MINERALOGIA – SPECIAL PAPERS
Volume 44, 2015

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

Contemporary challenges in the mineralogical sciences

Abstracts and field trip guide

Sandomierz, Poland, 8-11 October 2015

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

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The XXIInd Meeting of the Petrology Group of the Mineralogical Society of Poland and this issue of ***Mineralogia - Special Papers*** were financialy supported by the Polish Ministry of Science and Higher Education subvention and ACME Analytical Labs, PANalytical B. V. and A.G.A. Analytical.

PL ISSN 1899-8518

Printed:
Wydawnictwo Naukowe "Akapit", Kraków
Kom. 608 024 572
e-mail: wn@akapit.krakow.pl; www. akapit.krakow.pl

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

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organized by

Mineralogical Society of Poland

together with

Department of Geochemistry, Mineralogy and Petrography, Faculty of Earth Science, University of Silesia

KATEDRA GEOCHEMII,
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Sandomierz, Poland, 8-11 October 2015

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

Contemporary challenges in the mineralogical sciences

Dear Colleagues,

The 22nd Annual Meeting of the Petrology Group of the Mineralogical Society of Poland in 2015 is being held in the beautiful city of Sandomierz. The main topic of the meeting is *Contemporary challenges in the mineralogical sciences*. Annual Meetings of the Petrology Group have always been an excellent opportunity to present and discuss the most recent achievements of the society's members and its friends. This book of abstracts offers a glimpse to what can be expected during the 22nd Annual Meeting. Oral presentations and posters will cover a wide spectrum of topics related to geochemistry, mineralogy, and petrology-of rocks from the Tatra Mts., the Bohemian Massif, the Holy Cross Mts., and numerous other localities. Some of those presentations depict general problems of mineralogical sciences, others are focused on solving more regional problems by either overviewing the existing data or by providing new detailed data, but all of them are interesting and significantly contribute to our understanding of petrological processes and regional geology. All of the contributions to the Annual Meeting document an impressive progress in research that has been done by the investigators since the last Annual Meeting of the Petrology Group of the Mineralogical Society of Poland.

On behalf of the Organizing Committee we wish the participants fruitful and enjoyable meeting hoping that it will stimulate further research in the field of mineralogical sciences.

The Organizing Committee

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

Contemporary challenges in the mineralogical sciences

Oral and poster contributions

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Historical scenario signature of oil migration in barite mineral

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In this study, barite as well as galena collected from ore deposits in Iraq was investigated in terms of fluid inclusions and isotope geochemistry for the purpose of identifying the historical scenario of the oil migration. This objective relied on the fact that the origin of ore deposits involved oil field brine water that partially mixed with hydrothermal fluids of magmatic origin (Awadh 2006). Fluid inclusions are investigated within the epigenetic barite using ultraviolet fluorescence micro-spectrophotometry. Galena associated barite is also investigated for lead isotopes composition and age determination. All data obtained along with the paragenetic sequence of ore minerals are employed to provide geological evidence of the oil migration pathway and timing and, eventually, for the construction of the historical scenario of oil migration. Two phases of galena (early and late) was recognized, corresponding to 120 m.y. and 30 m.y. respectively. The specific hydrocarbon events are characterized by the oil migration that started before 70 m.y. ago and continued to 30 m.y. ago.

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Geochemistry and petrography of polymetallic sulfide ores and carbonate host rocks in the Alanish occurrence, north of Iraq

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The polymetallic Alanish occurrence is one of widespread Zn, Pb deposits in northern Iraq along the northern passive margin of the Arabian plate (Awadh et al. 2008). These deposits are hosted by carbonates cropping out in several dolomitized zones within the Chia Zari Formation (Late Permian). It is an epigenetic strata-bound occurrence of Mississippi Valley Type deposited from a mixture of formation water with oilfield water derived from sedimentary basins under high heat flows (Awadh et al. 2009) .

The dominant metals in the mineralization (Zn and Pb with a considerable amount of Fe as well as lesser amount of Ag and Cd) occur as primary sulfides (sphalerite, galena, pyrite, marcsite, acanthite and greenockite). Open spaces and cavity filling of small paleo-karsts, replacement, veins and veinlets are the dominant features of the mineralization. Supergene solution action on primary sulfides gave rise to gossan and secondary carbonates consisted of smithsonite, cerussite and goethite. Multiple stages of ore-bearing fluids intruded Chia Zari carbonates; the earlier stage was characterized by Fe-rich fluids and the later stage depleted of Fe.

Massive and disseminated sphalerite are the main features. The disseminated ore is synchronized lath-shape barite. Pyrite and marcsite are often isomorphosed to goethite. The minerals acanthie and greenockite are reported for the first time in Iraq; they occur as tiny crystals in blebs within the massive sphalerite.

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Variable post-magmatic mineral assemblages and bulk-rock chemistry of the Góry Suche Rhyolitic Tuffs (Permian, the Intra-Sudetic Basin, SW Poland)

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The Góry Suche Rhyolitic Tuffs (GSRT) are part of the Lower Permian Volcanic Complex of the Intra-Sudetic Basin, a late Palaeozoic intramontane trough in the eastern part of the European Variscan Belt. The GSRT, outcropping in a NW-SE trending belt 50 km long and up to 10 km wide, originated in voluminous caldera-forming eruptions (c. 100 km^3 of magma in total), with the majority of tephra deposited as ignimbrites. The NW segment of the GSRT, up to a few hundred metres thick, comprises both non-welded and welded ignimbrites, and the thinner SE segment consists of non-welded ignimbrites. Several primary petrographic and geochemical characteristics of the tuffs (e.g., textures, immobile element ratios) are rather uniform along the outcrop. However, the NW and SE segments are different in terms of post-magmatic / diagenetic mineral assemblages, as well as in bulk-rock chemistry of some mobile elements.

The main components of the tuffs are altered glass shards and small pumice fragments accompanied by c. 5-20% of phenocrysts of K-feldspar, albitized plagioclase, quartz, minor opaques and rare biotite. Accretionary lapilli are locally abundant. There are minor lithic clasts, such as texturally variable rhyolites and xenoliths of andesitic rocks, sandstones, mudstones and clay-rich rocks. Secondary minerals replacing the primary components and phases comprise, predominantly, quartz, K-feldspar and albite as well as calcite, dolomite, kaolinite and other clay minerals (illite?). Such a mineral assemblage is typical of the NW segment of the GSRT. However, in the SE segment, the above minerals are accompanied by significant amounts of analcite, replacing glass shards, filling voids and locally forming aggregates of euhedral crystals. In terms of bulk-rock chemistry, the analcite-free samples from the NW show higher contents of K_2O and SiO_2 as well as lower LOI and Na_2O, whereas the analcite-rich samples from the SE show the opposite features.

The above mineralogical and chemical characteristics can be tentatively linked with different post-magmatic processes which affected the NW and SE segments of the GSRT. The K- and Si-rich chemistry and K-feldspar and quartz-rich secondary mineral assemblages in the NW can be related to vapour-phase crystallization in hot tephra immediately after its deposition. The Na-rich chemistry and analcite-rich assemblages in the SE can be linked to interactions with groundwater and/or alkaline diagenetic solutions.

Acknowledgements: The study has been supported from the internal UWr grant 1017/S/ING to MA and from the PGI-NRI grant 61-2601-1401-00-0 to HA. Microprobe analyses were carried out at the Ruhr-Universität Bochum as part of scientific collaboration between RUB and UWr.

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Geochemical variation of mafic, monogenetic volcanic centres in the Cenozoic Strzelin-Ziębice Volcanic Field (SW Poland)

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The Strzelin – Ziębice Volcanic Field (SZVF), located c. 100 km east of the Ohře Graben in the Fore-Sudetic Block, represents a small but characteristic example of a mafic, monogenetic volcanic field typical of the Cenozoic Central European Volcanic Province and other continental, intraplate provinces worldwide. K-Ar ages of the volcanic rocks indicate two stages of activity, in the Oligocene at 30-25 Ma, and in the Miocene at 23-20 Ma (Badura et al. 2005 and references therein). Four main volcanic centres (near Targowica, Dębowiec, Żelowice-Kowalskie and Gilów-Gola) and minor scattered outcrops comprise variably eroded scoria cones, plugs and lava flows of nephelinite, alkali basalt and trachybasalt composition. Major and trace elements were analyzed in 21 samples, and Sr, Nd and Pb isotope compositions in 6 representative samples. The very high magnesium numbers and MgO and Ni contents in the nephelinites (up to c. 65 and 13 %, and 250 ppm, respectively) are typical of primitive, mantle-derived magmas, although lower values in some basalts and trachybasalts (down to 45, 5 and 90, respectively) may be due to some fractional crystallization of, mainly, olivine and clinopyroxene. Major and trace element data and Sr, Nd, Pb isotope ratios clearly distinguish nephelinites from basalts-trachybasalts, implying different mantle sources and melting conditions involved in the formation of these compositionally different magmas. The Sr, Nd and Pb (^{206}Pb/^{204}Pb) isotope ratios (c. 0.7030-0.7035, 0.5129-0.5130, and 19.6319-20.0430, respectively) range among the most extreme in the Central European Volcanic Province (e.g. Wilson, Downes 2006 and references therein) and indicate a depleted mantle component, the European Asthenospheric Reservoir, as the dominant magma source. Each of the main volcanic centres in the SZVF is distinctive from the others in terms of its compositional range (e.g. magnesium numbers, Zr/Nb ratios, isotope ratios). Geological data together with the variation of geochemical characteristics in time and space show that successive volcanic centres at the SZVF were formed by compositionally unique magma batches, and that the composition of these magma batches was mainly constrained by specific combinations of source characteristics and melting conditions, with shallow-level differentiation processes playing a lesser role.

Acknowledgements: The study has been supported from the internal grant 1017/S/ING from the University of Wrocław and from the Czech Science Foundation project P210/12/1990.

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Mineralogical characterization of historic mortars as a tool in discrimination of construction phases of historic buildings – a case study of the Lubiąż Abbey (SW Poland)

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The Lubiąż Abbey is located about 50 km northwest of Wrocław. It is a complex of numerous buildings, erected and developed by Cistercian monks. This complex comprises: 1) the church of the Assumption of the Virgin Mary, 2) the cloister, 3) the Abbatial Palace and 4) numerous outbuildings (*e.g.,* brewery, granaries etc.). The oldest are relics of Romanesque buildings, found within the church and the cloister. The most important later reconstructing phases took place at the end of the thirteenth century (Gothic style) and at the beginning of sixteenth century (Baroque style). Despite the numerous archaeological works that have taken place, the detailed inner structure of the complex is not well constrained. Thus, the aim of this research was to use other than conventional archaeological tools to discriminate all of the construction phases. To achieve this, a detailed petrographic study (polarizing microscopy, SEM-EDS, DSC-TG, XRD) of mortars and plasters sampled from the Abbey was performed.

The results allow us to conclude that all of the investigated mortars have abundant filler, dominated by quartz, with uncommon feldspars and lithic grains, and with no significant differences in grain-size distribution. The main differences lie in the mineralogy of the binder. On this basis, we distinguish three different groups of mortars. The first group is characterized by calcitic binder, strongly inhomogeneous, rich in lime-lumps, and enriched in patches of Fe-oxyhydroxides. Mortars constituting the second group exhibit almost pure calcitic binder, with less common lime-lumps. The third group differs significantly in that the mortars have binder composed of a mixture of calcite, magnesite and hydromagnesite occurring in different proportions. The first two groups represent mortars prepared on the basis of lime calcined from calcitic rocks (limestones, marbles) rich in Fe-bearing minerals and pure calcitic rocks, respectively. The third group comprises mortars prepared using lime calcined from dolomites of dolomitic marbles.

The position and relative stratigraphy of mortars in the Abbey suggest that the first group belongs to the oldest, i.e., Romanesque construction phase. Mortars included in the second group are Gothic, whereas the dolomitic mortars belong to the Baroque phase. The application of petrographic methods to the investigation of historic mortars proved to be valuable in differentiating the construction phases.

Acknowledgements: the research was supported by the National Science Centre Project (UMO-2012/07/B/ST10/03820).

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Fluid migration across the Carboniferous/Permian unconformity in SW Poland: clues from authigenic tourmaline

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The Permian volcanic- and sedimentary rocks that subcrop in the basement of the Fore-Sudetic Monocline, SW Poland, overly a thick clastic Carboniferous succession. It is believed that both rock successions underwent different diagenetic cycles in different times – the Carboniferous sediments, forming the Variscan externides, were folded, thrust, and underwent peak diagenesis (locally low-grade metamorphism) before the Permian (e.g., Speczik, Kozłowski 1987), whereas the Permian rocks of the post-Variscan cover were not folded and were buried to a maximum depth of ~3-5 km in the Jurassic (Karnkowski 1999). This paper shows evidence of boron metasomatism that altered both rock successions, indicating (liquid) fluid migration across the Carboniferous/Permian unconformity.

Boron metasomatism is manifested by the common occurrence of authigenic tourmaline in various Carboniferous and Permian rocks: volcaniclastic conglomerates, sandstones (greywackes and arenites), and shales. Fifteen samples taken from a chosen well core were studied in detail by polarising microscopy, SEM, microprobe, PGNA, and XRD. Tourmaline crystals occur in various forms: as radiating, fibrous aggregates filling fine cavities, as grain replacements, disseminated crystals in clay-rich matrix, monopolar authigenic overgrowths on detrital tourmaline grains, and in thin dolomite-quartz veins. Typical are fine dimensions and acicular form of the authigenic tourmaline – individual crystals do not exceed 100 μm in length and 1 μm in width; they occur commonly in the < 2 μm fractions separated for the analysis of clay minerals. The tourmaline-bearing rocks are enriched in boron up to 4000 ppm. There is a clear reversed relationship between the content of tourmaline and kaolinite in the rocks, suggesting that kaolinite was tourmalinised preferentially. The chemical composition of the authigenic tourmaline is similar to that described by Pieczka et al. (2011), i.e., it is X-site vacant tourmaline (magnesio-foitite).

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Variability of major and trace elements in the Otalżyno-, Huczwa- and Stoczek peat bogs

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The contents of major and trace elements in three peat bogs were studied. The Otalżyno peat bog, located north of Kartuzy (northern Poland), is a raised sphagnum bog. The peatland site Huczwa, located to the north-east of Tomaszów Lubelski, is a rush fen, while the Stoczek peat bog, occupying a section of the Tyśmienica valley within the limits of Stoczek village, is a sedge and moss peat bog. Test samples were prepared by cutting cores (Otalżyno – 4.9 m, Huczwa – 8.8 m and Stoczek – 3.5 m) into 10-centimetre sections. In the peat samples, after the full acid digestion, contents of Li, Be, Se, Rb, Ag, Sb, Cs, Tl, Th and U, and REE (Sc, Y, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) were determined by ICP-MS, those of Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sn, Sr, Ti, V and Zn by ICP-OES, the Hg content by TMA, and the organic carbon (TOC) by coulometry.

In the peat, the lowest contents of major elements, trace elements and rare earths, but not organic carbon, were found in the raised peat bog at Otalżyno. The peat from the Huczwa fen displays higher contents of major and trace elements, and rare earths than those in the Otalżyno bog. The peat from the Stoczek deposit (fen) has the highest contents of the studied elements. It was found that differences in the contents of elements in the peats are strictly dependent on the chemistry of the rocks occurring in the areas surrounding the bogs. Peats from the Huczwa fen, which formed in an area of loess (dominated by quartz and calcium carbonates) are much more deficient in trace elements and REE than the peat from the Stoczek deposit (also fen) that formed in an area of tills (in addition to calcium carbonate, quartz, clay minerals and abundant accessory minerals are present). In the peats, trace elements display a significant correlation with contents of Al, Fe and S, a lower correlation with P, an even lower- and lesser correlation with Ca, and only the slightest correlation with organic carbon (no correlation in the Otalżyno deposit and a negative correlation in the Stoczek and Huczwa fens).

Factor analysis revealed the presence of the grouping Al, K, Mg and Na with most of the trace elements (Ba, Be, Co, Cr, Ti, V, Li, Rb, Cs, Tl, Th and U) and with REE in all of the bogs. This factor can be defined as lithological. Other factors distinguished differ for low- and raised peat bogs. In the fens (Huczwa, Stoczek), calcium and strontium are combined, and in the Otalżyno raised bog, calcium groups with copper, phosphorus and organic carbon. In the fens, a factor combining the occurrence of iron with arsenic (Huczwa peatland) or with heavy metals (lead, mercury and copper - Stoczek) is also evidentt.

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Distribution of moldavites in Lower Silesia, Poland

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Moldavites are impact glasses which were produced by the high-temperature melting of the Tertiary ObereSüβwasser Molasse during the NördlingerRies impact in Germany (Řanda et al. 2008; Magna et al. 2011; Žák et al. 2012). Tektites ejected during the Ries event had been discovered from three substrewn fields in the Czech Republic, Germany, Austria (Trnka, Houzar 2002 and references cited therein) and in southwestern Poland (Brachaniec et al. 2014). From three sandpits (Gozdnica, Mielęcin, North Stanisław), 16 Polish moldavites have been collected. All of the fragments were found within the lower Upper Miocene sediments (Pannonian age) of the so-called Gozdnicka Formation (Szynkiewicz 2011). The moldavite weights vary from 0.15-0.53 g. Their shape is usually ellipsoidal. In case of the Gozdnica area, one specimen of moldavite is complete, without any transport features. The largest specimen from the Gozdnica sandpit have a much darker green colour than the smaller tektites from other sections. It also possesses a less corroded surface. In BSE images, bubbles and lechatelierite inclusions are typically observed. EMP data show that the SiO_2 content of the Polish moldavites range from 76.28-78.31 wt%. Palaeoenvironmental reconstruction (Badura, Przybylski 2004) shows that all of the investigated tektites are paraautochthonous. Their occurrence suggests that they were fluvially transported from the Lusatian area.

Acknowledgements: This project was financially supported by NCN grant no 2014/13/N/ST10/04921.

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Preliminary SEM investigation of some bivalve shells

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Shell is a biomineral structure occurring in the Mollusca and Brachiopoda groups which has developed as a result of the so-called ‘arms race’. It is a product of mantle (pallium), and is composed mainly of calcium carbonate (in the form of calcite and/or aragonite) constituting at least 95% of its weight, and of various biopolymer compounds forming the organic matrix.

The main aim of this research is to describe the morphological diversity of microstructures present in the shells of a few selected recent bivalve species. The studied bivalve species were: great scallop (*Pecten maximus*), lyrate Asiatic hard clam (*Meretrix lyrata*), common cockle (*Cerastoderma edule*), sand gaper (*Mya arenaria*) and blue mussel (*Mytilus edulis*). The bivalves reveal various internal microstructures.

Every shell sample was used for thin-section preparation and also fractured. The material was investigated using an ordinary optical microscope as well as a Philips XL 30 ESEM/TMP scanning electron microscope (SEM) equipped with an EDS (EDAX) detector. X-ray analyses (XRD) were undertaken using a Panatytical X’Pert PRO MPD PW 3040/60 equipped with Theta-Theta geometry. The analyses were carried out at the Faculty of Earth Science in the University of Silesia, Sosnowiec.

According to the XRD results, the shells are mostly built of pure Ca-rich carbonates (calcite and/or aragonite). The internal structures are underlined by thin prismatic crystals of the carbonates. Their size and orientation varies between bivalve species. The most massive with greatest carbonate crystals occur in *M. arenaria*. The most prismatic, elongated and thick crystals of the carbonates are characteristic of species such as *M. edulis* and *P. maximus*. Conchiolin, as an organic material, occurs as layers alternating with the carbonates crystals. Its presence was confirmed by some EDS spectra.

This study shows that the internal shell microstructure, and the shell morphology and thickness, is adapted for survival in a constantly changing environment and also to increase the probability of surviving predator attack. Moreover, more detailed studies on molluscan structures might contribute to the design of highly efficient mechanically resistant nanomaterials in the future.

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Weathering processes of Turonian cherts from Ożarów (NE margin of the Holly-Cross Mountains

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In the early Bronze Age mine "for potters" in Ożarow, Turonian cherts known in the archaeological literature as "Ożarow flint" were exploited. (Budziszewski 2008, Budziszewski, Michniak 1984) It was used for the production of sickle blades. In the bed of the primary raw material, chalcedone-opal nodules (noduls) of varying sizes, a dark, steel-gray color and bright discoloration are macroscopically visible. The rock, as used on most archaeological sites is, in contrast, of light gray colour. Transformed in this way, monuments also show substantial variability in hardness and shear strength. In order to define the weathering processes that caused the observed changes in the rocks, micro analyses using optical- and electron microscopy were carried out. Weathering seems to have involved relatively fast weathering of carbonates, entailing a significant weakening of the material and change in its color. Analysis of the weathering process is key to the identification of artifacts made from this material discovered on archaeological sites remote from the source mine.

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Monazite alterations and geochronology in the Jawornik granitoid and host metasedimentary rocks (Sudetes Mts., SW Poland)

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Post-magmatic alterations of monazite in the Jawornik granitoid from the Sudetes Mts are documented. The alterations involved partial replacement by (1) allanite, epidote and, occasionally, apatite, by (2) cheralite, allanite and a mixture of clay minerals, Fe oxides and possible unknown rare earth element (REE) phases and (3) K-feldspar, cheralite and titanite. Various monazite replacement reactions induced by alkali-rich fluids indicate the local character of the post-magmatic processes on a thin section. The monazite was tested for maintenance of the Th-U-Pb system during the alteration processes. Electron microprobe dating of altered- and unaltered monazite grains yielded similar dates ranging from 361-326 Ma with a weighted average 343±4 Ma (MSWD=0.84, n=24) related to monazite crystallization during emplacement of the granitoid. For comparison, monazite in the paragneiss in contact with the Jawornik granitoid (within the same thin section) is preserved unaltered or partially replaced by allanite. These monazites yielded dates from 370-326 Ma with a weighted average of 344±5 Ma (MSWD=1.10, n=24). Monazite in mica schist at a greater distance from the contact with granitoids, provided dates from 368-312 Ma with a weighted average of 337±5 Ma (MSWD=0.77, n=37). The 344-337 Ma ages document the timing of monazite (re)growth during prolonged Variscan metamorphism. The geochronological results, being consistent with previous works (Białek, 2014; Skrzypek et al., 2014), indicate that partial alteration of monazite does not necessarily disturb internal domains in the Th-U-Pb system and that monazite dating may provide meaningful data for granitic rocks affected by fluid-induced post-magmatic processes. The variability of the alteration products demonstrated the local character of the chemical system inducing alteration processes on a thin section scale.

Acknowledgements: This work was funded by ING PAN research funds (project "REE").

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Rheic Ocean history imprinted in zircon from metabasites: a case of the Western Tatra Mountains (Poland/Slovakia)

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The Rheic Ocean started to develop from the rifting of Avalonia from Gondwana during Ordovician times and closed during the Variscan Orogeny. Despite this generally accepted geodynamic scenario, there are still some disagreement about the timing of the opening and closure of the Rheic Ocean in different parts of Europe. In the Western Tatra metamorphic complex, amphibolite intercalations are present among metapelitic sequences. Despite petrographical and geochemical variations among different types of amphibolites, they all show modified MORB-like chemistry. The protolith rocks were probably tholeiitic basalts, differing in lower crustal contamination, intruding basin floored by attenuated continental crust.

Zircon crystals were separated from layered amphibolites from Ziarska Valley and from an eclogite boudin from Baranèc Mt. In CL, the zircon crystals from the amphibolite reveal a core-rim structure with cores displaying prominent oscillatory zoning and structureless rims. Cores were dated by SIMS U-Pb at ca 499±5 Ma and show $\delta^{18}O_{VSMOW}$ in the range 4.8-6.3‰. Highly luminescent internal rims are characterized by $\delta^{18}O_{VSMOW}$ = 1.9-3.5‰. Outer rims are dated at ca 345±2 Ma and show $\delta^{18}O_{VSMOW}$ values in the range 7.7-8.4‰. In the eclogite, mono-phase zircon crystals are dated by SIMS U-Pb at ca 351±3 Ma and characterized by $\delta^{18}O_{VSMOW}$ in the range 4.7-6.0‰.

The zircon cores in the amphibolite can be interpreted as reflecting the magmatic crystallization stage. They have typical mantle $\delta^{18}O_{VSMOW}$ values. The local lowering of $\delta^{18}O_{VSMOW}$ could be a consequence of melt interaction with the meteoric water during the initial stage of rifting and Rheic Ocean opening. The age of the zircon outer rims (ca 345 Ma) and the age of metamorphic homogenization of zircons from the eclogite (ca 350 Ma) fit (within error) to the age of granitoid magmatism in the Tatra Mountains and can be interpreted as the age of the final closure of the Rheic Ocean. High $\delta^{18}O_{VSMOW}$ values from zircon rims might be a result of crystallization from felsic melt formed during migmatization.

