compared with moldavites from the Czech Republic.

Scanning electron microscope observations, including BSE images and EDS analyses were obtained by using a Philips XL30 ESEM/TMP equipped with EDS (EDAX type Sapphire) detector at the Faculty of Earth Sciences, University of Silesia. Fragments of both types of the tektites were put into epoxy in aluminum ring. The final casting form was polished on one side.

The morphology of both tektite types show presence of linear, parallel grooves. Sometimes, vesicles up to 80  $\mu\text{m}$  in diameter are visible. The main mass of the Polish moldavites is represented by acidic glass with the typical content of:  $\text{Si} > \text{Al} > \text{K} > \text{Na} > \text{Ca} > \text{Mg} > \text{Fe}$ . Only lechatelierite (?) as a very pure silica is noted in all samples, Polish as well as Czech, and occurs mostly as irregular and elongated inclusions. Statistical distribution of lechatelierite (?) inclusions in tektites is bigger in moldavites from the Czech Republic than in Polish ones.

EDS analysis of Polish moldavites compared with data from world wide literature, shows a close similarity with other moldavites from the Central European tektite strewnfields. This clearly confirm their impact origin.

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## Experimental investigation into the relative stabilities of xenotime, (Y,HREE)-fluorapatite, and (Y,HREE)-epidote as a function of pressure, temperature, and fluid composition

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Xenotime, (Y,HREE)-apatite and (Y,HREE)-epidote/allanite stability relations during metamorphism strongly depend on pressure, temperature, and fluid composition. For instance, it has been shown that relative stabilities of allanite and xenotime in the low amphibolite facies pelites are sensitive to variations of both, temperature and CaO/Na<sub>2</sub>O ratio in the host rock (Janots et al. 2008). This study constrains relative stabilities of xenotime, (Y,HREE)-fluorapatite, and (Y,HREE)-epidote as a function of pressure, temperature, and a high activity of Ca vs. Na in the fluid.

The experiments at 2-10 kbar and 450-750°C were performed using a cold-seal autoclaves on a hydrothermal line (2-4 kbar runs) and piston-cylinder apparatus (6-10 kbar runs). The starting materials included inclusion-free crystals of the NWFP xenotime, albite (Ab<sub>100</sub>) or labradorite (Ab<sub>37</sub>An<sub>60</sub>Kfs<sub>3</sub>), K-feldspar, garnet, biotite, muscovite, SiO<sub>2</sub> and CaF<sub>2</sub>. Fluids included 2M Ca(OH)<sub>2</sub>, and Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O. Ca. 30 mg of solids and ca. 5 mg of fluid were loaded into 3x15 mm Au capsules and arc welded shut. Experiment durations were 16, 8, 6 and 4 days at 450, 550, 650 and 750°C, respectively.

The xenotime alteration is observed in all runs. The experimental products include (Y,HREE)-britholite or (Y,HREE)-fluorapatite in all runs, and a mineral with a composition similar to the sodic clinoamphibole in runs with (Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>+H<sub>2</sub>O). (Y,HREE)-epidote formed only in runs at 650°C and 8-10 kbar with 2M Ca(OH)<sub>2</sub>. These results are partially consistent with the relative stabilities of xenotime and (Y,HREE)-epidote observed in nature, showing that high Ca bulk content with high Ca/Na ratio promotes stability of (Y,HREE)-epidote.

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## Experimental, fluid-aided, low temperature mobilization of Y+REE and actinides between (Y+REE)-bearing phosphates and silicates

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The study explores mobilization of Y+REE and actinides between monazite (or xenotime), fluorapatite/britholite and silicates as a function of high Ca vs. Na activity in the fluid, under conditions replicating low-temperature metamorphism. The experiments were performed utilizing a cold-seal autoclaves on a hydrothermal line. The starting solids included inclusion-free crystals of the Burnet monazite (or NWFP xenotime) + albite ( $\text{Ab}_{100}$ ) (or labradorite,  $\text{Ab}_{37}\text{An}_{60}\text{Kfs}_3$ ) + K-feldspar + biotite + muscovite  $\pm$  garnet +  $\text{SiO}_2$  +  $\text{CaF}_2$ . Fluids included 2M  $\text{Ca}(\text{OH})_2$ , and  $\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$ . Mixed solids (20-30 mg) and fluid (5 mg) were loaded into 3x15 mm Au capsules and arc welded shut. Experiments were run at conditions of 2 kbar/250°C, 2 kbar/350°C over 40 days, and 4 kbar/350°C over 20 days.

Starting minerals are not altered in experiments with 2M  $\text{Ca}(\text{OH})_2$ , except 4 kbar/350°C runs, where partial dissolution on monazite and xenotime surface is observed, and britholite or britholite-(Y), respectively, are formed.

All monazite experiments with  $\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$  fluid resulted in alteration of starting minerals and formation of new phases. Monazite is strongly dissolved on the surface, and high internal porosity formed. Monazite alteration via fluid-mediated coupled dissolution-reprecipitation resulted in partial mobilization of Th, U and Pb. Consequently, the altered monazite domains yielded Th-U-total Pb dates from ca. 86 to 635 Ma, significantly lower than ca. 1072 Ma age of the original monazite. Released Th and U substitute mostly in steacyite formed in all runs, while REEs supplied REE-rich apatite formed in experiments at 2-4 kbars/350°C.

The xenotime grains are dissolved on the surface in all runs with  $\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$  fluid. Y-rich apatite, britholite-(Y) and mineral with composition similar to gerenite-(Y) formed.

Experimental results show that both monazite and xenotime are not stable in the system with high Ca-Na bulk content, under conditions of low-temperature metamorphism. Mobilization of REEs and actinides extensively increases in the presence of fluorine-bearing, alkali fluid. Alteration of monazite leading to disturbance of the Th-U-Pb system way below diffusional closure temperatures provides additional implications to chronological studies on monazite.

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## Experimental investigation into the relative stabilities of monazite, fluorapatite, and REE-epidote/allanite as a function of pressure, temperature, and Ca vs. Na activity in the fluid

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The stability relations of monazite, fluorapatite and REE-epidote/allanite as a function of P-T conditions and Ca vs. Na activity in the fluid were experimentally constrained. Experiments at 2-10 kbar and 450-750°C were performed using a cold-seal autoclaves on a hydrothermal line (2-4 kbar runs) and piston-cylinder apparatus (6-10 kbar runs) over 4-16 days. The starting materials included inclusion-free crystals of the Burnet monazite + albite (Ab<sub>100</sub>) or labradorite (Ab<sub>37</sub>An<sub>60</sub>Kfs<sub>3</sub>) + K-feldspar + biotite + muscovite + SiO<sub>2</sub> + CaF<sub>2</sub>. Fluids included 2M Ca(OH)<sub>2</sub>, and Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O. 20-30 mg of solids and 5 mg of fluid were loaded into 3x15 mm Au capsules and arc welded shut.

All experiments resulted in monazite alteration and formation of new phases. REE-fluorapatite and britholite are stable in a wide P-T range in both systems with high Ca and high Ca-Na activities. High activity of Ca in the fluid promotes alteration of monazite and formation of REE-epidote, REE-rich fluorapatite and britholite. In contrast, presence of Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O fluid, with bulk CaO/Na<sub>2</sub>O ratio of 1.0 in the system, retards formation of epidote.

The experiments so far support thermodynamic modeling (Spear 2010) indicating that increased Ca bulk content expands stability field of allanite relative to monazite towards higher temperatures. The influence of CaO/Na<sub>2</sub>O ratio in bulk content on the relative stabilities of monazite and REE-epidote in experiments is in agreement with natural observations from the amphibolite-facies Alpine metapelites (Janots et al. 2008).

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## Experimental study of the thermal transformation of siderite from the coal waste dump in Katowice-Wielonowiec, Poland

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Siderite is ubiquitous in coal waste dumps as it accompanies Carboniferous coal seams being exploited in the Upper Silesian Coal Basin. It occurs as layers interbedded with the coal seams and as concretions (sphaerosiderites), usually small in size. A sample of siderite (25 cm in diameter), collected from the coal-waste dump located in Katowice-Wielonowiec, Poland, consists of the minerals siderite (76%), dolomite (6%), quartz (7%), illite/muscovite (5%) and chlorite, kaolinite and feldspars (2%).

Samples of the siderite were baked under oxidizing conditions in a pipe furnace (PRC 65M Czylok) in separate experiments at temperatures of 400°C, 700°C, 900°C, and 960°C, all held for 5 hours. They were then heated in a thermal chamber (mri Radiation) coupled to a diffractometer (Bruker axs D8 ADVANCE). Phase compositions were checked up to 1200°C. A Scanning Electron Microscope (SEM-EDS), and a Field Emission Electron Probe Microanalyser (FE-EPMA) were used to confirm the chemical compositions of newly-formed mineral phases.

Magnesioferrite ( $\text{Fe}_2\text{MgO}_4$ ) appears in traces at 400°C. It is joined by minor wüstite ( $\text{FeO}$ ), graphite and very minor periclase ( $\text{MgO}$ ) at 420°C. High amounts of periclase and likely tetragonal maghemite are recorded in the range 700-800°C. Olivine also begins to appear in this range. At 900°C, periclase is absent, consumed by the formation of more olivine and the unit cell parameter  $a$  of the spinel phase has changed from 8.3998 Å (420°C) to 8.383 Å. At 1120°C, reflections for the spinel phase appear to correspond to magnetite ( $a \sim 8.306$ ) rather than magnesioferrite. This suggests migration of Mg from the primary structure of the spinel phase into the olivine-type. At the same time, reflections for olivine are shifted towards more fayalitic composition, suggesting additional consumption of wüstite. The main products of siderite transformation at 1200°C are: magnetite,  $(\text{Fe}^{3+}_{1.54}\text{Al}_{0.46}\text{Si}_{0.01}\text{Ti}_{0.01})_{\Sigma 2.02}(\text{Fe}^{2+}_{0.74}\text{Mg}_{0.20}\text{Mn}_{0.01}\text{Ca}_{0.01})_{\Sigma 0.96}\text{O}_4$ , i.e.,  $\text{Mag}_{59}\text{Hc}_{18}\text{Mfr}_{16}\text{Sp}_6\text{R}_1$ , where R stands for remaining end-members, i.e., jacobsite, galaxite, ulvöspinel, qandilite, and equivalents of harmunite ( $\text{CaFe}_2\text{O}_4$ ) and krotite/dmitryivanovite ( $\text{CaAl}_2\text{O}_4$ ); olivine,  $(\text{Mg}_{1.20}\text{Fe}^{2+}_{0.69}\text{Fe}^{3+}_{0.06}\text{Ca}_{0.04}\text{Mn}_{0.03})_{\Sigma 2.02}(\text{Si}_{0.96}\text{Al}_{0.02})_{\Sigma 0.98}\text{O}_4$ , i.e.,  $\text{Fo}_{59}\text{Fa}_{31}\text{Lh}_3\text{Co}_2\text{Te}_1$ ; P-bearing hedenbergite-diopside-esseneite-(...) pyroxene,  $\text{Ca}_{1.02}(\text{Fe}^{2+}_{0.42}\text{Mg}_{0.27}\text{Fe}^{3+}_{0.20}\text{Al}_{0.05}\text{Mn}_{0.03})_{\Sigma 0.97}(\text{Si}_{1.30}\text{Al}_{0.37}\text{P}_{0.13})_{\Sigma 2.00}\text{O}_6$ ; aluminous (clino) ferrosilite-rich pyroxene,  $(\text{Fe}^{2+}_{0.49}\text{Mg}_{0.31}\text{Al}_{0.18}\text{Ca}_{0.02}\text{Mn}_{0.01})_{\Sigma 1.00}(\text{Si}_{0.97}\text{Ti}_{0.01})_{\Sigma 0.98}\text{O}_3$ ; magnesiowüstite,  $(\text{Fe}_{0.58}\text{Mg}_{0.30}\text{Ca}_{0.10}\text{Al}_{0.01})_{\Sigma 0.99}\text{O}$ , i.e.  $\text{Wus}_{59}\text{Per}_{31}\text{Lm}_{10}$ . This composition compares well with that of 'paralava'-like bodies, commonly found on burning coal-waste heaps.





## Thermal waters in an active subduction zone in Southern Peru

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The ascent of thermal waters in Southern Peru is connected with neotectonic movements which are the result of active subduction of the Nazca plate under the South American lithospheric plate. Water samples were collected during the Polish Scientific Expedition to Peru in 2010 and 2012 from a number of springs, streams and lakes in the vicinity of the Colca River between the villages of Chivay and Canco. The river course mainly follows active W-E and NE-SW faults. The springs sampled gush from different rock formations at different altitudes (1393 – 4752 m a.s.l.).

Water samples were collected in eight areas: (1) Canco – thermal springs flowing from sedimentary the siliciclastic Yura Group of Jurassic-Cretaceous age; (2) Huambo – river and karst springs in travertines; (3) Mucurca – lake on the colluvium of the Cenozoic volcanic Barroso Group; (4) Pinchollo – geyser and thermal springs gushing from Cenozoic rocks of the volcanic Barroso Group, and from nearby streams; (5) Yanke – thermal springs among Pleistocene lake sediments; (6) Chivay – thermal springs within the siliciclastic Murco Formation of Cretaceous age covered by volcanics of the Andahua Group; (7) Sallihua – thermal spring flowing out from a Quaternary alluvial fan and (8) Sibayo – thermal spring rising from colluvium of Mesozoic sandstones. Efflorescences of sulphate- and carbonate composition bloom around the geyser and thermal springs with temperatures ranging from 40-82°C.

The thermal waters are of three geochemical types. The first type is dominated by calcium and bicarbonate ions with an electrical conductivity (EC) ranging from 670-1130 µS/cm. The second is sodium-chloride water type with an EC in the range 1700-5560 µS/cm. The third type is sodium-chloride-sulphate with an EC between 5020-5200 µS/cm. It was confirmed, that  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  concentrations in all collected samples depend mainly on lithology of aquifer.

Hot geyser water mixing with river water results in the calcium-sulphate water type. This implies that regardless of the depth of its reservoir, river water descends deeply along fault planes to mix with hot water rising along cross-cutting faults from volcanic strata at depth.



## Peridotitic xenoliths from Pilchowice basanite (SW Poland)

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The basanite from Pilchowice (SW Poland) belongs to the alkaline lava occurrences forming the Polish part of the Central European Volcanic Province. The outcrop of basanite is located at the Intra-Sudetic fault, the major Variscan dislocation in NE part of the Bohemian Massif. The basanite, known for abundant rhönite (Ladenberger et al. 2006 and references therein) contains numerous, usually small (<10 cm) peridotitic mantle xenoliths. Their protogranular texture (olivine up to 8 mm, common kink bands) is obliterated by intense fissuring and fragmentation of the grains. Olivine, ortho- and clinopyroxene and sparse spinel are the primary minerals; clinopyroxene occurs only in the part of the studied samples. The olivine (Fo<sub>90.2-91.5</sub>) contains 0.35-0.45 wt. % NiO. Clinopyroxene-free harzburgites contains Al poor orthopyroxene (mg# 0.92, 0.02-0.03 atoms of Al per formula unit, pfu in the following) and Cr-rich spinel (cr# 0.8). The clinopyroxene-bearing peridotites contain orthopyroxene slightly richer in Al (mg# 0.92, 0.04 atoms of Al pfu) and mildly Al impoverished clinopyroxene (mg# 0.92, 0.09 atoms Al pfu). The temperatures of equilibration recorded in ortho- and clinopyroxene pairs are close to 900°C. One of the peridotites contains clinopyroxene with abundant spongy rims. The orthopyroxene occurring in this rock is Al-rich (mg# 0.92, 0.12 atoms Al pfu) and the primary (non-spongy) clinopyroxene is Al-enriched (mg# 0.92, 0.17 atoms of Al pfu). Major element mineral composition in these rocks suggests that they preserved depleted chemical characteristics, which has been little changed by later metasomatic events, excepting the sample containing spongy clinopyroxene. The analyses of trace element content in clinopyroxene reveal strong cryptic metasomatism in all the samples, with REE patterns enriched in LREE. The Ti and Zr/Hf negative anomalies in PM-normalised diagrams are of different extent suggesting various (silicate and/or carbonatite) nature of the metasomatisng agents.

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## Dust from metal smelters: mineralogy, leaching and contaminant bioaccessibility

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Non-ferrous metal smelters are important point sources of pollution. In this contribution we present data on mineralogy and leaching behaviour of dusts from one secondary Pb smelter located in Central Europe and several Cu smelters from Africa (Zambia, Namibia). Dry climate and strong winds are believed to be responsible for dispersal of contaminated dust particles in areas affected by mining, mineral processing and smelting (Ettler et al., 2012). We evaluated the solid speciation, leachability and potential bioaccessibility of metals (Co, Cu, Pb, Zn) and As in fly ashes and slag dusts. Dusts were highly enriched in inorganic contaminants (up to 273 g Cu/kg, 8.9 g Co/kg, 39 g Pb/kg, 21 g Zn/kg and 437 g As/kg). Based on XRD, SEM, EPMA and HRTEM investigations, major contaminant-bearing phases were cuprospinel ( $\text{CuFe}_2\text{O}_4$ ), chalcantite ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), delafossite ( $\text{CuFeO}_2$ ), arsenolite ( $\text{As}_2\text{O}_3$ ), galena ( $\text{PbS}$ ), anglesite ( $\text{PbSO}_4$ ), sphalerite ( $\text{ZnS}$ ), elemental Cu and Pb chlorides (Vítková et al., 2011; Ettler et al., 2005). The pH-static leaching tests indicated that contaminants were released from the fly ash mostly at low pH (Vítková et al., 2011). We also adopted *in vitro* methods based on simulated gastric fluid (SGF) and simulated lung fluid (SLF). The maximum bioaccessibilities in SLF were relatively low (Co 16%, Cu 2%, Zn 1.2%, As 2.9%), whereas values higher than 20% were obtained for SGF (Co 80%, Cu 50%, Zn 77%, As 83%). The obtained data indicate that a severe health risk related to smelter dust ingestion/inhalation should be taken into account particularly in dry areas in African countries. This study was supported by the Czech Science Foundation (projects no. 13-17501S and P210/12/1413) and IGCP project no. 594.

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## Rock-forming P-bearing ternesite from pyrometamorphic rocks of the Hatrurim formation, Israel

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Ternesite,  $\text{Ca}_5(\text{SiO}_4)_2\text{SO}_4$ , is a rare mineral, originally described from altered xenoliths in Eifel volcanites (Irran et al. 1997). Its anthropogenic analogue is known from burned dumps in Lapanouse-de-Sévérac, Midi-Pyrénées, France (Eytier et al. 2004). We have found ternesite in larnite pyrometamorphic rocks of the Hatrurim formation at two localities: Hatrurim Basin, the Negev Desert and Jebel Harmun, the Judean Desert, Israel (Novikov et al., 2013). Ternesite from larnite pyrometamorphic rocks was detected as intergrowths of poikilitic metacrystals up to 0.5 cm in size, associated with larnite, fluormayenite, ye'limite, fluorellestadite, gehlenite, brownmillerite, shulamitite, spinel. Ternesite replaces fluorellestadite. Ternesite from larnite rocks of the Hatrurim formation is different in composition from ternesite from the Eifel by its high  $\text{P}_2\text{O}_5$  content up to 7.5 wt.%. The cell parameters of ternesite from the Jebel Harmun (*Pnma*, orthorhombic):  $a=6.8428(1)$ ,  $b=15.3921(2)$ ,  $c=10.1836(1)\text{Å}$ ;  $V=1075.12\text{Å}^3$ , are slightly different from cell parameters of ternesite from the type locality:  $a=6.863(1)$ ,  $b=15.387(2)$ ,  $c=10.181(1)\text{Å}$ ,  $V=1075.1\text{Å}^3$  (Irran et al. 1997). Refinement of the ternesite structure by single-crystal X-ray methods and comparison of bond lengths with those of the ternesite structure by Irran et al. (1997) showed that phosphorus incorporates into the Si- and S-tetrahedra. Occurrence of ternesite in pyrometamorphic rocks of the Hatrurim formation as poikilitic metacrystals does not fit to the general scheme that suggests the formation of high-temperature mineral associations in fine-grained larnite pyrometamorphic rocks of sanidinite facies at dry conditions. Instead ternesite formed at HT in the presence of a fluid phase (sulphate-bearing melt?).

