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VIII Meeting of the Mineralogical Society of Poland

Mineralogical Sciences in XXI Century:
Where Do We Go?

&

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

Migmatites: Contemporary Views and Examples

Abstracts and field trip guide

Bukowina Tatrzańska, Poland, 21-23 October 2011

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VIII Meeting of the Mineralogical Society of Poland

Mineralogical Sciences in XXI Century:
Where Do We Go?
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XVIII Meeting of the Petrology Group of the Mineralogical Society of Poland

Migmatites: Contemporary Views and Examples

organized by

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together with

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AGH – University of Science and Technology

Institute of Geological Sciences of the Jagiellonian University

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Bukowina Tatrzańska, Poland, 21-23 October 2011

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GENERAL SESSION

FIELD-TRIP GUIDE

VIII Meeting of the Mineralogical Society of Poland and XVIII Meeting of the Petrology Group of the Mineralogical Society of Poland

The joint VIII Conference of the Mineralogical Society of Poland and the XVIII Session of the Petrology Group of the MSP at Bukowina Tatrzańska, 21-23 October 2011, have two headline topics: “Mineralogical sciences in the 21st century: Where do we go?” and “Migmatites: contemporary views and examples”, respectively. The VIII Conference aims at reviewing and discussing selected key issues and trends in modern mineralogical sciences, and defining possible future developments in these and related areas of the Earth sciences. Obviously, it is impossible, within a short session, to make any kind of comprehensive review of current issues within all three major branches of the mineralogical sciences: geochemistry, mineralogy and petrology, not to mention related interdisciplinary fields such as cosmology, environmental sciences, new technologies and material sciences, prospecting for mineral resources, geoengineering, biochemistry, biomineralogy, medical mineralogy and so on. However, a few invited lectures during the general session of the Conference cover selected hot topics of the modern mineralogical sciences, and these are supplemented by several other presentations related to the main topic of the Conference. All these can stimulate discussion on recent perspectives within these areas of the Earth sciences. The scientific outcome of this part of the Conference, hopefully, will contribute to the initiative of identifying “100 mineralogical questions that, if answered, would have the greatest impact on resolving current and future challenges in the Earth, planetary and environmental sciences” (see Harrison 2011). Our discussion can help to better define also the current condition of the mineralogical sciences in Poland and to confirm the key position of mineralogy and related disciplines, along with other Earth sciences, within the currently modified structure of the Polish Academy of Sciences (see Janeczek, Marynowski 2011).

The headline topic of the XVIII Session of the Petrology Group of the MSP, “Migmatites: contemporary views and examples”, concerns fundamental issues in the study of the continental crust, such as partial melting processes at deep crustal levels during orogenic processes and their large-scale geodynamic consequences. The importance of migmatites in recent geological research has been illustrated by the impressive edition of the “Atlas of migmatites” published by the Mineralogical Association of Canada (Sawyer 2008). Apart of that, review papers on migmatite-related problems are collected in a thematic volume of Elements (7/4): “When the continental crust melts” (Sayer et al., eds. 2011). Our session, comprising a few invited talks and several other specific presentations, may contribute to this important research issue.

Traditionally, our Meeting includes also an open session, with many presentations covering a wide spectrum of problems of the mineralogical sciences. It is significant that many papers have been submitted by young scientists and PhD students from Poland and from other countries.

On behalf of all Members of the Mineralogical Society of Poland and all the Guests of the Meeting, I wish to express sincere thanks to the organizers, in particular to Maciej Manecki and his Colleagues of the Kraków Branch of the MSP, for their initiatives and effective arrangements.

Welcome to the Meeting at Bukowina! Let it be a fruitful scientific event and leave the most pleasant impressions from your stay in the unique Polish Tatra Mountains!

Ryszard Kryza
President of the Mineralogical Society of Poland

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VIII Meeting of the Mineralogical Society of Poland

Mineralogical Sciences in XXI Century: Where Do We Go?

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21 - 23 OCTOBER 2011

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POLSKIE TOWARZYSTWO MINERALOGICZNE