Acknowledgements: This study was supported by NCN grant No 2012/07/B/ST10/04366 (to AG).

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Assessing seasonal variations of atmospheric deposition in the Świętokrzyski National Park: A multi isotope approach on lichens

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The concentration and C, N, S and Pb isotope compositions/ratios of atmospheric pollutants enter into the organic compounds inbuilt in the lichen thallus. They could thus serve as an excellent passive tracer of atmospheric deposition for a well-defined area over the period of lichen growth.

The main aim of this study was to try to assess eventual seasonal variations in atmospheric contributions using a multi isotope approach (C, N, S, Pb) coupled with the analysis of corresponding metal concentration in lichens.

Lichen (*Hypogymnia physodes)* samples were collected during heating (1-3 February 2013) and vegetative (11-13 July 2013) seasons. A total of 20 sampling locations were chosen, 18 in the Świętokrzyski National Park (ŚPN) and 2 in its closest vicinity. Samples were collected on both bark and branches of *Abies alba* trees.

For each sampling location, we also analysed concentrations of atmospheric pollutants (SO_2 and NO_2 using the Amay-Krochmal method, and CO_2). For the CO_2, we analysed its corresponding carbon isotope composition ($\delta^{13}C(CO_2)$) by CF-IRMS. During the heating (h) and vegetative (v) seasons, the atmospheric SO_2 and NO_2 ranged from 0.8 to 22.8 $\mu g\cdot m^{-3}$ (h), < 0.1 to 1.9 $\mu g\cdot m^{-3}$ (v) and from 5.8 to 13.2 $\mu g\cdot m^{-3}$ (h) 0.9 to 9.4 $\mu g\cdot m^{-3}$ (v), respectively. CO_2 concentrations and $\delta^{13}C(CO_2)$ values varied from 477 to 672 ppm (h), from 390 to 545 ppm (v) and from -13.0 to -8.6 ‰ (h), from -10.2 to -4.0 ‰, respectively.

$\delta^{13}C$ and N isotope composition ($\delta^{15}N$) in lichens varied from -27.5 to -25.6 ‰ (h), -28.0 to -25.6 ‰ (v) -11.5 to -7.1 ‰ (h) -12.2 to -7.3 ‰ (v), respectively. Values of $\delta^{34}S$ and metal concentrations, currently being analysed. will be discussed at the conference.

Based on current results we can conclude as follows: (i) During both the heating and vegetative seasons, atmospheric CO_2 mainly reflects assimilation/respiration processes; (ii) the maximum SO_2 concentrations are observed at the highest altitude and in open locations indicating long-distance deposition of regional pollutants as well as during heating season; (iii) the maximum NO_2 concentrations were observed close to local roads (local pollutants) and were a bit higher during the heating compared to the vegetative season; (iv) there were no significant differences in $\delta^{15}N$ observed in lichens collected during the heating and vegetative seasons, a result, perhaps, of the same nitrogen source impacting the investigated area during both seasons; (v) differences in Pb isotope ratios were observed between winter and summer seasons although both indentify an industrial origin.

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Metamorphic modifications of the Braszowice-Brzeźnica chromitites

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The Braszowice-Brzeźnica chromitites form small elongated bodies hosted by serpentinized olivine-tremolite rocks (Delura 2012). They display three main textural varieties, namely, massive, nodular and disseminated. The particular varieties show a wide spectrum of Cr-spinel to chlorite matrix ratios, and of grain sizes. Rarely, analyzed samples are brecciated or display a centimeter-scale indistinct layering. The single Cr-spinel grains are usually deformed, with irregular cracks filled with chlorite.

The Braszowice-Brzeźnica chromitites are slightly to strongly altered. The metamorphic processes have influenced the chemical composition of the Cr-spinel as well as that of the silicate matrix. The Al-Cr-Mg-spinel is progressively replaced by Cr-Fe-rich and Al-Mg-poor spinel ("ferrichromite") along cracks and grain boundaries, without grain-shape modification. The process is reflected in the development of alteration rims surrounding primary Al-Cr-Mg-spinel cores. Primary olivine and scarce pyroxene, which formed the original matrix, have been transformed into a random chlorite mass (Cr-bearing clinochlore). The alteration processes also resulted in the formation of millerite or rarer heazlewoodite and godlewskite which either form minute inclusions within the spinel alteration rims or occur interstitially.

On the basis of chemical heterogeneity of the spinel grains, their optical properties, the shapes and the sizes of mineral inclusions, up to three distinct alteration rims may be evident. In nearly fresh chromitites, only one rim (rim I) can be found whereas, in more altered ores, up to three rims of variable width occur (rims I, II and, rarely, III).

The chemical compositions of altered spinel phases indicate that the Braszowice-Brzeźnica chromitites could have experienced lower-amphibolite facies conditions and minor low-temperature alterations reflecting greenschist-facies conditions. The alteration rims observed were developed in response to metamorphic events that may be ascribed to the various stages of the formation of the Central Sudetes. Rim I may have formed during the initial serpentinization, before obduction Rim II was formed under the higher temperature metamorphic conditions obtaining during obduction. Finally, rim III can be ascribed to post-obduction processes connected with exhumation and late Variscan granitoid magmatic events as has been suggested by Kądziałko et al. 2006.

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Geochemical background as a source of reliable quality guidelines for trace elements in soils

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Trace elements originating from geogenic sources in soils overlap with elements released from anthropogenic sources. This creates difficulties in establishing reliable quality standards for potentially toxic trace elements in soil. Moreover, if a trace element exceeds its maximum permissible level in soil as a consequence of natural high concentration in the environment, it is not recognized as a contaminant (see for example The Regulation of the Minister of the Environment on the Soil Quality Standards, 2002).

Here, we propose that threshold values (the upper limit of geochemical background range) should be used for development of reliable site-specific soil quality standards for trace elements. The results of geochemical background evaluation in three historical metal ore mining areas in the Holy Cross Mts were compared to maximum permissible levels of selected trace elements in the soils of Poland (The Regulation of the Minister of the Environment on the Soil Quality Standards, 2002; Table 1). Arsenic, cadmium, chromium, nickel, lead and zinc were determined in 181 soil samples after *aqua regia* extraction by the ICP-MS method. For more detail about the analytical procedure used and the geochemical background calculation method, refer to Gałuszka et al. 2015.

Table 1. Threshold values and maximum permissible levels (MPL) for selected trace elements in soils of three historical mining sites in the Holy Cross Mts.

Element	Parameter	Karczówka (n=61)	Miedzianka (n=62)	Rudki (n=58)
As (mg/kg)	Threshold	16	36	30
	MPL in protected areas	20		
	MPL in industrial areas	60		
Cd (mg/kg)	Threshold	1.7	2.0	3.2
	MPL in protected areas	1		
	MPL in industrial areas	15		
Cr (mg/kg)	Threshold	65	63	50
	MPL in protected areas	50		
	MPL in industrial areas	500		
Ni (mg/kg)	Threshold	17	39	42
	MPL in protected areas	35		
	MPL in industrial areas	300		
Pb (mg/kg)	Threshold	219	73	1716
	MPL in protected areas	50		
	MPL in industrial areas	600		
Zn (mg/kg)	Threshold	158	175	202
	MPL in protected areas	100		
	MPL in industrial areas	1000		

Distinguishing between natural- and anthropogenic input of trace elements in soils is very difficult at historical metal-ore mining sites. Though very high concentrations of metals in soils in these areas are inherited from the mineralized bedrock, anthropogenic sources of metals from mining and ore processing cannot be neglected. That the spatial distribution of elements in the post-mining sites is highly heterogeneous only makes soil-quality assessment more difficult. Usually, for practical reasons, the lowest concentrations of elements found in the soil of the mining/post-mining area are considered as the background level. This approach is not useful for recognition of site-specific background concentrations (Hudson et al. 1997). Contamination assessment in areas where geochemical background is highly variable should be done according to uniform criteria (Armiento et al. 2011).

The threshold values at the post-mining sites in this study are higher than the maximum permissible levels (MPL) for most of the elements in soils of protected areas in Poland and usually lower than MPL in soils of industrial areas. The Karczówka and Miedzianka sites are nature reserves and the Rudki area is located within the Świętokrzyski National Park buffer zone. According to the Polish regulations, soils at these three sites should be classified as category "A" with the most restrictive quality standards. However, these standards seem to be unrealistic because of the high geochemical background concentrations related to mineralized bedrock. To overcome this problem, it would be necessary to establish site-specific quality standards for trace elements in soils of historical metal ore mining areas. The upper limit of the geochemical background range calculated using statistical methods (e.g., the iterative 2σ technique) for each of the elements would be a good basis for establishing reliable quality guidelines.

Acknowledgements: This study was supported by the Polish National Science Centre (NCN), project no. DEC-2011/03/B/ST10/06328.

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Petrology, geochemistry and petrogenesis of Neogene adakitic domes, (Quchan – Esfarayen Magmatic Belt), NE Iran

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Subduction-related adakite rocks located in the north part of the Sabzevar ophiolite zone (northeast Iran) range from andesite to rhyodacite in composition. Here, we investigate the magma supply system of these subvolcanic hypabysal rocks. The Sabzevar ophiolitic zone (SOZ) is a part of the eastern Tethyan ophiolitic belt and a remnant of Cretaceous Tethyan oceanic lithosphere which was obducted during the late Cretaceous to early Paleocene interval. The ophiolite is intruded by widespred subvolcanic stocks, domes and dykes of intermediate to felsic composition.The subalkaline rocks ranging from 41±2.1 to 2.7±0.2 Ma in age reported between Sabzevar and Quchan (north Iran) become younger northwards, reaching late Miocene to Late Pliocene ages in Quchan. The volcano represents the last relevant magmatic episode in the region between Quchan and Sabzevar. These rocks are subalkaline andesites to dacites, with calc-alkaline affinity, and mafic alkaline rocks. The dacite rocks occur as isolated plugs, domes and dykes intruding andesitic rocks. All andesite and dacite samples display negative anomalies in Nb- Ta, P and Ti; anomalies in Pb are positive or negative. The low Y, low Yb (< 2 ppm), high La/Yb, high Sr, as well as the silicic character and low 87 Sr/86 Sr of some samples (down to 0.7040) are in agreement with an origin of the magmas by partial melting of a garnet-bearing, plagioclase-free source. This source could be represented by the metamorphosed basalts of an oceanic crust forming the slab (possibly as old as Variscan) foundering after the cessation of subduction. The adakitic composition of these rocks suggests post-collisional melting of oceanic slab and/or mafic lower crust, possibly triggered by an asthenospheric rise after slab break-off or intramantle delamination.

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Episodic construction of the Tatra Mountains granitoid pluton: geodynamic consequences for the Variscan collision scenario.

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The Tatra granitoid pluton (Central Western Carpathians, Poland/Slovakia) is an example of a composite polygenetic intrusion, comprising many magmatic pulses varying compositionally from diorite to granite and intruding the active Variscan shear zone. In this study, zircon U-Pb ages were used to trace the magmatic processes and to construct the geodynamic scenario of Variscan collision.

The U-Pb LA-MC-ICP-MS zircon dating of successive magma batches indicate the presence of magmatic episodes at 368±9 Ma, 364±5 Ma, 360±5 Ma, 355±8 Ma and 345±4 Ma, Together with the formerly published data, the magmatic events cover a time span of 30 Ma of magmatic activity, starting from 371±6 Ma to 337±6 Ma. The partial resorption and recycling of former granitoid portions ("petrological cannibalism") was a result of the incremental growth of the pluton by subsequent intrusion of following magma fractions, representing crystal mushes of high viscosity. The temperature was in the range of 750-850ºC for the time span of ca 30 Ma.

The presence of the inherited zircon cores suggests that the collision and granitoid magmatism involved crust of Cadomian consolidation age (c. 530 Ma and 518 Ma) forming the Proto-Carpathian Terrane, crust of Avalonian affinity (462 Ma, 426 Ma) and melted metasedimentary rocks of volcanic arc provenance, melted during successive collisions and prolonged subduction of oceanic crust during Rheic Ocean closure. The differences in granitoid composition are the results of different depths of crustal melting: more felsic magmas were generated in the outer zone of the volcanic arc, while more mafic magmas were formed in the inner part of the supra-subduction zone. The source rocks of the granitoid magmas covered the compositional range of metapelite-amphibolite and represent both lower- and upper crust.

Acknowledgements: This study was supported by NCN grant No 2012/07/B/ST10/04366 (given to AG).

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Palaeoproterozoic post-magmatic cooling of the Phalaborwa Complex, South Africa, constrained by U-Pb apatite dating

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The Palabora Complex in the Limpopo Province of South Africa, which intruded into Archean granite basement, is the only carbonatite complex hosting a primary Cu and a phosphate deposit. Thermochronological studies using apatite, in addition to the existing U-Pb zircon and baddeleite ages, complement the petrogenetic investigation of the Phalaborwa Complex and contribute to the debate of carbonatite magma batches replenishing the large pyroxenite intrusion causing disequilibrium crystallisation in a magmatic-hydrothermal system.

Apatite crystals were separated from carbonatite and phoskorite, sampled from the Loolekop and northern pipes of Phalaborwa Complex. The apatite sample from the phoscorite yields a LA-ICP-MS U-Pb lower intercept Tera-Wasserburg age of 1972±17 Ma, in agreement (within uncertainty) with a cooling Rb-Sr whole-rock age of the complex (2013± 93 Ma; Yuhara et al. 2005). A LA-ICP-MS U-Pb apatite analysis from the northern area yields an age of 2008±22 Ma (carbonatite sample). The data suggest relatively slow cooling of the Phalaborwa Complex, with cooling rates less than 15°/Myr (Yuhara et al. 2005), especially when compared with a U-Pb zircon age of 2060±2 Ma (Wu et al. 2011) marking the final stages of the Cratonic magmatism. The very steep REE fractionation patterns and negative Eu anomalies (carbonatite: $Ce_N/Yb_N = 372\text{-}482$; $Eu/Eu^* = 0.47\text{-}0.48$; phoscorite: $Ce_N/Yb_N = 146\text{-}159$; $Eu/Eu^* = 0.67\text{-}0.73$) suggest low oxygen fugacity in the parent melts which probably represent magma batches differing in fractionation ratio.

Acknowledgements: This study was supported by NCN grant No 2012/07/B/ST10/04366 (to AG).

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Variscan post-collisional cooling and uplift of the Tatra Mountains constrained by U-Pb apatite and titanite dating

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Apatite is a common accessory mineral in magmatic and metamorphic rocks which recently has been used in high-temperature thermochronological studies. The closure temperature of the U-Pb system in apatite is 350-550ºC (Schoene, Bowring 2007) while that of titanite is 660-700ºC (Scott, St-Onge 1995) making both minerals useful phases to constrain the high temperature cooling paths of crystalline basements.

Apatite and titanite crystals were separated from Western Tatra amphibolites, sampled both from the southern and northern metamorphic cover. The titanite sample yields a LA-ICP-MS U-Pb lower intercept Tera-Wasserburg age of 345.3±4.5 Ma, in agreement (within uncertainty) with the youngest U-Pb zircon age of granitoid magmatism in the Tatra Mountains (345-340 Ma). LA-ICP-MS U-Pb apatite ages from the northern metamorphic cover yield ages of 351.8±4.4 Ma (SM sample), 346.7±5.9 Ma (TB sample) and 342.6±7.1 Ma (RW sample). U-Pb apatite ages from the southern metamorphic cover yield an age of 344±11 Ma (GHM sample).

Taking into account the zircon U-Pb age of 345-340 Ma from the youngest granitoid magmatism, and the similarity in ages obtained from mineral systems with substantially different closure temperatures (ca 200º), we suggest relatively rapid cooling of the whole Tatra massif, with cooling rates much higher than the previously suggested 30º/Myr (Moussalam et al. 2012) during the final stages of the Variscan collision and uplift.

Acknowledgements: This study was supported by NCN grant No 2012/07/B/ST10/04366 (to AG).

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Petrography and geothermobarometry of selected mica schists from the Kamieniec Metamorphic Complex near Baldwinowice (Fore-Sudetic Block) – preliminary report

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The crystalline basement of the Fore-Sudetic Block in the Kamieniec Metamorphic Complex (KMC) comprises a volcano-sedimentary succession dominated by mica schists intercalated with acid- and basic metavolcanics, marbles, paragneises and small inliers of HP eclogites. This rock complex bears a strong record of Variscan reworking. PT conditions of Variscan tectonothermal events were previously estimated at ca 550 – 590 ^{o}C and 7.5 up to 12 kbars.

For the purpose of this study, we investigated a micaschists sample collected ca 18 km north of Kamieniec Ząbkowicki, in the vicinity of Baldwinowice. The sample is composed of garnet porphyroblasts (1.2 – 3.0 mm in diameter) set in matrix differentiated into micacesous and quartztose laminae and comprising isolated and relatively small plagioclase grains (ca 0.05 - 0.1 mm and occasionally 0.2 - 0.5 mm in diameter). Commonly, garnet grains contain inclusions composed of quartz, plagioclase and muscovite. Muscovite found both in matrix and as inclusions in garnet is characterized by a low paragonite content (Na/(Na+K) = 0.12±0.03) and differs in phengite concentration (Ms1 – Si^{+4} = 6.45±0.05 a.p.f.u. and Ms2 – 6.24±0.04 a.p.f.u. in the matrix and Ms3 – Si^{+4} = 6.14±0.04 a.p.f.u. as inclusions in garnet). XFe [=Fe/(Fe+Mg)] of biotite ranges from 0.53-0.59. In terms of Ti^{+4} content, biotite can be divided into two groups. Bt1 (Ti^{+4} = 0.23±0.03 a.p.f.u.) occurs in proximity to garnet porphyroblasts and as cores of larger biotite grains, whereas Bt2 (0.18±0.02 a.p.f.u.) occurs in the rock matrix or as rims of larger flakes. Garnet forms porphyroblasts reaching up to 2.5 – 3.0 mm in diameter. It is characterized by a normal growth zoning pattern with spessartine content decreasing from cores ($Alm_{50-57}Py_{3-5}Spe_{22-23}Gr_{13-23}$) towards rims ($Alm_{60-73}Py_{6-8}Spe_{8-14}Gr_{8-21}$). Occasionally, garnet rims show reversals in zoning trends (spessartine increase and almandine decrease, $Alm_{63-65}Py_{7-8}Spe_{12-15}Gr_{12-16}$), which can be attributed to retrograde cation exchange perhaps with resorption of garnet. Matrix plagioclase is represented by oligoclase (Pl1 An_{22-28}), but scarce larger grains (0.2-0.5 mm) show more anorthitic cores (Pl2 An_{31-34}). Plagioclase inclusions in garnet show Ca^{+2} rich (An_{20-28}) and Ca^{+2} poor compositions (Pl3 - An_{1-2}).

Estimation of maximum PT conditions preserved in the mica schists was performed using the average PT mode in Thermocalc software (version 3.33, tcds55).The mineral assemblage Gt, Pl1, Ms1 and Bt1 yielded 622±31^{o}C and 9.6±1.0 kbar, whereas Gt, Pl1, Ms1 and Bt2 yielded 624±32^{o}C and 9.2±1.1 kbar. Inferred temperatures of metamorphism are relatively high but similar within error. Interestingly, the calculated thermal peak of metamorphism is slightly higher than postulated by earlier workers.

Acknowledgments: The study was financed by ING UWr. grant no 1017/S/ING.

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Preliminary research of organic matter biodegradation by indigenous microorganisms isolated from hydrocarbon seeps area

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The effect of microbial activity on the molecular composition of organic matter is an important aspect of organic-geochemistry research. As the following examples show, changes in the distribution of organic compounds may significantly affect the results of research and, thus, paleoenvironmental and paleoclimatic interpretations, as has been repeatedly raised in the literature (e.g., Killops, Killops 2005; Peters et al. 2005).

This study provides evidence for direct biodegradation of organic matter including crude oil compounds extracted from sandstone samples, and from concretions within the sandstone, taken from the natural hydrocarbon seeps area in the Flysch Carpathians of south-eastern Poland. It was confirmed that the community of indigenous heterotrophic microorganisms, including hydrocarbon-degrading bacteria isolated from the sandstone and grown under aerobic conditions, could utilize the sandstone's organic matter as the sole carbon and energy source. Isolated microorganisms were incubated using the mineral Starkey medium using rock samples as the source of microorganisms.

The results focus on aliphatic fraction and some popular ratios based on compounds from this group. It was noted that relative concentrations of short-chain n-alkanes increased with decreases in long-chain compounds. Moreover, in the rock sample after microbiological experiment (2B), a significant change in the distribution of straight-chain compounds was noticed. In the abiotic control (2H), such changes were not observed. As a result of biotic processes. nearly all long-chain n-alkanes (> 27 carbon atoms in the chain) were removed. Simultaneously, an increase of n-alkanes with a chain length of C_{15} - C_{27} was noted.

Changes in relative concentration of n-alkanes and isoprenoids are expressed in variations of ratios based on n-C_{17}, n-C_{18}, and pristane (Pr) and phytane (Ph). Values of all commonly-used ratios decreased for all applicable variants (Pr / Ph, Pr / n-C_{17}, Ph / n-C_{18} + Pr Ph / n-C_{17} + n-C_{18}). The ratio showing the relation between short- and long-chain n-alkanes changed variously.

The distribution of tricyclic- and pentacyclic triterpenoids also changed. For example, a decrease in the relative relative concentrations of αβ stereoisomers, and the almost completely removal of βα compounds, in the distribution of pentacyclic triterpenoids was observed.

The indicator based on 18α(H)-22,29,30-trisnorneohopane (Ts) to 17α(H)-22,29,30-trisnorhopan (Tm), i.e., Ts/Tm (Ts/(Ts+Tm), varies slightly between samples. A significant increase (one order of magnitude) was found for environmental parameters based on the tricyclic triterpenoids. Within regular steranes, small changes in the relationship between individual diastereomers were noted. This study confirmed that microbial activity can have a significant effect on organic matter composition. Microorganisms introduce changes in the distribution of various groups of organic compounds.

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Geochemistry, Tectonic Setting and Geotechnical Properties of Safaga Dokhan Volcanics, Eastern Desert, Egypt: Late Neoproterozoic Magmatism

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The tectonic setting of the Dokhan Volcanics is one of the controversial topics in the geology of Egypt. These rocks have been investigated petrographically and geochemically since the 1980's at different outcrops. However, no agreement has been achieved regarding their tectonic setting and the genesis of their magmas. In order to solve this problem, a new study were conducted on the Dokhan Volcanics of the Safaga area (Gabel Nuqara). Revelation of their geochemical signature, tectonic setting, and their geotechnical properties, was the aim. The Safaga Dokhan Volcanics are one of the northernmost outcrops of the Arabian–Nubian Shield. These rocks, located about 8 km to the west of Port Safaga, comprise two main rock suites, namely, (a) an intermediate volcanic suite, consisting of basaltic andesite, andesite, and their associated pyroclastic rocks, and (b) a felsic volcanic suite composed of dacite, rhyolite, and ignimbrite. Geochemical investigation revealed that the two suites display well-defined major and trace element trends and a continuum in composition with wide ranges in SiO_2 (52 -75.7wt%), CaO (9.2-0.2wt%), MgO (5.3-0.01wt%), Sr (1367-7ppm), Zr (689-173ppm), Cr (up to 207ppm) and Ni (< 94ppm). These rocks are characterized by a strong enrichment in LILE relative to HFSE and are affiliated to the related alkaline to calc- alkaline - transitional magmatism. The magmatic evolution of these rocks was governed by two main processes involving (a) fractional crystallization of plagioclase, pyroxene, amphibole, magnetite in the intermediate varities and of k-feldspar, biotite, apatite, magnetite, and zircon in the felsic varities, and (b) crustal contamination process which participated, to some extent, in the evolution of these rocks as indicated by the wide range of K/Rb (522-203ppm), Rb/Zr (0.04-0.7ppm) and Ba/Nb (1316-58ppm) values. Values of these ratios do not significantly change during fractional crystallization but do change through crustal contamination (Davidson et. al 1988) and assimilation – fractional crystallization processes (DePaolo 1981). The proposed tectonic setting for the Safaga Dokhan Volcanics involves a transition between subduction – collision – post collision tectonics. The studied Dokhan Volcanics originated as a result of partial melting of the lower crust (Rb/Nb average = 4.2 ppm) with slight accumulation from underlying upper mantle. Mineral chemistry studies reveal that pyroxenes range from diopside to augite and crystalized in a temperature range from 1150-1250°C, that amphiboles are members of the calcic amphibole group and plot in the magniseohornblende field, and that the constituent plagioclases range widely in composition from An_{52} to An_{56} in basaltic andesite, An_{41} to An_{46} in andesite and An_{17} to An_{32} in dacite. Oscillatory normal zoning occurs in the intermediate varities. Alkali feldspar has a sanidine composition.