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## Potentially new ${}^Z\text{Ti}^{4+}$ -dominant garnet species of the schorlomite group

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Xenoliths within ignimbrites of the Upper Chegem Caldera, Northern Caucasus (Kabardino-Balkaria, Russia) are unique objects where great number of mineral species of the garnet supergroup were detected. These are minerals of the schorlomite group: kimzeyite, kerimasite, schorlomite; of the garnet group: andradite, grossular, uvarovite, morimotoite; and also ungrouped katoite. During the 2009-2011 six new garnet species were described from these xenoliths: bitikleite  $\text{Ca}_3(\text{Sb}^{5+}\text{Sn})\text{Al}_3\text{O}_{12}$ , usturite  $\text{Ca}_3(\text{Sb}^{5+}\text{Zr})\text{Fe}^{3+}_3\text{O}_{12}$ , dzhuluite  $\text{Ca}_3(\text{Sb}^{5+}\text{Sn})\text{Fe}^{3+}_3\text{O}_{12}$ , elbrusite  $\text{Ca}_3(\text{U}^{6+}_{0.5}\text{Zr}_{1.5})\text{Fe}^{3+}_3\text{O}_{12}$ , which formed a new bitikleite group; toturite  $\text{Ca}_3\text{Sn}_2(\text{Fe}^{3+}_2\text{Si})\text{O}_{12}$  and irinarassite  $\text{Ca}_3\text{Sn}_2(\text{Al}_2\text{Si})\text{O}_{12}$  complemented the schorlomite group (Grew et al. 2013). Recently in cuspidine zone of the xenoliths, minerals of the garnet supergroup with very complex composition were established:  $\text{Ca}_3(\text{Zr}_{1.10}\text{Sn}_{0.38}\text{Sb}^{5+}_{0.38}\text{Ti}^{4+}_{0.08}\text{U}^{6+}_{0.02}\text{Hf}_{0.01}\text{Sc}_{0.01})_{\Sigma 2}(\text{Fe}^{3+}_{1.55}\text{Al}_{0.82}\text{Ti}_{0.42}\text{Si}_{0.21})_{\Sigma 3}\text{O}_{12}$  (1) and  $\text{Ca}_3(\text{Sn}_{1.00}\text{Zr}_{0.75}\text{Sb}^{5+}_{0.20}\text{Fe}^{2+}_{0.02}\text{U}^{6+}_{0.01}\text{Hf}_{0.01}\text{Sc}_{0.01})_{\Sigma 2}(\text{Fe}^{3+}_{1.40}\text{Al}_{0.78}\text{Ti}_{0.48}\text{Si}_{0.34})_{\Sigma 3}\text{O}_{12}$  (2). Taking into consideration that these garnets are represented by complex solid-solution their classification should be based on the dominant valence rule and double-site occupation (Hatert and Burke, 2008). Both the above mentioned garnets belong to the schorlomite group as cation charge at (Z) tetrahedral site is 9.63 (1) and 9.82 (2), respectively (Grew et al., 2013). According to the octahedral site (Y) occupation and dominant type of three-valence cation at Z site, the first garnet is an analog of kerimasite ( ${}^Y\text{R}^{4+}>{}^Y2\text{R}^{5+}$  and  ${}^Y\text{Zr}>{}^Y\text{Sn}$  and  ${}^Z\text{Fe}^{3+}>{}^Z\text{Al}$ ), and second one – the analog of toturite ( ${}^Y\text{R}^{4+}>{}^Y2\text{R}^{5+}$  and  ${}^Y\text{Sn}>{}^Y\text{Zr}$  and  ${}^Z\text{Fe}^{3+}>{}^Z\text{Al}$ ). In all known minerals of the schorlomite group with ( $\text{R}^{3+}_2\text{R}^{4+}$ ) double-site occupation Si is the predominant cation at the Z site. In the described garnets  ${}^Z\text{Ti}^{4+}>{}^Z\text{Si}$ , what allows to consider above listed phases with crystal chemical formulae (1) and (2) as potentially new mineral species of the garnet supergroup belonging to the schorlomite group:  ${}^Z\text{Ti}$ -analog of kerimasite and  ${}^Z\text{Ti}$ -analog of toturite.

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## Application of ICP-MS and portable XRF in the study of soils from three historical areas of metal ore mining in the Holy Cross Mountains, Poland

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Soils at historical metal ore mining sites are enriched in potentially toxic trace elements due to natural processes (weathering of bedrock) and geoanthropogenic impact (ore mining and processing). Although metal ores have yet not been extracted in the Holy Cross Mts, the mining tradition in this area dates back to prehistoric times. Different metals, including Fe, Pb, Cu, U and Ag, were extracted in many parts of the Holy Cross Mts.

This study focuses on determination of trace metals in soils at three sites: Karczówka, Miedzianka and Rudki. Karczówka is a hill located in the western part of the city of Kielce. Lead was extracted in this area from the Medieval times up to the 17<sup>th</sup> century. Miedzianka Mt., situated in the westernmost part of the Holy Cross Mts, was the biggest copper and silver Medieval mining center of the region. Hematite in turn was mined as an iron ore for primitive furnace smelting during the Roman Empire at Rudki located at the Łysogóry fault (north of Holy Cross Mt.). After the Second World War, pyrite and uraninite had also been extracted there until 1971. Karczówka and Miedzianka are designated as nature reserves, whereas Rudki occurs within the Holy Cross Mts National Park buffer zone. This is the reason why environmental quality should be given high priority in these protected areas.

The principal objective of this study was to compare the element contents determined with an inductively coupled plasma mass spectrometry method (ICP-MS, model Elan DRC II) with those derived from field portable X-ray fluorescence spectrometry measurements (FP-XRF, model NITON XL3T 960 GOLDD+). About 60 samples were collected at Karczówka Mt. Prior to ICP-MS determinations, metals were extracted from soil samples with aqua regia, whereas FP-XRF measurements were preceded by minimal sample treatment (air-drying, grinding, sieving). The concentrations of abundant elements in soils are comparable and strongly correlated for both analytical methods. The study has shown that a low-cost, rapid, direct, non-destructive analysis of contaminated soils by FP-XRF (Kalnicky, Singhvi 2001) can be an alternative to trace element determinations by ICP-MS.

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## Assessing anthropogenic pressure on the Świętokrzyski National Park – preliminary results from a SCN multi-isotope approach from bioindicators

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The aim of this study is to assess the anthropogenic pressure in the Świętokrzyski National Park (ŚNP) coupling both quantitative (concentrations of atmospheric pollutants) and qualitative analyses (sulphur, carbon and nitrogen stable isotope compositions of bioindicators). Lichens (*Hypogymnia physodes*) and air samples were collected during the heating season (1-3 February 2013) from 20 points located in the ŚNP and its vicinity. The lichens species were sampled from bark and branches of *Abies alba* trees. The air samples were analysed for SO<sub>2</sub> and NO<sub>2</sub> concentrations using the Amay-Krochmal method with passive samplers, and for δ<sup>13</sup>C(CO<sub>2</sub>) and CO<sub>2</sub> concentration by CF-IRMS. Results for atmospheric SO<sub>2</sub> ranged from 0.77 to 22.82 µg·m<sup>-3</sup> with a mean value of 8.05±5.47 µg·m<sup>-3</sup>, and for NO<sub>2</sub> from 5.84 to 13.22 µg·m<sup>-3</sup> with a mean value of 7.52±1.94 µg·m<sup>-3</sup>. C and N concentrations in lichens varied from 43.3 to 52.2% with an average of 48.0±2.4% and from 0.8 to 3.1% with an average of 1.8±0.7%, respectively. In lichens δ<sup>13</sup>C values varied from -23.1‰ to -21.5‰ with an average value of -22.3±0.6‰. δ<sup>15</sup>N ranged from -11.8‰ to -8.1‰ with an average value of -9.7±1.2‰. Atmospheric CO<sub>2</sub> concentrations and δ<sup>13</sup>C(CO<sub>2</sub>) values are currently analysed and results will be discussed by the time of the conference.

Preliminary data indicate that: (i) δ<sup>13</sup>C value shows a slightly negative relationship with altitude (that may reflect natural stress factors: temperature, relative humidity *etc.* as well as anthropogenic pressure; e.g. tropospheric O<sub>3</sub> and CO<sub>2</sub>) and shows no relationship with the corresponding C concentrations, (ii) δ<sup>15</sup>N shows a slightly positive relationship with altitude and a slightly positive relation with N concentrations (that may reflect natural conditions or contribution from gasoline combustion from road traffic). S concentration (both sulphates and organic S) and their corresponding δ<sup>34</sup>S are currently analysed and will help better constrain anthropogenic contributions (results will be presented during the conference).

Spatial analysis of our results shows that: (i) NO<sub>2</sub> concentrations increase near main roads; (ii) SO<sub>2</sub> concentrations increase with higher altitude and near deforest areas; (iii) C and N isotopic depletion in lichens may reflect long distance transport of anthropogenic air pollutants (CO<sub>2</sub> and NO<sub>x</sub>) derived by local dominant W and NW wind direction.



## Fe-oxides in deep-water sediments (Mikuszowice Cherts, The Silesian Nappe, Polish Outer Carpathians) - evidence of bacterial iron mineralization?

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This paper presents new data on the biomineralogy of Mikuszowice Cherts, the series of the Late Cretaceous deep-water spiculites from the Silesian Nappe (SN). The Upper Ligota Beds, called the Mikuszowice Cherts is a turbiditic sequence. Samples for biomineralogical studies were collected from quarry in the Barnasiówka Range.

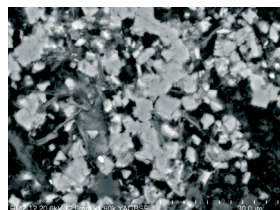


Fig.1. Remnant after bacterial filaments- iron oxide crystals.

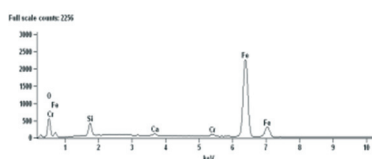


Fig.2. Microprobe analyses of the iron oxide crystal

Bacteria are found in every environments including the extreme, where they can be the only life forms e.g.: deep-marine sediments or deep sea hydrothermal. Bacterial processes can form iron minerals. Ferric Fe(III) oxides forming with bacteria effect characterize a highly insoluble and very often are preserved in sediments (Croal et al, 2004).

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## Geotectonic and regional significance of metaboninites from the Nové Město belt

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The Nové Město belt in the central part of the Sudetes comprises greenstones and amphibolites which show geochemical characteristics of tholeiitic basalts varying from depleted, N-MORB-like, to dominant, variably enriched intermediate between N-MORBs and E-MORBs, to enriched basalts intermediate between E-MORBs and OIBs. The mantle source to protolith of metatholeiites was heterogeneously metasomatised by subduction-derived component and by low-degree OIB-like melts generated in the garnet stability field. A variegated and heterogeneous input of components typical of both within-plate enrichment and active supra-subduction zone suggests the tectonic setting of back-arc basin of magma generation (BAB).

Metatholeiites are accompanied by rare high-Ca metaboninites (Mg# 71–74, TiO<sub>2</sub> 0.29–0.46 wt.%, CaO/Al<sub>2</sub>O<sub>3</sub> 0.8–1.1, Zr/Nb 77, [La/Yb]<sub>CN</sub> 1.00). Geochemical features of these rocks are akin to high-Ca boninites recognized in ophiolites of Troodos, Oman or Koh (New Caledonia) and also in back-arc basins of North Tonga and of the Dachadaban area (the North Quilan, China); they are similar also to metaboninites found in the Neoproterozoic basement in the SE part of the Teplá–Barrandian (the Kralupy–Zbraslav and the Štěchovice Groups; Ilnicki 2013 and references therein). The geochemical models show that the boninites were generated at ca. 1370–1470°C by 15–20% partial melting of the residual source depleted by an earlier tholeiitic melt extraction. The formation of the boninitic magma was preceded by metasomatic enrichment of the refractory mantle source by melts derived from sediments and amphibolites constituting the subducted slab.

The occurrence of boninites in the Nové Město belt relates the study area to the Teplá–Barrandian zone, as the only one in the Bohemian Massif where boninite dykes were also found. In the regional context, the association of boninites and the BAB tholeiites in the Nové Město belt is interpreted as a part of the back-arc system of the Cadomian volcanic arc preserved in the south-eastern part of the Teplá–Barrandian domain. Moreover, the generation of the boninite magma could have been related to ridge subduction and slab break-off under conditions of vanishing activity of the Cadomian back-arc zone.

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## Evaluation of sorption of peat to metal ions ( $\text{Zn}^{2+}$ and $\text{Cu}^{2+}$ ) as a tool in study of chemical structure of humic substances

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Chemical features of humic substances which are responsible for sorption of heavy metals result from presence and availability of reactive functional groups (i.a. carboxyl, phenol, hydroxyl), but binding mechanisms are different for different metals. Understanding these mechanisms may be useful in the characterisation of macromolecular matrix of humic substances.

Peat sediments contain organic matter, which is in general called humic substance. This substance is complex, complicated and variable in terms of molecular structure. It is a dynamic system which is subjected to constant transformation and nature of these changes depends on environmental factors: botanical composition, activity of soil fauna and microorganisms, hydrological and redox conditions and physical and chemical properties of the substrate. Fluctuations of those factors have an influence on the structure and properties of the peat as well as on the structure of the substances contained in humus.

Finally products of humification collectively called as humic substances can have various chemical compositions depending on the conditions under which they arose.

Popular spectroscopic techniques such as NMR, EPR, IR, allow to explore the complex structure of humic substances. Nevertheless, all these techniques are quite expensive. An alternative tool in research of molecular properties of humic substances may be a method involving the adsorption capacity towards heavy metal ions (such as  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ ). Basing on knowledge of the mechanisms of sorption of heavy metal ions by humic substances a relatively inexpensive and easy to use tool of exploring structure of humic substances can be obtained.



## Modelling the Kłodzko-Złoty Stok magma system using amphibole and two pyroxene geothermobarometry

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The Kłodzko-Złoty Stok granitoid intrusion is cross-cut by a number of dykes. Zircon dating (Mikulski et al., 2012) and careful field examination suggest that the dykes are comagmatic with the granitoids, and can provide information about deeper magma system levels unattainable from the granitoids alone. We have modelled the spatial structure of the magma system using P-T conditions determined for the crystallization of calcic amphiboles (Ridolfi and Renzulli, 2008) and/or two pyroxenes (Putirka, 2008) in the granitoid intrusion and related dyke rocks.

In general the P-T diagram and amphibole compositions show a variety of trends of which the most extreme can be interpreted as a result of different melt sources. Amphiboles from a spessartite from Mąkolno define a steep trend ranging from 2300 – 200 MPa and 950 – 800 C°, in contrast to zoned amphiboles from a pyroxenite located west of Złoty Stok which form a parabolic trend (2400 – 100 MPa and 1200 – 700 C°). The pyroxenite very probably originated as a mafic cumulate of a precursor magma. The P-T conditions calculated from two pyroxenes from a large dyke from the Bardo mountains near the Kłodzko-Laskówka road, overlap part of the last trend. Table 1 gives preliminary depths calculated from P.

This is the first quantitative model covering the whole magma system of a Variscan granitoid intrusion.

Table 1. Preliminary depth of magma chambers calculated

depth (km)	~30-35	~20	~14-15	~8-10	3-5 (granitoid body)
dyke rocks	Mąkolno lampr.	Droszków lampr.	all	all	andesite/ dacite vein

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## Pressure-temperature evolution of the HP-LT rocks from Nordenskiöld Land, Svalbard

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Recent fieldwork in western part of Nordenskiöld Land has established the presence of blueschists which occur in form of isolated bodies of different size and are enclosed within metasedimentary units. They are dark green and consist mostly of greenish amphiboles and reddish garnet. Blueschists are strongly retrogressed and the original progressive and peak HP assemblages are vastly replaced by later, lower pressure assemblages. However, garnet, actinolite, titanite and in minor amounts ferroglaucophane and phengite constituting the peak assemblage as well as epidote and pumpellyite belonging to the progressive assemblage, survived the retrogression. Garnet contains voluminous inclusions of epidote, chlorite, titanite, albite. Its composition varies from  $\text{Alm}_{62}\text{Prp}_0\text{Grs}_{36}\text{Sps}_2$  in the rims to  $\text{Alm}_{49}\text{Prp}_1\text{Grs}_{33}\text{Sps}_{17}$  in the cores. Gradual changes in chemical zoning as well as bell-shaped spessartine content profiles imply one-step, progressive garnet growth.

Since there is no suitable geothermobarometer available for the peak mineral assemblage, the pressure-temperature (P-T) conditions were estimated using the phase equilibrium modeling in the NCKFMnASHTO system using Perple\_X software. Modeling is based on bulk-rock chemistry and garnet and phengite compositional isopleths. P-T estimates indicate peak pressure conditions at c. 20kbar and 480°C. Chlorite + phengite + actinolite + ferroglaucophane + garnet + sphene + quartz are inferred to represent peak metamorphic assemblage, stable under high-pressure low-temperature (HP-LT) conditions. Blueschists from Nordenskiöld Land indicate a geothermal gradient of 7°C/km, which provides evidence for a unique cold subduction event in Paleozoic. These results are in agreement with the P-T estimates for the HP-LT metasediments of the Vestgötabreen Complex in the Motalafjella area (Agard et al., 2005), which occur to the north from the research area.

New evidence for blueschist facies metamorphism in Nordenskiöld Land suggests that the extent of the Caledonian HP-LT metamorphism on Svalbard is larger than previously supposed. These blueschist facies rocks may be an equivalent of the high pressure unit known from Oskar II Land (Motalafjella region), but more geochronological and petrological studies is needed to confirm this hypothesis.

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## Provenance of very low-grade metasedimentary rocks of the Variscan accretionary prism of the Kaczawa Mts. (SW Poland): preliminary geochemical data

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The Kaczawa Unit, together with neighbouring basement units, forms a structural mosaic of the Sudetes (SW Poland) at the NE edge of the Bohemian Massif. The provenance of metasedimentary and metavolcanic rocks that form the Kaczawa Complex, as well as their metamorphic P-T-t paths, are key questions for the hypothesis that the Kaczawa Unit comprises fragments of the Variscan accretionary prism. These questions have become particularly important since the 1970's when some of the rocks were classified as *mélange* rather than fragments of coherent stratigraphic successions as previously thought.

In an earlier study (Kostylew, 2007), metamudstones from the northern part of the Kaczawa Unit (Rzeszówiek and Chelmiec sites) were discussed. Here we present and preliminarily interpret new results of bulk-rock chemical analysis of 13 samples from various metasedimentary rocks (*mélange*, metamudstones, metasandstones and phyllites) from different structural parts of the Kaczawa Unit.

The provenance of metasedimentary rocks of the study area is assessed based on the Chemical Index of Alteration (CIA) and discrimination function analysis, using major-element and selected trace-element data (i.e. Eu/Eu\*, Zr/Sc, Th/Sc, Th/U and Gd<sub>N</sub>/Yb<sub>N</sub>). The results point to acidic igneous rocks of the upper crust as the likely main source for the protoliths of the metasedimentary rocks, possibly with a subordinate component of depleted mantle sources in the case of the Radzimowice Slates. Trends in major and trace elements compositions reveal both active and passive continental margins as possible tectonic settings of sedimentation. Overall data obtained are significantly scattered which can be an effect of diverse provenance areas for the metasedimentary rocks of various structural units of the Kaczawa Mts., as well as at least the possible two different geotectonical settings of deposition.

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## REE-rich allanites from a plagiogranite occurrence in South Othris, Greece

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Allanite-(Ce) is an important accessory phase, found within the plagiogranitic metaluminous rocks of the Paleokerasia ophiolitic mélange formation in South Othris, Greece. They form complex zoning patterns, having been affected by post-magmatic fluids. The plagiogranites whole-rock chemistry suggests that they were formed in extensional tectonic oceanic settings. Mineralogical and spectroscopic studies were carried out on the allanites, which are characterized by high LREE (e.g.  $\text{Ce}_2\text{O}_3 < 12.3$  wt%),  $\text{TiO}_2$  ( $< 4.07$  wt%) and low Th and Y contents. Allanite analyses have been separated into two groups, 1 (a, b) and 2. Group 1a corresponds to ferriallanite and exhibits relatively high  $\Sigma\text{REE}$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , FeOt, MgO and MnO contents, as well as the lowest  $\text{Al}_2\text{O}_3$  and CaO contents, whereas the LREE patterns are moderately fractionated [ $(\text{La}/\text{Nd})_{\text{CN}} = 1.19\text{--}3.10$ ;  $(\text{La}/\text{Y})_{\text{CN}} = 6.26\text{--}90.83$ ; Fig 1]. The high  $\Sigma\text{REE}$  and  $\text{TiO}_2$  contents, as well as the low  $\text{Al}_2\text{O}_3$ , MnO, and  $\text{ThO}_2$  are similar with allanites from extensional type granites (cf. Hoshino et al. 2006; Vlach and Gualda 2007). Group 1b differs in having highly fractionated LREE and the lowest HREE [ $(\text{La}/\text{Nd})_{\text{CN}} = 1.92\text{--}4.33$ ;  $(\text{La}/\text{Y})_{\text{CN}} = 170.22\text{--}552.62$ ]. Group 2 corresponds to allanite zones which have been affected more by post-magmatic processes, exhibiting the lowest  $\Sigma\text{REE}$  values, low  $\text{SiO}_2$ ,  $\text{TiO}_2$ , FeOt, MgO and MnO contents, but relatively high  $\text{Al}_2\text{O}_3$  and CaO contents. Their REE patterns are similar to Group 1a but are less fractionated. Raman spectra of the analyzed allanites show that these are characterized by a number of bands with the most intense arising at  $\sim 377$ , 478, 508 and  $654\text{ cm}^{-1}$ . Weaker bands appear at  $\sim 188$ , 212, 417, 887 and  $952\text{ cm}^{-1}$ . It seems a relation exists between the Raman band intensities and the REE contents of the zoned allanites

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## **Cu-Ag secondary mineralization in post-exploitation waste disposals of Cu-Ag Kupferschiefer deposit (SW Poland)**

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The aim of this work is characterisation of the Cu-Ag secondary mineralization in the post exploitation waste disposals of Cu-Ag Kupferschiefer deposit, Gilów and Żelazny Most. The study is also focused on the mobility of Ag released from Ag-bearing Cu sulphides during weathering.