The application of ICP-MS to the study of Acid Mine/Rock Drainage waters

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The inductively coupled plasma-mass spectrometry (ICP-MS) was introduced in the eighties of the 20th century to identify and quantify over eighty elements in a few minutes. The first ICP-MS instrument was manufactured by PerkinElmer SCIEX in 1983 (PerkinElmer SCIEX, 2001). ICP-MS is a rapid multi-element technique providing ppb or even ppt detection limits. Apart from its great sensitivity, this technique is characterized by a wide dynamic range, the ability to determine isotopes, spectral simplicity and a general lack of interferences for elements with masses greater than 70 (Crock et al. 1999). However, some ICP-MS interferences are derived from matrix effects, instrumental drift, and isobaric overlap of some elemental isotopes by molecular ions formed in the plasma, for example ^{40}Ca and ^{40}Ar, ^{56}Fe and $^{40}Ar^{16}O$ or ^{75}As and $^{40}Ar^{35}Cl$ (Koenig et al. 2010). All elements have at least one isotope free of isobaric interferences, but on the other hand less abundant isotopes will decrease detection limits of these elements (Wolf 2005). ICP-MS has widely been used for determinations of toxic elements such as As, Cd, Sb, Th, Tl, U, rare earth elements (REE), precious metals and refractory elements (Nb, Mo, Re, Ta, W) in a variety of geologic, environmental and biological samples (e.g. Lichte et al. 1987; Crock et al. 1999; Nordstrom et al. 2000). Moreover, this technique has the ability to measure isotope abundances of most elements between mass 6 (Li) and mass 238 (U). It also enables performing isotopic dilution to improve the accuracy of analysis. That is the reason why ICP-MS also found a valuable application in the certification of reference materials (CRM). Of a variety of sample introduction techniques, laser ablation (LA) is commonly used for studying minerals and rocks (Lichte, 1995). ICP-MS is applicable to many areas of geology, environmental sciences, biology, medicine, forensics, archeology, including the study of acidic waters. Coupling ICP-MS with chromatographic and electrophoretic methods, e.g. high performance liquid chromatography (HPLC) gives opportunity for elemental speciation studies (Vonderheide et al. 2007).

In the ICP-MS instrument the liquid sample is introduced to a nebulizer where a flow of argon converts the liquid into fine droplets (aerosol). The droplets then pass through the spray chamber to the tube or injector of the torch and into the argon plasma (6000°C). The ionized elements pass through the interface and the ion lens that focuses the ions into the quadrupole region. After that the ions are sorted by the mass-to-charge ratio in the mass spectrometer and measured by the detector (PerkinElmer SCIEX, 2001).

Inactive or abandoned sulfide-ore and coal mine sites, tailings piles as well as mineral deposits and mineralized rock formations that occur at or near the surface create a potential hazard to the environment throughout the world. The oxidation of pyrite and iron-bearing sulfides, a process called Acid Rock Drainage (ARD) or Acid Mine Drainage (AMD) when induced by mining activity, generates acidic metal-bearing waters that jeopardize natural waters, soils and biota (e.g. Nordstrom, Alpers 1999; España et al. 2008; Migaszewski et al. 2008, 2009; Graham, Kelley 2009; Kwong et al. 2009). There are two classes of mine waters showing low pH, namely: acidic and extremely acidic waters (Lottermoser 2007). The former ones (pH<5.5) occur in base metal, gold and coal mines whereas extremely acid waters (pH<1) are generated in sulfide oxidation environments that lack acid buffering minerals. In general, ARD/AMD waters belong to high ionic strength solutions which usually need dilution prior to ICP-MS analysis. These waters exhibit high concentrations of elements varying from tens to thousands of mg/l. The ICP-MS technique is most frequently used for determination of Ag, As, Bi, Cd, Co, Cu, Mo, Ni, Pb, Sb, Zn and REE in ARD/AMD waters. Of these elements, arsenic is of great concern because it usually shows raised levels in pyrite. Arsenic is remobilized during weathering creating an environmental and toxicological risk. ICP-MS is used to measure the total arsenic concentrations, however, coupled with other techniques (e.g. HPLC-ICP-MS) ICP-MS may be applied to study As speciation. The problem with As determination by ICP-MS is the presence of high chloride concentrations in acidic waters. Because $^{40}Ar^{35}Cl$ has the same mass-to-charge ratio value, this pair interferes with ^{75}As. As mentioned above, REE (lanthanides, Sc, Y) are usually determined with ICP-MS. Although these analyses are complex due to formation of polyatomic ions (e.g. $REEO^+$ or BaO^+) and optimization of analytical procedures to correct these interferences (Merten, Büchel, 2004), ICP-MS has certain advantages over other analytical methods that include: low detection limits (ng/L) and the possibility of multi-element determinations.

Table 1. REE concentrations in water bodies of the Podwiśniówka–Marczakowe Doły area (Dec 15, 2010)

Element (ppb)	Podwiśniówka acidic pit pond	Marczakowe Doły acidic pond	Marczakowe Doły fish pond
Ce	7.02	21.08	0.27
Pr	0.93	2.78	0.08
Nd	3.87	11.67	0.28
Sm	1.28	3.90	0.10
Eu	0.37	1.10	0.04
Gd	1.87	5.72	0.09
Tb	0.28	0.85	0.01
Dy	1.30	3.96	0.06
Ho	0.26	0.80	0.01
Er	0.59	1.96	0.04
Tm	0.08	0.27	0.01
Yb	0.47	1.54	0.03
Lu	0.07	0.26	0.01
Sc	1.95	3.49	1.13
Y	6.50	24.65	0.59
La	2.63	7.55	0.30

The authors determined REE in two acidic pond waters in the Wiśniówka mining area near Kielce (south-central Poland). For this purpose, an ICP-MS/MS instrument (model ELAN DRC II, Perkin Elmer) was used. The results are presented in Table 1.