Where the study area is located on the Red Sea coast, it is considered a promising site for the future of tourism and economic activities and a perfect position for establishing solar energy stations. Besides the geochemical- and petrological studies, rock mechanical studies are currently necessary to provide geotechnical data that will support upcoming developmental activities.

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Pollution detection in Lublin and problems of destruction processes in petroarhitecture details

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Lublin is the voivodeship town since the Middle Ages. The first houses were already built in this place in the early Middle Ages. During the Renaissance, it was a flourishing city, as is shown in a number of monuments and buildings. In later centuries, particularly during the partitions, Lublin became a provincial town but, in the twentieth century, recovered again the status of the regional town and passed a number of changes (Rozwałka 1997, 2006). At the time of the PRL, Lublin housed various manufacturing plants, most of which did not withstand the political changes (Gawrecki 1964, 1974). At the moment, the biggest source of emissions are still fumes and dust from heating homes in winter and pollution from vehicular traffic.

Samples were collected within the old town and observations made on the corrosion of architectural details. These samples were tested for metals related to the issue of pedestrian activity and observations on architectural details helped distinguish several types of corrosion associated with human activity. In Lublin there are numerous examples of the use of stone in the details of various types of architecture. These rocks respond differently to destructive factors related to human activity.

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Petrography of basic types of Turonian flints from the north-eastern margin of the Holy-Cross Mountains

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We present the results of mineralogical-petrographic and geochemical investigations of several basic types of Turonian flints from the north-eastern Mesozoic margin of the Holy Cross Mountains which were used in the Neolithic and Bronze Ages (Gościeradów flint, Janików flint, Ożarów flint, Świeciechów flint and Zawada flint; Libera 2002; Szeliga 2008). Though these flints display differences in their macroscopic properties, these are usually insufficiently diagnostic for precise raw material identification during analyses of archaeological inventories. To distinguish the character of individual types based on their mineralogic and petrographic features, microscopic analyses of a series of representative samples of flint raw material from different parts of the Turonian outcrops and on archaeological artefacts found at the early Neolithic site in Tominy (Ożarów commune) were performed. The microscopic investigations were conducted using a polarized light microscope and a scanning electron microscope (SEM - EDS). The results enable us, on the one hand, to define some probable characteristics of individual types of Turonian flints and, on the other hand, to identify some of these flints in the archaeological flint inventory from Tominy connected with the settlement of early agricultural communities in the early Neolithic (6th-5th millenium BC).

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PGE mineralization in the gabbro rocks from the Monchegorsk Region (Kola region, Russia)

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Numerous different types of metamagmatic- and metasedimentary rocks occur on the Kola Peninsula located in the northern part of the Baltic Shield. In the central part of Kola, the Monchegorsk Massif is located in a deep-seated fault zone at the junction between the Keivy terrane, the Murmansk domain, and the Kolmozero-Voron'ya greenstone belt. The Patchemvarek gabbroanorthosite is a lenticular intrusion (up to 2 km thick) consisting of variably altered leucogabbros and fairly uniform medium-grained metagabbroanorthosites. In the Patchemvarek gabbroanorthosite (2925 ± 7 Ma), zones of sulphide mineralization with increased Au, Pt and Pd concentrations have been demonstrated (Kudryashov, Mokrushin 2011). According to Bayanova et al. (2009), the ore-bearing intrusions formed earlier in the Kola belt (Fedorov-Pana and other intrusions at 2530-2450 Ma) and at some later stage in the Fenno-Karelian belt (2450-2400 Ma). These rocks have a massive structure and granoblastic texture with plagioclase varying from bytownite to labradorite and mafic minerals represented by amphibole and epidote. Accessory minerals include zircon, titanite, apatite, and Ti-magnetite. Rock samples were analyzed using a Leica DM2500P optical microscope and a Hitachi SU6600 scanning electron microscope with EDS at the Department of Geology and Lithosphere Protection (UMCS, Lublin, Poland). Inclusions of platinum arsenide (sperrylite, PtAs2) and other PGE phases were found in the samples with sulphides. This first discovery of sperrylite suggests the possible presence of platinum-group element mineralization in the Archaean gabbroanorthosites. Sulphur isotope analysis of selected sulfide phases made at the Institute of Physics (UMCS), Lublin, on a dual-inlet and triple-collector mass-spectrometer confirm a number of consecutive stages of mineralization in these rocks.

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The calculated P–T path for the metabasites in the E part of the Izera Complex (West Sudetes, SW Poland) and its regional implications

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The P-T path of metamorphism has been reconstructed for heterogeneously-deformed metabasite veins hosted by orthogneisses of the Izera complex in the northern part of the Karkonosze-Izera massif (West Sudetes). These orthogneisses with embedded metabasites and their envelope of mica schists were combined into the lowermost Izera–Kowary unit of the massif and interpreted as the Early Palaeozoic continental crust of the Saxothuringian domain (crystalline basement) affected subsequently by the Variscan metamorphism.

Microtextural relationships coupled with the compositional variability of metabasite minerals (e.g., growth zoning of Ca-amphibole) has allowed for the distinction of a sequence of mineral assemblages consistent with a Barrovian-type metamorphism, reflecting a progression from greenschist- to amphibolite-facies conditions at medium pressures. Conventional geothermobarometric estimates for prograde stages indicate a M_1 event at 350–460°C and 4.8–7.5 kbar followed by a M_2 event at 535–570°C and 6.2–8.2 kbar. The results of thermodynamic modelling (isochemical phase diagram P–T sections calculated with Perple_X'07 software) for the M_2 event are similar (545–600°C at 5.9–8.3 kbar). However, for the preceding M_1 event, the modelling suggests higher pressures of 8.1–11.2 kbar at 500–530°C. The model for a final M_3 stage indicates temperatures of 465–520°C at 3–5.2 kbar. The proposed P–T path for the Izera metabasites is in contrast with that reported by Žačková et al. (2010) for the mica schists from the south-eastern part of the Karkonosze–Izera massif (blueschist facies conditions $\geq$ 18–19 kbar at 460–520°C followed by isothermal decompression to 10.5–13.5 kbar and retrogression at $<$ 8.5 kbar at $<$ 480°C) hitherto included in one lithotectonic entity, the Izera–Kowary unit. Such a dramatic difference suggests that that the crystalline basement and metasediments of the Kowary–Izera unit were not always adjacent during their history. In turn, the P–T data for the Izera metabasites correlate with the metamorphic record in the western part of the Saxothuringian crust implying a similar development of the Variscan metamorphism along the eastern margin of the domain.

Acknowledgments: The study was supported by the Polish Ministry of Science and Higher Education (*606/P04/95/08*) and Faculty of Geology, Warsaw University (*BSt–170204*).

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Assessment of carbon isotopic composition variability and the humification degree of organic matter in selected profiles of peat bog in the Jizera Mountains

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Peat is the organic product of accumulation formed by the process of humification of organic matter. It consists of a humic substance as well as plant remains at different degrees of humification. Humic substances are a dynamic system undergoing biochemical- and chemical transformation. The final products of humification may be characterized by a variety of chemical compositions, depending on the conditions of the humification process and the degree of decomposition. It is also reflected in different carbon isotopic compositions ($\delta^{13}C$).

Peat bogs and wetlands play an important role in the global carbon cycle, particularly in the processes of accumulation and release of CO_2 and CH_4. As carbon isotopic composition depending on isotope fractionation in biological material may vary and change over time, it can provide information about the record of geochemical changes. Carbon isotopic analysis provides important information about the direction and rate of changes in the analyzed environment.

This presentation presents an analysis of variability of the carbon isotopic composition ($\delta^{13}C$) and the degree of humification degree of a peat profile, as well as an attempt to correlate these two factors. The results presented are an introduction to extensive research on the variability of the carbon isotopic composition in the process of humification of organic matter. The research will allow us to make a more accurate interpretation of geochemical processes occurring in the peat environment during the process of humification.

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Fluid inclusion analysis of minerals in sedimentary rocks in Poland - an overview and remarks

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Fluid inclusions - tiny portions of palaeofluids - may be trapped in the cements of sedimentary rocks, i.e., in the minerals filling pore space. Studies on fluid inclusions widely performed in different areas in Poland, i.e., in the Baltic Sea region, in the Polish Lowlands and in the Carpathians, have focused on fluid characteristics in geological material, microthermometric measurements and the application of fluid inclusions as geothermometers, generally in the context of petrological- and geochemical research (e.g., Jarmołowicz-Szulc 1998, 2001, 2011). Fluid inclusions were analyzed in the carbonates, quartz and anhydrite cements of Cambrian, Carboniferous and Rotliegend deposits in different boreholes drilled in northern- and central parts of Poland and/or in Paleogene rocks on the surface in the south-east. These studies involved microscopic inclusion characteristics ("fluid inclusion petrolography"), observations of fluorescence and cathodoluminescence, and microthermometry. Due to the different types of minerals, different inclusion features were observed. Inclusion homogenisation temperatures from the minerals and rocks lie in different intervals reflecting inclusion type, position and localization. Fluid densities are differentiated and the chemical systems are more or less complicated depending on their geological histories. The microthermometric results have been compared with those of isotope analyses (C, O, Sr). The data reflect the migration of fluids in time, the formation of cement generations in different basins and the origin of quartz veins.

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The Gardnos impact structure

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The crater of the Gardnos meteorite is a geological phenomenon that lies in Norway, about 125 km from Oslo (Kalleson et al. 2009). The structure is well seen in the outcrops of impact breccias and post-impact deposits that form a circle with a radius of about 5 km. Two main types of impact breccia may be observed there. The autochtonic *Gardnos breccia* is a massive, coherent clastic rock which breaks through the clasts. It consists of poorly sorted, slightly rounded clasts of finely-crystalline granites or granite-gneisses. The breccia exhibits a monomictic character. The large clasts are surrounded by a matrix built of fine rock fragments and black organic matter. Main and accessory minerals present in the clasts display sizes ranging from 0.1-1.0 mm. The minerals are polycrystalline. Biotite, stilpnomelane, opaque minerals, titanite and zircon are accessories. This breccia is structurally not homogenized. *Suevite breccia* is macroscopically a compact massive rock – greenish to grey to dark green in colour. On fresh surfaces or breaks, irregular- or elongated black fragments of recrystallized glass ca 1-2 cm in size and surrounded by the fine grained green matrix may be noted. In thin section, the suevite is seen to be polymictic breccia with small fragments built of recrystallized melt, rock and mineral clasts. The matrix is also a fine-grained mixture of rock and mineral fragments. Fragments > 1 mm represent only 15 volume% of the rock. Lithic clasts are predominant and polymictic. Granitic clasts dominate over those of amphibolites, quartzites and ultramafites. Recrystallized glass clasts of sizes varying from 1-10 mm represent from < 5-10 volume% of the rock. They display irregular, elongated, ameboid or spiral shapes and contain finer mineral clasts (e.g., quartz).

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Zircon U–Pb ages and O isotopes of the Jawornik, Bielice and Kłodzko-Złoty Stok granitoids, the Sudetes

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The collage geological structure of the Sudetes was established as a result of complex tectonic processes, mainly related to the prolonged Variscan amalgamation of Gondwana-derived lithostratigraphic units (terranes) and the Laurussia continent. The northern- and eastern boundaries of the Orlica-Śnieżnik Dome, often considered as terrane boundaries developed as shear zones, include elongated granitoid bodies, namely, the Kłodzko-Złoty Stok (KZ) and Jawornik granitoids in the north and the Bielice granitoids in the east.

For these granitoids, U-Pb SIMS SHRIMP zircon geochronology and oxygen isotope analysis on zircons and quartz were carried out. The timing of crystallization of each sample was based on ~15 analyses from commonly oscillatory zoned, magmatic zircons. Three dated samples of the Jawornik granitoids yield ages of 347±2, 334±2, and 334±3 Ma. In these samples, pre-Variscan zircon cores reveal a distinct inherited age component (545-639 Ma and ~1.0 Ga). Dating of the Bielice granitoids provide U-Pb zircon ages of 355±2 and 336±2 Ma. Three samples of the main body of the KZ pluton give ages of 340 ±3, 336 ±2 and 314 ±2 Ma. Nearly the same ages are obtained for a dioritic enclave (332±2 Ma), a microdiorite dyke (332±2 Ma) and pyroxene-amphibole bearing rock (333±2 Ma) associated with the main KZ pluton. As in the case of the Jawornik granitoids, one of the samples of the KZ pluton reveals a Neoproterozoic inherited component. In the Jawornik and Bielice granitoids, values of δ^{18}O(Zrn) cluster around 5.5-7.0‰ and they are ~4-5‰ less than δ^{18}O(Qz) separated from the respective samples. In the KZ pluton, most of the analyzed Variscan zircons show relatively constant δ^{18}O(Zrn) values falling within the range of ~5.7-7.5‰. The sample containing inherited zircon cores reveals more elevated values of ~8-10‰ which indicate a significant contribution of the upper crust in the formation of this granitoid. Comparison of δ^{18}O(Zrn) to δ^{18}O(Qz) indicates that most Qz–Zrn pairs fall between isotherms of 600 and 900°C. However, some of the KZ samples reveal lower temperatures that demonstrate post-magmatic disturbance of O isotopic equilibrium in the quartz grains. The U-Pb and O zircon isotopic data suggest that the KZ, Jawornik and Bielice granitoids were mainly generated in the lower crust in the Variscan late collisional configuration. Subsequently, they were emplaced along the major regional tectonic boundaries inferred to represent Variscan suture zones.

Acknowledgments: This study was financed by MNiSW grant N307 112436 during the period 2009-2011.

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Petrology, geochronology and stratigraphy of the Młynowiec-Stronie Group, the Orlica-Śnieżnik Dome (the Sudetes)

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The Orlica-Śnieżnik Dome (OSD, the Sudetes), contains two traditionally distinguished metavolcano-sedimentary formations, the Młynowiec Fm. and the Stronie Fm. Due to disputable protolith ages of these subunits, their mutual stratigraphic relations remain uncertain. A thin horizon of light quartzites (the Goszów quartzites) occurs between these formations that, for years, has been considered as a basal unit of the Stronie Fm.

Our research on the Goszów light quartzites and adjacent rocks indicates the stratigraphic continuity of the Młynowiec and Stronie Fms. The light quartzites form three different, locally intercalating varieties: pure quartzites, Kfs-bearing quartzites and mica-rich quartzites. Th-U-total Pb monazite dating performed on the light quartzites (8 samples), mica schists (6 samples) and paragneisses (4 samples) reveals two age clusters of ca 364 Ma and 335 Ma, confirming the presence of distinct, latest Devonian and Visean monazite-forming events in the OSD. The monazite study also reveals an early Palaeozoic monazite age of ~494 Ma that was obtained only for the Kfs-bearing quartzites. The U-Pb zircon study performed on two samples of the quartzites revealed that ca 490 Ma zircons form 90% of the zircon population in the Kfs-bearing quartzites, and 10% in the adjacent Kfs-absent, pure quartzites. Field and petrographic studies, supported by the geochronological data, suggest that the light quartzites originated mainly from quartz sands intercalated by pelitic rocks, with occasional admixtures of volcanogenic, tuffitic material. The Early Palaeozoic monazite and zircon age of ca 490-495 Ma is thus interpreted as the protolith age of the Goszów light quartzites. It indicates their temporal affinity with the protoliths of the other ca 500 Ma metavolcano-sedimentary rocks of the Stronie Fm.

The tectonometamorphic record of the light quartzites, compared to the under- and overlying mica schists and paragneisses, indicates that the whole Młynowiec-Stronie group is an integral, lithotectonic unit, with no visible structural or metamorphic discontinuities. Structural studies and thermodynamic modeling indicate that the development of tight N-S-trending folds and an axial penetrative schistosity resulted from E-W directed tectonic movement and metamorphic progression from 500ºC to 640ºC and 6-7 kbar at which the assemblage Grt(rim)-Bt-St-Ms-Qz developed in the light quartzites and adjacent rocks.

Acknowledgments: This study was funded by the NCN grant no. 2011/03/B/ST10/05638.

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Evidence from titanite composition for the mixing of felsic and lamprophyric magmas in the Kłodzko-Złoty Stok intrusion

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The high volatile contents of lamprophyric magmas inhibit zircon crystallization and promote incorporation of Zr into titanite (Seifert 2003; Ventura et al. 1999). In a study of the Kłodzko-Złoty Stok intrusion (KZSI), we have found that lamprophyre and felsic magma interactions were much more common than previously thought.

The composition of titanite, present in melanocratic dykes, cumulates, gabbros and some granitoids, especially whose with macroscopic mingling textures, provides complementary evidence of lamprophyre involvement in magma evolution. Euhedral titanites from a dacite dyke SE of Chwalisław have up to 0.1 wt% of Zr in their cores. The lamprophyric nature of the parent of this dyke can be proven by LA-ICP-MS results on amphiboles. An alkaline dyke from Rogówek has up to 1.5 % Zr in the titanite cores. Here a lamprophyric origin can be proven by other means, such as Sr-apatites, and chlorite (replacing biotite) overgrown by a Kfs-Qtz-Pl mass. The Fe/Al ratio in titanite exceeds 3 (up to 25) and agrees with the extremely high OH concentration in the melt (Ventura et al. 1999).

The Zr concentration in titanite has also helped us to interpret rocks where the interaction with lamprophyric melts is not obvious. Gabbro-diorites from Żelazno (dated at 340 Ma by Mikulski et al. (2013)) have the largest observed titanite crystals, with Zr enrichment in the outer segments (not regular rims) (> 0.14%). This observation can explain the fact that amphibole rims around massive pyroxenes formed as a result of gabbro interaction with lamprophyric melt. Ultramafic cumulates (hornblendites) from the SE side of KZSI have whole rock Zr concentrations up to 500 ppm but no zircons have been found. Titanites, however, contain 0.1% of Zr and suggests that cumulates are of lamprophyric origin rather than derived from gabbro-diorite-tonalite magmas.

Acknowledgements: This work was supported by project N N307 634840 financed by MNiSW.

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New perspectives on the metamorphic diamond hunt in the Scandinavian Caledonides and worldwide

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Within the Scandinavian Caledonides, ultra-high pressure (UHP) mineral indicators have been recognized at three different structural levels: in the uppermost allochthons of the mountain belt in the Tromsø Nappe (Janák et al. 2013), at middle structural levels in the Seve Nappe Complex (SNC; Majka et al. 2014), and deep in the hinterland in low structural levels in the Western Gneiss Region of Norway (e.g. Smith 1984; Dobrzhinetskaya et al. 1995). These discoveries, along with those of coesite in the Alps (e.g., Chopin 1984), and microdiamond in the Kokchetav Massif, Rhodopes, Alps, Bohemian Massif etc. (e.g., Dobrzhinetskaya 2012) provide an unambiguous message: "Seek in the right place, in the right mineral and with the right technologies and you will find!"

Key lithologies in the diamond hunt are gneisses that host self-evident UHP rocks. They are usually thought to be of granulite- or amphibolite-facies conditions. Thus they do not attract as much attention as do eclogites or peridotites, although these gneisses volumetrically prevaile in all UHP terranes worldwide.

The gneisses from the SNC in Jämtland, exemplified here, contain plagioclase and sillimanite and have never been suspected to have experienced UHP metamorphism. Careful search for remnants of the peak pressure stage in garnets resulted in the identification of mineral assemblages containing, e.g., kyanite and phengite, that allowed for estimation of pressure conditions at 2.8-3.2 GPa (Klonowska et al. 2014). Further examination of garnets resulted in the finding of microdiamonds (Majka et al. 2014). Garnet is a perfect vessel for mineral inclusions that can reveal the P-T evolution of a rock. Moreover, the existence of a minor amount of the C-saturated fluid in the garnet-gneisses at the near peak-pressure stage, a condition easily fulfilled in, e.g., metasediments, allows formation of diamonds. Recent discoveries of diamonds in the SNC have essentially changed the geologists' perspective on the subduction-eduction processes that have led to the formation of the Scandinavian Caledonides.

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A new interpretation of gaps in zircon age distributions in deep crustal "hot zones" – evidence from the Sesia Magmatic System (Ivrea–Verbano Zone and Serie dei Laghi, Southern Alps, Italy)

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Advection of heat by the intrusion of mantle-derived magma is frequently invoked as the driver of high-temperature metamorphic events in the deep crust, thus forming so-called deep crustal "hot zones". One of the best places worldwide to study this process, especially the temporal relationships thereof, is the deep crustal section of the Ivrea-Verbano Zone of NW Italy.

The Ivrea–Verbano Zone and the adjacent Serie dei Laghi constitute a complete section of the (pre-)Variscan Adriatic continental crust, which was intruded at different levels by coeval magmas of Permo-Carboniferous age, collectively referred to as the "Sesia Magmatic System".

Radiometric age data demonstrate that igneous pulses began intruding the deep and middle crust no later than 314 Ma, an age corresponding to that inferred for regional granulite-facies metamorphism and predating by more than 20 m.y. the well-documented, main magmatic pulse at about 292 to 282 Ma forming the so-called Mafic Complex. A gap in zircon age information from 316±3 Ma to 276±4 Ma, observed in the deep-crustal granulite-facies paragneisses overlaps a similar gap from ca 314 to 283 Ma between igneous and reset zircons in a closely associated mafic–ultramafic sill. On the other hand, U/Pb zircon ages demonstrate intrusive activity upwards in the section in the middle and upper crust during these time gaps.

Numerical modelling shows that high temperatures in deep crustal "hot zones" may persist for millions of years, so continued episodic intrusions of magma may sustain high temperatures in granulites which remain partially molten for about 30 m.y. Thus, the observed age gaps may reflect prolonged maintenance of temperatures above the stability field of zircon. The re-emergence of a zircon-age record with ages < 275 Ma then reflects final cooling to temperatures beneath the zircon U-Pb closure temperature after the emplacement of the Mafic Complex.

In higher sections of the crust above the "hot zones", lower overall temperatures prevailed and so a "normal" sequence of intrusion events is recorded by the zircon ages.

Thus, a far reaching conclusion of these findings is that a gap in a hight-T geochronological record within a high-grade terrane might not necessarily mean an absence of events, but instead may record the occurrence and duration of a thermal peak.

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Imprint of a lower crustal cracking front at a fast-spreading ridge in the gabbros of the Ślęża ophiolite (SW Poland)

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The onset of fracturing is an important factor in the evolution of both modern and ancient lower oceanic crust. In fast-spreading rift environments, fracturing provides the initial permeability for the penetration of seawater into the lower oceanic crust. Models for the cooling of the oceanic crust suggest that fracturing in fast-spreading environments begins at a downward-propagating "cracking front". The earliest µm-scale hydrothermal veins crosscutting lower crustal mafics are interpreted as an imprint of such phenomenon (Manning et al. 2000).

According to textural (i.e., crosscutting) relationships, the earliest metamorphic event in the gabbroic section of the Ślęża ophiolite is connected with a distributed, microscopic crack network that can be interpreted as a fossil remnant of a "cracking front". The microscopic network is spatially associated with the grain boundaries of primary igneous phases and microcracks crosscutting them. On the scale of individual thin sections, microcracks are evenly distributed troughout and shear offsets are rare. Plastic deformations are restricted to ubiquitous L-S crystal shape fabrics and undulatory extinction of primary pyroxene which imply movement of crystal-liquid suspension (mush) troughout the lower crust and refer to magmatic flow fabrics in fast-spreading rift environments (MacLeod et al. 1996).

The microscopic crack network provided conduits that delivered first fluids and drove rock/fluid reactions. These reactions promoted the growth of metamorphic amphiboles, epidote-group minerals, secondary calcic plagioclases and secondary Ti minerals (titanite and anatase). Such mineral asemblages entirely fill and seal microcracks (< 100 µm wide).