The samples were collected from three, 6 meters deep drill holes. The mineral identification and planimetry were performed using reflected light polarizing microscope. Preliminary non-standardized chemical analyzes were performed utilizing FEI QUANTA 200 Field Emission Gun Scanning Electron Microscope equipped with the energy dispersive spectrometer (EDS) at the Faculty of Geology, Geophysics and Environmental Protection of the AGH-University of Science and Technology in Kraków. Chemical composition of minerals was determined using a Cameca SX-100 electron microprobe at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances of the Warsaw University.

The primary Cu sulphides are present in samples from both waste disposals. The main minerals include chalcocite, bornite, chalcopyrite and stromeyerite. Malachite is a secondary mineral formed during weathering in the Gilów waste disposal, while Cu chloride compositionally similar to atacamite group minerals is formed in the Żelazny Most waste disposal. The secondary minerals commonly form rims on the Cu sulphides, indicating partial replacement of primary phases. The Ag released from Ag-bearing Cu sulphides (up to ca. 5 wt.%) substitutes in newly formed, secondary minerals (up to ca. 0.5 wt.% Ag).

The minor concentrations of Ag in secondary Cu carbonates and Cu chlorides is strictly related to limited amounts of Ag relatively to Cu released from altered primary ore minerals. It has to be noted, that stability and formation of Ag-bearing minerals during weathering is controlled by pH-Eh conditions. Therefore, multiple factors controlling mobilization of Ag and formation of secondary minerals has to be considered.

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## Low-temperature metasomatic processes recorded by CuS-Cu<sub>5</sub>FeS<sub>4</sub>-CuFeS<sub>2</sub> phases – example from Cu-Ag Kupferschiefer deposit (SW Poland)

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Metasomatic processes, in general, result in re-equilibration of mineral assemblage driven by changes of pressure, temperature and/or local chemistry. The particular example of process leading to mineral replacement by a new phase(s) is a fluid-mediated coupled dissolution-reprecipitation (Putnis 2002). This study concerns metasomatic mineral sequence recognized in Cu sulphides from the Cu-Ag deposit.

Samples were collected from the Cu-bearing shale enriched in Ag (>100 ppm Ag) from the Lubin Mine (Kupferschiefer Deposit, SW Poland). The ore mineralization in the sample is dispersed in the shale or forms thin ore veinlets. The dispersed ore mineralization includes chalcocite, bornite, pyrite with rare native Ag and stromeyerite. Ore veinlets include intergrowths of, from core to rim, chalcocite, "half-bornite", bornite and chalcopyrite. The "half-bornite" zone shows zoning related to variations in Ag content.

The recognized textures represent sequence of ore minerals replacing chalcocite driven by changes to the conditions of temperature, pH, Eh, and hydrothermal fluid composition (cf. Reed & Palandri 2006). Such metasomatic alterations are interpreted as resulting from the fluid-mediated coupled dissolution-reprecipitation process.

*Acknowledgements:* Chemical analyzes of minerals were performed using JEOL JXA-8530F Hyperprobe field emission electron microprobe in the CEMPEG, Uppsala University and Cameca SX-100 electron microprobe at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances of the Warsaw University. This work was supported by the National Science Centre research grant (No 2011/03/N/ST10/04619).

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## Carboniferous (Mississippian) bentonites in the Sudetes (SW Poland): preliminary results of field and laboratory investigations

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This report summarizes preliminary data from fieldwork and laboratory investigations on Carboniferous (Mississippian) bentonites in the Sudetes carried on within the research project *Bentonites in the Visean of the Sudetes*. The main aim of the project is to correlate the isotopic zircon ages of the bentonites with their biostratigraphic position and to provide new geochronometric constraints for chronostratigraphic subdivisions of the Carboniferous (*c.f.* Kryza *et al.*, 2011).

Based on rather scarce information from earlier publications (*e.g.* Żakowa, 1958), bentonites have been searched for in 13 exposures of the Carboniferous molasse-type deposits in the Central Sudetes: 7 in the Intra-Sudetic Basin, 5 within the Góry Sowie Massif and 1 in the Bardo Unit. In a few profiles (Ptasia Góra, Jugów, Paprotnia), macrofauna has been found, whereas in others, it is rather scarce or absent. In Konradów, Głęboki Wąwóz, Szczawno and Ciechanowice, macroflora is present, while in Szczawno, Piaskowa Góra, new trace fossils have been discovered. Preliminary assessment of the fossils confirms a Mississippian (Visean-Namurian) age of the strata.

Bentonites have been found in four localities: Konradów, Ptasia Góra, Szczawno and Paprotnia. In other profiles, clay-rich layers in muddy sediments have also been sampled for test mineralogical investigations and stratigraphic correlations. Based on preliminary X-ray diffraction and thermal analysis results, the study bentonites are composed mainly of dioctahedral smectite–beidellite; some contain a mixed-layer I/S mineral, illite and kaolinite.

Selected samples of the bentonites and clay-rich sediments have been processed for zircon separation. In 18, out of 29 selected samples, zircon separates have been obtained. Morphology of zircons from the bentonites confirms their volcanic affinity. Selected zircon separates will be dated using adequate isotopic techniques (LA-ICP-MS, ion microprobe, ID-TIMS).

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## Xenoliths from Steinberg (Upper Lusatia, SE Germany): probes of lithospheric mantle beneath Central Europe.

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The basanite occurring in the Steinberg quarry (2 km to the west of Ostritz village, ca 15 km to the south of Görlitz in Lusatian part of Saxony, Germany) belongs to the Central European Volcanic Province. Numerous peridotite xenoliths of size not exceeding 8 cm occur in some places in the basanite.

Two kinds of peridotite occur in xenoliths from Steinberg. The peridotite I (6 xenoliths) has a protogranular texture. In some xenoliths the grains are intensely fissured. It consists of olivine (88.86 – 91.64 % Fo, 0.32 – 0.48 wt. % NiO), orthopyroxene (mg# 0.91 – 0.92, Al 0.05 – 0.13 apfu, Ca 0.01 – 0.06 apfu, but with small variation of Ca and Al in single xenolith), clinopyroxene (mg# 0.93 – 0.95, Al 0.04 – 0.16 apfu, Ca 0.86 – 0.97 apfu), and spinel (mg# 0.57 – 0.64, cr# 0.41 – 0.54). Clinopyroxenes from peridotite I are depleted in REE relative to primitive mantle. Their REE patterns are U-shaped. The peridotite II (1 xenolith) is consist of olivine (72.77 – 77.53 % Fo, 0.02 – 0.11 wt. % NiO), orthopyroxene (mg# 0.76 – 0.77, Al 0.15 – 0.20 apfu, Ca 0.02 – 0.03 apfu), clinopyroxene (mg# 0.83 – 0.85, Al 0.18 – 0.26 apfu, Ca 0.87 – 0.90 apfu) and spinel. Locally, it exhibits the cumulate texture. Clinopyroxene from peridotite II is characterized by flat REE pattern, slightly enriched relatively to primitive mantle, with weak positive Eu anomaly.

Peridotite I records strong depletion event, followed by enrichment by silicate alkaline melt or fluid. The agent was possibly CO<sub>2</sub> – bearing as is suggested by high Th – U and Sr contents in clinopyroxene (e.g. Dasgupta et al.). The forsterite and nickel contents in olivine occurring in peridotite II are typical for lower crustal cumulates.

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## Megacrysts of diopside from the Cenozoic Ostrzyca Proboszczowicka basanite (SW Poland)

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The basanite occurring in the Ostrzyca Proboszczowicka Hill close to Złotoryja (Lower Silesia) is one of over 300 hundred outcrops of Cenozoic alkaline volcanic rocks forming the north-eastern part of Central European Volcanic Province in SW Poland.

The few centimetre (typically 1.5 – 3 cm) clinopyroxene megacrysts occur sparsely in the basanite. The megacrysts are black in hand specimen and emerald-green or rarely yellow in thick (100 µm) section. They appear to be the anhedral fragments of broken crystals of larger size. Some have singular euhedral faces preserved. The sector-zoning is common; locally the sectors show internal zoning. Abundant, euhedral, large apatite crystals up to 7 mm in length or scarce, euhedral yellow 5 mm diopside crystals of older generation occur as intergrowths in the megacrysts. The 1 - 2 mm reaction fringes cover the margins of megacrysts. The megacrysts have the composition of iron-rich diopside (mg# = 0.61 – 0.68), contain significant sodium (0.09 – 0.12 atoms per formula unit, a pfu in the following), are Cr-free and Ti poor. Aluminium content varies from 0.13 to 0.27 a pfu, and that of Ca is 0.89 – 0.92 a pfu. Some sectors are enriched in Al (0.17 – 0.27 a pfu) and Ti (0.04 - 0.05), whereas others contain 0.13 – 0.15 atoms of Al pfu. The fringes contain 0.23 – 0.39 atoms of Al pfu, are calcic (0.92 – 0.96 a pfu) and titaniferous (up to 0.12 atoms of Ti pfu). The clinopyroxene crystals occurring in the basanite groundmass have the composition of subsilicic diopside (Si down to 1.6, Ca up to 1.1 atoms pfu; Al: 0.21 – 0.48, Cr: 0.00 – 0.02, Ti: 0.05 – 0.14, atoms pfu, cf. Fig. 1). The PM normalised REE patterns are typical for clinopyroxene in equilibrium with silicate melt. The fringes are much more rich in LREE (ca. 100 x PM) relative to the rest of grains (ca. 10 x PM) showing that the melt composition evolved between the place of crystal growth and the place of fringe formation (most probably in the vent during host lava eruption).

Textural relationships (large broken crystals with intergrowths of euhedral apatite and older generation diopside) suggest that the megacrysts are fragments of very coarse-grained cumulate. Major and trace element composition suggests that the megacrysts formed at significant depth (lower crust? upper mantle?) from the LREE enriched alkaline melt. That melt was very rich in phosphorous which enabled its saturation in apatite at the early stages of solidification.

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## **Apatite as a monitor of magma mixing – a multi-method approach**

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Apatites from the Karkonosze granitoid pluton were studied using several analytical and data-processing techniques including Cathodoluminescence (CL), Field-Emission Electron Microprobe (FE-EPMA), Particle-Induced X-ray and Gamma Emission (PIXE, PIGE), and Polytopic Vector Analysis (PVA). Each method was applied to visualize and interpret the effects of mixing of mantle-derived mafic and crust-derived felsic melts, along with the fluid overprint.

FE-EPMA, CL and PIXE/PIGE data reveal distinct changes in melt composition indicated by complex zonation patterns in individual grains. Alternating violet and yellow luminescence suggests rapid and multiple transitions from more alkaline to more acid environment during crystal growth. In early stages of intensive mixing with highest proportions of mafic melt, apatites display bimodal REE/Y ratios – increased in zones with mantle affinity and decreased in those parts that crystallized from more felsic melt. The ratio decreases with melt evolution. Chemical composition of apatites from all stages of magma mixing was employed to model the number and composition of magma sources, using a mathematical algorithm named Polytopic Vector Analysis. It analyzes a data population from every system formed from mixing of several components and derives the number and composition of these components and their proportions in every sample. Simulation for whole-rock chemistry gives satisfactorily results for three components – mafic, felsic and post-magmatic fluids. However, in case of apatites, the distribution of trace elements between the components disagrees with whole-rock chemistry. According to these results, the fluid component contains most of the REEs and Y, whereas, considering whole-rock chemistry, the mafic magma is most enriched in REEs and Y. Such difference in trace-element distribution may be caused by a different scale of processes that we observe in whole-rock and mineral chemistry. Fluid overprint is less visible in large-scale whole-rock geochemistry, whereas its influence is more significant in individual minerals. Factors like local saturation, diffusion rates, partition coefficients for varying melt compositions and presence of other accessory phases, have also to be taken into account.

Every method exposes different aspects of apatite formation in the mixing system and is crucial to understand the influence of such heterogeneity on apatite composition. PVA reveals different types of information depending on the input data – whole-rock chemistry gives us magma composition whereas apatite is a better proxy for fluid composition.

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## Heavy minerals from the Baga-Gazriin Chuluu A-type granite (central Mongolia)

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The territory of Mongolia is located in the central part of huge tectonic structure called Central Asian Orogenic Belt (Altaids). The major dislocation zone crossing the middle of Mongolia is Mid-Mongolian Tectonic Line (MMTL) which was formed as the result of closure of Mongol-Okhotsk Ocean (Tomurtogoo et al. 2005). The Mesozoic (T/J) Baga-Gazriin Chuluu (BGCh) granitic pluton outcropping at the area of ca. 120 km<sup>2</sup> lies within the tectonic zone marked by faults connected with the MMTL (Machowiak et al. 2013). The geochemical composition of BGCh granites is typical for A-type granites. The pluton is accompanied by numerous greisen veins, tungsten-tin and REE mineralization. The BGCh granites represent 3 textural variations: coarse-grained, medium-grained and fine-grained. The mineral composition of all the granitic textural subdivisions appeared to be almost identical. Apart from quartz the main rock constituent is K-feldspar (as perthite). In minor amount the granites contain laths of plagioclases with polysynthetic twinning (no zonal crystals) and dark micas (in different modal proportions) – mainly biotite and zinnwaldite with numerous inclusions of very small grains of zircon and monazite. In some samples small flakes of muscovite and white lithium mica are found. In all textural types (but not in every sample) fluorite and topaz are observed. The above-mentioned minerals occur in the studied granites in different proportions and form grains of different size (Machowiak and Stawikowski 2013).

The composition of heavy mineral assemblages in BGCh granite shows that most common minerals are monazite, topaz, fluorite, cassiterite, zircon and opaque minerals. Monazite and zircon usually represent inclusions in dark micas and form euhedral and subhedral crystals. Topaz, fluorite, cassiterite and other minerals built anhedral crystals. Depending on the degree of greisenization, variable contents of topaz, fluorite and mica aggregates (usually biotite–zinnwaldite) are observed.

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## Polymetamorphic rocks of northern Wedel Jarlsberg Land (Spitsbergen) - missing link between Southwestern and Northwestern Svalbard's Basement provinces?

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Svalbard's Caledonian basement is divided into Northeastern, Northwestern and Southwestern basement provinces. Caledonian high-pressure (HP) rocks are known only from the two latter. In the Northwestern Province eclogites occur. They form mainly dykes cutting across or boudins enclosed within augen gneisses of the Tonian age. In the Southwestern Province, clearly exotic blueschists and eclogites are thrust onto Late Neoproterozoic low-grade metasediments. The subject of this study is the so-called Magnethøgda sequence occurring within the Southwestern Province in Wedel Jarlsberg Land. The sequence consists of augen gneisses, minor amphibolites and shists and it is thrust onto low-grade Late Neoproterozoic metasediments. The goal of this research was to investigate both age and metamorphic conditions of the Magnethøgda sequence.

For the P-T estimates, shists have been chosen as the most suitable lithology. The schists consist mainly of garnet (Grt), muscovite, biotite, chlorite and quartz. Two generations of Grt can be distinguished. Garnet-I builds inclusion rich cores, whereas Grt-II forms either rims on Grt-I cores or separate euhedral grains. Their composition varies from Alm68Pyr8Grs9Spss9 in the cores to Alm49Pyr2Grs31Spss18 in the rims. The P-T conditions were estimated using the phase equilibrium modeling in the NCKFMMnASHT system using Perple\_X software. Preliminary P-T estimates indicate the growth of Grt-I at c. 550 °C and c. 5 kbar, whereas Grt-II has been growing under high pressure greenschist to blueschist facies conditions (c. 500 °C and 12 kbar). Ion microprobe U-Pb zircon dating of accompanying augen gneisses yielded c. 950 Ma for the protolith (zircon cores) and c. 635 Ma age for metamorphic overprint (zircon rims). Previous K-Ar geochronological data suggest that the sequence in question was also subjected to the Caledonian metamorphism. In such scenario, Grt-I is interpreted to be c. 635 Ma, whereas Grt-II to be Caledonian.

As mentioned above, Caledonian HP rocks in Svalbard are known from Northwestern and Southwestern basement provinces, whereas Tonian igneous rocks from the Northwestern Province only. Thus we propose that the Magnethøgda sequence represents a missing link between the Northwestern and Southwestern provinces. The sequence notices c. 950 Ma igneous event typical for the Northwestern Province, c. 640 Ma amphibolite facies metamorphism known from the Southwestern province (possibly also from the Northwestern) and then HP Caledonian overprint known from both provinces. These results call for re-consideration and possibly re-interpretation of the Svalbard's Caledonian basement division.



## Changes in bulk and molecular composition of extractable organic matter caused by weathering of a Tournaisian marine black shale

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A detailed study on paleoweathering of a Lower Carboniferous (Tournaisian) black shale from the Kowala quarry in the Holy Cross Mountains of Poland, revealed significant changes in total organic carbon (TOC) and total sulfur (TS) amount. Paleoweathering resulted in a 97 % decrease in TOC and total loss of sulfur, as well as changes in carbonate contents, extract yields and percentage yields of the organic fractions. The decrease in TOC is accompanied by a distinct reduction of organic compound concentrations, but the degradation range differs in the individual weathering zones. The less stable compounds such as low molecular weight aromatics (e.g. methylnaphthalenes, dibenzofuran, dibenzothiophene), isorenieratane and its diagenetic products, or maleimides decrease significantly or disappear already in the partially weathered zone, while the more stable polycyclic aromatic hydrocarbons (PAHs) decrease only in the weathered and highly weathered zones. Besides the organic matter (OM) content, the influence of paleoweathering on the distributions of organic compounds is important in the context of paleoenvironment, source and maturity interpretations. Almost all biomarker parameters change their values in the highly weathered zone, but such ratios as, e.g. the 2-MeH (methylhopane index), are almost totally resistant to change. The aryl isoprenoid ratio (AIR) values decrease gradually with weathering. This modifies completely the potential interpretation of the nature of the photic zone anoxia. In addition to degradation of OM, some PAHs like benzo[*b*]fluoranthene increase in concentration in the partially weathered zone due to their formation from phenyl-derivatives. The correct recognition of paleoweathering in outcrop and drill core samples aids in the proper interpretation of biomarker parameters and contributes to a better understanding of the processes which took place during weathering (Marynowski et al., 2011).

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## First report on mantle xenoliths from Cerro Chenque, Patagonia, Argentina

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Alkali basalts of Pliocene – Quaternary age occur along Patagonia in Argentina. The rocks have typical intraplate OIB-like geochemical characteristic. Volcanic activity in this back-arc region is related to subduction of Nazca and Antarctic plates beneath South American Plate (Bjerg et al., 2005).

The Cerro Chenque occurrence of peridotitic, pyroxenitic and gabbroic xenoliths has been discovered during 2013 field works in Patagonia. The presented results are based on preliminary study of two protogranular/porphyroclastic spinel lherzolite xenoliths (CH13 and CH28). Composition of rock-forming phases varies between the xenoliths (Tab.1). Olivine, opx and cpx are relatively magnesium-rich (Tab.1). Opx-cpx equilibrium temperatures are unusually low and close to 720°C. The REE pattern of cpx from xenolith CH13 suggests its equilibration with silicate melt, whereas that of CH28 cpx is U-shaped and may indicate the influence of subductions related melts. Opx in both xenoliths is strongly LREE depleted.

Table 1. Main chemical features of minerals forming xenoliths CH13 and CH28. Classification after Morimoto (1989)

	Ol Fo	Opx classification /mg#	Cpx classification /mg#	Spl mg#/cr#
CH13	91.0-91.5	Enstatite/0.92	Al, Cr-diopside/ 0.93-0.94	0.75-0.76/ 0.33-0.36
CH28	91.0-91.3	Cr-enstatite/0.92	Cr-diopside/ 0.94-0.95	0.71/ 0.43-0.46

Our preliminary results on Cerro Chenque xenoliths show that the sampled lithospheric mantle has multi-stage history, including (1) significant melting event and (2) enrichment by various metasomatic agents.