The preliminary study exhibited a distinct abundance of these elements in the Marczakowe Doły acidic pond ("yellow boy") vs. the Podwiśniówka acidic pit pond. The same element relationships were also documented in January, February and March of 2011. This evidence may suggest that the Marczakowe Doły acidic pond is recharged with pyrite oxidation products derived from a different unexposed pyrite zone. It is interesting to note that the control small fish pond located about 150 m north of the Marczakowe Doły acidic pond displays markedly lower contents of REE. This may indicate that the Marczakowe Doły ponds are recharged from two different rock formations, and furthermore, may provide the evidence for the location of the "yellow boy" pond within a fault zone.

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Mineralogy of Mars: characterization of Martian paleoclimate from arid hot and arid cold analogues on Earth

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For almost a decade, the exploration of Mars has benefitted from hyperspectral data sets that made possible detailed mineralogical mapping and interpretations of the Martian surface composition. Both infrared spectrometers OMEGA onboard Mars Express and CRISM onboard Mars Reconnaissance Orbiter revealed an impressive variety of the mineralogical formations on Mars, including phyllosilicates, sulfates, iron oxides and mafic minerals - pyroxenes and olivines (Bibring et al. 2006; Mustard et al. 2005, 2008).

Mafic rocks are thought to be abundant at the surface of Mars. The evidence of the basaltic surface composition comes from the characteristic absorption bands of olivine and pyroxene, and the mineralogical abundance modelling (Poulet et al. 2009). The TES/MGS data have suggested that the basalts in the northern hemisphere are mainly fresh, whereas in the southern hemisphere they are mainly altered (Wyatt, McSween 2002). This has been confirmed by interpretation of the OMEGA/MEx and CRISM/MRO datasets (Bibring et al. 2006; Mustard et al. 2008; Salvatore et al. 2010). In addition to the orbital data, the spectra obtained in situ unambiguously demonstrated the presence of basalts at the Spirit rover landing site in Gusev crater (McSween et al. 2004). The basaltic rocks have also been found at the Pathfinder landing site (Bell et al. 2002), despite a different environmental setting - the Ares Vallis floodplain.

Of interest is whether information on paleoclimate conditions of the basalt alteration can be retrieved from the measured basalt spectra. The new data on spectral signature and chemical composition of altered basalts in both arid cold and arid hot regions on Earth have been compared to the Martian near-infrared (NIR) spectra. The selected basalts on Earth are located in the Udokan area of Siberia, and in the Ogaden region of southeast Ethiopia.

Detailed mineralogical characterization of basalt weathering, which is necessary for understanding the evolution of the Martian conditions, requires a multi-technique approach. However, even the variety of approaches used (polarization microscopy, X-ray diffraction, SEM, Raman spectroscopy) did not succeed in explaining the whole range of NIR absorption bands observed, especially in the Udokan basalts.

The studied basalts, despite their dramatic differences in alteration conditions, have very similar bulk rock NIR spectra. Broad absorption bands in the bulk rock spectra, especially related to -OH and H_2O absorptions make difficult to recognize smaller bands of critical importance in identifying some alteration minerals. The NIR spectra of the Martian bulk rocks are, therefore, unlikely to distinguish between basaltic rocks that were altered in arid hot versus arid cold environments. This study suggests that analyses of rock powders may help to discriminate between both environments: the rock powders altered in arid hot environment have a first-order positive spectral slope in the range 0.9-2.0 µm, whereas those altered in arid cold environment have a first-order negative spectral slope. This might help in evaluating different hypotheses of the Martian paleoclimate conditions, if the analyzed surfaces have powder-size granulometry. Two different types of alteration observed in the Ogaden - surface oxidation associated with spheroidal weathering and penetrative weathering - cannot be distinguished either in the NIR bulk rock and the powder spectra. This suggests that different processes of alteration of basalts under a given climate might be difficult to distinguish in the NIR spectra of the Martian surface.