On the basis of the nature of the crack network of the Ślęża ophiolite gabbros, it is inferred that they represent deformation in the semibrittle field. Such semibrittle conditions occur after the gabbros cool below the plastic – brittle transition (~750°C) and are diagnostic for cracking fronts in fast-spreading rift environment (Manning et al. 2000)

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Assessing environmental anthropogenic pressure in Lower Silesia based on atmospheric PM$_{10}$: carbon isotopic and OC/EC ratio approach

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Our investigation of PM$_{10}$ samples gathered in 2011 pertains to Lower Silesia. The 173 samples (ca 25 for each of eight sampling points) were collected in two regional background stations (group I) at Osieczów (Oś) and Czerniawa (Cz), one industrial station (group II) at Działoszyn (Dz) and five urban background stations (group III) at Nowa Ruda (NR), Świdnica (Św), Polkowice (Po), Legnica (Le) and Zgorzelec (Zg) the Voivodeship Inspectorate for Environmental Protection (VIEP) employees. Due to the sampling point characteristic, even 157 µg·m^{-3} (NR), 152 µg·m^{-3} (Le) or 115 µg·m^{-3} (Św and Po) of PM$_{10}$ mass concentration were noted, while 50 µg·m^{-3} is the CAFÉ Directive limit. In order to determine the origin of carbon in PM$_{10}$, the carbon isotopic composition (^{13}C/^{12}C) was measured using EA-CF-IRMS and organic- and elemental carbon concentration (OC/EC) was measured by Thermal-Optical Carbon Aerosol analyser.

The coupled data of δ^{13}C values (especially calculated isotopic mass balance) as well as OC and EC composition yield complex information that allows identification of the quality and quantity sources of air pollution. Based on the mathematical calculation of the isotopic mass balance, we drew the following conclusions. (i) In the heating season, the contribution of coal to the total carbon pool in PM$_{10}$ varies from 26.1-39.1% (group I), 49.1% (group II) and 40.6-97.3% (group III) whereas the contribution from transport varies from 60.9-73.9% (group I), 50.9% (group II) and 2.7-59.4% (group III). (ii) In the vegetative season, the contribution of coal to the total carbon pool in PM$_{10}$ oscillates about 2.8% (group I), 23.2% (group II) and 21.8-87.9% (group III) whereas the contribution from transport oscillates around 96.6% (group I), 65.5% (group II) and 7.6-73.8% (group III), and biogenic input fluctuates around 0.6% (group I), ca 11.4% (group II) and 0.3-4.5% (group III). Finally, using percentage contributions of specific sources, the real quantity input (µg·m^{-3}) of each source in the whole mass of PM$_{10}$ was calculated.

Coupled carbon isotopic signatures and OC/EC values of PM$_{10}$ allow the following conclusions. (i) Over the whole year in each analysed localisation, fossil fuels dominated the combustion input (coal used in heating/energy production and diesel/gasoline used in transport), though in differing proportions depending on area. (ii) Biogenic input in the total PM$_{10}$ fraction is, surprisingly, negligible in each analysed localisation and can be excluded as a potentially important PM$_{10}$ source.

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P-T-t evolution of the Pinkie unit of SW Svalbard Basement Province

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Here we present the pressure-temperature-time (P-T-t) evolution of the Pinkie unit (Prins Karls Forland, SW Svalbard). This unit consists mainly of laminated quartzites and metapelites which are overthrust by the lower-grade lithologies of the Grampian Group. The Pinkie unit was subjected to at least amphibolite facies metamorphism, and represents the highest grade metamorphic rocks on Prins Karls Forland.

Metamorphic zoning from chloritoid through staurolite, up to kyanite zone is apparent in the Pinkie unit. Five Barrovian zones have been distinguished in the metapelites: 1) Cld+Chl+Ms, 2) Grt+Chl+Ms+Bt, 3) Grt+St+Ms+Bt, 4) Grt+St+Ky+Ms+Bt, 5) Gt+Ky+Ms+Bt. The discontinuous reactions have been modeled in the K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O (KFMASH) system. The M1 assemblages and the D1 structures are heavily overprinted by a pervasive D2 mylonitic pattern.

Garnet occurs as two textural types. Garnet I builds huge (≤ 3 cm), subhedral to anhedral, strongly deformed and crushed porphyroblasts. It contains numerous inclusions, mainly of quartz and ilmenite. Garnet II forms small (≤ 0.5 cm), pure euhedral grains. The growth of garnet II is interpreted as a product of the staurolite breakdown reaction. Mn in the garnet exhibits bell-shaped zonation and Ca shows an almost flat profile through the grain. Mg and Fe are scattered (X_{Alm}=0.75-0.85, X_{Prp}=0.05-0.1). These elements could have been mobilized by fluids during the D2 event. Staurolite forms porphyroblasts full of quartz inclusions. Occasionally, staurolite overgrows garnet I. It is Fe-rich with X_{Fe}=0.81-0.83 and is characterized by Zn=0.05-0.07 a.p.f.u. Micas define the main foliation. Biotite is characterized by X_{Fe}=0.52-0.59, and Si in muscovite varies from 3.02-3.06 a.p.f.u.

SIMS U-Pb geochronology on detrital zircons from the Pinkie unit quartzite yielded ages as young as Neoproterozoic (0.95-1.05 Ga), with dominant populations around 1.4 and 1.6 Ga. Monazite from three different garnet-bearing lithologies has been dated using the chemical technique. It occurs as inclusions in garnet and staurolite as well as in the matrix, occasionally surrounded by allanite+apatite coronas. The age of metamorphism was estimated to be 370-360 Ma. Hence our study provides the very first evidence for a Barrovian metamorphism of Ellesmerian age in the High Arctic. So far, only "cold" deformation of this age was recognized in Svalbard.

Acknowledgments: This study is supported by the NCN research project No 2013/11/N/ST10/00357.

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The Pinkie metapelites from Svalbard: an excellent target to apply Thermoba-Raman-try

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A residual pressure in mineral inclusions may develop during exhumation and cooling, thanks to their high compressibility and expansion compared to the host mineral. The position of Raman bands of different minerals depends on pressure and/or temperature (e.g., Kohn 2014). It means that the shift in the Raman band position measured in an inclusion hosted by another phase can be translated to the pressure and/or temperature of the inclusion entrapment. This approach, called Thermoba-Raman-try, is based on well-known physical properties of minerals and it is independent of chemical equilibrium in the system. Recently, the Thermoba-Raman-try technique using the Raman shift of quartz inclusions in garnet (QuiG; Spear et al., 2014) has been validated by experiments.

Here, we used the QuiG barometry to determine peak pressure for metapelites of the Pinkie unit from SW Svalbard. This unit is composed mainly of laminated quartzites and metapelites representing a Barrovian-type metamorphic sequence. Five metamorphic zones are distinguished in which chloritoid, staurolite and kyanite are observed. These rocks are strongly deformed and were affected by penetrative mylonitization and associated fluid influx, circumstances that make P-T estimation using conventional methods based on mineral equilibria very difficult, if not impossible. Garnet forms big (up to 3 cm) elongated and partially crushed anhedral porphyroblasts containing mostly inclusions of quartz and ilmenite. Several garnets from the Grt+St+Ms+Bt, Grt+St+Ky+Ms+Bt and Grt+Ky+Ms+Bt zones were chosen for preliminary QuiG studies. The wavelength shift of the main (464 cm^{-1}) band of quartz was measured in inclusions of 30-60 μm in size. The results suggest that the garnet from the aforementioned zones grew at c.7-9 kbar at 550-650°C. Our results, coupled with the mineral reactions observed and compared to the KFMASH petrogenetic grid for the pelitic system, allow us to pin-point the pressure conditions under which the peak mineral assemblages were formed.

This study is supported by the NCN research project No 2013/11/N/ST10/00357.

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The Lower Carboniferous sandstones in the Wielkopolska-Silesia zone prospective for tight gas search

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The Lower Carboniferous sandstones in the Wielkopolska-Silesia zone are a part of the flysch sediments of Viséan and lower Namurian age. This complex is built of alternative claystones, mudstones, sandstones and conglomerates, the thickness of which varies from some hundreds to some thousands of meters. The sandstones prospective for the occurrence of tight gas occur at the depth where the top of the Lower Carboniferous deposits is 1-3 km. Quartz is the main component of the grain fabric and it prevails over feldspars and rock fragments (Krzemiński 2005). Lithoclasts locally predominate over the quartz and the feldspars. Plagioclases are more abundant than potassium feldspar. Muscovite and chlorites predominate over biotite. Zircon, tourmaline and rutile are the most common heavy minerals. Rock fragments are mostly represented by fragments of metamorphic- and volcanic rocks. Pyroclastic material is common (quartz with volcanic glass inclusions or with corrosion effects, fragments of acidic- and neutral volcanic rocks). The grain fabric is bound by the mostly recrystallized matrix and by the cement. Most commonly, the Lower Carboniferous sandstones display a total porosity of about 1-2% and a very low permeability. In the sandstones analyzed, the effects of the following diagenetic processes may be observed, namely, compaction, cementation, replacement and alteration, and dissolution. Straight intergranular contacts, undulated mica flakes or undulated plastic rock fragments are the effects of mechanical compaction. Cementation is dominated by the occurrence of layered silicates. Among the minerals that have been identified are diagenetic muscovite, illite, chlorite and kaolinite (Krzemiński 2005). Carbonates such as Fe-dolomite or ankerite, calcite and siderite are subordinate. Autigenic quartz in the form of overgrowths on quartz grains, and anhydrite, have been sporadically observed. The process of replacement is a very common diagenetic process. The carbonatic, locally anhydritic pseudomorphs after feldspar grains and rock fragments, as well as the replacement of the matrix mainly by carbonates, are visible results of this process. The alteration corresponds to the albitization, argillitization and chloritization of most feldspars and the illite recrystallization to muscovite. As the dissolution of feldspar grains pre-dated their albitization, the results of this process are poorly seen in the sandstones.

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Carboniferous (Mississippian) bentonites in the Sudetes (SW Poland): a summary of mineralogical and geochemical data

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Based on field observations and macroscopic features, further supported by geochemical and geochronological data, the studied Carboniferous bentonites and associated clay-rich sediments of the Central Sudetes have been subdivided into three groups: A – yellow bentonites (A1 from Ptasia Góra in Wałbrzych and A2 from Paprotnia, the Bardo Mts.), B – "green bentonites" (B1 from Szczawno, and B2 from Konradów), and C – mudstones of the background sediments enclosing the bentonites.

Mineralogical analysis was performed on extracted clay fractions < 2 μm, and included X-ray diffraction (Siemens D5005, Co radiation, Fe filter, raw separates and additional runs after glicolation, and after annealing at 550°C) and thermal analysis (Derivatograph, 25-950°C). The analyses revealed that Group A bentonites are composed of mixed-layer I/S, illite and kaolinite, Group B bentonites of illite, smectite and kaolinite (+/- chlorite), and the mudstones of group C of quartz, illite and chlorite.

Group A bentonites show the highest LOI (c. 13 wt%) and Al_2O_3 (c. 27%), and relatively low SiO_2, Fe_2O_3 and Na_2O. They are also richer in incompatible elements - Zr, Nb, Hf, Y, HREE, U and Th. Bentonite B1 has also high Al_2O_3 (~27%) but different concentrations of some other elements. The mudstones of Group C and bentonite B2 plot closely, having rather high Si, Fe, Na, Ti, Ba, Cr, Ni and low LOI, Al, Hf, Y, U, Th and Ta.

In the multi-element diagram normalized to the primordial mantle, all the samples are rather similar, with a decreasing trend from the most to the least incompatible trace elements, and with several distinct anomalies. In the diagram normalized to the upper continental crust, the plots are broadly horizontal, at c. 1 – 2 x the normalization values for the upper crust. There are many distinct anomalies, including two positive – for Th and U in bentonites A. The patterns for the pairs of bentonites B and their background mudstones are broadly parallel, with significantly higher values for the bentonites.

Conclusions:

1. Chemical features of Group A bentonites, e.g. high concentrations of incompatible elements: Zr, Nb, Hf, Y, HREE, U and Th (but low Ti and LREE) suggest their possible affinity to intermediate rocks (andesites?) of magmatic-arc setting.
2. Group B bentonites are not homogeneous. Bentonite B1 displays some geochemical similarities and dissimilarities compared with Group A, thus it might be related to a different type of volcanic eruption. Bentonite B2 shows geochemical similarity to the surrounding mudstones. This suggests a different origin for this clay, e.g., via mixing of volcaniclastic material with "background" sediment during deposition or re-deposition.

Acknowledgements: The study was supported from the Research Grant of the National Centre of Science, NCN, Poland, No. 2011/01/B/ST10/05112.

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Tracing mantle origin: O and C isotope analysis of single calcite grains from carbonatites – new data from NE Poland

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Stable isotopes of carbon and oxygen have long been used to identify the genesis of carbonatites, in particular for differentiating mantle origin. The attribute for primary igneous carbonatite (PIC) was defined as co-variation of isotopic ratios in the range δ^{13}C −3.1 to −7.7 ‰ and $\delta\ ^{18}$O +5.3 to +8.4 ‰ relative to V-PDB (δ^{13}C) and V-SMOW (δ^{18}O) respectively. We present a new dataset comprising secondary ion mass spectrometry determinations of $^{13}/^{12}$C and ^{18}O/^{16}O in single grains of calcite from samples assembled during earlier expeditions of Polish Geological Institute to known worldwide carbonatite-alkalic complexes, namely, Hoggar in Algeria (Al) and Lugingol in Mongolia (Mo) as a frame of genetic reference, and from two deep boreholes in NE Poland Tajno (Ta) and Wigry (Wi) that still remain an object of petrogenetic consideration. Past exploration and research activities were already completed when an isotopic study was performed on the side. The results of the additional investigations including ranges of C-O ratios permil, standard error and number of measurements n, are summarized in Table 1.

Table 1. The range of stable isotope (O, C) data for calcite separates from Hoggar, Algiera (Al), Lugingol, Mongolia (Mo) carbonatites, and from deep boreholes in NE Poland Tajno (Ta) and Wigry (Wi). Isotope data are based on replicate measurements of natural standard NBS-18 Fen carbonatite.

sample	$\delta\ ^{13}$C [‰]	±[‰]	$\delta\ ^{13}$C[‰]	±[‰]	$\delta\ ^{18}$O[‰]	±[‰]	$\delta\ ^{18}$O[‰]	± [‰]	N,
PIC	-7.7		-3.1		5.3		8.4		
Al	-11.79	0.41	1.27	0.39	3.37	0.13	12.38	0.12	n=121
Mo	-4.44	0.43	8.78	0.39	-4.45	0.15	12.25	0.12	n=91
Ta	-9.33	0.44	6.49	0.48	5.86	0.11	24.39	0.12	n=79
Wi	-3.22	0.36	8.65	0.32	20.92	0.14	26.05	0.12	n=33

The δ^{18}O and δ^{13}C compositions of calcite from subvolcanic calciocarbonatite of Ta, exhibits continuous shift from the PIC field that could be indicative of either Rayleigh fractionation, with magma crystallization and cooling, or late-stage fluid infiltration. Similar variations of $\delta\ ^{13}$C and $\delta\ ^{18}$O ranges are evident in the Al and Mo samples, though many O-C isotopic ratios of Al, Mo Ta falling into the PIC, and strictly linked to magmatic phases, are believed to represent primary isotopic signatures of the mantle. A calcite dyke from the Wi borehole reveals, however, a more uniform O-C isotopic composition that differs significantly from the PIC field; in this case, any relation to primary igneous origin (e.g., carbonatite) should be questioned.

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Paleoproterozoic age of charnockite from the Łanowicze borehole, confirmed by U-Pb zircon measurements on SHRIMPIIe/MC

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Charnockitic rocks in NE Poland have been recognized in only four deep boreholes within the Precambrian crystalline basement of the East European Craton. They have traditionally been included within the 1.5 Ga Mazury Complex where an AMCG rock suite is dominant. Emplacement of the AMCG was connected with a post-collisional tectonic setting– with a local extensional regime alongside W-E trending lineaments within continental crust. An age investigation by CHIME revealed the presence of possibly older charnockites in Łanowicze PIG-1 (Bagiński, 2006) within the Mazury Complex. This possibility has been confirmed using SHRIMP IIe/MC. The aim of this contribution is to present new U–Pb age data obtained on zircon single grains and to discuss the timing of charnockite generation.

Different contents of Th, U, Pb in monazite grains hosted by charnockite from Łanowicze record two different events in their history: older Paleoproterozoic at 1785±40 Ma and younger Mesoproterozoic at 1445 ±35 Ma (op. cit). There is also a zircon SIMS age of 1805±16 Ma. A new investigation using EPMA CL imaging reveals that zircon zoning does not reflect the concentric patterns typical of simple igneous growth but is rather similar to high-grade metamorphic textures. Zircons from Łanowicze- PIG 1 borehole currently dated using the SHRIMP IIe ion microprobe yielded a wide range of ages. The new results document that crystallization of charnockite took place at 1827±16 Ma, followed by high-grade regional metamorphism, in contrast to monazite, which recorded only granulite-facies and cooling processes. All results are consistent with the main orogenic event in the area. Moreover, ages of approximately 1.5 Ga were noted rarely in thin metamorphic overgrowths. They are pointers to the formation of the AMCG suite. The zircon data show that charnockites in the Łanowicze area were formed and metamorphosed mainly during Late Svecofenian continental accretion. These charnockitic rocks are approximately 300 million years older than the charnockite–mangerite components of the AMCG suite within the Mazury Complex. At ca 1.5 Ga, the charnockites were partially remelted and mixed with the AMCG suite rocks, probably in a post-collisional setting. The whole suite now possesses a geochemical signature from both events.

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Phosphates from Annopol (East Poland) - preliminary results of rare earth elements analysis

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At the end of the Early Cretaceous (Albian), the major part of the Central Europe, including Poland, was affected by a marine transgression (e.g. Marcinkowski 1974).In the Late Cretaceous, an epicontinental sea adjacent to the Tethys Ocean to the south, and including the area of the current Annopol Anticline, was dominated by carbonate sedimentation (Leszczyński 2012). Continuous sediment deposition was occasionally disturbed by decreases in sedimentation, up to the formation of discontinuity surfaces, which were accompanied by the accumulations of fossils, very often phosphatized (Olszewska-Nejbert 2004).

In the Annopol area, within the top part of the Albian sequence, the ‘Phosphorite Beds’ have been distinguished (Radwański 1968). Until 1970, the phosphates from this locality were the subject of exploitation. The Annopol phosphates are mostly concentrated in sandy marls with glauconite. The zones of phosphorite accumulation usually co-occur with rich fossil associations consisting of shark teeth and bones, vertebrae and teeth of marine reptiles, incl. plesiosaurs and ichthyosaurs, and the remnants of chimeras and turtles (e.g., Radwański 1968; Machalski et al. 2009).

The ‘Phosphorite Beds’ can be divided into a lower horizon dominated by large phosphorite concretions and an upper horizon with a predominance of smaller nodules. The two horizons belong to the highly condensed succession of sediments that have been interpreted as a zone of hardgrounds and burrowed omission surfaces / erosional surfaces (Machalski, Martille 2013). The origin of the Annopol phosphorite concretions is still not fully understood. Presumably, the accumulation of phosphates was associated with the abundance of biological life due to the global increase in organic productivity after the Cretaceous marine transgression, and with accumulations of various skeletal substances (e.g., Olszewska-Nejbert 2004). The large-scale heterogeneity of the paleontological record, with fossils that are certainly in an *ex situ* position, could be the result of multiple sediment redeposition events.

In this study, the phosphorite samples were collected from the exposures occurring at the land surface level. Two samples were subjected to chemical analysis, including contents of REE. Sample 1 represents the phosphorite lower horizon and comes from a large (~12 cm in diameter) fragment of a phosphorite concretion. Sample 2, representing the upper horizon, is one of the smaller nodules (~3 cm in diameter) originally cemented by marly-sandy sediments.

In the samples, the P_2O_5 content is 30.2% (for both samples), $CaCO_3$ is ~43% and SiO_2 ~11%. Differences in the contents of major elements between the two analyzed samples are minuscule. Besides, the analyzed phosphorite concretions are characterized by the following contents of selected trace elements: Sr (~144 ppm), Ba (56 and 85 ppm), Zr (33 and 38 ppm), Hf (2.5 and 4.3 ppm), Ta (0.2 and 0.28 ppm), W (302 and 46 ppm), Tl (0.14 and b.d.), Pb (30 and 21 ppm), Bi (b.d. and 0.3 ppm), Y (31.4 and 30 ppm) Th (1.52 and 2.53), U (98.2 and 35.3 ppm). Particularly noteworthy is the high content of uranium, especially in Sample 1. Rare earth elements display slightly increased concentrations in the studied phosphorites. Their contents in Sample 1 amount to 165.5 ppm, with LREE = 146.8, and HREE = 18.8, while for the Sample 2 the total REE = 144.3 ppm with LREE = 129.1 and HREE = 15.2.

The results of these preliminary determinations shed some new light on the depositional and diagenetic stages of the development of the Albian ‘Phosphorite Beds’ from Annopol. Previous studies indicate a relative increase in global P accumulation rates during the Late Albian (Föllmi 1995). A highly-elevated global sea level triggered the intensification of oceanic water exchange. The increase of deep-water circulation led to redistribution of dissolved P from deeper parts of the water reservoirs (Soudry et al. 2006). A similar scenario is proposed for the Annopol area. Subsequently, at the early diagenetic stage of the ‘Phosphorite Beds’, which occurred already in a reductive environment, U (hexavalent) diffused from seawater into the sediments. It was continuously reduced and finally precipitated as submicroscopic segregations of uranium minerals (mainly uraninite) that were probably absorbed by phosphatic material (Baturin, Kochenov 2001). The enrichment in rare earth elements could be the result of their complexation with P ions.

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Phase equilibria and metamorphic evolution of the UHP kyanite-bearing eclogite from Międzygórze, northern Bohemian Massif

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The eclogite is finely foliated with garnet- and omphacite-dominated bands. Garnet forms anhedral to subhedral porphyroblasts, rarely containing inclusions of kyanite, rutile and quartz. Omphacite, kyanite, phengite and quartz form the main matrix assemblage, accompanied by accessory rutile, apatite, zircon and Fe-oxides. Zoisite is found partly or completely overgrown by garnet, and rarely in the matrix. The peak pressure assemblage is considered to be Grt-Omp-Ky-Phg-Q-Ru. Omphacite contains rod-shaped inclusions of SiO_2 oriented parallel to the c-axis. It is partly decomposed to a diopside-plagioclase symplectite, whereas phengite decomposes to a biotite-plagioclase symplectite. Rare late amphibole is also present in the matrix.

Garnet is zoned mainly in regard to grossular, pyrope and almandine distribution, whereas spessartine is always flat. Compositional step profiles either give an impression of normal core to rim zoning with increasing pyrope, slightly decreasing almandine and rather stable grossular or reveal multiple core domains without any zoning, separated by local pyrope highs and grossular lows. The cores contain 37-38 mol% of pyrope and 26 mol% of grossular, whereas the rims contain up to 39 and 24 mol%, respectively. Omphacite is characterized by jadeite up to 37 mol%, Ca-Tschermak up to 3.2 mol% and Ca-Eskola up to 2.6 mol%. Phengite contains up to 3.33 Si apfu.

The P-T conditions were derived using a combination of Grt-Omp-Ky-Phg thermobarometry and P-T pseudosection modeling in the NCKFMMnASHT system. To calculate the peak-pressure, omphacite with the highest jadeite content, maximum grossular of garnet and phengite with the highest Si were used.

The obtained P-T conditions are 2.8-3.05 GPa and 770-835°C. These results fall above the quartz-coesite boundary, thus pointing to ultra-high pressure conditions during formation of the Międzygórze eclogite. The retrograde assemblage lacks typical high temperature minerals. Hence the inferred retrogressive path suggests simultaneous decompression and cooling.

All authors of this contribution are active members of the International Eclogite Conference (IEC) initiative and would like to dedicate this contribution to the memory of Professor Nonna Bakun-Czubarow, who represented Poland on the IEC Coordination Committee.

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The use of rare earth elements and stable S and O isotopes for fingerprinting pollution sources: a Serwis case study (Holy Cross Mountains)

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The results of rare earth element- and stable-isotope determinations on environmental samples can be used for tracing pollution sources and for the prediction of migration pathways. Information about the environmental fate of pollutants is especially important in cases of potential toxicity and possible adverse effects on biota. Active- and old mining waste disposal sites, especially in metal ore mining areas, pose serious environmental problems, including groundwater contamination. To study this issue in detail, a remediated old mining disposal site and the area surrounding the Serwis locality in the świętokrzyskie province has been selected for geochemical investigation (Migaszewski et al. 2015a, b).