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## Xenolithic jigsaw - lithospheric mantle beneath Central Europe

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The lithospheric mantle occurring beneath Bohemian Massif in Central Europe has been sampled in Cenozoic times by numerous lavas. Recent studies (e.g. Puziewicz et al. 2011) show that mantle in this region is mostly anhydrous, harzburgitic, and was subjected to various kinds of metasomatic events. Our data from Lower Silesia and Lusatia show that in some sites two populations of mantle peridotites characterized by different major element composition of olivine and pyroxenes of mantle peridotites occur. Population “A” (minimal opx-cpx equilibration temperatures ~800 °C or no equilibrium between cpx and opx) contains olivine Fo<sub>90.5-92.0</sub>, whereas the population “B” (temperature ~1000 °C) contains olivine Fo<sub>87.5-90.0</sub>. The study of population “B” shows that it originated due to refertilization (“Fe-metasomatism”) of more Mg-rich peridotites by silicate melts percolating through lithospheric mantle. The peridotites belonging to population “A” were supposedly the protolith of those of the population “B”. Part of the population “A” peridotites contain clinopyroxene of mg# 94–95, typical for low temperatures of equilibration.

In some sites (e.g. Krzeniów) the trace element patterns show that decreasing mg# of cpx in population “A” peridotites is due to gradual replacement of primary lower-temperature mineral assemblage by the later higher-temperature one. This suggests that the variation of mineral chemistry is rather due to chromatographic effect than to vertical variation in lithospheric mantle temperatures (Christensen et al., 2001).

The data on Central European lithospheric mantle are insufficient, sometimes exceptive and allowing various interpretations of history of the same lithologies. We suggest that the lithospheric mantle has a mosaic structure, and consists of the mantle roots of plates assembled during Variscan orogeny intermingled with upwelled and “lithospherized” asthenospheric mantle and further reworked by Cenozoic volcanism.

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## Freiberg strategy for high temperature synthesis of multi trace element doped reference materials for resource technology

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Quality assurance of natural raw materials (e.g. ores) with beam-based microanalytical methods requires a proper set of homogeneous, matrix-matched reference materials (RMs) doped with trace elements relevant to resource technology applications. A set of synthetic minerals and glasses – tantalite, pyrite/chalcogenide glass, feldspar/feldspathic glass - has been synthesized using the Czochralski, flux and sol-gel method respectively.

Dark brown tantalite crystals have been grown by the Czochralski method from the melt of composition  $\text{Fe}_{0.6}\text{Mn}_{0.4}\text{Ta}_2\text{O}_6$  (melting point of about 1600°C) with the use of an Ir crucible and a protective atmosphere consisting of 85% Ar, 10% CO<sub>2</sub> and 5% CO. A growth rate of 1 mm/h and rotation rate of 10 rpm were applied. The crystals were doped with Sc, Ti, Y, Zr, Hf, La, Ce and Nd at 1000 µg/g per element.

Pyrite-like chalcogenide glass was synthesized from the melt composed of natural pyrite (Krantz GmbH), PbCl<sub>2</sub> flux and excess sulfur (Merck) in a molar ratio 1:2:1. The batch was finely ground, spiked with Au, Pt, As, Sb and Co of natural origin (TU Bergakademie mineral collections) at trace concentrations, mechanically homogenized and subsequently placed in a sealed quartz glass ampule. The ampule was evacuated (10<sup>-3</sup> bar), inserted in an induction oven and heated to 700°C. The melt was kept under such conditions for 5 hours and subsequently cooled at a rate of 5°C/h down to 500°C and then at 20°C/h down to room temperature.

Pure, stoichiometric end-member feldspathic glasses (K- and Na-Fsp) were prepared from metal alkoxide precursors (VWR, Sigma-Aldrich, Alfa Aesar) using sol-gel chemical synthesis method. The alkoxides were dissolved in a mutual solvent, spiked with a set of trace elements, placed in a glass reactor, heated up to 80°C and vigorously stirred and refluxed for several hours. Reaching the gelation point, the solutions were hydrolyzed, underwent polycondensation, cooled down and left to dry in a fume hood for 10 days. Solidified gels were then fired up to 500°C in an oven.

Back-scatter Electrons imaging (BSE), Electron Probe Microanalysis (EPMA) and Particle Induced X-ray Emission (PIXE) were used to determine purity, composition and chemical homogeneity of the synthesized materials. Quantitative and qualitative elemental spatial distribution maps have been obtained for major and trace elements for each matrix. Homogeneity of the matrices was evaluated using petrologically sensitive statistical analysis.



## Mineral and chemical composition of biomass ash

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Biomass is considered as important non-fossil renewable energy source. Its share in co-combustion with hard coal in power plants in Poland increases. Chemical and mineral compositions of biomass ash differ significantly from coal ash. Addition of biomass significantly modifies the composition and properties of fly-ash and influences possibilities of its application. The study is based on mineralogical and chemical analysis of ash obtained at temperature ca 470°C from various types of biomass.

Variation of chemical composition of biomass ash is very high. SiO<sub>2</sub> content varies from ca. 68 wt. % to 1.4 wt. %; Al<sub>2</sub>O<sub>3</sub> from 3.8 wt. % to 0.1 wt. %; Fe<sub>2</sub>O<sub>3</sub> from 2.9 wt. % to 0.35 wt. %; MgO from 11.07 wt. % to 2.04 wt. %; CaO from 37.9 wt. % to 3.05 wt. %; Na<sub>2</sub>O from 1.17 wt. % to 0.02 wt. %; K<sub>2</sub>O from 35.17 wt. % to 3.32 wt. %; P<sub>2</sub>O<sub>5</sub> from 36.2 wt. % to 0.74 wt.%. According to chemical classification of ash (Vassilev, Vassileva 2007) all samples represent calisalic type.

Chemical composition of biomass used as fuel can vary significantly because it is related not only to vegetation type but also to soil conditions influencing vegetation growth and composition of detrital components (derived from soil, atmospheric dust particles deposited during cultivation or storage).

Broad range of variation of chemical composition of biomass ash is reflected in its very variable mineral composition. Several samples are rich in K and Mg phosphates, other rich in carbonates (e.g. calcite, fairchildite, kutnahorite), sulphates (arcanite, anhydrite), oxides (lime, periclase, Fe oxides), silicates (wollastonite, enstatite, K-feldspar) beside other components as quartz or cristobalite. Addition of these components to coal ash results in high variability of composition and properties of ash obtained in co-combustion.

The real influence of biomass co-combustion with coal on fly-ash composition is related not only to the chemical and mineral composition of biomass ash but also ash content in biomass. It varies from below 1 wt. % to 10.5 wt. %.

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## Seasonal variations of arsenic concentrations in waters of the acid mine drainage Podwiśniówka area

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Arsenic is a toxicant that draws global attention. This metalloid forms different minerals or isomorphic substitutions in many sulfides including pyrite. Thus, of special interest in the study of As are acid rock/mine drainage (ARD/AMD) areas. The concentrations of As in AMD and thermal waters may reach several tens and even hundreds ppm (Henke 2009).

The study area encompassed Podwiśniówka and Marczakowe Doły acid ponds, and Marczakowe Doły fish pond located about 5 km north of Kielce (Migaszewski et al. 2008, 2013). The crypto- and microcrystalline pyrite occurring at the western wall of the Podwiśniówka quarry contains about 1% As. However, the concentrations of this element are not uniformly distributed in pyrite, ranging from 0.0X to 14%.

The concentrations of As in the Podwiśniówka acid pit pond and the Marczakowe Doły fish pond waters were similar, varying from 2 to 106 ppb and from 8 to 105 ppb, respectively. In contrast, the Marczakowe Doły acid pond water showed distinctly higher As contents in the range of 53 to 589 ppb. The pond waters examined also exhibited seasonal variations in As contents with the most distinctive variability in the Marczakowe Doły acid pond. In general, winter periods favored higher concentrations of As, for example 511 ppb and 589 ppb in January and February of 2012. This seasonal variability may be explained by changes in pH, temperature and redox conditions combined with geochemical interactions within the water-ochreous precipitate-colloid system. Weathering of pyrite releases As which is trapped by unstable schwertmannite. The transformation of this mineral into ferrihydrite at the pH of 2.5-4.5 and subsequently into goethite at the pH of 3-7 leads to desorption of As. The decrease in the pH causes reductive dissolution of iron oxyhydroxides triggering also the release of As.

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## **Birbirite - strongly ferruginous silicate metasomatite from the weathered zone of the Szklary serpentinite massif (Lower Silesia) – preliminary report**

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The name of birbirite comes from the Birbir River in Ethiopia, where the first time were described "birbirites" which consist essentially of secondary silica and limonite, and are derived from the dunite through alteration and concentration processes (Molly, 1959). Such rock was recently described from the Szklary Wzgórze Siodłowe Ni deposit of the saprolitic type (Mikulski, *in press*). This Ni deposit is located near Ząbkowice Śląskie within the Niemcza Tectonic Zone on the Fore-Sudetic Block (Mikulski, 2012). Formation of this Ni deposit underwent in several stages connected first with strong serpentinitization of Devonian peridotites and ultramaphic cumulates (the lower member of the Sudetic Ophiolitic Complex; Majerowicz, 1979) by Carboniferous Strzelin granitoids, which further were subject of intensive multiply weathering in Cenozoic (Niśkiewicz, 1967).

In 3 boreholes drilled in 2007 within the southern parts of the Szklary - Wzgórze Siodłowe Ni deposit near Bobolice, at depth interval from ca. 16 to 20 m, rusty in color, hardly silicified and porous metasomatic rock – birbirite was recognized. This is strongly ferruginous silicate rock in which amorphous silicates and aggregates of hydrated Fe-oxides and hydroxides (limonites) dominate. Besides, in vertical profile of birbirite (every 0.5-1 m) thin veinlets (1-3 cm) of white-grayish chalcedony and fine-grained quartz may appear. Chalcedony forms narrow collomorphic structures around porous part of the rock. Under the ore-microscope were also recognized small (<40 µm) remnants of magnetite, Cr-magnetite and chromite that are subject of replacement by hematite and Fe-hydroxides, single sulfides (pyrite and chalcopyrite) and in chalcedony veinlets very rare single gold grains (<10 µm). Chemical composition (XRF) of birbirite from Bobolice is as the following: SiO<sub>2</sub> ~89-94 wt%, Fe<sub>2</sub>O<sub>3</sub> – 2.8-6.8 wt%, MgO ~2 wt%, Al<sub>2</sub>O<sub>3</sub> – 0.2-0.5 wt%, MnO – traces and LOI – 1-2 wt%.

Intensive supergene weathering and fluctuation in the underground water level caused exchanges in pH-Eh conditions responsible for elements migration within Ni-bearing ferruginous saprolite. Mg and Ni from olivines were almost completely removed but Si was strongly enriched and recrystallized in birbirite as amorphous silica accompanied by recrystallized Fe in the form of hydroxides.

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## Geochronological constraints on metamorphism of eclogites from Piława Górna (Góry Sowie block, Sudetes)

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Amphibolites and migmatitic gneisses mined at the Piława Górna contain several meters thick bodies of retrogressed eclogites. The primary eclogitic assemblage consists of garnet, omphacite, quartz, clinozoisite, rutile, and kyanite. The retrogressed assemblages comprise amphibole, sodic diopside, orthopyroxene, plagioclase, spinel, corundum, ilmenite and biotite. The peak metamorphic conditions of the eclogite stage were estimated 730–840°C at 2.0–2.5 GPa. The studied eclogites show strong affinity to volcanic arc or back-arc basin basalts and it is presumed that the magma to the protolith of the rocks could have been generated in a supra-subduction setting. The Lu–Hf isochrone age of each sample was defined by three garnet fractions, clinopyroxene and whole rock. Two least retrogressed samples with preserved eclogitic assemblage yielded Lu–Hf isochrone age ranging from 389.5±2.1 Ma to 390.3±1.6 Ma. The age of highly retrogressed and amphibolitised sample is 385.8±1.1 Ma. The age of eclogite metamorphism is similar to the age of HP–HT episode of the Sowie Góry granulites (395–390 Ma; Kryza, Fanning 2007), and is within time span of the HP metamorphism reported for the Śnieżnik granulites (~387 Ma; Anczkiewicz et al. 2007). It also corresponds to the HP event recognised in mafic eclogites of the Münchberg nappe (390–380 Ma). The obtained age of ca. 390 Ma is interpreted as an approximation of the pressure peak of the eclogite stage, preserved in the Góry Sowie block. Additionally, it coincides with the age of tectonic incorporation of the mantle rocks into the Góry Sowie gneisses (389±1.6 Ma).

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## Magnetic petrology of Precambrian metadolerites from St. Jonsfjorden area, Central Western Spitsbergen, Svalbard

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Metadolerites within the Precambrian calcareous metapelites and marbles in the St. Jonsfjorden area were selected for paleomagnetic study. The protoliths of the examined rocks were small Neoproterozoic sills/dykes intruded into the Precambrian successions which were metamorphosed in greenschist facies during Caledonian Orogeny (Ohta 1985).

Nine metadolerite samples have been investigated by a combination of ore microscopy and microprobe (EPMA). Rock-magnetism investigations, including determinations of maximum unblocking temperatures ( $T_{ub\ max}$ ) and coercivity spectra of ferromagnetic minerals, based on: SIRM (saturation isothermal remanent magnetization) decay curves and three-component IRM (isothermal remanent magnetization) procedure described by Lowrie (1990). Coercivity of remanence ( $H_{cr}$ ) has been determined using Vibrating Sample Magnetometer (VSM). All of the examined samples revealed a minor content of high coercivity spectra fraction (saturation field–2.9T) and the dominance of low coercivity fraction (saturation field–0.16T) with distinct ranges of  $T_{ub\ max}$  = 450–600°C. The IRM saturation fields do not exceed 0.2 T and the  $H_{cr}$  is within the range 20–40 mT.

The ferromagnetic mineral associations which consist of ilmenite are commonly overgrown by titanite, anatase(?), goethite, pyrrhotite, chalcopyrite, pentlandite, and pyrite. The ferromagnetic phases which evolved during the magmatic stage were recrystallized during greenschist facies metamorphism accompanied by a high activity of CO<sub>2</sub>-rich aqueous fluids expelled from the host rocks. During these processes all generations of Ti-rich magnetite and oxy-exsolved hematite in ilmenite have transformed into titanite or have been dissolved. The textures of the sulphide aggregates and their intergrowths with late silicates suggest that they have also recrystallized. The current mineralogical composition of ferromagnetic phases corresponds well with the rock-magnetic data. The metamorphic processes have completely reset the Ti-rich magnetite and hematite phases within the metadolerites, and the paleomagnetic data record the geotectonic history of Western Svalbard from Late Silurian time onwards.

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## Mineralogy of antimony ores mined at Dębowa in the Bardzkie Mts (Sudetes), SW Poland

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The „Reiche Silber Glück” adit at Dębowa village is the only known place in Poland, where the antimony ores were mined. The adit was excavated in the Upper Devonian through Lower Carboniferous highly pyritized greywackes of the Bardo-Młynów Unit. The ore samples for the study were collected from „Reiche Silber Glück” adit during the spring 2013 field work. The aim of this presentation is to show mineralogy of the primary (hydrothermal) and secondary (weathered) mineral associations from the collected ore samples that have been investigated by a combination of ore microscopy, X-ray powder diffraction, and electron-microprobe analysis. This is the first report that shows detailed mineralogy of antimony sulphide- and sulphosalt-veins from the vicinity of Dębowa.

The antimony ores form thin braided veinlets occurred within clayey zone, ca. 1 m thick, which was developed as a result of intense hydrothermal alteration of the host greywackes along tectonic fault zone. The clayey material consists of fine grained quartz and illite. The ore veins range from 0.5 to 3 cm in thickness. The Sb vein-type mineralization is younger than dispersed pyrite mineralization within host rocks. Taking into account mineralogy of ore and gangue components three vein types were recognized: **(I)** quartz veins, up to 2 cm in thickness, containing sphalerite, jamesonite, boulangerite, bournonite, Ag-rich tetrahedrite (up to 1.8 wt.% Ag), chalcopyrite, stibnite, and gersdorffite; **(II)** massive stibnite veins, up to 3 cm in thickness, filled mainly by stibnite containing numerous intergrowths of sphalerite, rare inclusions of jamesonite, boulangerite, galena, chalcopyrite, covellite, pyrite and small amount of arsenopyrite commonly included within quartz aggregates; and **(III)** Mn-bearing ankerite veins, up to 2 cm in thickness, containing dispersed grains of sphalerite, jamesonite, boulangerite, stibnite, and galena. The weathered assemblages are represented by yellowish Sb-ochres (stibiconite, bindheimite), scorodite, pitticite, hydroniumjarosite, cerusite, smithsonite, malachite, ferrihydrite, gypsum, aragonite, and native sulphur.

Genesis of the examined sulphide mineralization is related to hydrothermal processes within greywackes of the Bardo-Młynów Unit at their contact with the Kłodzko–Złoty Stok granitoid intrusion. The ore vein system represent medium to low temperature zone (below 300-250°C) of ore mineralization, distal in relation As-Au ore zone known from the Złoty Stok area.





## Dynamic evolution of the volcanic body from the Wołek Hill (Sudetes, SW Poland) based on fluid inclusions from mantle xenoliths

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Fluid inclusions (FI) entrapped in rock-forming minerals of mantle origin are powerful tools for understanding fluid migration during mantle metasomatism, and the dynamics of the hosting magmas. In this contribution, we present preliminary results based on FI hosted in olivine (Ol) and orthopyroxene (Opx) of mantle xenoliths from Wołek Hill, ~9 km SW from Wilcza Góra. We have recognized several groups of FI entrapped at the same time (Fluid inclusion assemblage, FIA) and have tested the Roedder's rules to assess the reliability of the FI data. In most cases, FI display rounded and oval shape with size below 10  $\mu\text{m}$ , but larger FI with dendritic shape occurs. Some of FI > 8  $\mu\text{m}$  show halos of secondary FI indicating re-equilibration due to overpressure. We have performed microthermometric measurements of CO<sub>2</sub>-rich FI from mantle xenoliths affected by cryptic metasomatism. Among several crystals, we have selected one Ol and one Opx crystal containing several FIAs. Sixty-eight FI analyzed are CO<sub>2</sub>-FI, based on first melting temperature. All CO<sub>2</sub>-FI studied homogenize to liquid at temperature ( $T_h$ ) < -2°C. We have analyzed two FIAs hosted in Ol and six isolated FIs in Opx. The two FIAs hosted in Ol show average of  $T_h$  -6.5°C ( $\pm 3.1$ , 34 FI) and -13.3°C ( $\pm 3.8$ , 11 FI) respectively. The isolated FI show  $T_h$  varying from: -24.8°C to -6.3°C, indicating that primary isolated FI show generally higher density than secondary FI hosted in olivine as it should be expected. Densities estimated from  $T_h$  of FI show a narrow range from 0.94 to 1.05 g/cm<sup>3</sup>. These densities correspond to pressures of 0.7-0.9 GPa based on the equation of state and assuming temperature of entrapment of 1100°C. The calculated pressures correspond to depths of 24-30 km, assuming an average crustal density of 2.8 g/cm<sup>3</sup>. The estimated depths likely represent MOHO depths and are consistent with values found previously by Ladenberger et al. (2009). The preliminary data available on FI show no evidence of magma accumulation at shallower depths than the Moho, but further investigation are still necessary.

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## The diversity of the Ca content in the olivines from mantle xenoliths (Wolek Hill, SW Poland) – preliminary evaluation of the EPMA data using PIXE measurements

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Ca content in olivine (Ol) is one of the best indices for processes occurring in the Earth's upper mantle (e.g. metasomatic enrichment, partial melting) or during extraction of mantle xenoliths to the Earth's surface (e.g. xenolith - host-rock interactions).

The detection limit of EPMA analysis is influenced by analytical conditions, but also by a degree of sample's heterogeneity (e.g. secondary fluorescence). Precise measurements of Ca content, particularly in depleted mantle rocks, is challenging and obtained results can be questioned.

Based on previous observations, the Wolek Hill xenoliths could be divided into three groups: I) with visible modal metasomatism; II) with dominant signs of cryptic metasomatism; III) without any signs of metasomatism.

EPMA analyses were performed with a Cameca SX-100 at the University of Warsaw using an accelerating voltage of 15 kV, current 20 nA and 40 s acquisition time (20 s peak and 2x10 s background). The detection limit was ca. 200-250 µg/g. One set of measurements was made under special conditions (15kV, 100 nA, 100 s) – with the detection limit of ca. 20 µg/g.

PIXE (Particle Induced X-ray Emission) measurements were performed at the HZDR in Dresden using a 3 MeV proton beam, current 1-1,5 nA and acquisition time 3 hrs for each scan (size ca. 60-65 µm and 30 µm; time per point ~ 10 s). The detection limit was ~ 6 µg/g for the full scan or ~ 200 µg/g per point.