The study area is located in the Dębno Valley, north of the Łysogóry Range (north-central part of the Holy Cross Mountains). The bedrock of this valley consists of Ordovician and Silurian clayey shales with siltstone and graywacke interbeds covered with Quaternary sediments (mostly tills and fluvioglacial sands). The study encompassed an abandoned mining waste disposal site and neighboring farmer's wells at the village of Serwis. The low-grade ore tailings were derived from the inoperative pyrite-uranium mine situated about 1.6 km north of the study area at the small town of Rudki. The reclamation of the mine tailings pile, which was performed in 1972-1973, turned out to be unsuccessful. This is evidenced by the presence of numerous unvegetated muddy patches and acidic pools. The principal objective of this study was to determine any potential influence of uranium and other toxic elements on the farmer's wells. Moreover, an attempt was made to use rare earth elements (REE) and stable O and S isotopes as pollution geotracers.

The concentrations of selected trace elements (Ag, As, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, U, Zn) and REE in technogenic soils, and acid pool- and farmer's-well waters were determined using an ICP-MS instrument (model ELAN DRC II, Perkin Elmer). In addition, the dissolved sulfates in water samples were analyzed for stable S and O isotope ratios by a dual-inlet and triple-collector isotope ratio mass spectrometer (MI-1305 model with modified inlet and detection systems) whereas the delta H and O values of water samples were determined on-line on an Picarro L2120-i Analyzer. The chemical analyses were performed at the Environmental Analytical Laboratory of Jan Kochanowski University whereas isotope analyses were done at the Mass Spectrometry Laboratory, Institute of Physics and in the Faculty of Geosciences, Maria Curie-Skłodowska University in Lublin.

The acid tailings pool waters showed exceptionally high concentrations of REE (range of 99.89-1065.50 μg/L) with a predominance of MREE (Sm-Ho). The NASC-normalized roof-shaped REE patterns displayed Gd excursions which are rarely found in acid mine drainage (AMD) areas, for example in the former "Podwiśniówka" acid pit pond near Kielce (Migaszewski et al. 2014). In contrast, the farmer's well waters are distinctly impoverished in REE. This suggests that these elements are adsorbed, co-precipitated, structuraly substituted by iron oxyhydroxides, oxyhydroxysulfates and clay minerals during infiltration of rainwater or meltwater to perched aquifers. It is interesting to note that absorption and immobilization of REE by mineral phases, organic matter, microorganisms and plants has been documented in many case studies (e.g., Johannesson, Lyons 1995; Merten et al. 2004; Romero et al. 2010).

Soils at the abandoned mining waste disposal site show heterogeneous distribution of trace elements, as was previously documented by Uzarowicz and Skiba (2011). The impact of the reclaimed tailings pile on some farmer's wells is evidenced by raised levels of SO_4^{2-} ions up to 577 mg/L and the $\delta^{34}S\text{-}SO_4^{2-}$ signatures (0.7–4.0‰) which are similar to those recorded in acid tailings pools (0.3–3.1‰). This conclusion is also backed up by the site variable dendrogram that groups these wells into one cluster linked to the acid pools.

The Serwis reclaimed tailings pile is a good example of AMD water generation in a nearly circumneutral environment. The isotopic data point to an iron oxidation path of pyrite leading to acidification of pool waters. This study has shown that the reclaimed mine tailings pile at Serwis jeopardizes the local perched aquifers that recharge farmer's wells with water.

Acknowledgement: This study was supported by the Polish National Science Centre (NCN), project no. DEC-2011/03/B/ST10/06328.

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Sulfur isotope analysis of sulfide minerals – a remake done by SHRIMP IIe/MC

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Sulfur isotope data from sulfide minerals are a powerful tool for identifying sources of ore mineralization. It is also a petrogenetic indicator of sulfur contamination of magma through interactions with country rocks during emplacement of intrusions. Commonly, the sulfur isotope measurements are performed on bulk mineral separates However, a new option is to provide sulfur isotopic signature by in-situ measurements on ion microprobes. It allows in-situ exploration of isotopic heterogeneities on a very small scale, avoiding internal defects or other-phase inclusions.

A collection of pyrite grains from the Radzimowice Au-As-Cu abandoned deposit (sample 10B, Table 1) and from the Leszczyniec Fe prospect (sample M-13, Table 1) for which isotopic signatures were previously diagnosed by conventional methods (Mikulski 2007) was selected for evaluating the accuracy and precision of sulfur isotope analysis by SHRIMP IIe/MC. The pyrite standard Ruttan was used during the analytical session to calibrate isotope ratios and to monitor the precision of the SHRIMP IIe/MC.

To perform in-situ measurements of three isotopes of sulfur ^{32}S, ^{33}S, ^{34}S with high spatial resolution and analytical precision, a primary ^{133}Cs+ ion beam was focused to approximately 16-18 μm at the surface of single grains mounted in epoxy resin. An electron gun was oriented normal to the sample surface and gold coating provided charge compensation.

9 analyses of reference Ruttan pyrite grains with ref. value of δ^{34}S = 1.2 ± 0.1‰ (VCDT) gave an average of δ^{34}S = 1.189 ± 0.08‰ with standard deviation of 0.53.

The results obtained during the tests on SHRIMP indicate good agreement with conventional method and demonstrate some differences between samples in terms of the melt geneneration; 10B originated from a dominantly igneous protolith (δ^{34}S values > 0‰) whereas M-13 involved some partial melting of a sedimentary protolith (δ^{34}S < 0‰).

Table 1. Sulfur isotopic composition of pyrites from the Sudety Mountains

sample	δ^{34}S_lab. SHRIMP	δ^{34}S lab.L .	δ^{34}S lab.W.
10B/Radzimowice	0.53± 0.14‰, s.d= 0.69	0.62‰	0.96‰
M-13/Leszczyniec	-2.40± 0.08‰ s.d= 0.62	-2.37‰	-2.65

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Minerals from selected peats (the Kietrz peat bog, Poland): preliminary SEM investigation

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Peats as biogenic sediments are one of the most heterogeneous deposits due to their physical and chemical properties. The study focused on mineral distribution in selected peat profiles, a feature which depends on many geochemical factors. The sampling area is the peat bog in Kietrz in southern Poland (50˚04'37.2" N, 18˚02'44" E), in the mesoregion of the Głubczycki Plateau belonging to the Silesia Lowland macroregion. Three independent peat profiles, K1 (1.95 m), K2 (3.50 m), K3 (3.60 m). were collected from different parts of the peat bog.

The dried peat samples were investigated using a Philips XL30 Environmental Scanning Electron Microscope (ESEM) with EDAX analyzer. The analyses were carried out at Faculty of Earth Science, University of Silesia.

Three different types of minerals with different origin were noted. The first type comprises primary minerals, mostly represented by iron sulphate (pyrite?) and calcium carbonate (calcite?). The second type is represented by calcium sulphide (gypsum?), Fe-rich oxides/hydroxyloxides (limonite?) which are characteristic products of the oxidation/weathering of the primary minerals. The third type is represented by rare distributed detrital minerals, e.g., zircon, apatite, feldspar and quartz.

The mineral suite, their distribution in the studied profiles, comparison with changing pH, TS and CC enables distintinction of levels differing in chemistry and mineralogy. The most significant factors having an effect on the minerals are peat chemistry, groundwater chemistry, and the pH and redox conditions pertaining during peatland evolution

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Carbonaceous material from the Pepper Mts Shale Formation – a Raman microspectroscopic study

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Carbonaceous matter (CM) has been found within clay shales and mudstones of middle Cambrian age. The studied deposit belong to the Pepper Shale Formation outcropping in the Pepper (Pieprzowe) Mts, Poland. The Raman microspectroscopy method has been used to estimate a temperature of CM alteration in conjunction with palynological studies.

Raman microspectroscopy of the carbonaceous matter shows two broad bands at 1000-1800 cm^{-1} and 2500-3100 cm^{-1}. The temperature of CM alteration, estimated on the basis of the Kouketsu et al. (2014) model, is lower than 200°C for goethite bacterial cells. A more precise assessment of temperature is complicated due to the presence of goethite peaks overlapping with those from the CM first order region. The temperature obtained for pyrite bacterial cells is ~180°C.

Based on the palynological studies, the organic matter shows differences in thermal maturation; the organic cells display a wide degree of colour alteration from transparent to various tints of brown. Dark brown walls of cells assembled in algal coenobia might have undergone humification in terrestial environments, before river transport into, and final deposition in a marine environment, where cyanobacterial filaments have been commonly deposited where they lived. This fact may suggest that groups of microfossils with darker colors underwent initial stages of decay before their redeposition and/or in different earlier environments.

Acknowledgements: The study was financed by AGH project No 15.11.140.642. (to Naglik), AGH GGIOŚ-KMPiG No 11.11.140.319 (to Natkaniec-Nowak), GGIOŚ KGOiG No 11.11.140.173. (to Bąk) and GGIOŚ KGZiG No 11.11.140.320 (to Toboła).

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Inclusions in authigenic quartz from the Pepper Mts Shale Formation – a Raman microspectroscopic study

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Authigenic crystals of quartz found within druses in mudstones from the Pepper Mts Shale Formation (Holy Cross Mts) were investigated by Raman microspectroscopy to obtain a temperature of thermal alteration of those rocks. Deposits from the Pepper Mts are nowadays interpreted as a sedimentary complex subjected to advanced stages of diagenesis.

Mudstone mineral compositions are dominated by sharp-edged, nonundulatory quartz grains accompanying by micas altered to chlorites. According to Przewłocki (2000), chlorites also occur as a product of clay-mineral transformation during burial diagenesis at temperatures above 100°C. The presence of authigenic crystals of quartz may indicate that the mudstones were also affected by hydrothermal fluid circulation.

Specimens of quartz differ both in color and size. Transparent specimens occur in association with yellow, brown and even black quartzes. Individual quartzes show a wide variation in size from a few millimetres up to 1.5 centimetres. The composition of fluid inclusions consist of methane proven by peak ~2917 cm^{-1}, nitrogen with diagnostic peak ~ 2329cm^{-1}, H_2S with characteristic peak ~2598 cm^{-1} (Burke, 2001) and carbonaceous material showing two board bands in the area of 1000-1800 cm^{-1} and 2500-3100 cm^{-1} (Kouketsu, 2014). The crystallization temperature of the quartz, estimated on the basis of Kouketsu (2014) conceptional model, is ~300°C. These results indicate that the mudstones from the Pepper Mts were altered at higher temperature than was previously supposed and that diagenetic alteration preceded a hydrothermal event.

Acknowledgements: The study was financed by AGH project No 15.11.140.642. (to Naglik), AGH GGIOŚ-KMPiG No 11.11.140.319 (to Natkaniec-Nowak) and GGIOŚ KGZiG No 11.11.140.320 (to Toboła).

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An EMPA study of the Early Bronze Age artifacts from southern Poland and its bearing on ore provenance

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Metal artifacts from graves dated to the third millennium BC from the western part of Little Poland were studied by means of electron microprobe and SEM-EDS to ascertain their chemical composition and ore provenance. The graves were discovered during excavations of burial mounds at sites in Kolosy and Miernów (Kazimierza Wielka district), and in Żerniki Górne (Busko Zdrój district; Włodarczak 1998; Kempisty and Włodarczak 2000, and references therein). These Late Neolithic and the Early Bronze Age graves were assigned to ca 2600-2400 BC (Corded Ware culture) and ca. 2200-1900 BC (older and classic phase of the Mierzanowice culture).

Metal artifacts chosen for analyses represent typical forms common for grave furnishings from Little Poland, namely, ornaments (mostly ear rings) and knife-shaped objects or awls interpreted as items used in flint manufacturing. Twelve pieces of the copper artifacts (a few cubic millimeters in volume) were cut and mounted in Araldite resin blocks and analyzed for their chemical composition with a CAMECA SX100 (Faculty of Geology, University of Warsaw) and a Hitachi SU-70 UHR Schottky FE-SEM (Faculty of Materials Science and Engineering, Warsaw University of Technology).

The studied fragments of the Early Bronze artifacts are characterized by the presence of corrosion layers developed at the surface of the objects, while the inner parts of the samples (copper matrix with Cu ranging from 94-99 wt% comprising As, Sb, Ag, Ni and Sn admixtures), host numerous Cu-O, Pb-Sb-O, Pb-As-O, Sn-Co-Ni-Se intergrowths (inclusions) of different shapes and varying spatial distribution.

Taking into account the chemical composition of the objects and their intergrowths, four metal groups were distinguished:
1) Strongly enriched in As (up to 2.0 wt%) and Ag (up to 0.7 wt%) with Pb-Sb-O inclusions;
2) enriched in As (0.2–0.6 wt%) and depleted in Ag with Pb-As-O inclusions;
3) strongly enriched in Ag (0.2–0.6 wt%) and depleted in As (< 0.1 wt%) with Pb-Sb-O inclusions;
4) strongly enriched in Ni (up to 1.7 wt%) with Co (up to 0.1 wt%) with high concentrations of Sb (0.8–3.0 wt%) and Ag (0.4–1.2 wt%), and with Sn-Co-Ni-Se inclusions.

The concentration of Ag, Sb, As and Sn in the Early-Bronze copper artifacts and the presence of intergrowths and their chemical composition are key indicators enabling recognition and determination of the mineralogical composition of the processed ores. Our study indicates that sulphosalt-rich ores were mainly used for manufacturing the Cu alloys. Based mostly on the content of Sb, As and Ag in the intergrowths, the worked ores most probably comprised tetrahedrite and tennantite with varying proportions of both minerals. Less often, ores with very small amounts of Sn-bearing phases were used by the Early-Bronze Age smelters. The presented chemical features of the studied artifacts may serve as indicators of ore(s) provenance, pointing to the Carpathian deposits in Slovakia and/or Hungary. The most probable ore sources were complex sulphide-sulphosalts and weathered Cu ores mined at Špania Dolina (Starohorské Mts, Central Slovakia) because of well-documented Neolithic mining activity in this area (Tocík, Zebrák 1989). Other deposits that are extremely tennatite- and tetrahedrite-rich with enhanced Ag contents, e.g., hydrothermal siderite tetrahedrite ores at Slovenské Rudohorie (Slovakia) and in the Rudabanya area (Hungary) should not be ruled out at this stage of the research.

Acknowledgments: The study was financed by the National Centre of Science (NCN) grant SONATA nr UMO-2012/05/D/HS3/04128 "ARCHAEOMETALLURGY OF COPPER. The Carpathian centers of metallurgy in the Early Bronze Age" (leader: U. Bugaj).

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Rare earth elements in the Kupferschiefer series of SW Poland

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In marine sedimentation dominated by deposition of clay and organic matter, the distribution of REE depends primarily on the composition of the terrigenous source material, biogenic material composition and redox conditions in bottom waters. However, the final distribution of REE in the sediments depends on the diagenetic processes or interaction of sediments with fluids. Therefore, metalliferous black shales tend to be more strongly enriched in REE relative to typical black shales. The occurrence and distribution of REE in the Permian Kupferschiefer series of SW Poland is closely associated with different geochemical zones, including the Rote Fäule hematitic footwall alteration. The most characteristic regularity in the variation of REE concentration is a gradual depletion in REE content outward from the oxidized zone (Rote Fäule) and from rocks of pyritic and polymetallic mineralization, through rocks with copper mineralization up to hematite mineralization in the oxidized zone (in terms of a division into zones of mineralization). The same trend can be observed with respect not only to specific groups of REE (LREE, MREE and HREE), but also to all rare earth elements, and Y and Sc. The systematic increase in the concentration of REE (especially MREE) towards Rote Fäule reflects the secondary supply of REE by fluids (MREE> HREE> LREE) and their migration. The differences in the distribution of REE in variously oxidized rocks indicate redistribution of REE by upwelling and spreading oxidizing fluids. The nature of REE distribution in the Kupfershiefer series of SW Poland implies changes in the physical and chemical conditions during the secondary mineralization process leading to remobilization of particular elements. In summary, it may be concluded, that differences in the distribution and concentration of REE between the shales barren in copper (with pyrite and polymetallic mineralization) and the copper shales as well as oxidized shales resulted from superposition of the original REE concentration and secondary enrichment associated with additional REE supply and further redistribution.

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REE bearing minerals in carbonatite veins from the Tajno massif (East European Platform, NE Poland)

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The Tajno alkaline-carbonatite complex, which is known only from drillings, occurs within the south-eastern part of East European Platform (NE Poland).The carbonatite rocks were identified by Ryka (1992) as veins cutting the ijonite and syenites and cementing the chimney breccia. The Tajno massif was emplaced during the Early Carboniferous (Demaiffe et al. 2013).

Samples of carbonatite rocks from the Tajno IG4 borehole were studied as a potential REE deposit. The main aim of the research was to determine the prospective intervals within the Tajno IG4 borehole materials. Moreover, the identification of REE-bearing mineral paragenesis, as well as detailed sampling and further laboratory analysis were also the matter of investigations.

"In situ" chemical analyses of borehole materials were performed using the handheld XRF Olympus Delta 50 Premium spectrometer (4W Ta anode X-ray tube, 50 kV). Prior to analyses of the natural rock samples, the parameters of the spectrometer was optimized for rare earth elements such as Y, La, Ce as well as for other critical elements such as Zr, Hf, U and Th. Handheld XRF non-destructive analyses allowed the identification of mineralized trends and anomalies within the drill-core material at the ppm level.

Contents of La and Ce were chosen as indicators of the occurrence of REE-bearing minerals in the analyzed rocks. Spot XRF-analyses were executed for each meter of drill core (1300 analytical points over ca 1200m). The graph of La and Ce content vs. sample depth in the Tajno IG4 borehole exhibits high differentiation. Contents of La are in the range between 30-7193 ppm (average ca 177 ppm) and those of Ce are between 38-5204 ppm (average ca 255 ppm).

Detailed chemical compositions of minerals was determined on selected samples with higher content of REE elements using a Cameca SX 100 electron-microprobe in the PGI-NRI laboratory. The main REE-bearing minerals are REE-carbonates such as bastnasite, parisite, synchisite etc., and the REE-phosphates monazite and REE-apatite. The occurrence of the REE bearing silicates perrierite and zircon were also identified. The presence of minerals with higher contents of REE's such as rutile and ilmenite were also detected. Carbonates (Sr-calcite and ankerite), fluorite, K-feldspars, albite and quartz as well as micas (mainly phlogopite) sulphides (pyrite, chalcopyrite and sphalerite) and sulphates (barite and celestine) occur in the carbonatite veins.

Acknowledgments: This research is supported by the Ministry of the Environment of Poland from the sources of the National Fund for Environmental Protection and Water Management.

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Zechstein polymetalic mineralization on the northern part of the Fore-Sudetic Monocline

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The aim of this study was to identify, and geologically and mineralogically characterize mineralization on the Fore-Sudetic Monocline in the Wilcze area, located in the northern part. Work was carried out on samples from deep boreholes which were affirmed by metallic mineralization. So far, due to the considerable depth of deposition (about 2500 m) the mineralization has not become a target for the mining industry. Many ore minerals were identified, the relationships between individual ore- and rock components examined, and detailed descriptions of the host rock lithologies were made using a microscope in transmitted and reflected light.

Important ores, the high price of copper, the demand for this metal - all are issues related to exploration and extraction that are essential and important for the economy. Since the 50's in Poland, when the copper ore deposit in Lubin-Sieroszowice was first documented, intensive mining operations have been conducted in the southern part of the country.

The study area is located in the northern part of the Fore-Sudetic Monocline, far away from the area of current proven reserves. This is an area designated as prospective for the exploration of copper ore deposits. The analysis and investigation was carried out on samples from six boreholes. A research microscope with reflected light coupled to a Nikon Nikon camera (Sight DS-5Mc), and with computer software (NIS-Elements AR), was used for the research. Pictures using lenses with magnifications of 5x, 10x, 20x and 50x could be taken. Recognition of ore minerals was carried out on the basis of their optical characteristics such as degree of reflection, color, relative relief, anisotropy and internal reflections. EPMA analysis shows that the most abundant ore minerals are located in PZ1. Documented sulfides are pyrite FeS_2, chalcopyrite $CuFeS_2$, covellite CuS and bornite Cu_5FeS_4.

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Morphology, internal structures and geochemistry of zircon from selected granitoids of the Tatric crystalline basement (Central Western Carpathians)

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The zircon crystallization history may provide unique insights into magma petrogenesis. This paper focuses on the morphology, internal structures and chemistry of zircon crystals, selected from geochemically and isotopically well-characterized granitoids from the Tatric crystalline basement. Three samples of granitoids were collected from Rohacz Płaczliwy *RP*, Koszysta Wielka *KW* (Tatra Mts.) and Chopok *ChP* (Low Tatra Mts.) to show that zircon is a useful tracer for magma processes and provides an additional record of magma sources.

Zircon crystals from all samples are colourless to light yellow and vary in length from ca 100-350 µm. All analysed zircon crystals are perfectly euhedral, differing only in their aspect ratios ranging from 1:1 to 1:4. Zircon crystals from sample RP represent mostly S1 (24%), L1, L2, S2, L4, S6 subtypes (Pupin 1980), giving low IA and IT indexes (IA= 298; IT= 278). Most grains exhibit oscillatory zoning characteristic of magmatic growth (single-phase crystals). Some crystals have inherited components (cores) surrounded by oscillatory zoned rims. Zircon crystals from sample KW belong to subtypes L1 (40%), S1, S6 and S11 (Pupin,1980), giving lower IA and higher IT indexes (IA= 214; IT= 294). CL investigations show that the short- and normal prismatic crystals usually exhibit two different domains: a homogeneous to weakly growth-zoned internal part (core) surrounded by a rim with fine to broad oscillatory zoning. The long prismatic crystals show only oscillatory zoning. Zircons from sample ChP represent mostly subtypes S5 (15%), S3, G1, L5, S1, L2 and L1, giving higher IA and similar IT indexes (IA= 468; IT= 276). Zircon morphologies from samples RP and KW indicate an aluminous magmatic environment (granitoids of crustal or mainly crustal origin), whereas the zircon crystals from sample ChP are typical for calc-alkaline and K-calc-alkaline series granitoids (granitoids of crustal and mantle origin; Pupin 1980).

Microprobe analyses show a positive correlation between P and Y in all analysed crystals, suggesting the xenotime-type substitution $Zr^{4+}+Si^{4+}\leftrightarrow(Y, REE)^{3+}+P^{5+}$. The crystal domains with oscillatory zoning are characterized by Zr/Hf ratios in the range 33-68 (RP), 41-58 (KW) and 29-48 (ChP).

Acknowledgements: This study was supported by NCN grant No 2012/07/B/ST10/04366.

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Diversification of rare earth element contents in the Poznan Clays

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The “Poznan Clays”, formerly called “The Poznan Series”, occurring in Central and Northern Poland were formed in a large inland alluvial-lacustrine basin. Variability in these series is based on the region occurrence as well as on their lithostratigraphy. The clays have characteristic tinges: green clays, grey clays and red (flaming red) clays.

129 samples were collected from 18 deposits of the clays. After complete acid digestion, contents of rare earth elements were determined by inductively coupled plasma mass spectrometry (ICP-MS). Contents of major- and traces elements were determined by WD-XRF and ICP-OES, and mercury by mercury analyzer.

Differences were found in element content depending on clay lithotype. Red clays have the highest contents of REE ranging from 58.7-1709 mg/kg with an average content of 178 mg/kg and a geometric mean of 140 mg/kg). In green clays, REE contents range from 82.9-376 mg/kg (average content 173 mg/kg; geometric mean 160 mg/kg). In gray clays, REE contents range from 83.9-546 mg/kg (average content 177 mg/kg; geometric mean 158 mg/kg). Some samples of the red clays have the highest REE contents. The study shows that green clays are characterized by higher average contents of Rb, Sr, Cr, Ni, and the major elements Ca, Mg, Na and K. Grey clays have higher Hg, Zr, Ba, Zn contents and lower contents of Fe, Mg, Cr, and V. In red clays, higher contents of As, Cu, Fe and Mn were found. Variability of REE elements depending on the region of their occurrence was noted in the clays. The highest REE contents characterize clays from the Wielkopolska and lubuski region and the lowest, clays in the Opolski and Upper Silesian regions. Interestingly, in the Wrocławski region nearby, there are two deposits with the smallest REE contents and one with the highest amount. Small positive europium- and cerium anomalies in clay samples from 17 deposits was noted. The study reveals differences in the contents of rare earth elements in the “Poznan Clays” depending on lithological variety and region of deposition.

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Morphology of zircon crystal grains in metasediments from the western part of the Orlica-Śnieżnik Dome

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The existence of a Neoproterozoic to Ordovician rock succession has lately been reported from the Orlica-Śnieżnik Dome (OSD) located in the Central Sudetes. This has led to interpretations that the OSD may represent a vestige of a recycled Saxoturingian crust (Chopin et al. 2012; Mazur et al. 2012). In this context, special attention has always been paid to thin horizon of light Goszów Quartzites (GQ) exposed in the eastern part of the OSD. The horizon has been interpreted as yielding a Cambrian age (Jastrzębski et al. 2010) or, in contradiction, as representing the youngest Early Ordovician member of the volcano-sedimentary succession (Mazur et al. 2012). Similar light quartzites are also known from the western limb of the OSD. Recently, based on geochemical similarities, it has been suggested that quartzites from both parts of the dome represent the same lithostratigraphic horizon (Szczepański and Ilnicki, 2014).

Our goal was to study the morphologies of zircon grains from light quartzites cropping out in the OSD in order to constrain their possible similarities and provenance. Our investigations show that, in terms of roundness, elongation and crystal morphology, there are striking similarities between quartzites from both sides of the OSD. Moreover, it seems that the main source of the euhedral zircon fraction, with morphologies dominated by {110} and {211} forms, were most probably granitoids of ca 500 Ma known from the OSD and widespread in the Saxothuringian Zone.

Acknowledgments: The study was financed by ING UWr. grant no 1017/S/ING.

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Sesquiterpenoids and diterpenoids from Lower Jurassic sub-bituminous coal from the "Blanowice Formation", southern Poland

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The "Blanowice Formation" of Late Pliensbachian–earliest Toarcian age is located in the Silesia-Cracow Monocline. This area represents the southernmost, peripheral limits of the Early Jurassic epicontinental basin in Poland. The Lower Jurassic strata in this area consist mostly of continental deposits (Gedl 2007).

Sesquiterpenoids and diterpenoids are large groups of hydrocarbons which occur widely in nature (Noble et al. 1985). Sesquiterpenoids ($C_{15}H_{24}$), terpenes with three isoprene units are mainly represented by unsaturated hydrocarbons, alcohols and acids, constituents of essential oil and resins (e.g., Pietsch, König 2000). However, they are also common in conifers as well as in other plants such as angiosperms and bryophytes (Otto and Wilde, 2001). Diterpenoids ($C_{20}H_{32}$) have four isoprene units and they are found in higher plants, fungi, insects and marine organisms (Hanson 2005).

Two samples of sub-bituminous coal from the "Blanowice Formation" have been analyzed for sesquiterpenoids and diterpenoids using gas chromatography-mass spectrometry (GC-MS). One sample was taken from the clay pit in Mrzygłód, while the other was collected from the Wysoka Lelowska 47Ż drill core.

The sesquiterpenoid and diterpenoid distributions differ considerably in the two samples. The aliphatic fraction of the Wysoka Lelowska 47Ż sample contains relatively abundant C_{14}-C_{16} bicyclic sesquiterpanes including the drimane-type and eudesmane-type compounds and their rearranged products. The series of bicyclic compounds are believed to have been formed from a hopanoid precursor by degradation and reduction, or rearranged in early diagenesis (Alexander et al. 1984). Aromatic sesquiterpenoids in the Wysoka Lelowska 47Ż sample are represented by isoledene, methyl ionene, 1,2,3,4-tetrahydro-2,2,5,7-tetramethyl-naphtalene, α-muurolene, calamenene, cadalene, eudalene and 2,5-dimethyl-1(3-methylpentyl)-naphtalene. Among diterpenoids, tricyclic compounds predominate with norisopimarane, 8,13α-Dimethylpodocarpane, isopimarane and norpimarane as the most abundant. Bicyclic diterpenoids are absent, while tetracyclic compounds are represented by 16-Nor-labda-8(17),13-dien-3-one, phyllocladane and *ent*-Beyerane.

In the Mrzygłód sample, diterpenoids predominate significantly in the whole aliphatic fraction (Fig. 1). The most abundant compounds are tricyclic diterpenoids with isopimarane having the highest peak. Bicyclic diterpenoids are essentially composed of labdane-type compounds, namely, 14,15-Bisnorlabdane, 16-Norlabdane, 8α(H)-Labdane and 8β(H)-Labdane, while tetracyclic diterpenoids are represented by 16-Nor-labda-8(17),13-dien-3-

one, cassane, cleistanthane, phyllocladane, *ent*-Beyerane and hibane (Fig. 1). The sesquiterpenoid distribution is much less diverse compared to the Wysoka Lelowska 47Ż sample. In aliphatics, only drimanes and homodrimanes are present with isomers with 8β(H)- configuration as the most abundant compounds. Aromatics are represented by isoledane, methyl ionene, guaiazulene and 2,5-dimethyl-1(3-methylpentyl)-naphtalene.

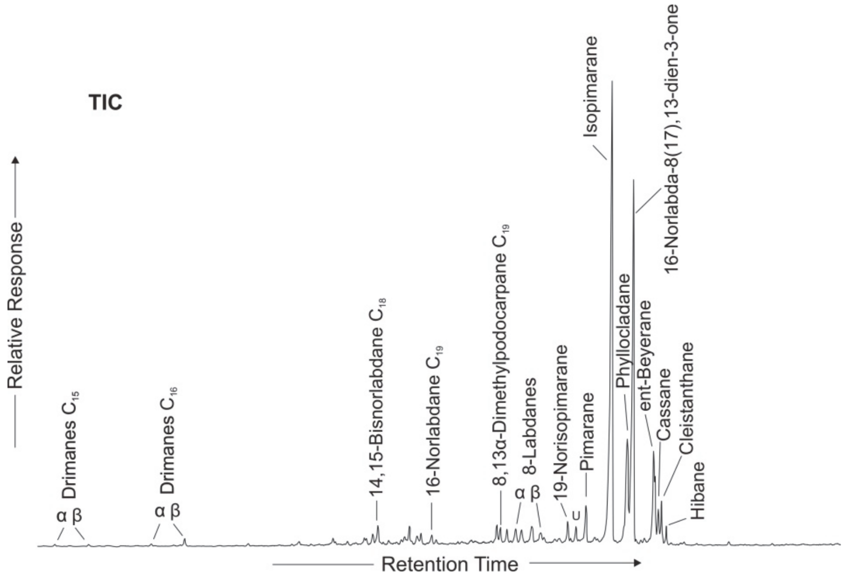

Fig. 1. Total ion chromatogram of the aliphatic fraction of MR7 sample showing the definite predomination of diterpenoids in the extract.

The presence of sesqui- and diterpenoids in such a high amounts in the two samples clearly indicates that resin plants were the major constituents of the Blanowice coal.

This work was supported by the NCN grant: PRO-2012/05/N/ST10/00486.

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Thermobarometry of the Hamadan pelites migmatite within the Alvand aureole, West Iran

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Intrusion-related migmatites comprise a substantial part of the high-grade part of the Alvand aureole in the Hamadan, western Iran. In this region, abundant Al-rich metasedimentary rocks and various granites occur. Migmatites consist of melanosomes with Bt+Sill+Grt+Crd+Sp±Opx and leucosomes with Grt+Pl+Kfs+Qtz. High-grade metamorphic rocks of the area contain assemblages of the upper pyroxene hornfels facies to lower sanidinite facies rocks. Field relations, mineral parageneses and P-T estimates suggest that intrusion of granitic magma and concomitant partial melting of metasedimentary units were the main processes for migmatization. The first appearance of orthopyroxene in these rocks marks the transition from upper pyroxene hornfels- to lower sanidinite facies conditions. Peak metamorphism took place at 650-750°C and ~2-4 kbar; such HT/LP metamorphism is caused mainly by advective heat derived from granitic intrusion. Regional metamorphism, magmatism and subsequent contact metamorphism occurred due to arc construction and collision during subduction of a Neo Tethyan seaway and subsequent oblique collision of Afro-Arabia (Gondwana) with the Iranian microcontinent in the Late Cretaceous–Early Tertiary.

In order to work out the melting temperature and to see if heat was high enough for melting, pressure and temperature for each metamorphic phase was estimated using conventional thermobarometry methods such as cation exchange reaction thermometry, multiple equilibria calculations, GASP barometry and petrogenetic grids. The Fe-Mg exchange between garnet and biotite thermometer using different calibrations was applied. Solution models of Helffrich and Wood (1989) and Ganguly and Saxena (1984) were used for garnets. For pressure estimation, the GASP (garnet-sillimanite-quartz- plagioclase; Koziol and Newton 1988) barometer was employed. The outer parts of garnet and biotites with highest Ti contents were used to find the peak temperature. Plagioclase, however, does not show significant zoning. P-T estimation for peak metamorphic parageneses gives a temperature of 650-700ºC and a pressure of 2 kbar. Furthermore, using multiple equilibria (by THERMOCALC program version 3.2, Holland and Powell 1998), temperature and pressure was calculated for the formation of the metapelitic rocks. Activities of biotite, muscovite, garnet and plagioclase end-members were calculated using the AX program of Holland and Powell (1998). On the basis of these data, the studied rocks were at a depth of 6-12 km when they experienced the peak metamorphic temperature. This reflects a mean geothermal gradient of about 58°C/km, which is in range of contact aureoles. Therefore, peak metamorphism occurred under high temperature and low pressure conditions (LP/HT metamorphism) and reflects high heat flow in this part of the crust. This suggests a genetic link between granite ascent from the deep crust and the high-temperature/low pressure contact metamorphism in the upper crust.

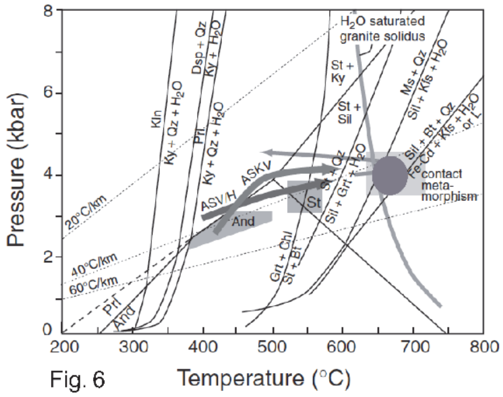

Fig. 6. Pressure‑temperature diagram. Al2SiO5 triple point from Holdaway (1971); other equilibria calculated using database and software of Berman (1991).

The research involved field work, petrographic studies, and criteria used to infer that leucosomes are products of partial melting. The results enabled us to make some conclusions regarding the partial melting of the Hamadan pelites in the Alvand aureole:

1- Intrusion of the Alvand complex (Cretaceous-Tertiary) into the host metapelitic rocks (Jurassic schists) created pelitic hornfelses and anatectic migmatites in the Alvand aureole.
2- Partial melting in the Alvand aureole was restricted to pelitic bulk compositions.
3- Temperatures appropriate for partial melting, cotectic compositions and igneous microstructures in the studied rocks support the conclusion that leucosome and mesosome formed due to anatexis.
4- The first appearance of orthopyroxene in these rocks marks the transition from the upper pyroxene hornfels to lower sanidinite facies conditions, and is attributed to the process of fluid-absent partial melting.
5- Peak metamorphism in the migmatitic rocks of the Alvand aureole took place at 650-750°C and ~2-4 kbar (HT/LP) reflecting the high heat flow.

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Condition of the Precambrian crust formation in northwest Iran

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The Takab Precambrian rocks with a variety of metamorphic and igneous rocks including pelitic schists, gneiss, meta-ultramafic, amphibolites, calc-silicate and granitoids crop out in the northwest of Iran. In the context of the structural subdivisions of Iran, the Takab Complex has been assigned to the Central Iran Zones; it seems to have more affinities to this zone from the viewpoint of stratigraphy, lithology and age data. P-T conditions of metapelitic and meta-ultramafic rocks those attributed to most orogenic belts. On the other hand, geochemical studies of metapelitic- and gneiss protoliths relate these to magmatic arc tectonic settings. All these characteristics, and the presence of paleo-suture zones and ophiolitic rocks around the high grade metamorphic rocks, suggest that an island-arc type cratonization formed the Takab Precambrian basement. This complex belonged to a greater late Neoproterozoic-early Paleozoic orogenic system that was active along the Proto-Tethyan margin of the Gondwanaland supercontinent, extending at least from its Arabian margin to the Himalayan margin of the Indian subcontinent.

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The optical core scanner DMT CoreScan3 – a tool for structural and petrographical core studies and for gathering geological information

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The optical core scanner **DMT CoreScan3** is a new tool in the Polish Geological Institute – the National Research Institute for the projects undertaken by the Geological Survey of Poland. This is the first equipment of its kind in Poland. The mobile scanner works on drill core material. Its first Polish application has been the recording and analysis of the **Bibiela PIG-2** borehole (planned depth of 1500 m), started in the Spring of 2015.

A standard procedure prior to the core analysis is the photographic recording of the primary condition of the core. A quick, partly automated registration of a high resolution image is possible with a scanner before the analyses which may interfere with the core structure. The **DMT CoreScan3** allows scanning of the cores rotated through 360° along the axis of the cylinder, resulting in a developed rock image. Recording of the cut cores and cores in boxes is also possible. The aim of the software application is the formation of a digital library of drilling core images with all parameters of the drilling. The drill core recording begins with drilling parameters (as e.g. localization, name, scanning data, geologists, etc.).

After computing, the entire core image is imported to the drilling card which can be modified in respect to the range of the conducted studies and analyses. The core images may be analyzed in terms of structural and petrographical features, both in quantitative and statistic modes, using additional software modules. The following structural parameters may be estimated based on the core images: orientation of the layering, fissures, faults and veins (in combination with a core orientation and borehole deviation), geomechanical parameters of the rock (RQD, FD, FS). Mineral phases may be distinguished, the total concentration of minerals, their percentage in the rock, the rock's porosity and its distribution, and structural features (a shape and grain size distribution) may be determined thanks to special software for petrographic analyses. The results are transferred to the borehole cards. Due to the software, these borehole description cards may be also supplied with the results of other studies (mineralogical, stratigraphical, geophysical, etc.).

All studies demand a proper choice of filters and image parameters. Thus, an operating geologist must really have experience in conducting the optical analyses. The data obtained are at ”online” access and they represent the elements for further comparisons, arrangements etc. The whole data base in the form of the “the drilling core image library” will contribute to the geological information resources of the PGI-NRI National Geological Archives.

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A multi-tool methodology of data processing for research on small amounts of extraterrestrial matter originating from multistage processes.

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Introduction

Contemporary challenges of mineralogical sciences are focused on the use of multi-tool methodologies of data collecting and data processing. The presentation aims to test the usability and credibility of the method which can be subsequently used to reconstruct the origin and evolution of phases formed in a heterogeneous environment.

Primordial geochemical signatures are frequently obscured due to multiple overlapping processes. To confirm the multiple changes in the system, research on individual phases is highly recommended. Successful definition and examination of complex mutual relationships in the major-trace element composition, including their mobility and the successful reconstruction of the origin and evolution of the system, depends on the proper choice of method of data processing and modelling.

Data acquisition and processing

This study reports the volatile concentrations in fluorapatite coexisting with merrillite from the NWA 2975 shergottite obtained by a multi-tool approach: electron microprobe and polarized synchrotron FTIR- and Raman-spectroscopy. We combined the focused ion-beam sample preparation technique with polarized synchrotron-based FTIR (Fourier Transform Infrared Spectroscopy) and Laser-Raman spectroscopy to identify structurally bound OH, F, Cl and CO_3 groups in fluorapatite from the NWA 2975 shergottite. TEM, LA ICP MS and CL studies have also been performed.

Depending on the method of apatite formula recalculation, the FTIR-based quantification of the incorporated OH, expressed as wt % H_2O, is in broad agreement with, or systematically a little less than the H_2O concentration calculated according to electron-microprobe analyses of F and Cl and mineral stoichiometry. The TEM research indicated that the recognized volatiles budget of fluorapatite is strongly related to its magmatic origin and was not altered during post-magmatic events. It also revealed the presence of a second generation of apatite. CL data point to week interaction with fluids in the marginal parts of crystals leading to a third apatite generation. Based on all the pieces of information collected using this multi-tool methodology, a geochemical model of the origin of the phosphate sequence is constructed.

Acknowledgments: The study was financed by NCN 2011/01/B/ST10/04541.

***MINERALOGIA - SPECIAL PAPERS**, 44, 2015*
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Thermal maturation determination of the Silurian black shales from the Holy Cross Mountains, Poland, using petrographical and geochemical methods

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One of the main methods used to measure the thermal maturation of sedimentary rock sequences is vitrinite reflectance (Hunt 1996). However, the method can only be applied to organic matter which occurs in sedimentary rocks younger than Upper Silurian. The reason for this limitation is related to the paucity of higher land plants before the Devonian. Measurement of the maturation of Silurian and older sedimentary rocks is however possible using macerals other than vitrinite. Zooclasts (graptolites, chitinozoans, and scolecodonts) and other organic participles (e.g., solid bitumen) have been successfully used as equivalents of vitrinite in Lower Paleozoic rocks (e.g., Poprawa 2010; Petersen et al. 2013; Suárez-Ruiz et al. 2012). Here, the complex characteristics of the thermal maturation of the Lower Silurian graptolite shales from the Holy Cross Mountains (HCM) are presented for the first time. A number of independent methods have been used to measure the thermal maturity of Silurian rocks. The main method used was vitrinite equivalent reflectance measured on graptolite rhabdosomes (Fig. 1), supported by Rock-Eval analysis and GC-MS measurement of organic compounds. For this research, 34 graptolite shales and 2 concretions from 11 boreholes and 3 outcrops were sampled. Black shales are characterized by diverse TOC values varying from 0.24-7.85%. Having calculated vitrinite equivalent reflectance using three different formulas, we propose that the most applicable values for the Silurian rocks are those based on Schmidt et al. (2015) equation:

$$\mathrm{VLR} \leq 0.75\%: \mathrm{VR_{eq}VLR} = 0.9916\mathrm{VLR} + 0.1590;$$
$$\mathrm{VLR} > 0.75\% \;\&\; \leq 1.50\%: \mathrm{VR_{eq}VLR} = 0.9046\mathrm{VLR} + 0.3786$$

Based on this formula, the values range from % 0.71 $\mathrm{VR_{eqv}VLR}$ (the vitrinite equivalent reflectance of the vitrinite-like macerals) to % 1.96 $\mathrm{VR_{eqv}VLR}$. Alternative, complementary methods including Rock Eval pyrolysis and parameters based on organic compounds (CPI, Pr/n-C_{17}, Ph/n-C_{18}, MPI1 and MDR) from extracts did not prove adequate as universal thermal maturity indicators. We have confirmed previous suggestions that Llandovery shales are the most likely Silurian source rocks for the generation of hydrocarbons in the HCM.

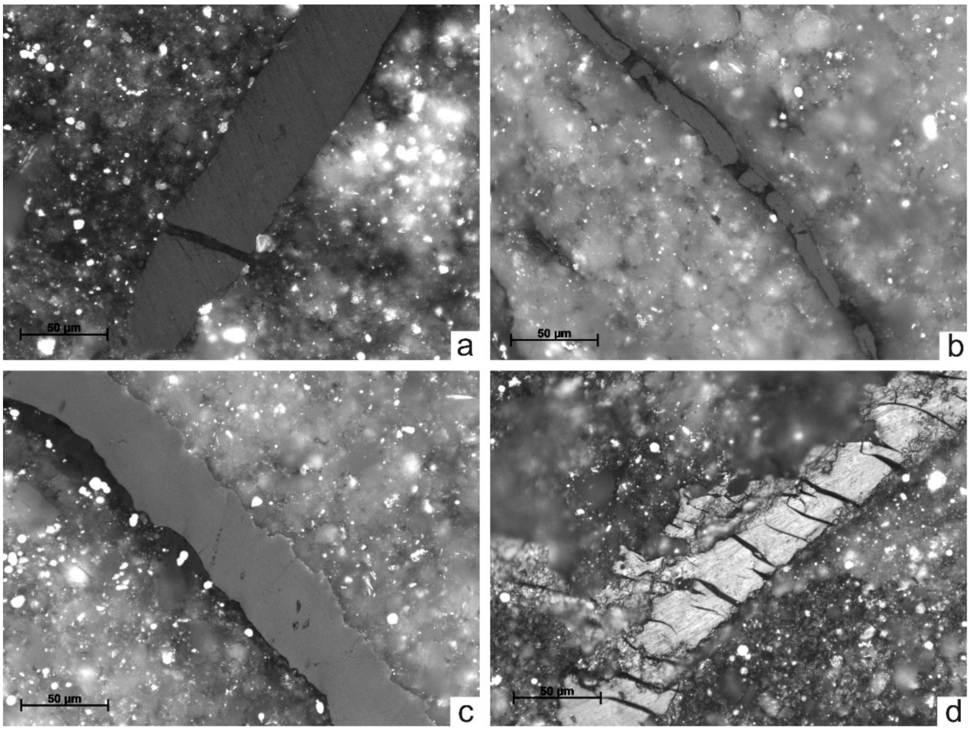

Fig. 1. Photomicrographs (white reflected light, oil immersion) of parts of graptolite rhabdosomes. Reflectance value increases gradually from (a) to (d). (a) Llandovery shale, Zbrza PIG-1, HCM, Poland (b) Wenlock shale, Zagórze IG-1, HCM, Poland (c) Wenlock shale, Kleczanów PIG-1, HCM, Poland (d) Wenlock shale, Daromin IG-1, HCM, Poland.

Acknowledgements: This work was supported by the NCN grants: 2012/07/B/ST10/04211 (to WT) and 2014/13/N/ST10/03006 (to JS). The research was supported by Wroclaw Research Centre EIT+ within the project NanoMat (POIG.01.01.02-02-002/08) financed by the European Regional Development Fund (Innovative Economy Operational Programme, 1.1.2).

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Biooxidation of chalcopyrite by new isolated *Acidithiobacillus* sp. 13Zn with mixed cultures

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Bioleaching is the extraction of metals from ores by applying living organisms. It is an alternative resource-saving and environmentally friendly method for metal recovery. Due to these characteristics, bioleaching of chalcopyrite by pure and mixed cultures of *Acidithiobacillus* sp. 13Zn, *Leptospirillum* sp. CC and *Acidithiobacillus caldus* has been investigated. The mixed cultures of newly isolated *Acidithiobacillus* sp. 13Zn, and iron oxidizing *Leptospirillum* sp. CC or sulfur oxidizing *A.caldus,* oxidize chalcopyrite more actively than a pure culture of *Acidithiobacillus* sp. 13Zn. Thus, the presence of *A.caldus* and *Leptospirillum* sp. CC in the mixed culture increases the dissolution of iron from chalcopyrite by about 1.26 and 1.14 times, respectively. The presence of chemolithotrophic bacteria, especially pure and mixed cultures, such as *Leptospirillum* sp. CC and *A.caldus*, allows enhancing of the extraction of copper from chalcopyrite by 1.32 and 1.26 times. In the bioleaching of chalcopyrite, the association of *Acidithiobacillus* sp. 13Zn with sulfur oxidizing bacteria *A.caldus* was more effective.

Pyrite (FeS_2) and chalcopyrite ($CuFeS_2$) are the most abundant and refractory sulfide minerals. The commercial application of chalcopyrite bioleaching is limited because of its slow rate. The main cause of the low dissolution rate of chalcopyrite is passivation of its mineral surface. Reaction products of bioleaching such as elemental sulfur and iron-hydroxide (jarozite) precipitate on the mineral surface and prevent its further dissolution by restricting flow of bacteria and reaction products to and from the mineral surface [5].

According to literature data, in commercial bioleaching processes the most important bacteria are iron- and sulfur-oxidizing *Acidithiobacillus ferrooxidans,* sulfur-oxidizing *Acidithiobacillus thiooxidans* or *Acidithiobacillus caldus* and iron- oxidizing *Leptospirillum* spp. bacteria [1-3]. Moreover, the dominant bacteria in the bioleaching processes operated at 45−50°C are *Leptospirillum ferriphilum* and *A. caldus* [4].

The objective of the current study is to investigate the bioleaching of chalcopyrite by a newly isolated strain *Acidithiobacillus* sp. 13Zn and its associations with other iron- and sulfur-oxidizing bacteria, as well as the influence of physicochemical factors.

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Quartz-apatite veins in metamorphic rocks of the Holy Cross Mountains

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The presence of low- and very low-grade metamorphic rocks (phyllite) in the Holy Cross Mountains was described for the first time almost a decade ago (Salwa 2006, 2009). These rocks are intensely tectonically deformed - folded and faulted and cut by numerous hydrothermal veins with different mineralogical compositions. Four dominating types include, i.e., quartz, quartz-chlorite, siderite and siderite-dolomite veins, revealing different relationships with tectonic deformations. Apatite has been detected recently in quartz and quartz-chlorite veins. Their thickness rarely exceeds 1 cm but they commonly occur in groups of closely-spaced veins. The apatite crystals show correct crystallographic shapes. Exceptionally, they reach more than 1 mm in length and 0.2 mm in thickness, but usually they are much smaller. Larger crystals are usually fractured and broken, indicating that the crystallization took place before/during tectonic deformations. Cracks in crystals are mostly filled up with quartz and chlorites. The chemical composition of the apatite is consistent with fluoroapatite. Under microscope this mineral is colorless and has a bar or needle-like habit.