Compared to EPMA, PIXE has the advantage of providing elemental (all-at-once) distribution maps for many elements within a reasonable timeframe.

The measured Ca content in Ol is comparable for both methods – rather in the range than in specific µg/g values. Based on preliminary evaluation, for full scans, samples from the group I and II display values higher than 100 µg/g; samples from the group III, are depleted with values below 100µg/g (ca. 50 µg/g). In majority, scans are homogeneous but the increasing Ca content related to secondary cracks in Ol is also visible. Although, such enrichment is limited only to several microns.

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## **Mineralogy of soils developed on various ultrabasic rocks from Poland**

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Outcrops of ultrabasic rocks and derived soils are located in Poland only in Lower Silesia region (southwestern Poland). Ultrabasic rocks and associated soils occur in the Fore Sudetic Block (e.g., Szklary Massif, Gogołów - Jordanów Massif) and in the Sudetes (e.g., Popiel Hill, Śnieżnik Massif).

We examined several ultrabasic parent rocks and related soil profiles from the Fore Sudetic Block (Szklary Massif) as well as from the Sudetes (Popiel Hills and Śnieżnik Massif). Bedrocks for studied soils are represented by: (1) serpentinitised peridotite in the Szklary Massif, (2) serpentinite in the Śnieżnik Massif and (3) hornblende peridotite in the Popiel Hill. All studied soil profiles have similar pedogenetic characteristics (e.g., chemical composition, pH, position in a toposequence, grain size distribution etc.) however mineral composition of studied parent rocks is highly diversified. Serpentinitised peridotite from Szklary is composed of olivine (forsterite) and serpentine as major minerals, with minor amphiboles (tremolite and anthophyllite) and chlorite (clinochlore) and accessory magnetite. Serpentinite from the Śnieżnik Massif consists of serpentine group minerals (more than 80 vol. % of rock) and accessory chlorite and magnetite. Studied ultrabasic rock from the Popiel Hill contains olivine, orthopyroxene (enstatite), amphiboles (magnesian hornblende and tremolite) and serpentine as major minerals with accessory spinel, magnetite and ilmenite. Mineral composition of studied soils is complex and it generally depends on the type of bedrock. Soil minerals can be divided into three groups: (1) primary minerals inherited from parent rock (e.g., serpentine, olivine etc.), (2) phases having allogenic (aeolian and/or fluvioglacial) origin (e.g., quartz, feldspars etc.) (3) autigenic phases derived from weathering of (1) and (2) such as clay minerals (e.g., smectite, kaolinite etc.). Soil from Szklary is the most mineralogically complex among all studied soils. The diversity of soil from Szklary is manifested by larger proportions of smectites in soil clay fraction. They originate not only from serpentinite weathering under temperate climate but also from weathering crust which developed on Szklary ultrabasites during Neogene. Furthermore, soils from Szklary and Popiel Hill contain more important amounts of phases having fluvioglacial/aeolian origin than soil from Śnieżnik Massif. Besides in the latter we only observe traces of swelling phases (smectite or vermiculite), which indicates different degree of weathering from one site to another.

Based on results of our study we can conclude that major factor influencing the mineralogy of studied soils is type of an ultrabasic parent rock. However some other factors (e.g., local climatic conditions, presence/absence of materials of allogenic origin etc.) play also an important role and may significantly modify the mineral composition of soils developed on ultrabasic rocks.



## Modern and historical Cu-slags: from characterization to environmental impact

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Metallurgical slags are considered as waste materials potentially deteriorating environmental quality. Due to incomplete efficiency of pyrometallurgical process, they are enriched in toxic metals that may be mobilized during biogeochemical weathering, consequently leading to environmental pollution. Therefore, slags are currently perceived as undesirable for any dumping strategies. On the other hand, the fact that slags often display relatively high concentrations of metals makes them potential secondary resources for future metal recovery. However, before considering possibilities of slags reuse, their environmental stability should be regarded as the priority.

Due to the fact that smelting technologies have improved gradually since many years, waste obtained from a present day production may represent different chemical and phase composition compared to those resulting from historical industry. As the result of composition diversity, they may behave different in the environment. For that reason, characterization of the metallurgical wastes has been a purpose of our relevant attention.

Two types of copper slags representing different smelting technologies: historical and modern slags (including three kinds of samples collected from different stages of technological process) were chosen for this study.

Characterization of the wastes revealed that historical and modern slags display slightly different chemical and phase composition. Regarding bulk chemistry of the slags, our results demonstrated significant quantities of metals (up to): Cu: 13400 and 11425 ppm, Zn: 9359 and 76400 ppm, Pb: 738 and 26124 ppm, As: 315 and 3569 ppm, for historical and modern slags respectively. According to results obtained from mineralogical analyses, slags are composed of various mineral phases with the majority of silicates and glassy matrix. Additionally, historical and modern slags contain numerous metal sulfide inclusions such as: chalcopyrite, bornite, pyrrhotite and sphalerite occurring as volumetrically minor compounds. Moreover, major and minor phases show some variations in chemical composition having various metal concentrations.

Obtained results confirm that chemical and phase diversity of historical slags may vary from this presented by modern slags, hence their environmental behaviour has to be also considered individually. Therefore, geochemical stability of these wastes as well as possibility of their industrial application will be an objective of our further considerations.



## Moss-biodeterioration of sandstones in polluted environment: preliminary data from Wrocław historical buildings (SW Poland)

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Biodeterioration of building stones is a serious problem in preservation and conservation of historical buildings and monuments, especially in polluted environment conditions. This paper aims at presentation of preliminary results of investigation of biodeterioration processes of sandstone in monuments of the city of Wrocław. Study sites were selected where architectural stone was found to be covered with moss *Tortula muralis* Hedw. The study historical buildings are exposed to polluted urban atmosphere.

Samples of *T. muralis* moss and of the basis were collected from 6 sites in Wrocław: Architecture Museum, Pomeranian Bridge, National Museum, and churches of st. Augustine, st. Elizabeth and st. Magdalene. Additionally, six quarries were selected from which sandstones could have been used for the construction of the study buildings (from the vicinities of Lwówek Śląski, Bolesławiec, Radków and Szczytna).

The mosses growing on sandstone architectural elements in Wrocław are represented almost exclusively by *Tortula muralis*. The samples from the quarries revealed more variegated moss assemblages: apart from *Tortula muralis*, *Atrichum undulatum* and *Haplocladum microphyllum* are common. The drill-core samples of sandstones covered by mosses display distinct surface alteration zones, up to c. 2 cm deep, where the matrix of the sandstone has been largely removed and new mineral phases (e.g. gypsum) formed.

The collected samples of moss and its basis digests will be analyzed for a range of major and trace elements, and macronutrients (e.g. N, P, S, K, Ca, Mg) using adequate methods. Parallel petrographic, mineralogical and geochemical investigations (optical microscopy, XRD, DTA, SEM and EDS) are in progress.

There are only few examples of investigations of bryophytes impact on sandstone in architectural objects (e.g. Liscia et al., 2003). This study is expected to extend our understanding of the biodeterioration processes of stone monuments in terms of air pollution impact in large urban agglomerations, which is important for restoration and conservations works.

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## Garnet hornblendites of the Niedźwiedź Massif (SW Poland): the remnants of the Variscan andesitic volcanic arc root

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The Niedźwiedź Massif in SW Poland consists of garnet hornblendites with subordinate garnet clinopyroxenites and leucotonalite schlieren containing igneous epidote. The garnet-hornblende assemblage records peak metamorphic conditions at 12 – 13 kbar and 790 °C (Puziewicz & Koepke 2001, Neues Jahrbuch für Mineralogie Monatshefte 2001: 529-547). The hornblendites and clinopyroxenites are intermingled with products of their metamorphic retrogression under amphibolite, epidote-amphibolite and pumpellyite-actinolite facies conditions (Puziewicz 2006, Neues Jahrbuch für Mineralogie Abhandlungen 183: 1-11).

The hornblendites whole-rock trace and REE patterns are typical for tholeiites. Locally, the remnants of magmatic layering in the centimetre-scale occur. Primary hornblende has the composition of Si-rich tschermakite (mg# 0.49 – 0.56) and is characterised by (primitive mantle normalised) bell-shaped REE patterns. Part of hornblende grains exhibits igneous zonation with mg# decreasing outwards. Garnet cores are rich in intergrowths of titanite and solidified melt inclusions consisting of quartz + plagioclase ± hornblende ± epidote, whereas the rims are free of inclusions. The primary garnets have the composition close to  $\text{Alm}_{50}\text{Sp}_{2}\text{Py}_{17}\text{Gr}_{31}$  with mg# 0.22 – 0.26. The tonalite schlieren contain oligoclase and igneous epidote. Clinopyroxenites consist of diopside, garnet, subordinate plagioclase and hornblende and accessory titanite. The diopside is chemically homogeneous. It is slightly depleted in REE's relative to primitive mantle, its REE patterns are bell shaped (impoverished in LREE and HREE) or flat with slight LREE depletion.

The mineral assemblage of Niedźwiedź garnet hornblendites is typical of high-pressure crystallization of wet andesitic/tholeiitic magma. The crystallized melt inclusions as well as the layering suggest that the hornblendites are cumulates of evolved andesitic to tonalitic magma. Part of the grains occurring in the Niedźwiedź garnet hornblendite preserved primary igneous features (magmatic zonation and REE patterns of amphibole, crystallized melt inclusions in garnet and titanite, occurrence of magmatic epidote in tonalitic schlieren). Many of the grains record high P/T metamorphism which might be due to in-situ cooling of cumulates and which overprints the igneous features. This was followed by retrogressive metamorphism and foliation development during exhumation of the rocks. In conclusion, the garnet hornblendites and garnet clinopyroxenites originated in a deep-seated evolved andesitic magma chamber in the supra-subduction environment.



## Geochemical and mineralogical composition of the internal sediment occurring with Zn-Pb ores from the Silesian-Cracow region, Poland

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An “internal sediment” - the clayey, organic matter-rich sedimentary rock that fills caverns in the bottom parts of ore bodies and open spaces between the collapse breccia fragments have been reported numerous times in Zn-Pb ores from the Silesia-Cracow region (e.g. Sass-Gustkiewicz, 1996), but detailed studies on its molecular and mineralogical composition from different localities have not been undertaken so far. Preliminary tests of internal sediments from 2 mines: “Pomorzany” and “Trzebionka” using X-ray diffraction (XRD), gas chromatography coupled with mass-spectrometry (GC-MS), total organic carbon (TOC) and total sulfur (TS) measurements were carried out. Based on XRD data and Rietveld refinements, the “Trzebionka” samples are more dolomitic (88-94%wt) than the “Pomorzany” samples with 57%wt average dolomite content and relative high gypsum amount (20-35%wt). The ore minerals (pyrite, sphalerite, marcasite) content is highly variable, however the “Pomorzany” sediments are richer with the total ore mineral amount of 15%wt. Traces of sulfates, such as jarosite- and alunite group minerals, higher hexahydrate and gypsum, content, points out distinct weathering processes in the bed. Geochemical investigations indicate that studied sediments are organic matter (OM) rich, while contents of TS are highly variable and depend on the degree of sulfides mineralization. In “Pomorzany” samples, OM content varies from 7% to 15% TOC and 2-20% TS. “Trzebionka” samples usually contain slightly less OM (4-13% TOC) and ore minerals (1-9% TS). The study of OM extracts using GC-MS revealed its immature nature. All of the tested samples contain hop-13(18)-ens, hop-17(21)-ens and 17 $\beta$ , 21 $\beta$ (H)-hopanes, compounds typical for an immature OM. The distribution of *n*-alkanes differs significantly between samples from each mine. “Trzebionka” samples characterized by definite prepredominance of short- over longchain *n*-alkanes, what usually is interpreted as derived from marine precursors, while “Pomorzany” samples show bimodal distribution with peaks at *n*-C<sub>17</sub> and *n*-C<sub>27</sub>. These differences in *n*-alkanes distribution may indicate a multi-sourced origin of OM in internal sediments from Silesia-Cracow Zn-Pb ores.

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## Chlorite-mica stacks and chlorite in phyllites from Podmachocice (Holy Cross Mts., SE Poland)

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The occurrence of metamorphic rocks within the Łysogóry Unit of the Holy Cross Mts. (SE Poland) has been recognized only recently (Salwa, 2006, 2009). As yet, the rocks are known from only one locality. They are significantly tectonised and reveal a simple mineralogical composition, restricted mainly to quartz, very fine-grained white mica and chlorite. The latter two minerals commonly form the chlorite-mica stacks (Milodowski & Zalasiewicz, and refs. therein). In such aggregates biotite most often occurs as a host-mineral, while intergrowths of chlorite and white mica are rare.

Two types of stacks can be observed. The first type is associated with less tectonically involved rocks and shows „pillow-like” shapes. Chlorite in such „pillows” crystallizes between sheets of chloritized, undeformed biotite. The second type of chlorite-mica stacks with more complicated internal textures has been recognized in intensively tectonised (developed slaty cleavage and crenulation cleavage) phyllites. The stacks were formed as a result of a passive dragging of the host-mineral between cleavage planes during deformation. Sheets of detrital micas were strongly deformed in a ductile regime and form well-defined small folds. Syntectonic chlorite fills the spaces between sheets of deformed biotite. Automorphic crystals of chlorite have been observed in the most tectonically deformed phyllites. This chlorite is often zoned, with cores showing composition of chloritized biotite and rims of pure chlorite. This suggests a progressive transition from the chlorite-mica stacks to automorphic chlorites. Some of chlorite crystals are slightly rotated between the cleavage planes, suggesting they crystallised before the final termination of tectonic deformation.

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## **Why some halite speleothems from the Wieliczka Salt Mine are coloured?**

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The Wieliczka mine various forms of halite speleothems are generally colourless, clear or milky. Much more rare but very beautiful and characteristic colourful dripstone formations can be found practically anywhere in the mine, on all exploitation levels, and practically in all groups of speleothems distinguished in Wieliczka, with only one exception – St. Kinga's hairs have never been observed coloured, even when they were growing from rusting metal pipes. These speleothems, e.g. stalactites, cauliflowers or crusts, reveal various hues, yellow to red to brown, being usually related to iron compounds without a real knowledge on their forms, occurrence and composition. To explain the origin of their colours the detailed study of the samples collected in the mine, including rust, brines, water extracts, and produced experimentally in the laboratory, has been undertaken, using SEM, XRD and AAS. It was found that the colourful speleothems are related mainly to the rusting metal elements, ubiquitous in the mine. The rust is composed of several iron oxides and hydroxides, like akaganéite, lepidocrocite, goethite, haematite, and magnetite. Coloured halite forms were probably covered by the ferric minerals suspension in the brine, both during their growth and afterwards. The mineral composition and the size, thickness, and continuity of mineral concentrations of iron seem to control the colour of the secondary rock salt. Intensity of colours of the speleothems is related probably to the type of a cover on crystals, a continuous film or finely dispersed micron-size mineral aggregates, whereas their hues stem from the colours of various iron minerals.



## Secondary Cu minerals from abandoned Radzimowice mine (Sudety Mts, Poland) and conditions of their formation

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Several mineral parageneses of secondary Cu minerals (SCM) are found as recently forming in abandoned mine galleries in Radzimowice. The first one is dominated by hydrous copper sulphates (HCS): langite, posnjakite, brochantite, and some devilline and malachite. Their crystallization, directly from mine waters, is modeled by both the concentration of  $\text{SO}_4^{2-}$  ions in solution and its pH. Langite and posnjakite are stabilized by relatively high  $\alpha\text{SO}_4^{2-}$  and pH values (6.0–7.5). An inflow of groundwaters causes a decrease of  $\text{SO}_4^{2-}$  and  $\text{Cu}^{2+}$  concentrations, a change of pH, and leads to dissolution of posnjakite and langite. Solutions with lowered  $\text{Cu}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations are parental for brochantite, the most stable HCS, formed under the pH of 4–7.5. No antlerite, which crystallizes at  $\text{pH} < 4$ , or tenorite, stable by  $\text{pH} > 8$  were found. Fluctuating chemistry of these solutions is also confirmed by the presence of malachite, which forms over a wide range of  $\text{CO}_3^{2-}$  concentrations, and devilline, which reflects locally high  $\text{Ca}^{2+}$  activity in the mine waters. HCS also dominate in the paragenesis II which, however, contains ferrihydrite, native Cu, cuprite, gypsum, and minor malachite, chalcoalumite and amorphous Cu-Al sulphates. Cuprite crystallizes at the surface of native copper. Its crystals show traces of dissolution; their coverage by HCS suggests reaction between cuprite and  $\text{SO}_4^{2-}$  ions. Ferrihydrite precipitates from solutions of the  $\text{pH} < 5.5$ . At the same time, the presence of brochantite is indicative of the pH of the 4–7.5 range. The presence of gypsum indicates the  $\alpha\text{SO}_4^{2-}$  value close to  $10^{-2.5}$  mol/l (i.e., saturation concentration of gypsum). Then, the stability fields of brochantite and ferrihydrite overlap in the pH range of ~5–6. Paragenesis III is dominated by woodwardite, with minor langite, chalcoalumite, and malachite. Cu-Al sulphates arise in zones where pH-low waters mix with neutral waters. There, a clear separation of Fe-rich precipitates of acid mine waters from blue deposit of Cu-Al sulphates is observed. Woodwardite binds Al, that is removed from solutions of an elevated pH. The presence of langite suggests the parent solutions have the pH of ~6–7.5. Field observations show, that woodwardite crystallizes from  $\text{CO}_2$ -undersaturated solutions (below  $10^{-4}$  mol/l  $\text{CO}_2$ ), by the pH of 7.39–7.55. An increase of  $\text{CO}_2$  concentration leads to the formation of malachite. The last paragenesis comprises chrysocolla, goethite and mottramite. The source of silica for the chrysocolla is decomposition of rock-forming minerals under the influence of acid mine waters. Migration of these waters outside the zones of sulphide oxidation and inflow of meteoric waters lead to the increase of pH of these solutions and binding of silica and  $\text{Cu}^{2+}$  ions. Vanadium may both come from rock-forming minerals (e.g., biotite) and magnetite, traces of which are present in the deposit and its surroundings.



## Reconstruction of the magma processes and continental crust evolution in the Halle Volcanic Complex

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The Halle Volcanic Complex (HVC) belongs to the Central European Basin Large Igneous Province (CEBLIP) and is located in NE Germany and its volcanic rocks outcrops as lava domes and laccoliths. The HVC is dominated by rhyolitic rocks (c. 200 km<sup>3</sup>), which were mainly emplaced as large laccoliths. The U/Pb age of zircons ranges from 289 to 301 Ma, inherited zircons are scarce (Breitkreuz et al., 2009).

We have chosen four localities within the HVC for detailed isotopic and chemical analyses of magmatic zircon.  $\epsilon_{\text{Hf}}$ ,  $\delta^{18}\text{O}$  and elemental concentrations of Zr, Hf, Th, U, REE have been measured in previously dated zircons from Spitzberg and Wettin and analysed zircons from 1044 and 1390 were dated in this study. On the basis of Hf content we divided zircon in two groups: zoned grains with low Hf core (8000 - 9000 ppm) and high Hf rim (10000 - 12000 ppm) and unzoned grains with constant low Hf concentration through grains (6000 - 9000 ppm). High Hf rims occur also as magmatic overgrowths on inherited cores. The diversity in  $\delta^{18}\text{O}$  (6.3 - 8.1 ‰) does not correlate with Hf concentration and  $\epsilon_{\text{Hf}}$ . Low Hf zircon is also characterised by higher Th/U and more diverse trace element contents compared to high Hf zircon.

Generally, the isotope and chemical characteristic of zircon grains is similar between localities and suggest an input of higher  $\epsilon_{\text{Hf}}$  magma towards the late stage of magma evolution, probably shortly prior to the final emplacement. Lack of correlation between  $\epsilon_{\text{Hf}}$  and  $\delta^{18}\text{O}$  implies that at least three sources contributed material to the ca. 300 Ma magmatism contrary to the simple two source contribution observed for the NE German Basin (Pietranik et al., 2013).

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## Rapid changes in redox conditions during Lower Silurian Ireviken Event – example from the basinal succession of the Holy Cross Mountains

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The Ireviken Event is characterized as a minor extinction event at the Llandovery-Wenlock boundary. Whole event took place during regression, after the onset of global sea-level fall and finished before the maximum lowstand (Calner, 2008). The mechanism responsible for the event originated most probable in the deep oceans, and made its way into the shallower shelf seas (Munnecke et al., 2003). Comparing to other worldwide sections, the Wilków profile is unique due to its deep-water type of sedimentation and therefore could provide important information about sedimentary environment. In present work, identification of redox conditions was carried out using pyrite framboid diameters and inorganic geochemical indicators. The size distribution of framboids supplies information about ancient redox environments at a fine scale resolution (Wignall & Newton, 1998). Almost 10 m before this Silurian event the absence of framboids is observed, what may suggest rather oxic conditions during sedimentation. The beginning of Ireviken Event is characterized by presence of tiny framboids what indicate very drastic change into sulphidic conditions in water column. After that euxinic pulse, conditions have changed gradually to more oxic / dysoxic with short period toward more anoxic conditions, what is revealed by larger pyrite diameters. Euxinic conditions in water column returned at the end of Ireviken Event and are continued at the upper part of the section. Comparing to pyrite framboid data, most of the geochemical parameters including U/Th, Ni/Co, V/(V+Ni) and V/Cr show mainly oxic to dysoxic conditions on the sea-floor with scarce anoxic periods. Differences between pyrite framboid and geochemical data could be explained as a result of an intensive sea level oscillations during this extinction event with periods of sulphidic conditions not always reaching the sea floor.