The source of phosphorus for the formation of the crystals were most likely brachiopod phosphate shells dissolved in hot solutions during the tectonic deformations and associated metamorphic changes.

The occurrence of quartz-apatite veins has been reported widely in phyllite localities, suggesting that the metamorphic processes and related mineral veins extended over a much larger area.

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Mineralogical study of historic stones and mortars from the Gothic tabernacle (St. Elisabeth's Church, Wrocław, Poland)

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This study presents a mineralogical characterization of natural and artificial stones, sampled from the late Gothic church tabernacle located in St. Elisabeth's Church in Wrocław. This tabernacle was built in the 15th century in the form of a tall, slender tower. The base of the tabernacle was made of sandstone, whereas upper decorations were made of gypsum mortar – artificial plaster stone. Due to a series of fires and devastation which affected the church and its tabernacle, the object studied underwent subsequent reconstructions and renovations that have obscured its original Gothic character. The aim of our study was twofold. Firstly, to identify and fully characterize the materials used in the tabernacle. Secondly, on the basis of results, to recognize and discriminate between construction phases and to determine the provenance of the natural stone.

A total of 16 samples were analyzed, including 5 samples of rock and 11 of mortar. All materials were investigated using 1) a petrological polarizing microscope, 2) computer image analysis, 3) X-ray powder diffraction and 4) thermal analysis.

The data obtained indicates that the natural rock can be classified as quartz arenite, dominated with quartz, with accessory feldspars and lithic grains and a clay-silica (chalcedony) cement. The petrographic characteristics suggest that the lower-Silesian, Cretaceous sandstones were used as a dimension stone for erecting the tabernacle. They could be derived from deposits of the North Sudetic- or Intra Sudetic Basins. To clarify this provenance, petrographic features of investigated samples in combination with their grain-size distribution were compared with corresponding literature data (Ehling 1999). The sandstones exhibit medians in the range of 0.23-0.33 mm with the first quartile ranging from 0.12-0.24 mm and the third quartile from 0.35-0.45 mm. These data fit best to Turonian-Coniacian sandstones from the North Sudetic Basin (outcrops in Jerzmanice, and Żerkowice, Rakowiczki).

According to mineralogical data, samples of gypsum mortar are divided into three groups. The most common is gypsum mortar, without filler (1st group). Less common is gypsum mortar with abundant quartz filler (2nd group). The least common is lime mortar rich in quartz filler (3rd group). On the basis of mortar mineralogy and their relative stratigraphy observed in the tabernacle, we suppose that mortars belonging to the first group represent original Gothic material, whereas mortars from the last two groups are younger and correspond to later restorations.

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Lechówka - the first fossil iron meteorite from the K-Pg clay boundary in Poland

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Discoveries of the fossil iron meteorites are quite rare. Until now, there was only one find, the Lower Cretaceous Lake Murray meteorite, which is a IIAB iron that is well characterized.

The Lechowka Quarry is located in eastern Poland, near the Polish-Ukrainian border. The section in the quarry is c. 4.25 m deep and c. 20 m long. In the Lechowka section, eight depositional units can be identified. The Lechowka outcrop is the first complete sedimentary record of the K-Pg boundary in Poland, as was confirmed by biostratigraphy and the PGE anomaly. The highest iridium peak (9.8 ppb), the highest value in all clay from the boundary, is located c. 10 cm below the boundary clay (Racki et al. 2011). In the boundary clay from the Lechowka outcrop, the paleometeorite found was located in the bottom part of the host layer.

The boundary clay in the Lechowka section is composed mainly of smectite–nontronite and montmorillonite which occur with kaolinite, mica, silica, augite and diopside. In the lowest part of the clay, microspherules have been recorded (Brachaniec et al. 2014). They are precursors of the boundary smectites, with shapes, sizes and chemical compositions similar to spherules described from K-Pg sections worldwide.

The fragments of meteorite and meteoritic dust have a metallic-grey color and have the characteristic appearance of having been weathered to a light brown, shaly material (Fig. 1). Scanning electron microscope observations and electron-microprobe analyses reveal two different zones in the investigated meteorite. These are (1) areas with preserved, primary Ni-rich minerals (taenite, kamacite and schreibersite) that are overgrown by (2) secondary Ni-rich magnetite and Ni-rich hydroxides (goethite). No relicts of silicates (e.g., olivines, pyroxenes) or chromites were noted.

The presence of primary kamacite, taenite and schreibersite enclosed in secondary Ni-rich oxides/hydroxyloxides confirms the extra-terrestrial origin of the material studied. It appears that the meteorite from Lechowka represents a single local fall.

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BSE investigation of products formed after metallurgical-slag elution tests - a case study from the Lipówka landfill in Strzemieszyce, southern Poland

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Two samples of metallurgical slag (LSW and LST) were investigated after 11 years exposure in lysimeters. Both originate from the Katowice steelworks which is one of the biggest iron producers in Poland. The samples were collected from the Lipówka landfill in Strzemieszyce. Slags are deposited there in 1985. They cover an area of 45 hectares. The exploitation of the slags as construction aggregate started at the end of the 90's. The sample LST was taken from an excavation to the bottom of the landfill, in the eastern part of the area. This part of the landfill was created in the late 80's, so it can be assumed that the sample was laid in a block of the landfill for about 15 years. The sample LST was taken from the landfill in 2004 and then placed in a lysimeter. The second sample LSW was taken from the landfill in 2004, a few days after its deposition on the landfill. It too was placed in a lysimeter. The primary suite of minerals in both samples is limited to quartz, larnite, melilite, gehlenite, srebrodolskite, calcite and magnetite. Occasionally, wustite and α-Fe was observed in the LST sample.

Mineral products of the elution test were investigated by using scanning electron microscopy. SEM observations, including BSE images and EDS analyses obtained using a Philips XL30 ESEM/TMP equipped with an EDS (EDAX type Sapphire) detector at the Faculty of Earth Sciences, University of Silesia.

Both samples are characterized by a similar suite of minerals. The most common mineral phases are potassium- and sodium sulphate, sodium chloride (halite?) and some silicates that contain Na>K>Ca>Mg>Al. The sodium sulphate dominates over the rest of minerals. It forms needle- and platy-like aggregates where crystals are up to 150 μm long, with the aspect ratio 35:1. Halite? crystals form normal, cubic crystals up to 10 μm in size. The silicate phase occurs rarely as wide and flat crystals which are the base for the other newly forming minerals. In the studied phases, other elements including, e.g., heavy metals, and small amount of Fe and Mn were not noted.

As the result of two experiments, little elution of Fe, Mn, Al, Si and marked elution of Na, K, Ca and Mg was found in the tests when water was used as a solvent. In conclusion, the slags could contribute to the growing pH and alkalization of the environment.

Acknowledgements: This study was financially supported by National Science Centre (NCN) Grant 2014/13/B/ST10/02403 (given to AG).

_MINERALOGIA - SPECIAL PAPERS__, 44, 2014_
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Cl – bearing minerals of the mayenite supergroup from three localities: Bellerberg, Germany; Shadil – Khokh, South Ossetia; Hatrurim Formation, Israel

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The mayenite supergroup consist of two group: the mayenite group (oxides) and the wadalite group (silicates), with the general formula $X_{12}T_{14}O_{32-x}(OH)_{3x}[W_{6-3x}]$ (Galuskin et al., 2015). In this work, we focused on mineral species of the mayenite supergroup, which exhibit Cl substitution at the W site: chlorymayenite $Ca_{12}Al_{14}O_{32}[\square_4Cl_2]$, chlorkyuygenite $Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]$, wadalite $Ca_{12}Al_{10}Si_4O_{32}[Cl_6]$ and eltyubyuite $Ca_{12}Fe_{10}Si_4O_{32}[Cl_6]$. We examined samples from three localities: the calcium - silicate xenoliths from the Bellerberg volcano, Germany; the calcium – silicate xenoliths from the Shadil Khokh volcano, South Ossetia; the schorlomitite – rankinite paralava from the Hatrurim Formation, Israel. The described minerals were found with other Cl – bearing minerals such as rusinovite $Ca_{10}(Si_2O_7)_3Cl_2$, rondorfite $Ca_8Mg(SiO_4)_4Cl_2$ or "chlorellestadite" $Ca_5(SiO_4)_{1.5}(SO_4)_{1.5}Cl$.

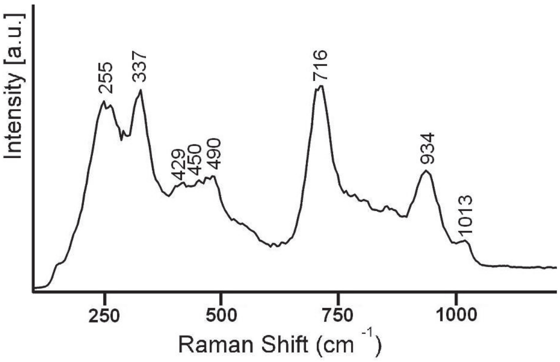

Fig. 1. Raman spectrum of wadalite from the Bellerberg volcano.

In the examined rocks, minerals of the wadalite group with variable ratios of Si:Al:Fe predominate. Minerals of the mayenite group were found rarely.

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Mineral transformations during natural weathering of fly ash after lignite combustion

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The aim of the research was to determine the mineral transformations which occur during natural weathering of fly ash after landfilling. The transformations of fly ash after lignite combustion were studied using X-ray diffraction (XRD) and scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). In order to determine mineral transformations, the following samples of fly ashes were examined: (FA1) "fresh" fly ash taken immediately after collection on electrostatic precipitator, (FA2) "fresh" fly ash transported in a water suspension and deposited in landfill, and (FA3) fly ash after four-year on a landfill. The pH of the samples was around 14 (FA1 and FA2), and 12.7 (FA3).

Based on powder XRD studies it was found that sample FA1 consists of quartz, anhydrite, lime, as well as traces of hematite, magnetite, K-feldspar, and calcite. Sample FA2 contains quartz as a predominant mineral. Moreover, ettringite, bassanite, vaterite, small amounts of portlandite, as well as traces of calcite and magnetite were found in sample FA2. The mineral composition of sample FA3 was similar to that of FA2. The main differences between the two were that portlandite was not found in sample FA3 and that there were relatively higher amounts of bassanite and vaterite in sample FA3.

The results indicate that the most evident mineral transformations taking place during the weathering of the fly ash studied concern Ca-bearing phases and sulphate minerals.

Lime CaO which is present in "fresh" fly ash, changes into portlandite $Ca(OH)_2$ after mixing with water and subsequent precipitation. Moreover, vaterite (a hexagonal polymorph of $CaCO_3$) is formed after taking CO_2 from the atmosphere and precipitation after drying the water suspension. As the weathering advances, portlandite disappears (dissolves or transforms into another Ca-bearing phase) and vaterite still remains.

Anhydrite $CaSO_4$ occurring in "fresh" fly ash transforms into secondary sulphates after mixing with water and subsequent precipitation form water suspension. The most abundant sulphates in weathered fly ash are ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$ and bassanite $CaSO_4\cdot 0.5(H_2O)$. These minerals are still present in fly ash after four-years of weathering.

Acknowledgments: The research was funded by the Polish National Science Centre (decision no. DEC-2011/03/D/ST10/04599).

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Bioleaching of pyrite by pure- and mixed cultures of chemolithothrophic bacteria

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The iron oxidizing chemolithotrophic bacterium *Leptospirillum ferrooxidans* for the first time was isolated and described in Armenia. Similar vibrioid microorganisms were then detected in uranium ores, acid drainage of copper ores, and acidic hydrothermal springs. Further, in spite of their inability to oxidize sulphur or its reduced compounds, it was revealed that *Leptospirillum* spp. bacteria assist in the oxidation of pyrite. Two strains of *Leptospirillum* spp. bacteria have been isolated from dumps of the Tandzut and Akhtala polymetallic ore deposits in Armenia. The optimum temperature for the growth of isolated strains was 37°C and 40°C respectively. The pH optimum was 1.7-2.0. The sulfide mineral oxidation ability of isolated strains was assessed by studying their affinity to pyrite. It was revealed that both strains indicate high a affinity to pyrite. However, their growth together with sulfur oxidizing *Acidithiobacillus albertensis* SO-2 (KP455986) significantly enhances the efficiency of pyrite bioleaching. It is believed that bioleaching of pyrite by *Leptospirillum* spp. bacteria occurs by means of indirect contact leaching.

The chemolithotrophic bacterium *L.ferrooxidans* capable of ferrous iron oxidation for the first time was isolated and described by Markosyan [4]. At present, the genus *Leptospirillum* includes: *Leptospirillum ferrooxidans* (Group II I group), *Leptospirillu ferriphilum,* "*Leptospirillum rubarum*" (Group II) and "*Leptospirillum ferrodiazotrophum*" (Group III). Bacteria of the genus *Leptospirillum* are Gram negative acidophilic motile vibrios which fix carbon dioxide using the energy of oxidation of Fe (II) ion [1, 3, 4, 7].

Recently, scientists have emphasized the importance of bacteria of the genus *Leptospirillum* and their mixed cultures with other bacteria in the biooxidation and bioleaching processes at temperatures above 40°C [2, 5-7].

Currently, it is considered that bacterial leaching of sulfide minerals mostly takes place by an indirect "contact" mechanism. According to this mechanism the oxidation of minerals is implemented by Fe (III) ions complexed with extracellular polymeric substances: $MS + 2Fe^{3+} \longrightarrow M^{2+} + S^{\circ} + 2Fe^{2+}$

The aim of the work was to study the main biological properties of isolated *Leptospirillum* spp. bacteria and their sulfide mineral oxidizing activity with reference to enhancing the efficiency of pyrite biooxidation and bioleaching processes.

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Katowice – Wełnowiec slags: from the furnace to the dump

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In the Katowice - Wełnowiec zinc smelter during the entire period of its operation, primitive smelting process called the "Silesian Method" was used. In this method, the ore-bearing dolomite with the addition of silica sand and coal was loaded with a shovel to the horizontal muffles building furnace. In the furnace, ore was melted with additions and zinc was vaporized. Zinc was collected in the clay condensers and molded into bars. Melting of the batch took place at a temperature of at least 930°C (total reduction of ZnO by carbon) however, for efficiency of the process, temperature might exceed 1000°C. Waste melt was removed manually and then transported to the landfill, where it was poured continuously in layers. Tested slag started crystallization right after leaving the furnace, but continuous melt load isolated the lowermost layers from rapid cooling.

Pyrometallurgical slag from Katowice - Wełnowiec, as in other Polish locations, consists of oxides (spinels, hematite), silicates (olivine, monticellite, zincite), silicates (pyroxene, melilite, feldspar, feldspathoid), sulphides (MnS-ZnS-FeS solid solution, pyrrhotite, galena) and apatite. Geothermometry was applied to determine the temperature during crystallization of the initial phases formed. The results are within the range of 1141 - 1353ºC. As the result of the continuous loading of the melt, multi-stage crystallization took place. It is reflected in petrographic images of the slags. Three zones can be distinguished: regular slag, a miarolitic zone with melilite and pyroxene crystals up to a few centimeters and a boundary zone between the last two. Not only do they differ in phase composition and morphology, but also in chemistry. It was determined that element migration took place during melt crystallization, enhanced by fluid presence. The unusual miarolitic segregations originated from volatile-rich (CO_2-dominated) residual melt by fractional crystallization, causing zinc-, fluorine- and phosphorus concentration in the last phases to crystallize. Local disequilibrium growth was imprinted in sector zoning of the pyroxenes, while the rapid changes in oxygen fugacity are marked by the presence of hematite, and Mn^{4+} substitutions in spinels.

Acknowledgements: This study was supported by NCN grant No. 2014/13/B/ST10/02403 given to Aleksandra Gawęda and scholarship for young researchers: restoration of the historic smelting process at zinc smelter Katowice - Szopienice on the basis of petrographic and geochemical data.

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Metallurgical slags from the “Trzebinia” smelting plant, Poland

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Slag samples were collected from the Trzebinia waste-dump, which is a remnant of the “Trzebinia” smelting plant, active from 1890 to 1965. A characteristic feature of the slags is the presence of dark-green and yellow patches, differing in phase composition.

When compared to the other slags described (e.g., by Puziewicz et al. 2007; Warchulski et al. 2015) with melilite as a main component, in the Trzebinia slags, feldspars predominate (up to 45 wt%). The first generation of feldspars is depleted in Pb and range from $Or_{1-7}Ab_{4-25}An_{96-67}$ to $Or_{83-73}Cs_{4-13}Ab_{11-9}An_{1-5}$. The second generation of feldspars forms granophyric intergrowths with quartz and is probably a product of crystallisation from the (Pb, Ba, Si, Al)-enriched melt in a following sequence: $Or_{\sim 2}pfsp_{7-14}Ab_{10-15}An_{80-69}$, $Or_{43-30}Cs_{5-43}pfsp_{29-7}Ab_{\sim 15}An_{\sim 5} \Rightarrow Or_{26-19}Cs_{5}pfsp_{37-57}zfsp_{\sim 3}Ab_{\sim 16}An_{17-8}$ (*pfsp*-$PbAl_2Si_2O_8$, *zfsp*-$CaZnSi_3O_8$). The Pb-rich alkali feldspars intergrown with plumalsite ($Pb_4Al_2Si_7O_{21}$), are replaced by Ca-Pb arsenates.

The second important slag components are pyroxenes. Pyroxene–rich areas of the slag are yellow in colour. Essenite-rich subsilicic diopside varying in the range of $Di_{51-65}Es_{42-31}$ are typical here. Silica-rich dark slag portions contain two-pyroxene assemblages: $Di_{65-13}Hd_{24-79}Es_{9-11}$, and the zincian pigeonites from intermediate to ferrous types ($En_{51-26}Fs_{35-64}Pe_{13-10}$). In the Ca-variety, the Pe (*petedunnite*) molecule is below 2.0 mol.%.

Two types of spinels (2-15 wt%) with a general formula $(Zn,Mg,Fe^{2+},Mn)(Fe^{3+},Al,Ti)_2O_4$ were found. The ferrite spinel chemistry corresponds to a complex solid solution of franklinite, gahnite, and magnesioferrite to magnetite ($Frk_{59-15}Mfr_{27-77}Spl_{12-5} \Rightarrow Frk_{25-15}Ghn_{10-8}Usp_{29-25}Mag_{35-50} \Rightarrow Ghn_{9-1}Usp_{14-2}Mag_{74-95}$). The aluminium rich spinel belongs to the hercynite-spinel and magnetite families ($Sp_{35-20}Hc_{43-5}Mag_{22-14}$). The mole fraction of the jacobsite end-member in all spinels does not exceed 4 mol.%.

Olivine is a minor component of the examined slags (up 5 wt%), sometimes forming monomineralic, mm-scale domains. Olivine is fayalitic in composition ($Fo_{3-24}Fa_{72-93}$), enriched in Zn (up to 7 mol% of $Zn_2[SiO_4]$), while La (*Larnite*) and Tp (*Tephroite*) never exceeds 1.5 mol.%. Willemite is characterized by a high iron content ($Wlm_{69-57}Fa_{25-43}Fo_{\sim 5}$).

Embedded angular fragments (remnants of the furnace lining), consist of mullite and quartz, and commonly exhibit partial melting. Possibly melting of these fragments and new melt assimilation caused the contamination of the slag-melt that resulted in its enormous silica enrichment. Patchy texture, however, suggests restricted elements mobility. Zn is concentrated in silica-poor melt portions, and Pb tends to concentrate in high silica (granophyric) melt batches.

Acknowledgements: This study was financially supported by the NCN grant 2014/13/B/ST10/02403 given to AG.

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Textural evidence for liquid immiscibility in a diabase sill from Zalesie, the Bardo syncline (the Kielce region) in the Holy Cross Mts

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In the area of the Holy Cross Mts, igneous rocks appear in the Kielce and the Łysogóry regions. In the Bardo syncline (the Kielce region), diabases were examined at the Bardo, Kędziorka, Widełki, Zbelutka, Zagórze and Zalesie localities. The thin (≤ 16 m) sill near Zalesie village (Kardymowicz 1957) shows the smallest grain size when compared to the others. Samples from its central parts comprise ophitic clusters of plagioclase and pyroxene as well as an abundance of mesostasis material (25-35%). Plagioclase laths and pyroxene grains with glassy inclusions (*sieve texture*) are also present. The mesostasis contains, as main phases, spiky ("swallow-tail"), skeletal and branching plagioclase ($Or_{3-6}Ab_{61-76}An_{20-36}$, ≤ 2.0 wt% FeO) and skeletal pyroxene ($Wo_{20-30}En_{20-30}Fs_{40-60}$) that, in some cases, have grown in clustered, fan-like aggregates. In addition, the quenched mesostasis contains skeletal Fe–Ti oxides, acicular microlites of apatite and patches of residual glass very often replaced by saponite. According to Philpotts (1982) the most striking feature of rocks exhibiting immiscibility is the presence skeletal magnetite. The amount of immiscible glassy mesostasis falls where magnetite forms equant grains in the more oxidized melts with their earlier crystallization. In the Zalesie sill, the mesostasis contains, in addition to the minerals mentioned above, also contains Fe-Ti-P-rich glassy (an. 1, 2; see the Table below) and crystallized globules in a silica-rich (rhyolitic) homogeneous glassy host (an. 3). The iron-rich spherical glassy globules tend to be attached to plagioclase surfaces while the crystallized globules, showing high variability in their texture and composition, are disseminated within the felsic glass. During subsolidus re-equilibration, they can be unmixed to silicate (Fe-clinopyroxene) and Fe–Ti–P-rich phases (apatite, magnetite). Thus the origin of Fe–Ti–P-rich globules, and of felsic glass of the mesostasis, is consistent with the evolution of a late interstitial melt under disequilibrium conditions promoted by rapid cooling of the lavas at low oxygen fugacity.

An. No	**SiO_2**	**TiO_2**	**Al_2O_3**	**FeO**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**	**Total**	
an. 1	19.46	7.58	4.35	16.97	0.44	1.08	27.63	0.27	0.36	20.97	99.11	
an. 2	29.25	14.78	6.14	47.26	0.29	0.02	1.15	0.41	0.64	0.59	100.53	
an. 3	67.92	0.68	14.12	2.34	0.06	0.08	2.44	2.90	2.82	0.50	93.86	
	Q	C	Or	Ab	An	Hy	Ol	Il	Ap	Total		
an. 1	6.06	3.50	2.13	2.28	0.05	22.04	0.00	14.39	48.73	99.19		CIPW Norm
an. 2	0.00	4.09	3.78	3.47	1.85	40.72	17.17	28.07	1.37	100.53		
an. 3	34.83	3.06	16.67	24.54	8.84	3.48	0.00	1.29	1.16	93.86		

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On the Wądroże Wielkie quartz rock mineralization (Sudetes)

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The Wądroże Wielkie granite-gneisses with accompanying quartz veins represent a part of the Kaczawa metamorphic unit and are localized in the Fore-Sudetic Block. The age of the granite-gneisses is 548±9 Ma, while the origin of the quartz veins is referred to the Herzynian orogenesis. The quartz rock is hydrothermal - metasomatic and connected with fault zones. The rock displays heterocrystalline-, hipautomorphic-, locally cataclastic structure, and a random porous texture. The results of the metasomatic alteration of the rock may be often observed in the form of the quartz erasing the earlier features of the rock. Relics of older quartz crystals in the younger quartz are characteristic. The quartz is the main rock component. Aggregates of kaolinite, sericite, Fe - hydroxides, Ti minerals and, locally, pyrite are relatively abundant. In some places, the chalcopyrite occurs in association with pyrite. This mineralization is accompanied by secondary Fe (mainly goethite) and Cu (koveline and chalkosite) minerals. Impregnations of small calcite rhombohedrons and fine irregular aggregates are relatively common. The calcite fills in some cavities, in the association with goethite. Small amounts of zircon, rarely with pyrite, may be noticed. Inclusions of titanium minerals (rutile, possible anatase and titanite) are present. The kaolinite, chlorite and illite fill in empty spaces and cavities. The kaolinite mostly forms impregnations. Less commonly, it occurs as fine-grained schliers in association with the Ti and Fe mineralization. Generally, a lot of minerals are present in the rocks whose origin is unrelated to hydrothermal-weathering activity.