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## Zircon (U-Th)/He thermochronology of the Permian Weissliegende sandstone in the Fore-Sudetic Homocline (SW Poland)

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Two fine-grained sandstone samples of Weissliegende series from the Rudna mine-field site (Fore-Sudetic Homocline) were investigated by low-T zircon (U-Th-[Sm])/He thermochronology (closure temperature of ~180°C) to reconstruct basin thermal history.

ZHe dating results for six sandstone-derived zircon grains represent Neoproterozoic (Cryogenian, Ediacaran), Late Devonian (Famennian) and Middle Triassic (Anisian) ages. Five zircon grains reflect older provenance helium ages, one sample revealed younger, post-depositional age (244±5.0 Ma). Due to highly abraded zircon crystals rims and possible zonation of U-Th isotopes we interpret raw ages as meaningful dataset not applying the  $\alpha$ -correction.

Most important findings might be summarized as follows:

- No thermal reset caused by temperature increase over 180°C was recorded by helium system in 5 from 6 totally analyzed grains. One zircon sample (11-1) resulted in younger post-sedimentary ZHe age.
- Reported basin post-sedimentary thermal structure is in accordance with available clays stable isotopes data for ore temperature formation (100-150°C).
- Total sedimentary burial for the Permian basin did not exceed 6 km applying 30°C/km geothermal gradient, which is consistent with existing paleogeographic models.
- Considerable age dispersion may reflect different source areas and/or difference in retentivity of zircon helium system. Analyzed Weissliegende sandstones might reflect in this case dynamic sedimentation environment with mixed sea and river source conditions.
- The single post-depositional age of 244±5.0 Ma correlates with available paleomagnetic data suggesting a mid-Triassic (230-240 Ma) age of Kupferschiefer mineralization.
- No thermal effect of overlaying evaporites (reaching 11 to 65 m) has been found.
- New approach to the Kupferschiefer mineralization age issue is suggested by applying (U-Th)/He analysis of the ore minerals (e.g. hematite, see Danišik *et al.* 2013).

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## Valleriite types and their significance for serpentinization, Turnagain Ni deposit, BC, Canada

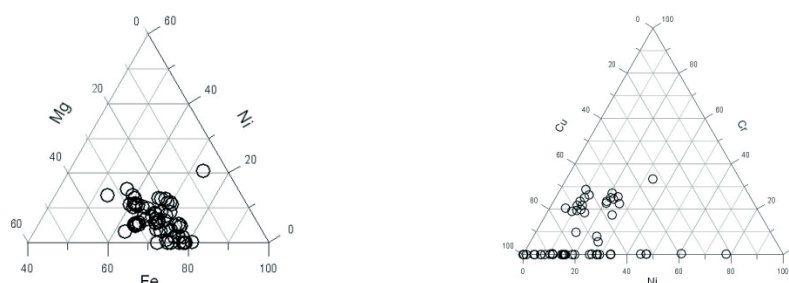
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The Turnagain intrusion, located approximately 70 km east of the town Dease Lake, British Columbia (Canada) is one of the (Uralian)-Alaskan-type mafic-ultramafic plutons. Alaskaites usually comprise: dunite, wehrlite, clinopiroxenite and hornblendite (Sheel et al, 2009). Turnagain deposit contains low grade 428 Mt of Ni ores (<http://www.hardnickel.com>) + some Cu and PGM's. The ores contain common valleriite type minerals: valleriite proper  $4(\text{Fe,Cu})\text{S}\cdot 3(\text{Mg,Al})(\text{OH})_2$ , haapalaite  $2(\text{Fe,Ni})\text{S}\cdot 1.6(\text{Mg,Fe})(\text{OH})_2$ , tochilinite  $6\text{Fe}_{0.9}\text{S}\cdot 5(\text{Mg,Fe})(\text{OH})_2$ , Cr-vallerite  $(\text{Fe}_{2.5}\text{Cu}_{1.0}\text{Ni}_{0.2})_3, 7\text{S}_4\cdot (\text{Mg}_{1.6}\text{Cr}_{0.4-0.6})_{2.2}(\text{OH})_{4.5}$ .

Cr varies in the valleriite studied between 1.69 and 6.16 wt.%. Cr-vallerite forms by replacement of chromite.



Rys. 1. Triplots of valleriite composition for 66 specimens.

Valleriite forms also oriented syntaxial/epitaxial micro to nano size sandwiches with antigorite.

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<http://www.hardnickel.com>



## Relationship of organic matter oxidation, Cu-mineralization, and trace element geochemistry, Nonesuch Shale, Michigan, U.S.A.

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The White Pine sediment-hosted copper deposit, for several decades an important copper source in the U.S.A., occurs in silty shales of the basal Nonesuch Formation and is regarded as an analog of the Kupferschiefer ores. The deposit is presumed to have formed from oxidizing, syn-diagenetic fluids generally migrating in underlying red bed sandstones and conglomerates of the Copper Harbor Formation. Flow ascending into the Nonesuch resulted in mainly stratiform mineralization as pore and fracture fillings in the basal 5 m; some vertical fracture fillings and breached shaly laminae mark cross-stratal flow.

The lowest 15 m of the Nonesuch can be divided into packages that display chemical and petrographic evidence of penetration by ascending fluids. Cu-mineralization as sulfides, is mainly restricted to the lowest 5 m and in places is accompanied by modest increases in Ag, V, and Zn. Vertical fracture fillings and breached shale laminae are most abundant here. The next 5 m package is low in sulfur, trace metals, and copper, although native copper occurs. The third 5 m package shows increased sulfur with modest increases in Cu, As, Cd, Mo, Pb, Sb. MREE/LREE is generally elevated in the lowest 10 m.

The Nonesuch hosts organic matter (OM) as kerogen, bitumen, and oil inclusions; total organic carbon (TOC) varies according to the 5 m packages above. TOC is <0.5 wt. % in the lowest 5 m package, <0.2% in the second package, and rises gradually above. OM is generally considered to have reduced the mineralizing fluid, driving the deposition of copper. Rock Eval pyrolysis data indicate that OM in or near the 5 m-thick ore zone is strongly oxidized and has not followed the normal maturation trend expected for OM deposited in lacustrine or shallow marine restricted basins.

We suggest that the geochemical zonation of the lowest 15 m of the Nonesuch may reflect evolution of the mineralizing fluid as it migrated upward. The oxidation of OM in Nonesuch immediately overlying the Cu-mineralization in particular indicates upward migration of fluids that carried Cu into the base of the Nonesuch. Comparison to data of Bechtel et al. (2002) from the Lubin-Sieroszowice Cu-mining district shows OM from the Cu-mineralized Nonesuch to be similar in degree of oxidation to that of Kupferschiefer where influenced by the Rote Fäule.

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## From Cadomian arc to Ordovician passive margin: Geochemical records preserved in metasedimentary successions of the Orlica-Śnieżnik Dome in SW Poland

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Chemical composition of metamorphosed siliciclastic rocks cropping out in the Orlica-Śnieżnik dome (Bohemian Massif) identify the main source for the Neoproterozoic sediments of the Młynowiec Formation, for the Cambrian variegated sediments interfingering with bimodal volcanics of the Stronie Formation and for the Goszów quartzites deposited during Late Cambrian/Early Ordovician. The Młynowiec Formation developed as a Cadomian magmatic arc along the northern Gondwana margin. In contrast, the variegated Stronie Formation being at least in part of supra-subduction affinities shows very similar chemical characteristics pointing to erosion of freshly exhumed Cadomian orogen and detritus deposition within the back-arc basin. On the other hand, the Goszów quartzites show contrastingly different chemical characteristics pointing to passive continental margin as a tectonic setting of depositional basin.

The geodynamic scenario providing explanation for the observed change in tectonic setting of deposition of documented volcano-sedimentary sequences includes three main stages: (1) Pre ~540 Ma evolution of an active continental margin and related back-arc basin terminated with collision and accretion of magmatic arc to Gondwana margin; (2) the Latest Neoproterozoic–Early Cambrian rift to drift transition (540–520 Ma) and development of depositional basin filled with detritus derived from remnants of the magmatic arc associated with volcanic activity bearing supra-subduction characteristics and (3) Gondwana breakup leading to formation of a shallow-water passive margin depositional basins fed with quartz-rich detritus resembling Early Ordovician Armorican Quartzites known from other parts of the Variscan Belt. Presented scenario is similar to what is documented for analogous Cadomian and Early Palaeozoic successions cropping out in the Saxothuringia and other regions of the Gondwanan Europe.





## Anomalous Be-rich bohseite from Julianna pegmatite (Piława Górna, Góry Sowie Block, Lower Silesia, Poland)

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Bohseite,  $\text{Ca}_4\text{Be}_3\text{AlSi}_9\text{O}_{25}(\text{OH})_3$ , was described in 2010 from Ilímaussaq Alkaline Complex, Kangerdluarssuk fjord, Greenland (Friis et al. 2010). It crystallizes in orthorhombic system (*Cmcm*) and forms a series with bavenite,  $\text{Ca}_4\text{Be}_2\text{Al}_2\text{Si}_9\text{O}_{26}(\text{OH})_2$ .

The bohseite-like mineral was found in a LCT-type core (albite zone) of mixed (NYF+LCT) Julianna pegmatite in Piława Górna quarry (Góry Sowie Block, Poland) (Szuszkiewicz et al. 2013). It occurs together with Fe-rich helvite, phenakite and unidentified Be mica-like minerals as an alteration products after a primary Be mineral, probably beryl. It forms fan-like or parallel aggregates of white platy crystals (up to 2 mm in length) with characteristic striation.

According to Lussier and Hawthorne (2011), maximum three Be atoms can be present in the bavenite structure. Bohseite from Greenland contains such Be amounts, and therefore it is considered as a Be-dominant end-member in the series. The compositions of the bohseite-like mineral from Piława Górna vary in the range of  $\text{Ca}_{3.98-4.10}\text{Na}_{0.00-0.04}\text{Be}_{2.84-3.77}\text{Al}_{0.34-1.16}\text{Si}_{8.89-9.00}\text{O}_{25}(\text{OH})_{2.74-3.48}\text{F}_{0.10-0.34}$ , reaching anomalous high Be of 3.77 apfu. The highest Be- and the lowest Al contents reported to date in minerals of the bavenite–bohseite series worldwide, widen compositional range of the series up to  $\text{Ca}_4\text{Be}_4\text{Si}_9\text{O}_{24}(\text{OH})_4$ .

Structural studies of bohseite from Piława Górna are currently in progress.

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## The first U–Pb dating of apatite from the Polish part of the Cieszyn magma province, Southern Poland

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On the area of the Cieszyn magma province, igneous rocks appear mostly as bodies, emplaced in mechanically weakened zones in Cretaceous sediments. The main products of the volcanic activity are sills, represented by: picrite, picroteschenite, teschenite and syenite. Previous  $^{40}\text{Ar}/^{39}\text{Ar}$  dating of amphiboles (ca. 120 Ma; Lucińska-Anczkiewicz et al., 2002) and  $^{40}\text{K}/^{40}\text{Ar}$  dating of teschenitic rocks in the Polish Outer Western Carpathians, performed on amphiboles, biotite and whole rocks (“amphibole” age ca. 112–90 Ma; “biotite” age ca. 138–133 Ma; whole rock age ca. 122 Ma; Harangi et al., 2003), confirmed their Cretaceous age.

Apatite crystals from different magmatic rocks from the Cieszyn igneous province of the Polish Western Carpathians were dated. All investigated apatite crystals can be classified as fluoroapatite with 1.6–3.7 wt% of F [ca. 1.4 atoms per 2 (OH, F, Cl)]. The apatite crystals are 0.1 to 0.8 mm long and 0.1–0.2 mm wide; in general stubby apatite in whole studied population dominate over acicular ones.

Three teschenitic rock samples from Boguszowice, Puńców and Lipowa yielded different ages:  $103 \pm 20$  Ma,  $119.6 \pm 3.2$  Ma and  $126.5 \pm 8.8$  Ma, respectively. The total, calculated age for all three samples is  $117.8 \pm 7.3$  Ma (MSWD 2.7) and is similar to “pyroxene” and “amphibole” ages given by Harangi et al. (2003). The considerable smaller scatter of results in the “apatite” ages than in published “amphibole” and “biotite” ages is probably caused by better apatite resistance on hydrothermal alteration than amphibole and/or biotite ones.

Lack of primary, magmatic zircon, monazite or xenotime makes apatite crystals the best phase which may be useful for detailed, U–Pb dating of the igneous rocks from the Cieszyn area. The apatite age might reflect the lowest limit of the magmatic activity in the Cieszyn magma province.

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## REE patterns and LA-ICP-MS U-Pb age of apatite from granitoid rocks of the Tatra Mountains (S-Poland) – a record of the granite origin and cooling history

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The Tatra granitoid is an example of the Variscan polygenetic, hybrid intrusion, formed by the multiple magma injections in the crustal shear zone. The prolonged time of intrusion (370 – 337 Ma) is a result of the long-lasting subduction and collision at the southern margin of Laurussia. Apatite is a common accessory mineral, present in all types of the granitoid rocks of the Tatra Mountains and important carrier of rare earth elements (REE). Trace elements content and LA-ICP-MS U-Pb age of apatite from different granite types were investigated.

Apatite from hybrid, monazite-bearing cumulative rock from the Western Tatra Mountains, dated for 344±3 Ma, shows 287-457 ppm Sr (mean value 397 ppm), 870-1300 ppm Y (mean value 1123 ppm) and low REE fractionation ( $La_N/Yb_N = 2.41-1.39$ ) and weakly negative slope of LREE with positive Ce anomaly ( $Ce/Ce^* = 1.08-1.69$ ).

Apatite from monazite-bearing layered High Tatra granite, dated for 339±5 Ma, shows 549-562 ppm Sr (mean value 583 ppm), 1542-2455 ppm Y (mean value 2150 ppm), very weak REE fractionation ( $La_N/Yb_N = 0.66-1.04$ ), negative Eu anomaly (0.39-0.44) and steeply negative slope of LREE with positive Ce anomaly ( $Ce/Ce^* = 1.10-1.15$ ).

Apatite from hybrid allanite-bearing diorite from the Goryczkowa Unit, dated for 340±4 Ma, shows 616-784 ppm Sr (mean value 692 ppm), 1006-1551 ppm Y (mean value 1367 ppm), REE patterns reflecting the mixed magma source ( $La_N/Yb_N = 0.51-2.41$ ;  $La_N/Sm_N = 0.19-0.84$ ), but all showing the almost constant, weakly positive Ce anomaly ( $Ce/Ce^* = 1.01-1.15$ ).

The presented data suggest that REE patterns of apatite could be a monitor of the origin of the parent rock and depend on the association of the other REE-bearing minerals (monazite-allanite).

Taking into account the relatively low closure temperature of the U-Pb system in apatite (ca. 560°C), the age of apatite marks the lowest limit of the magmatic activity. In the Tatra Mountains, the presented ages ca. 340 Ma support the thesis of the youngest magmatic activity at the 340 Ma and influence the mobility of Pb isotopes. In case of the Tatra Mountains 340 Ma could be taken as the key age for the Pb-isotope data calibration, pointing out the lower crustal origin with enriched mantle component for the Tatra granites.

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## Geology and petrology of Cenozoic volcanic rocks of Ostrzyca Hill in the Kaczawa Foothills, SW Poland

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The Ostrzyca Hill is one of the most famous outcrops of Cenozoic volcanic rocks in Lower Silesia in the eastern part of the Central European Volcanic Province. The hill is a basanitic neck rising 250 m above the surrounding plains built of Permian sandstones and conglomerates. The basanites exposed in the upper part of the hill show columnar joints with variable orientation and typical dips of c. 30°. No breccias or other volcanoclastic rocks are found. Comparison with adjacent, similar outcrops and other examples in published papers suggest that the original Ostrzyca volcano (a pyroclastic cone of Miocene age?) was eroded a few hundred metres (less than 1 km) below the pre-eruptive level. The basanite is porphyritic with seriate and massive texture. Clinopyroxene, olivine and rare plagioclase are phenocrysts. The groundmass is microcrystalline and consists of clinopyroxene, olivine, plagioclase, nepheline, spinel and apatite. The rock is melanocratic with low sum of the light minerals (c. 10%). Olivine has a normal zonation (Fo 0.87 – 0.75). The groundmass plagioclase is labradorite (An 50-60) and the spinel is aluminian titanomagnetite. Clinopyroxene (diopside, En 0.32 – 0.40, Wo 0.48 – 0.53) shows a weak zonation; compositional differences between phenocrysts and groundmass crystals are small. However, diopside megacrysts (up to c. 2 cm in size) tend to be enriched in Fe and depleted in Mg. There are also other xenoliths and xenocrysts (e.g. olivine aggregates, quartz crystals). The major and trace element geochemistry of the basanites is similar to neighbouring occurrences. Rather primitive magma composition is indicated by high contents of MgO, Cr, Ni (c. 12%, 480 ppm, 300 ppm, respectively). Modelling using the MELTS software (Ghiorso & Sack, 1995; Asimov & Ghiorso, 1998) and comparison of calculated and observed phase assemblages and compositions suggest that crystallization of the basanite magma, including the formation of olivine and diopside phenocrysts, occurred at shallow crustal levels. The clinopyroxene megacrysts possibly are xenocrysts that crystallized from a different, more evolved magma. The xenocrysts and xenoliths point to some contamination of the basanite magma by both mantle and crustal rocks.

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## Fractional crystallization recorded in the Zn-Pb slags from Piekary Śląskie-Bytom area

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In Zn-Pb slags the limited fractional crystallization could be observed, despite the limited space and closed system. The fractional crystallization is best recorded in large (up to 1 m) blocks of slag, where the outer part, due to undercooling conditions, has frozen rapidly and preserved the inner part from external factors. Cooling rim reduces also the temperature drop in block core, allowing phases to grow steadily, but not enough for equilibrium crystallization to be developed. As a result we observe large variety of phases showing well developed zoning.

Olivine crystals represents  $Fe_{60-95}$  and show Mg – Fe zoning, which reflects the cooling conditions during crystallization process. Kirschsteinte – monticellite series is uncommon and have complex chemistry corresponding to 32-63 mol.%  $CaFe[SiO_4]$ . Spinel is one of major phases and it generally covers chemical composition in system  $FeAl_2O_4 - ZnAl_2O_4 - FeFe_2O_4 - ZnFe_2O_4$ . Well-developed spinel crystals show (Ca, Fe) growing from the core to the rim. Pyroxene, present in all assemblages, has variable chemical composition, generally close to augite or diopside–hedenbergite enriched in CaO. Zoned crystals show Fe, Zn, Mn and Ti content rising from core to rim. Glass inclusions inside pyroxene crystals are common. Importance of melilite in slags is uncertain: it is main phase in some assemblages, while it is lacking in the others. Melilite composition ranges in system: åkermanite ( $Ca_2MgSi_2O_7$ ) – hardystonite ( $Ca_2ZnSi_2O_7$ ) – Fe-åkermanite ( $Ca_2FeSi_2O_7$ ). Feldspars are present in assemblages with higher  $SiO_2$  content, thus they do not co-exist with olivine, leucite and nepheline. Generally feldspars are represented by plagioclases, in some case second generation of feldspars is present as plumbean K-feldspar enriched in barium (up to 6,12 wt.% BaO). Leucite and nepheline on the other hand co-occur with olivine crystals and show many substitutions in elements like Ca, Ba, Sb, Zn, Na, Mg, Fe. Two main types of glass in slags have been distinguished: inclusive glass and residual glass. Differences in chemical composition between both types of glass allow to follow changes in slag melt during crystallization process. Amount of Ca and Al is higher in inclusive glass, while residual glass is enriched in Si, K and Ti. Also unique high-Pb (up to 53,22 wt.% PbO; average 44,98 wt.% PbO) residual glass is present in some assemblages, as a result of fractionation.

The observed sequence of crystallization is close to Bowen's one. Formation of each subsequent phase lead to the impoverishment of the melt in some elements and influences the chemical composition of following crystals. As the result, the composition of melt changed from tholeiitic basalt (inclusive glass) to alkali rhyolite (residual glass).