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Mineralogical study of sediments in the vicinity of the impact crater in the Morasko Meteorite Reserve

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In the area of the meteorite Morasko there are several craters. The deposits forming the edge of the biggest crater are glacial tills under which, at different depths, there are fine-clastic deposits, whose age was determined as Miocene-Pliocene (so called Poznań clays). These deposits in the study area are located on the surface. In some cases they are covered likely due to glacitectonic processes. Both on tills and clays, thin soils have developed; in the study area they are overgrown by Querco-Fagetea forest. In places, they include clay inserts, lenses and fine silt clasts of the substratum. In places, also, they are intercalated by black or gray organic material with fine and coarse mineral grains and rocks fragments.

About 5,000 years ago, a meteorite hit the soft till-sandy deposits and left traces in the morphology. The main objectives of the mineralogical studies are to (1) investigate the minerals in the clay fraction of the sediments around the craters, (2) see whether mineralogical studies indicate impact phenomena and (3) see whether weathering processes affect the composition of clay fraction.

The methodology involves the measurement of pH and macroscopic descriptions of deposits. Laboratory tests of the clay fraction prepared from the sediments, using the X-ray method, allowed determining the mineral composition of the tiniest fraction (< 2 microns). The method used was that of Jackson (1959), according to which the samples were tested in three stages: in an air-dry state, treated with ethylene glycol and roasted at a temperature of 550 degrees C. In addition, polished thin sheets were subjected to microscopic observation in reflected light. Two profiles of sediments were examined of a thickness of 180 and 220 cm situated close to the largest crater. Samples were taken every 20 cm.

The studied deposits show low pH diversity in the range 5.5-5.9. The colour of the sediment varies in the profiles from grey-black on the surface to yellow-grey to greyish brown. The clayey deposits also show variable colouring from grey-black (from the presence of organic matter) to reddish yellow (from the presence of goethite) to spotted red-greenish. The red colour is due to the presence of hematite. Lenses and clayey clasts in tills are greenish-grey, with no evidence of the presence of iron oxides and hydroxides. Deposits are inlaid with Fe and Mn hydroxides and, in some places, contain carbonate concretions which reflect soil processes. All the profiles have fragments of contemporary roots.

Microscopic analyses show a relatively small mineralogical variability of the clay fraction. In each of the studied profiles, clay minerals found in tills include kaolinite, illite and smectite minerals, with a touch of mixed-layer phases like smectite/illite. The surface samples also contain admixture of minerals of vermiculite structure, or of mixed-layer type minerals (vermiculite/smectite or vermiculite/illite). The vermiculite minerals of the surface samples indicate partial collapse due to temperature increase to 550 degrees C. The smectite minerals show swelling, which results in movement of the basal reflections from approx. 14 A to approx. 17 A after glycol. Kaolinite and illite reflections do not displace after glycol while, after roasting, illite reflections remain constant and the kaolinite structure collapses, resulting in the loss of kaolinite reflections.

In the Poznań clays, the composition of the sediments is well known. It is dominated by smectite minerals, with varying participation of illite and kaolinite. In a few samples collected at the surface, there are admixtures of mixed-layered minerals of the illite/smectite type. None of the tested samples revealed evidence of vermiculite, but quartz occurs as an admixture in every tested sample.

Microscopic observations have shown microclasts that consist of both till and clay. Tills are composed of petty-clastic quartz skeleton, with a minor contribution of alkali feldspar, plagioclase, pyroxene and amphibole that are "embedded" in the finer clay matrix. They are yellow-brown in colour. Other clasts found on the microscale are homogeneous clasts of green colour which are observed in microscopic images. They do not correspond to any of the optical characteristics of clay minerals identified by X-ray. It seems that they may be clay minerals affected by the impact which were originally Poznań clay clasts in glacial tills.

The investigated deposits show a variation in the vertical profile in terms of colour and composition of clay minerals. The colour results from the presence of organic matter, and iron oxides or hydroxides. In the surface samples, the presence of vermiculite was recorded, which does not appear in the sediments deeper than 40 cm. The tills have a different mineral composition (vermiculite-like, smectite, illite, kaolinite) to the Poznań clays (smectite-like, illite/smectite, kaolinite, illite). The impact could have resulted in clay clasts of grassy-green colour and so far unidentified mineral composition. Weathering processes (soil) lead to changes in the colour to reddish-yellow and reddish, and probably also to development of the vermiculite-like minerals.

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Mineralization of Emsian corals as a result of hydrothermal processes in the Bukowa Góra Formation - preliminary results

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The Bukowa Góra quarry is located in the NW part of the Łysogóry Block of the Holy Cross Mountains. The lower part of the Bukowa Góra section belongs to the middle and upper part of the Zagórze Formation. The upper part of the section comprises sediments of the Grzegorzowice Formation with three units: Bukowa Góra, Kapkazy and Zachełmie Members. The dark claystones of the Bukowa Góra Member (BGM) contains abundant fossil fauna represented by corals of the order Rugosa and Tabulata, brachiopods, crinoids, trilobites and bryozoans.

In this study, 20 specimens of corals containing a cavity in the central part of the skeleton were analyzed by means of Environmental Scanning Electron Microscope (ESEM) and powder diffraction (XRD). The recognized minerals are: quartz, feldspars (plagioclase), dolomite, siderite, pyrite, gypsum, chlorite, kaolinite and minerals of the illite-smectite group.

The primary low-Mg of the coral skeleton was completely replaced by dolomite, what is surprising in the light of apparently good preservation of originally calcitic dissepiments, septa, and other skeletal elements of the corals.

Hydrothermal minerals represented by a silicia-carbonate-sulfide system partially filled the cavities in the form of automorphic crystals. Large (< 1 cm) quartz crystals are often covered with a thin coating of Fe, Mn-rich oxides/hydroxyloxides. Carbonates (< 0.5 cm) are common. The crystallization process occurred in the Ca-Mg-Fe-Mn system. The calcite group is represented by Mg-calcite and siderite with Ca, Mg and Mn admixture in the lattice. The dolomite group is represented by ankerite with varying iron content and minor Mn substitution in the structure. The most common sulfide minerals are pyrite and chalcopyrite. Sphalerite crystals occur rarely. In the studied coral cavities, no Pb sulfides were found though the presence of galena is possible due to the high content of lead in some secondary minerals of, probably, the hollandite supergroup.

Based on the preliminary analyzes and mineralogical observations, a model of diagenetic processes during the geological history of the BGM is proposed. According to, e.g., Grabowski et al. (2006), dolomitization of the calcium carbonate, including corals in the BGM, was associated with burial and increased geothermal flux as a result of tectonic activity in the Holy Cross Dislocation Zone.

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Rare organic minerals on self-heating coal waste dumps - the Wełnowiec case

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Coal wastes in dumps may undergo self-heating that alters both organic- and mineral phases. The resulting decomposition of organic matter releases gases and liquids similar to those deriving from combustion (free access of O_2) or pyrolysis/coking (depleted O_2). Mineral efflorescences commonly bloom in active vents on dump surfaces. Mineral phases include native S, sal ammoniac, and, less often, Ca-, NH_4-, Fe-, Al-, K- sulphates. Among these, rare organic minerals such as hoelite (9,10-antra-quinone, $(C_6H_4)_2(CO)_2$), kladnoite (phthalimide, $(C_6H_4)(CO)_2NH$), kratochvilite (fluorene $(C_6H_4)_2CH_2)$), and ravatite (phenanthrene, $C_{14}H_{10}$) can occur (Žáček, Ondruš 1998; Jehlicka et al. 2007).

For this study, 16 samples of efflorescences from the Wełnowiec dump (Katowice) were collected. Their DCM extracts were analyzed on a GC-MS chromatograph (Agilent Techn.) with a DB-35 column. Chemical compositions and habits were detected using SEM-EDS and mineral phases by XRD.

The Wełnowiec organic efflorescences vary in their phases, amounts and compositions. Despite the fact that organic minerals occur together in and around active vents, their origins and formation mechanisms are different. Kratochvilite, hoelite, and ravatite come directly from coal-waste organic matter and occur in bitumen. During self-heating, they evaporate and precipitate, accumulating where temperatures are sufficiently low. Kladnoite, together with other organic compounds (benzamide, benzoic acid, phthalic anhydride) is synthesised within the dump as such reactive compounds that do not occur in fossil organic matter. Phthalic anhydride forms as a result of phthalic acid dehydrogenation which is followed by ammonia substitution giving phthalimide (kladnoite) – a multi-stage manner of formation that serves to exemplify the complex conditions within self-heating dumps.

Acknowledgements: This research was supported by the Polish National Scientific Centre (NCN grant No 2013/11/B/ST10/04960).

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Types of bituminous products formed during the self-heating of coal wastes - the role of prior weathering

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Coal waste dumps are the sites of several on-going processes such as the oxidation of organic matter which may lead to self-heating and self-combustion, and the weathering and leaching of self-heating products and of heavy metals. All of these processes can lead to significant environmental problems. The various processes do not act separately. The final features of coal wastes stored for many years are the result of the combination of all (Misz-Kennan, Fabiańska 2011).

The aim of this research is to recognize any relationship between prolonged weathering/oxidation of coal wastes and self-heating products. Coal waste samples were taken from the Słupiec, Przygórze, Okrzeszyn, and Piast dumps in Lower Silesia. Their DCM extracts were analyzed on a gas chromatograph with a DB-35 column coupled with a mass spectrometer (Agilent Techn.). Maceral composition was assessed by reflective light microscopy.

Significant differences in the chemical composition of self-heating products that relate to the absence/presence of coal-waste weathering prior to self-heating are revealed. Coal wastes which were self-heated as fresh unweathered rocks contain a wide range of geochemical markers and pyrolytical substances. The dominating compounds are either *n*-alkanes with the Gaussian-type distribution or aromatic hydrocarbons: PAHs and their alkyl derivatives. Biomarkers (e.g., pentacyclic triterpanes and steranes) are present and their distributions are easily recognized. The composition of bitumen in coal wastes subjected to self-heating after their weathering is distinctively different. Oxygen derivatives, e.g., aliphatic- and aromatic ketones and aldehydes dominate in such samples together with phenolic compounds and S_8. They form a large "hump" of unresolved compounds in the chromatogram baseline. Aromatic hydrocarbons are still present but their oxygenation products are also found. Moreover, extraction yields are often much higher in the case of coal wastes weathered prior to self-heating, possibly due to the decomposition of the organic matter macromolecule. Pre-heating weathering clearly promotes the formation of a wide range of substances potentially hazardous to the environment, and their greater abundance.

Acknowledgements: This research was supported by the Polish National Scientific Centre (NCN grant No 2011/03/B/ST10/06331).

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Characterizing microstructure and porosity in shales of the Sasin, Pasłęk and Pelplin Formations from the Baltic Basin

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Understanding of factors controlling permeability in gas-bearing shales is important to the building of any reliable reservoir models. Therefore, knowledge of porosity, pore-size distribution, total organic carbon (TOC) content, the mineralogy of shales and their microstructure are critical to understanding mechanisms for porosity development. We analyzed porosity, TOC and mineral composition for 10 samples from the Sasin, Pasłęk and Pelplin Formations from the Baltic Basin. Assessment of porosity was determined using KIP and WIP methods and compared with results of image analysis of scanning electron microscope (SEM) images performed for selected samples using the BSE technique. Moreover, detailed microstructure of a selected sample has been investigated using a combination of focused ion beam (FIB) milling and scanning electron microscopy (SEM).

There is no linear correlation between porosity and TOC or any one mineral, indicating a more complicated distribution of porosity for the investigated set of samples. The SEM technique shows pores in the size range of 10 nm to more than 1 000 nm. Interestingly, porosity calculated based on image analysis is considerably smaller than that based on KIP and WIP methods. This presumably demonstrates that most pores are smaller than the resolution of SEM imaging system, which accounts for the systematic underestimation of total porosity in SEM images. Backscattered electron (BSE) images of FIB cross sectioned shale surfaces show a complex microstructure. Energy dispersive spectroscopy of the shale cross sections indicates that clay, quartz, carbonate, pyrite, and kerogen are the most prevalent components. Pores are observed in both the kerogen and inorganic matrix. By using FIB milling and SEM imaging sequentially and repetitively, three-dimensional data sets of SEM images have been generated for a selected sample. This enabled reconstruction of the three-dimensional volume of the investigated shale sample and allowed for estimation of kerogen, inorganic matrix and pore volume percentages of the reconstructed shale volume.

Scanning electron microscopy images and 3D reconstruction document that the investigated shales show quite complex microstructure and are characterized by mixed-pore networks.

Acknowledgments: the study was supported from grant SHALESEQ (No PL12-0109): “Physicochemical effects of CO_2 sequestration in the Pomeranian gas bearing shales” funded by the National Centre for Research and Development.

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Stop 1. Krzemionki Opatowskie flint mine

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The prehistoric flint mine of Krzemionki Opatowskie is one of the most important historic sites in Poland, and one of the most spectacular Neolithic monuments in Central Europe. Krzemionki Opatowskie is located in the north eastern foreland of the Holy Cross Mountains within the Skarbka Oolitic Limestone unit of late Oxfordian age (Gutowski 1998). Flints occur within oolitic limestones (Fig. 1). Sedimentary structures point to an extreme shallow-water and tidal-flat environment. Flint horizons have fixed stratigraphic positions (Pieńkowski, Gutowski 2004). There are two morphological varieties of flint: striped and chocolate. The origin of this flint types is undoubtedly related to the early diagenetic stage of silica precipitation released earlier in the process of clay minerals decomposition. Decomposition takes place in a small depth, maximum several meters below the bottom surface (Pieńkowski, Gutowski 2004).The crucial role in the penetration of these solutions into bottom sediments, as well as in the formation of siliceous concretions, was played by the presence of silica precipitation centers in the form of burrows created in the sediment by various animals, but in this case primarily by decapods (Pieńkowski, Gutowski 2004).

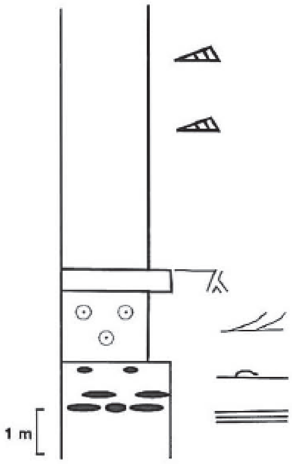

Fig. 1. Upper Oxfordian profile in Krzemionki Opatowskie flint mine (after Pieńkowski, Gutowski 2004).

In 1922, the geologist Jan Samsonowicz discovered an excellently preserved Neolithic mining field at Krzemionki Opatowskie, which ultimately proved to be the most important relic of prehistoric cultural heritage in Central Europe. Nowadays, we know of more than 20 prehistoric flint mine sites in Poland (Lech 2013). Mines had been active between about 3900 and 1600 years BC, according to radiocarbon dating (Doktor 2012). Striped flint was exploited in Krzemionki Opatowskie using various methods, the simplest being the sinking of regular pits about 2 m deep (Lech 2013). The unique historical value of Krzemionki Opatowskie lies in the application of the most sophisticated Neolithic mining techniques. Shafts were dug through the Pleistocene formations and sunk through the limestone layers beneath. When the flint-bearing level was reached, low galleries about 60-90 cm in height were cut from the shaft base, usually at a depth of about 5 to 8 m (Lech 2013). The hard limestone enabled the rich flint seams to be followed by means of galleries expanding into low underground chambers. The subterranean workings could reach a distance of 20 m from the shaft bottom and cover an area of several hundred square metres. The chambers were filled with heaps of limestone rubble between which narrow passages were left to allow movement in and out of the workings. In the galleries were preserved some simple pictograms drawn on the walls using charcoal from torches. The most outstanding of these is the so-called “orante”, a praying figure named from the Latin orare, to pray. Its meaning today is unclear, but it is likely that the image was connected with the religious beliefs of the Neolithic miners. The underground chambers of Krzemionki Opatowskie represent the most advanced form of flint mining in prehistoric Europe (Lech 2013). The hardness of the limestone enabled these to be hollowed out in order to excavate the maximum amount of precious rock, for which there was a high demand. Their structure is a monument to the high level of technology employed in the European Neolithic. The miners came to Krzemionki from nearby villages. They worked with picks of flint, stone and antler as well as hammers and levers. Wood and animal hide were also used in the making of mining tools. Striped flint acquired from Krzemionki Opatowskie was mainly used for making axe heads. These were the end product of workshops (Lech 2013).

Tourists first came to see the mines in the late 1950s after Tadeusz Żurowski cleared the underground parts in the vicinity of Shafts 1, 2 and 3. The idea for a subterranean gallery that would allow tourists to walk comfortably instead of crawling through narrow pits dates to 25 years later. Excavations conducted by the State Archaeological Museum in Warsaw in the late 1970s and in the 1980s led to the execution of the first short section of such an underground tunnel running around Shafts 1,2 and 3. The first tourist route was opened in 1985 (www.krzemionki.pl).

The tourist route in its present form is 465 m long, descending 11.5 m at the deepest point. It provides for an organized sightseeing of excellently preserved prehistoric mines of banded flint and introduces visitors to the geology of the region. Moreover, it shows how the prehistoric mines were protected and preserved in the past half a century. The underground tourist route in Krzemionki is a unique world example of such a monument that is open on a regular basis to visitors (www.krzemionki.pl).

Stop 2. Lower and upper Gromadzice section from the Holy Cross Mountains

Introduction

The early Jurassic is a time of mainly terrigenous, but occasionally also marginal-marine and marine sedimentation in a large epeiric basin extending across Poland.

Maximum thicknesses of these sediments reach up to 1400 m. Sedimentation in that shallow basin (less than 10-20 m deep), was especially sensitive to sea level changes (Pieńkowski 2004). The Hettangian deposit in the Holy Cross Mountains is divided into three formations: the Zagaje Formation, Skłoby Formation and Przysucha ore-bearing Formation (Pieńkowski 2004). Sediments of all Hettangian Formations consist of quartz and clay minerals (mainly kaolinite and illite), usually with siderite and/or goethite, and are characterized by the lack of carbonates (Brański 2008).

The two sections in Gromadzice village belongs to two Lower Jurassic, Hettangian Formations: Zagaje (lower section) and Skłoby (upper section). For general picture of the outcrops see Fig. 2.

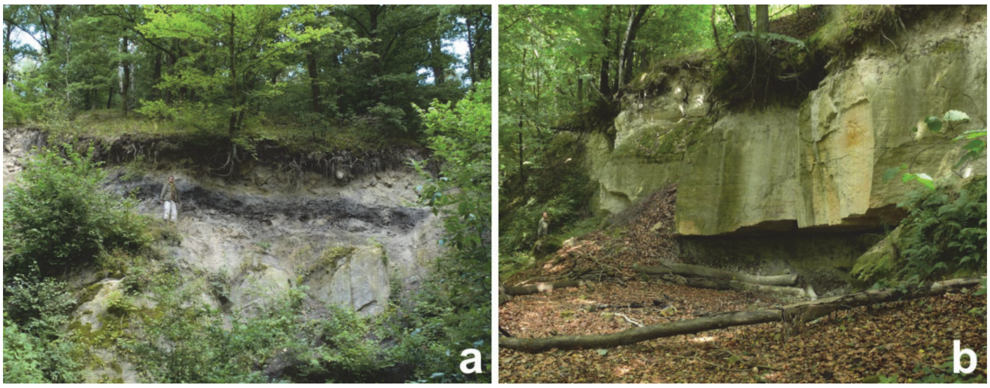

Fig. 2. General view of the lower (a) and upper (b) Gromadzice sections.

Lithology description

Zagaje Formation. The sedimentary rocks of the Zagaje Formation consist of conglomerates, passing upwards into sandstone/conglomerate lithofacies. These sedimentary systems represent alluvial fan and braided river deposition (Pieńkowski 2004). Higher up, the section is dominated by sandy-muddy rocks of a meandering-anastomosing river depositional system which change into mudstone/claystone lithofacies with palaeosols (Pieńkowski 2004).

Skłoby Formation. The Skłoby Formation in the Holy Cross Mountains is composed of diverse deltaic successions. Two basic types of deltas have been distinguished in the Early Jurassic deposits of Poland: wave-dominated (or mixed wave-fluvial) deltas in the upper Gromadzice outcrop and fluvial-dominated (birds-foot) deltas in the nearby Podole outcrop (Zatoń et al. 2009).

The cycle pattern of sedimentation of the upper Gromadzice is repeated, starting from course grained sandstones through mudstones with root tracers and ending with organic-rich, charcoal-bearing black shales (up to 25 % TOC), wrongly named as coals.

Interesting issues related to the Gromadzice sections

Dinozaur footprints. In the Gromadzice sections, footprints of predatory dinozaurs has been found, including *Kayentapus* and *Moyenisauropus natator* Ellenberger (Gierliński et al. 2001). In addition, footprints of young sauropods have also been identified and described (Gierliński 1997).

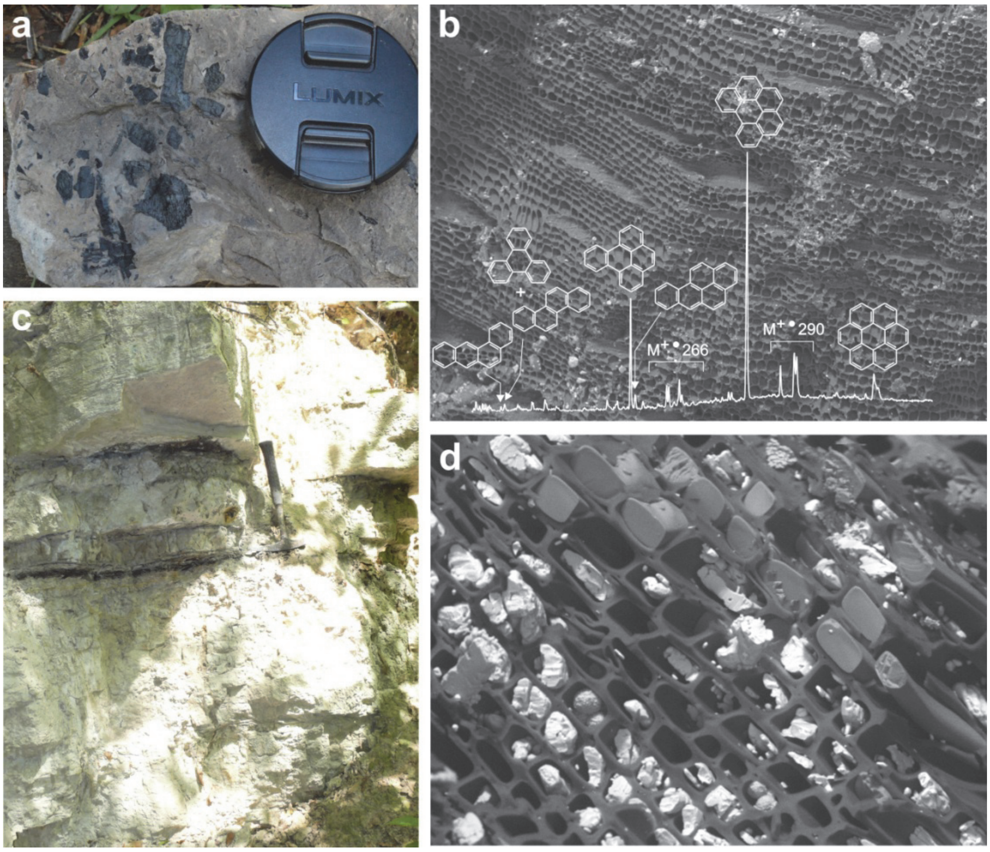

Fig. 3. (a) Macroscopically identifiable charcoals from the lower Gromadzice section. (b) SEM picture of a well preserved charcoal fragment and a TIC chromatogram of upper Gromadzice charcoal-bearing shale showing a high concentration of high-molecular-weight PAHs. (c) Part of the upper Gromadzice section with black charcoal-bearing shales intercalations. (d) Partially mineralized charcoal fragment.

Wildfire evidence. At both sections, charcoals and elevated concentration of polycyclic aromatic hydrocarbons (PAHs) have been identified and characterized (Fig. 3), showing evidence of wildfire activity during the Hettangian (Marynowski, Simoneit 2009). This was the first description of wildfires after the T/J boundary. Moreover, it was of importance because the occurrence of wildfire activity during the Lower Jurassic threw the new light on the concentration of O_2 during that period (Marynowski, Simoneit 2009).

Gastropod egg capsules. Fossil gastropod egg capsules have rarely been reported from the fossil record. In the upper Gromadzice section, they were found inside *Cardinia* bivalve shells, suggesting that the shells were the best medium for egg-capsule deposition (Zatoń et al. 2009). What seems to be even more interesting, chitin is preserved in these neritimorph gastropod egg capsules (Wysokowski et al. 2014). The identification of chitin in the Hettangian egg-capsules is the oldest documented occurrence of that biomolecule in Earth history.

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