## Cu-Zn slags from Røros (Norway): a case of rapid cooling and crystal nucleation

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The Røros mining town, designated as an UNESCO World Heritage Site in 1980, is located in Sør-Trøndelag District, in central Norway. Røros was established in 1644 and it is known of historical mining industry related to copper production in the years 1646–1977 (Jones, 1999; Prøsch-Danielsen, Sørensen, 2010). The Røros ore deposits belong to Cambrian-Silurian succession, deformed and metamorphosed during the Caledonian orogeny. The orefield is pyrite-rich polymetallic sulfide type (Barrie et al., 2010).

Slag pieces are composed of three parts: inner, composed of glass with dispersed rare crystallites, outer, characterized by the presence of dense net of needle-shaped crystallites and the 2-5 mm thick rim, composed of crystallite aggregates directed perpendicularly to the slag surface. Microscopic observations point out that nucleation was inhomogeneous and steered by both temperature gradient between the outer and inner parts and volatile contents. Volatiles decrease the rate of nucleation/crystallization, so the smallest crystal ratio in the internal part of the slag portions could be an effect of higher volatile content, expressed as higher vesicle content. The presence of sulphide remnants were noted in all parts of the slag portions and no correlation between the crystal ratio and their presence was noted. The main crystalline component is ferruginous olivine ( $\text{Fa}_{02-98}$ ; average  $\text{Fa}_{74}$ ), usually overgrown by the diopsidic pyroxene (97 mol. % diopside). A glass, filling the space between crystals, is basaltic in composition. Observations are in agreement with experimental studies underlining that in the same degree of undercooling olivine nucleate more readily than pyroxene, which is forming the rims on the olivine cores.

The presented results suggest the slag cooling could be an analogue of fast-cooling basalt lavas, with similar textures and similar sequence of crystallization observed.

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## Composition of coal combustion by-products: importance of combustion technology

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Coal combustion in energy-generating (electricity and heat) plants results in production of significant amount of by-products, e.g. fly-ash and slag (bottom ash). Because of relatively limited range of variation of composition of hard coal used in these plants and similar technologies of combustion used, the composition of fly-ash and slag from different plants was similar. Utilization of by-products of coal combustion increased meaningfully during last decades.

Nowadays, situation is changing, partly due to co-combustion of coal and biomass and modifications in combustion technology. We present data on the chemical and mineral composition of fly-ash and slag obtained from two types of boilers - pulverized fuel boiler and hybrid boiler with fluidized bed adopted also to be fired with pulverized fuel. The same fuel is used in both boilers thus all differences in composition are related to the technology of combustion.

Much higher value of loss of ignition is typical of fly-ash from fluidized bed boiler (11.2 wt. % comparing to 1.8 wt. % in pulverized bed boiler) what is related to abundance of not burnt coal (10.6 wt. % of total carbon content). It is present in irregular, porous, coke-like fragments. Fly-ash from both boilers is composed of quartz, mullite and amorphous glassy material but glass and mullite content is higher in pulverized fuel boilers. Spherical forms composed mainly of aluminosilicate glass dominate in fly-ash. Their size varies within broad range (from below 1  $\mu\text{m}$  to 50  $\mu\text{m}$ ). Other spherical forms are composed of Fe, Ca, Mg, Fe oxides. Beside spherical forms irregular porous glassy grains occur. The content of these grains is higher in fly-ash from fluidized bed boiler.

Slag from pulverized fuel boiler is composed mainly of irregular, often porous, glassy forms (aluminosilicate glass of variable composition with local accumulations of Ca, Mg and Fe oxides), glassy spherical forms and coke-like not burnt coaly matter. Mineral composition of this slag determined by XRD is simply – quartz, mullite and glass. Slag from fluidized bed boiler is different. It is composed of irregular fragments of sedimentary rocks of different types (mudstones, fine-grained sandstones). Results of X-ray diffraction analysis suggest that this slag is devoid of high temperature components (e.g. mullite, glass). Careful study in SEM (equipped with EDS) indicates that rocks are partly welded.

Differences in the composition of fly-ash and slag from both types of boilers are related mainly to the differences in the temperature of combustion.

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## Preliminary data on chromitite from Czernica Hill, Ślęza Ophiolite (SW Poland)

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The Gogołów-Jordanów serpentinite massif (SW Poland) is a member of pseudostratigraphic sequence of the Variscan Ślęza Ophiolite. The outcrop of serpentinites is 22 km long and up to 7 km wide. The serpentinites occurring in the central part of the Massif (Czernica Hill) contain grains and aggregates of Cr-spinel. Chromite accumulations occur as pockets, veins or dispersed grains within serpentine-chlorite mass. The chromitite host rock is usually completely serpentinized, but in places chromitite veinlets are surrounded by olivine. Such olivine grains are zoned - their edges are enriched in fayalite.

Chemical composition defines two groups of chromite: chromite I (Cr# = 0.49 - 0.58) containing 23.32 - 28.36 wt.% Al<sub>2</sub>O<sub>3</sub>, 40.29 - 48.10 wt.% Cr<sub>2</sub>O<sub>3</sub>, 15.10 - 15.50 wt.% FeO, 14.50 - 15.50 wt.% MgO and 0.10 - 0.25 wt.% Na<sub>2</sub>O and chromite II (Cr# = 0.71 - 0.73) containing 13.83 - 15.24 wt.% Al<sub>2</sub>O<sub>3</sub>, 54.85 - 56.65 wt.% Cr<sub>2</sub>O<sub>3</sub>, 16.71 - 18.04 wt.% FeO, 10.62 - 11.59 wt.% MgO and 0.45 - 0.52 wt.% Na<sub>2</sub>O. The TiO<sub>2</sub> content ranges between 0.10 and 0.15 wt.%, PGE and REE were not detected by the LA ICP-MS method. Chromite grains consist mostly of chromite I, whereas the chromite II forms irregular domains up to 150 µm, located mainly at grain edges and fissures.

The low TiO<sub>2</sub> content and intermediate Cr number are typical of chromites formed in mid ocean ridge setting, which originated due to reaction of peridotite and MOR basalt. The Gogołów-Jordanów chromitites are probably remnants after melt-rock interaction within Moho Transition Zone (MTZ) and mark the places of focused melt flow (Leblanc and Ceuleneer, 1992). In this context, chromium and aluminium come probably from peridotitic pyroxenes that react with basaltic melt. Chromites crystallized within small magma chambers as cumulates, when magma migration was blocked.

Chemical composition of chromite II (depletion in Al and Mg and enrichment in Cr and Fe relative to chromite I) suggest that this is altered phase after chromite I. Such alteration is typical for chromites that underwent greenschist facies metamorphism (Gonzalez-Jimenez, 2009).

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## Carbons in a carbon – analyses of organic carbon (OC) and elemental carbon (EC) in PM10 dust

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The main goal of the study was to investigate the origin of potential sources of atmospheric pollution in the study area based on determination of fraction of OC (organic carbon) and EC (elemental carbon) in the TC (total carbon) contained in PM10. The PM10 samples were collected on quartz filters Whatman QM-A by employees of Voivodship Inspectorate for Environmental Protection (VIEP) in Wrocław in 2011 at air monitoring point in Zgorzelec. It is the urban background monitoring station which in the future can be treated as a perfect point comparative for geochemical studies of other urban background stations in Lower Silesia. For further analyses selected 20 samples gathered on average every two weeks measurements. The PM10 concentration varied from  $10 \mu\text{g}\cdot\text{m}^{-3}$  (11.10.2011) to  $85 \mu\text{g}\cdot\text{m}^{-3}$  (9.11.2011), with an average of  $27.3 \mu\text{g}\cdot\text{m}^{-3}$ . Total carbon contribution in aerosols was between 30.78% (06.01.2011) and 60.73% (21.01.2011), with an average of 42%. The lowest OC content of TC was 77.8% (24.12.2011) while the highest was 86.2% (6.01.2011) with an average of 82.3%. The contribution of EC in TC ranged between 13.7% (6.01.2011) and 22.2% (24.12.2011), with an average of 17.7%. OC to EC ratio amounted to an average 4.8 what may be suggested the probable dominant emitter in the study area throughout the year coming from the low-emission which is the combustion of wood and coal. It could be also effect of secondary combustion origin aerosols applied from outside the town. Low contribution of EC in PM10 points to small input of transport pollutions and biomass burning in the particulate matter in Zgorzelec. Further research on the relations of OC and EC thus appears to be reasonable and may help in identifying sources of atmospheric pollution in the in Lower Silesia region.

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# **XX<sup>th</sup> Anniversary Meeting of the Petrology Group of the Mineralogical Society of Poland**

*From the deep Earth to the human's environment*

## ***Field trips guide***







## **Stop 1: Targowica, quarry of basalt (50°41'22.37"N 16°57'55.95"E). Miocene, basaltic scoria cone (structure, deposits, petrology)**

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### **Regional setting and evolution of volcanism in the Strzelin-Ziębice Volcanic Field**

Mafic to bimodal, intraplate volcanic activity, often associated with rifting, occurred in many parts of Europe in Cenozoic to Recent times (Wilson & Downes, 2006). The Ohře (Eger) Graben in the Bohemian Massif is a well-recognized site of such volcanism, and the Strzelin – Ziębice Volcanic Field (SZVF), located c. 100 km east of the Ohře Graben, in the Fore-Sudetic Block, is a small but characteristic example of a mafic, monogenetic volcanic field typical of the Cenozoic volcanism in Central and Western Europe (Fig. 1A).

The SZVF occurs upon the W-E trending Strzelin horst, bounded by the Rostoka-Mokrzyszów and Paczków grabens to the north and south, respectively. Neogene and Quaternary, alluvial and post-glacial deposits, cover most of the area and are up to several hundred metres thick in the grabens. The pre-Cenozoic basement comprises of Late Precambrian and Palaeozoic, crystalline rock series, which belong to the eastern part of the Variscan orogen. The roughly meridional structural trends in the basement are defined by the alignment of tectonostratigraphic units, shear zones and terrane boundaries (Fig. 1B). The location of the SZVF and the distribution of individual volcanic centres can be generally linked with block-type Cenozoic tectonics, which partly reactivated old dislocations within the Variscan basement (Oberc et al. 1975, Dyjor, 1995; Cwojdzinski & Jodłowski, 1982).

K-Ar age determinations of the volcanic rocks (Birkenmajer et al. 2004; Badura et al. 2005) and petrological data (Awdankiewicz, unpublished) suggest two distinct stages of Cenozoic volcanism in the SZVF:

- the older stage, dated at c. 30-28 (25?) Ma (Oligocene), which comprised the emplacement of nephelinites at Żelowice-Kowalskie and Pogroda, as well as trachybasalts at Dębowiec;
- the younger stage, dated at c. 23-20 Ma (Early Miocene), with eruptions of basalts at Targowica and Brukalice, as well as trachybasalts near Gilów-Gola.

The timing of volcanism in the SZVF is similar to other parts of Lower Silesia, although the volcanic rock assemblage is more specific: e.g. basanites, which are most widespread elsewhere (Białowolska, 1987), are lacking in the SZVF.

The volcanogenic deposits and original volcanic landforms of the SZVC are variably eroded, in places down to a subvolcanic level. Volcanic plugs, relics of lava flows and locally pyroclastic deposits are recognized (e.g. Birkenmajer et al. 1970, 2004) and some volcanic structures have been characterized in more detail (August et al., 1995; Awdankiewicz, 2005 and unpublished data). The eruptions of nephelinites were dominantly

effusive and resulted in the formation of lava flows (fields?), locally with up to 2-3 stacked aa-type lava sheets (e.g. at Kowalskie). The eruptions of basalts and trachybasalts ranged from effusive to explosive, Strombolian-type. The lavas and associated pyroclastic deposits occur at Dębowiec, Brukalice and, especially, at Targowica. The Sośnica Hill near Targowica, in the centre of the SZVF, is one of the best preserved examples of Cenozoic volcanoes in Lower Silesia, and it is well exposed in recently re-opened quarry.

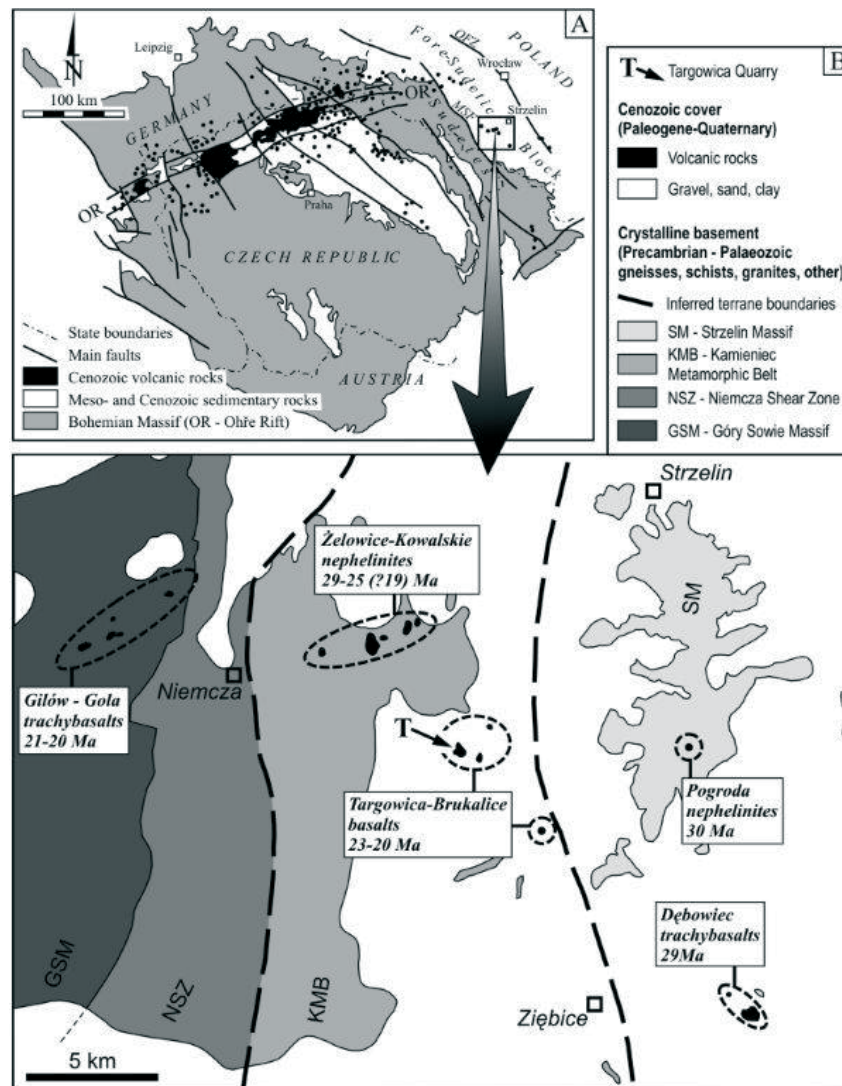


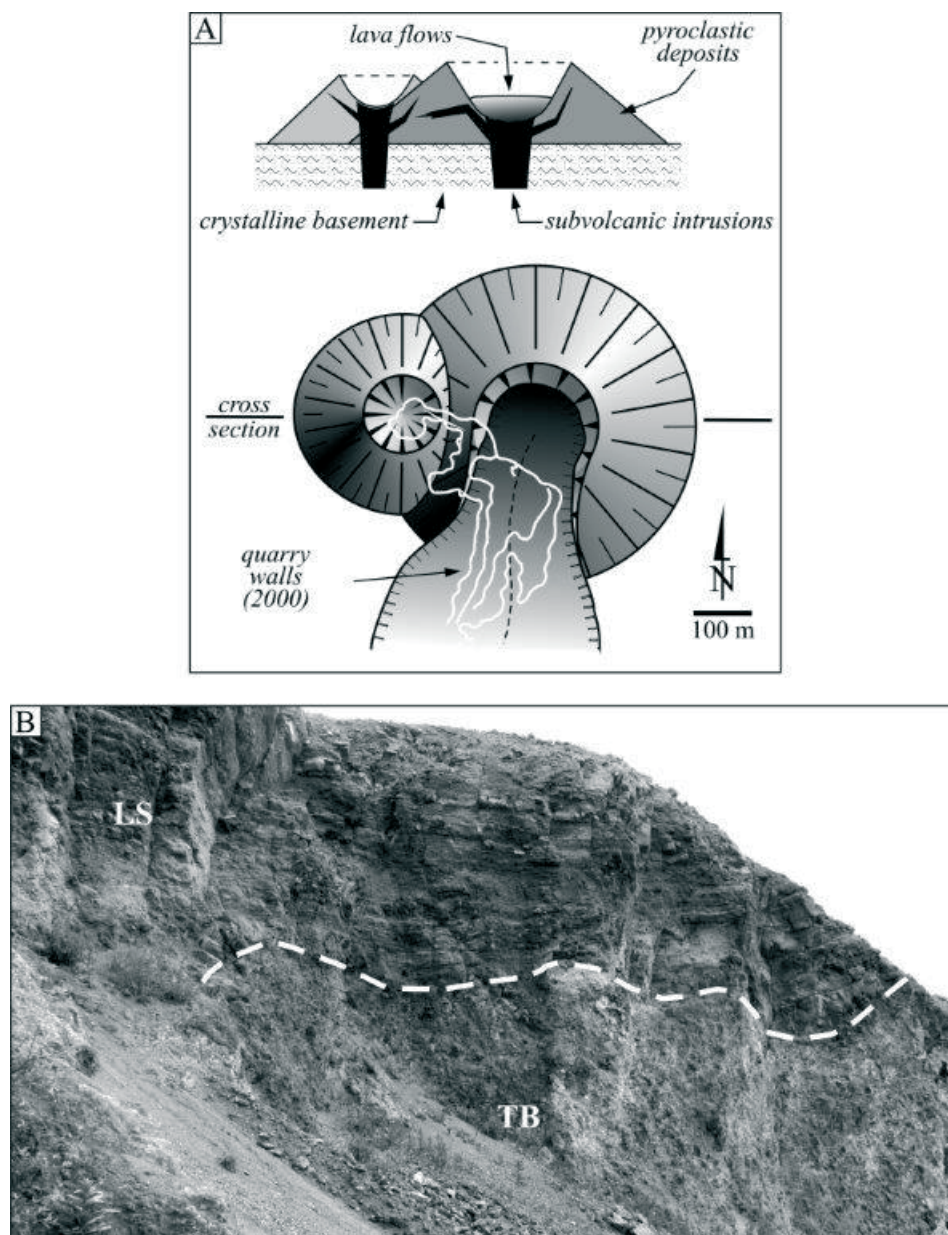
Fig. 1. A. Location of the Strzelin-Ziębice Volcanic Field relative to the Ohře (Eger) Graben in the Bohemian Massif (modified from Ulrych et al. 1999).

B. Geological sketch map of the Strzelin-Ziębice Volcanic Field highlighting the main outcrops of volcanic rocks and their age (based on Sawicki, 1967; Birkenmajer et al. 2004; Badura et al. 2005; Mazur et al. 2006; Awdankiewicz, unpublished). Location of the Targowica quarry is indicated.

### **The Sośnica volcano at Targowica: Structure, deposits, eruptive processes**

The structure and evolution of the Early Miocene Sośnica Hill volcano have been characterised by Awdankiewicz (2005). The original volcano (Fig. 2A) was a Strombolian scoria cone, c. 500-1000 m in diameter and 90-180 m high. A lava flow erupted from the central crater through a breach in the southern sector of the cone. A smaller, “parasitic” vent (cone?) possibly developed on the western flank of the main cone. The quarry walls expose various types of volcanoclastic deposits (Fig. 2B), ranging from non-bedded tuff breccias (predominant) to bedded lapillistones (less common). These deposits consist of volcanic bombs, scoria and a finer, ash-sized pyroclastic fragments. These rocks were deposited by pyroclastic fall related to mildly explosive, Hawaiian to Strombolian-type eruptions of the basaltic magma. The lithological variation reflects different styles of activity of the volcano: e.g. intense eruptive phases with rapid deposition of coarse, poorly sorted, bomb-rich material (the coarse-grained, non-bedded tuff breccias) as well as less intense eruptive phases with several more discrete eruptive episodes (the bedded lapillistones). The pyroclastic deposits are cut by subvolcanic intrusions, including a plug in the western part, as well as subvertical to inclined dykes and subhorizontal sheets in other parts of the cone. Basaltic lavas in the southern part of the cone partly filled the crater and flew out through the breach in the cone; in the proximal part the flow consisted of two main lobes. The lavas show columnar and platy joints of variable orientation, partly reflecting the palaeotopography, with the platy joints subparallel, and columnar joints perpendicular to the underlying surface. After the cessation of activity, the volcano has been substantially eroded. The present Sośnica Hill represents remnants of, mainly, the SE sector of the volcano, where the pyroclastic deposits were partly protected from erosion by a “framework” of plugs, intrusive sheets and lava flows.

Quarrying in recent years, after 2005, significantly modified the extent of the quarry and the sections exposed. In particular, the lava flow in the south was largely quarried away, and the advance of quarry walls to the north, west and east, outwards from the main vent, exposed thicker accumulations of pyroclastic deposits; alignment of flattened volcanic bombs suggest welding in some of these tuff breccias. Quarrying proceeds also downwards in the main vent area, where the coherent basaltic plug is exposed. Preliminary examination of the new exposures suggest that the volcano could have been smaller than in the reconstruction in Fig. 2A.



*Fig. 2. The Sośnica Hill volcano at Targowica.*

A. Reconstruction of the original form of the volcano relative to quarry walls around the year 2000 (modified from Awdankiewicz, 2005).

B. Pyroclastic deposits at Sośnica: non-bedded tuff-breccias (TB) rich in volcanic bombs, overlain by well-bedded lapillistones (LS). The quarry wall is c. 10 m high.



### Petrological aspects

Massive basalts from the internal parts of lava flows and subvolcanic intrusions are holocrystalline, porphyritic with microcrystalline groundmass and composed mainly of clinopyroxene (c. 50% by vol.) and plagioclase (23-25%) with smaller amounts of olivine and opaque minerals (11-21% and 14-15%, respectively). The phenocrysts (c. 5-10% by vol., typically <1 mm long) comprise olivine, clinopyroxene and rare plagioclase. Olivine phenocrysts are embayed and partly replaced by iddingsite. Some clinopyroxene phenocrysts show sieve-textured cores. Basalts from the margins of lava flows and intrusions, as well as basaltic fragments in the volcaniclastic deposits, are vesicular and hypocrySTALLINE, with abundant, opaque-rich interstitial cryptocrystalline or glassy material (tachylite). In addition, the basalts contain xenoliths of peridotites and other plutonic rocks as well as various polycrystalline aggregates of olivine, clinopyroxene and opaques, which may represent xenocrystic as well as cognate materials. A microprobe study shows that clinopyroxene is diopside, plagioclase is labradorite (An62-52), olivine is Mg-rich with normal zonation and (Fo84-65) and the opaque minerals comprise chromite and titanomagnetite. The post-magmatic minerals, found in vesicles and locally abundant in the pyroclastic deposits, are zeolites (phillipsite, natrolite, chabasite), clay minerals (smectites) and carbonates (calcite, dolomite; August et al. 1995; August & Awdankiewicz, 1999).

The recent data of Puziewicz et al. (study in progress) show that the xenolith suite from Targowica comprises mantle peridotites, gabbros and probably ultramafic cumulates. All the xenoliths are few centimetres in diameter. The mantle peridotites are depleted in terms of major element composition of rock-forming minerals (olivine Fo 91.0-91.5, orthopyroxene mg# 0.91-0.92, Al <0.08 atoms pfu, sparse clinopyroxene mg# 0.92 – 0.95, highly variable Al). The REE patterns of clinopyroxene are depleted in HREE and enriched in LREE). Some of the xenoliths contain carbonatite pockets.

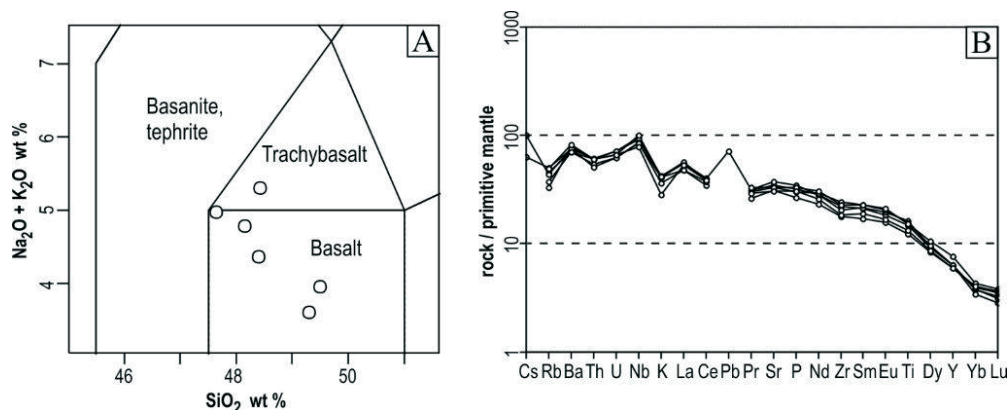


Fig. 3. Selected geochemical characteristics of the Targowica basalts.

A. Samples from Targowica area in a low-silica part of the TAS plot (Le Maitre et al. 2002). Two samples with the highest silica and lowest alkali contents are altered scoria fragments from pyroclastic deposits.

B. Primitive mantle-normalized plot for the basalts (normalization after Sun & McDonough, 1989).

Comments in text.

The major and trace element characteristics of the basalts reveal a fairly primitive composition (Mg# = 63, Cr = 220 ppm, Ni = 150 ppm), enrichment in several incompatible elements (e.g. Ba, Nb, Ta, La, Ce) as well as relative depletion in K, Rb and the heavy rare earth elements (Fig. 3B), typical of mafic alkaline lavas elsewhere in Lower Silesia and in

Europe (cf. Wilson and Downes, 2006). By analogy, these features suggest formation of the basaltic magma of Sośnica volcano at the transitional zone of garnet and spinel peridotites containing also phlogopite and/or amphibole, at low degrees of partial melting. The primary magma likely underwent some crystallization and fractionation of, mainly, olivine and clinopyroxene, on the way to the surface. However, the low volume and rate of magma supply, together with the simple structure of the magmatic feeding system typical of scoria cones (without bigger magma reservoirs) possibly inhibited more advanced differentiation and promoted rather rapid ascent and eruption of the mantle-derived melts. Referring to the motto of this meeting, “From the deep Earth to the human’s environment”, these were the deep-level factors, such as the mantle source characteristics and partial melting processes which largely determined the magma composition and eruptive style of the Sośnica volcano.

*Acknowledgements:* The comment on xenoliths was kindly written by J. Puziewicz.

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## Stop 2: Why is the Szklary Massif interesting for Earth scientists?

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### Introduction

The geological unit called the Szklary Massif forms a chain of hills and crops out in southern part of the Fore Sudetic Block (southwestern Poland). Geological and historical evolution of this site is complex (Fig. 1) which makes it an interesting study object for wide range of scientists: from mantle petrologists to environmental geochemists.

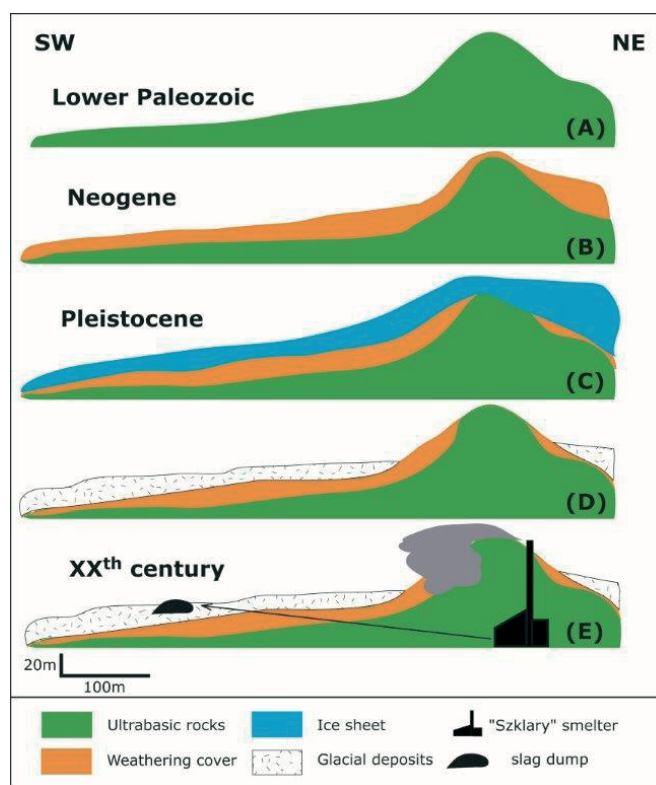


Fig. 1. Simplified picture presenting the evolution of the Szklary Massif.

The Szklary Massif is composed mostly of partially or completely serpentinized ultrabasic rocks belonging to a tectonically dismembered Paleozoic ophiolitic sequence

(Pin et al. 1988). Phase composition of ultrabasites from Szklary is dominated by serpentine group minerals, olivine, orthopyroxene and amphiboles (tremolite and anthophyllite) as major constituents whereas, chromite, Cr-magnetite, chlorite, clinozoisite and carbonates occur as accessory minerals (Niškiewicz, 1967, Gunia 2000, Kierczak et al., 2007; Figure 2).

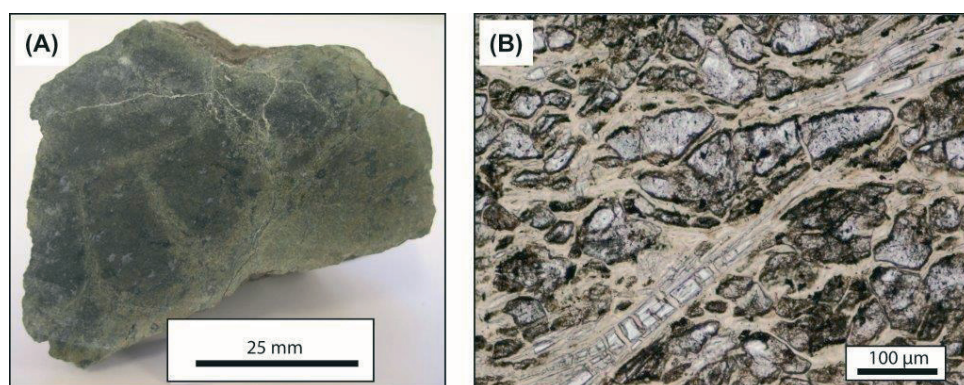


Fig. 2. Partially serpentinized peridotite from the Szklary Massif (A) macroscopic view (B) microphotograph taken under parallel polars.

During the Neogene, rocks from the Szklary Massif were subjected to a lateritic weathering, which produced a thick (in some places up to 50 m) rust-colored cover of altered rock with a structure typical of the New Caledonian laterites (Dubieńska *et al.* 2000, and references therein). The weathering cover is composed of iron oxides, oxyhydroxides and SiO<sub>2</sub> varieties (e.g., chrysoprase – a precious gemstone). In contrast with most laterites, the alteration crust in Szklary contains a great number of clay minerals which were formed not only as a result of chemical weathering under tropical climate but also due to hydrothermal metamorphism posterior to serpentinization (Dubieńska *et al.*, 2000; Sakharov *et al.*, 2004 and references therein). During Pleistocene the area of the Szklary Massif was covered by an ice sheet. Afterwards, as a result of a glacier regression, unweathered ultrabasic rocks have been exposed in the upper parts of the hills whereas fluvioglacial sediments overlay lower parts of the massif. From the Quaternary, the Szklary massif has been submitted to a temperate climate, and as a result of weathering of ultrabasic rocks, naturally enriched in some trace elements (such as nickel and chromium) a specific type of soil called "serpentine soils" was formed. These soils have distinctive properties caused primarily by a specific chemical composition of parent rocks. The parent ultrabasic rocks commonly cause infertility of serpentine soils, which results from the low ratio of calcium to magnesium, and the high content of nickel and chromium in the parent rock and the soil (Weber 1981 and references therein). However, ultrabasic ecosystems harbor a distinct, often endemic plant community (Brooks, 1987).

The lateritic cover of the Szklary Massif was exploited as a low-grade Ni-ore containing less than 2 wt.% of nickel (Niškiewicz *et al.* 1979). Mining and smelting in Szklary began in the late nineteenth century and lasted almost 100 years, until 1982. As a result of these industrial activities large amount of wastes (e.g., slags) was disposed on dumps in the surroundings. Generally, pyrometallurgical slags are important sources of inorganic contaminants (metals and metalloids) and its weathering leads to release of pollutants and

causes contamination of soils, ground and surface waters (Ettler et al., 2009; Lottermoser, 2005).

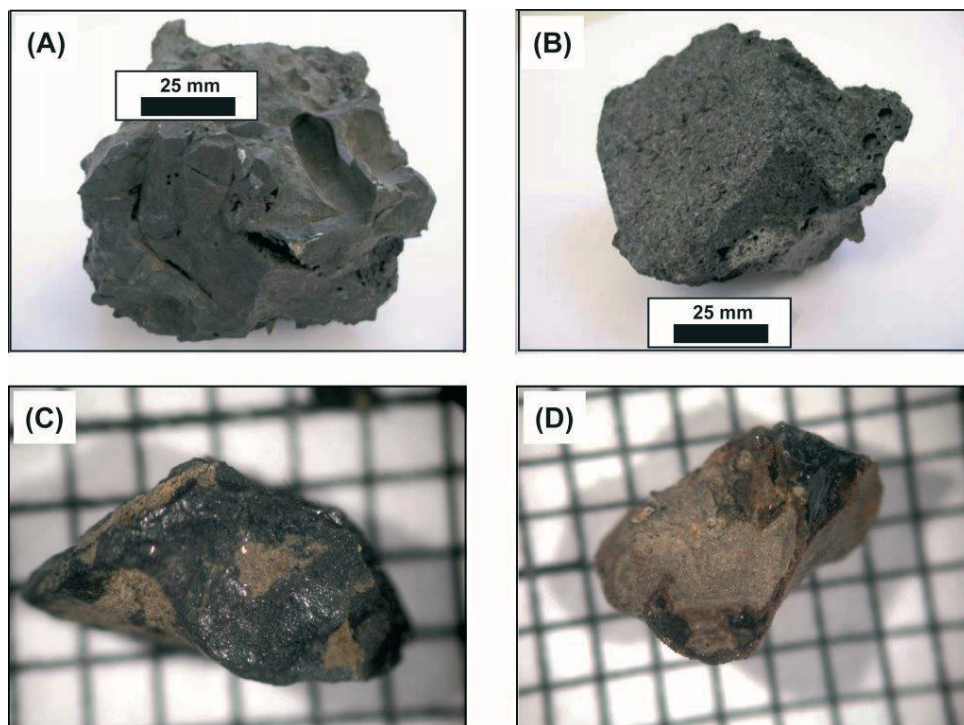


Fig. 3. Photographs of representative samples of the Szklary slags: (A) slag type 1 from waste dump, (B) slag type 2 from waste dump, (C) slag type 1 from cultivate field, (D) slag type 2 from cultivated field.

Two main types of slags occur in the waste dump of pyrometallurgical slags produced during reworking of lateritic ores of Ni in Szklary (Fig. 3). They consist of silicate glass, synthetic equivalents of clinopyroxenes (diopside, hedenbergite), melilite, olivines (forsterite, fayalite) and subordinate spinel (chromite), sulfides (pyrrhotite, pentlandite, heazlewoodite, digenite) and intermetallic compounds (awaruite, bronze, metallic Fe and Cu). Slags from Szklary contain important amounts of some metallic pollutants (e.g., Co up to 4000 ppm, Cr up to 6500 ppm, Ni up to 4000 ppm and Zn up to 400 ppm; Kierczak et al 2009). Thus they constitute potential source of pollution for the surrounding environment. Furthermore, waste dump in Szklary is covered by a thin layer of soil (Technosol) which contains considerably higher concentrations of Ni (up to 9 wt. %) and other metals (Kierczak et al., 2008).

In this context, an interesting feature of the Szklary Massif is that this site comprises two environments containing Ni and Cr from diverse origins: lithogenic (ultrabasic rocks, weathering crust and serpentine soils) and anthropogenic (waste dump composed of slags and covered by a Technosol).

Several papers were dedicated to study the stability and potential mobility of Ni and Cr in different types of materials (those of lithogenic and anthropogenic origin) from the Szklary Massif (Kierczak et al., 2007, Kierczak et al., 2008, Kierczak et al, 2009). The approach based on mineralogical characterization of Ni and Cr bearing phases and

complementary chemical extractions allowed discussion about potential mobility of these elements and revealed relative stability of Cr compared to Ni. Furthermore, it was pointed out that Ni from lithogenic sources (serpentine soil) has a higher potential mobility than Ni from anthropogenic sources (slags, Technosols).

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### Stop 3: The Kośmin quarry. Granodiorites of the Niemcza Zone

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Third point of field trip bring us to one of the igneous rocks of the Variscan basement in the NE part of the Bohemian Massif. The Kośmin granodiorite is characteristic because of its fabric, occurrence of feldspar porphyrocrysts in the groundmass rich in dark minerals and because of numerous dark enclaves. The granodiorites, termed as “syenites” (Cloos, 1922), are known since over the century. Their appearance fitted the ideas of “transformists” in the time of mid-XX<sup>th</sup> century discussion on magmatic vs. non-magmatic origin of granites, and the rock were used as the local example in that discussion (Dziedzicowa 1963).

The Niemcza Zone is narrow (<5 km in width) meridional zone of mylonitised gneisses, forming the sinistral shear zone located at the eastern margin of the Góry Sowie gneissic block (Mazur & Puziewicz 1995). The igneous rocks of the Niemcza Zone comprise fine grained biotite-hornblende diorites-monzodiorites exhibiting no deformation and medium grained porphyritic granodiorites with well defined igneous foliation/lineation (Puziewicz 1992). Geological relationships show that both group of the rocks are coeval, and that the diorites at least locally are older than the granodiorites (Puziewicz 1992). Recent study of Pietranik et al. (2013) shows that diorites intruded from 342 to 336 My.



Fig. 1. Outcrops of the medium-grained granodiorites (black) in the Niemcza Zone (based on figure in Puziewicz, 1992).



The Kośmin quarry is situated in one of the largest outcrop of the granodiorites (Fig. 1) and thanks to intensive mining offers good view of granodiorites, their large-scale textural variation and various kinds of enclaves.

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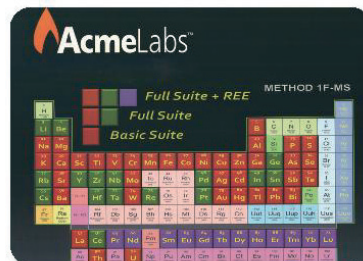
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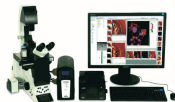
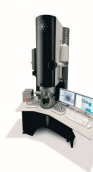
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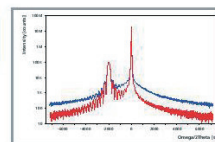
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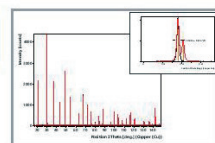
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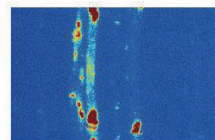
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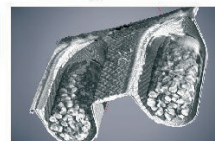
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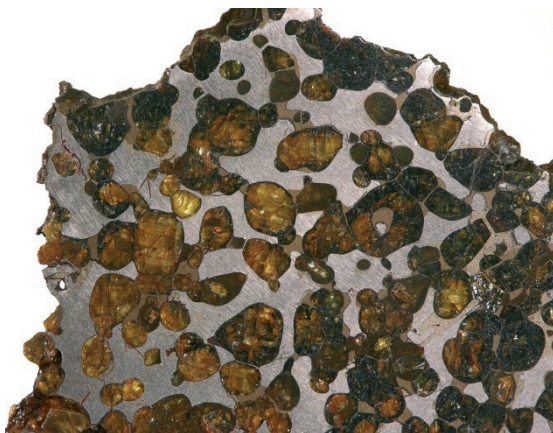
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Firma PerkinElmer, koncentrując się na dostarczaniu innowacyjnych rozwiązań i usług dla nauki i przemysłu, wychodzi naprzeciw Państwa potrzebom. Dzięki nam każde laboratorium ma dostęp do zaawansowanych metod analitycznych, zapewniających szybkie otrzymanie wyniku i spełniających najwyższe wymagania.

Nasze rozwiązania przeznaczone do analiz fizykochemicznych pomagają lepiej poznać badane próbki. Od monitorowania radioaktywnych i organicznych składników, do wykrywania śladowych ilości substancji, dzięki nieporównywalnym systemom eksperckim i szerokiemu zakresowi usług dostarczamy możliwość wnikliwej analizy, jak również zapewniamy bezproblemową i wydajną pracę laboratoriów. Jesteśmy partnerem, który pomaga w uzyskiwaniu najwyższej jakości i optymalnej dokładności na każdym etapie pracy, gwarantując przy tym wsparcie naszych specjalistów.

Nasza oferta w dziale analitycznych metod laboratoryjnych obejmuje m.in.:

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- analizatory pierwiastkowe **EA** mierzące m. in. ilość węgla organicznego i nieorganicznego,
- analizatory termiczne **STA**, **TGA** i **DSC** badające m. in. przejścia fazowe,
- mikroskopy i spektrofotometry podczerwieni **IR** określające m. in. rozmieszczenie oraz ilość minerałów w próbkach,
- materiały eksploatacyjne i akcesoria do urządzeń różnych producentów.



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