The Ogaden basalts are located in a much more arid setting than the Udokan basalts, but the hydration bands are deeper in the Ogaden spectra than in the Udokan spectra. Thus, an inverse correlation exists between rainfall and climate aridity, maybe related to the weathering effect of groundwater, or to the hydration state of the secondary minerals. Therefore, the strong hydration bands (e.g. Mustard et al. 2008) observed on many Martian spectra of mafic mineral-rich areas (Mustard et al. 2005) are not necessarily evidence of a past wet climate characterized by persistent water runoff during long-lasting wet seasons, but are also consistent with dry conditions, cold or hot, with only very limited or no precipitation.

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Mineralogical sciences in the XXI century: Where do we go? A Foreword

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1. Introduction

The headline topic of the VIII General Meeting of the Mineralogical Society of Poland (MSP) is designed to stimulate discussion about the current state and future challenges of the mineralogical sciences both in Poland and internationally. This is a hot topic addressed in vigorous discussions within national and international scientific societies, and considered at many international conferences and in leading international journals. The most spectacular debate on the current issues of the mineralogical and related sciences has been led in regular thematic issues of ***Elements***, An International Magazine of Mineralogy, Geochemistry, and Petrology. All of the 38 volumes of the Magazine, published between April 2005 and June 2011, have been devoted to important research issues in modern mineralogy and in related scientific disciplines. The theme was also present at the latest IMA Congress in Budapest, 2010, in special interdisciplinary sessions such as: Medical Mineralogy, Nanogeoscience, and the Nuclear Fuel Cycle.

At the Polish national level, "Perspectives and progress of mineralogical sciences in Poland" was the topic of the V Congress of the MSP in Cieszyn in 2003, where perspectives in mineralogy, petrology and geochemistry in Poland were outlined by Manecki (2003). The challenges of the modern mineralogical sciences have been addressed in many papers presented at conferences and workshops organized by the MSP, for example the review talk by Hovorka (2009) at the VII General Meeting of the MSP, Święty Krzyż, 2009: Mineralogy and petrology in the service of society: challenges for the 21st century. The current condition of the mineralogical sciences in Poland has recently been discussed in the Report of the Mineralogical Sciences Committee, Polish Academy of Sciences (Janeczek and Marynowski 2011). The role of mineralogy, petrology and geochemistry (and related sciences) in society and their position within the framework of science have recently been debated within the ongoing process of re-structuring the Polish Academy of Sciences (J. Janeczek, Letter to President of the III Department of PAS, 23.05.2011).

In a wider international context, it is worth noting an initiative proposed by the Mineralogical Society of Great Britain & Ireland: to establish a list of the ***100 most important questions in mineralogy***. The survey, following an article in Elements, June

2011, is being carried out by means of online data-collection and the results will be published in “Open Access” form. The organizers encourage the international mineralogical community to participate in this exercise and they invite also scientific societies, as well as governments and funding agencies, to take part in the debate. This type of initiative has a proven track record in other areas of science and could well be of great benefit to the future of mineralogical sciences.

2. Current issues in mineralogy, petrology, geochemistry and related sciences

The mineralogical sciences, like other fields of Earth sciences and of science in general, have two basic goals: (a) to extend our general knowledge, and (b) to solve practical problems vital for human society. Of importance here is the need to set a proper balance between theoretical aspects of science and practical/applied issues, the boundary between which is blurred: thus “theoretical” discoveries may become cornerstones for practice and new technologies. The fields of the theoretical mineralogical sciences cover a vast area, from physical, theoretical and experimental mineralogy, through various aspects of petrology and geochemistry, to applications of these sciences to other geosciences and related disciplines. Applied mineralogical sciences provide important contributions to solving basic practical problems concerning the human present and future, including:

- energy, mineral, water, and food resources,
- natural and man-made disasters, climate change, land-use impact, environmental pollution and wastes,
- new technologies, nanogeosciences, geoengineering, industrial mineralogy, gemology,
- biomineralogy and medical mineralogy,
- human heritage studies (archaeometry, petroarchitecture, stone deterioration).

The basic and most classical field of mineralogy is the discovery and description of new mineral species. Much attention has recently been paid to the mineral evolution (similar, in a way, to the evolution of life; Hazen et al. 2008), starting from a very few mineral species formed in the early Solar System, to over 4,000 minerals known recently (not including a great number of human-made “minerals”; see Zalasiewicz et al. 2011, this volume). It is also worth noting here recent discoveries (by an international team including members of the MSP) of new rare minerals of the garnet group, some containing uranium and other rare elements, which are of potential interest for nuclear-waste technology (Galuskina et al. 2010).

Beyond the Earth, modern mineralogy, petrology and geochemistry penetrate outer space and the Solar System (e.g. Elements, E, 7/1). The geological exploration of our cosmic neighborhood helps us to understand our own planet. Cosmochemistry and cosmomineralogy provide data that can be quite as important as the results of space missions. For example, cosmochemistry gives an accurate age of the Solar System, and constrains the composition of the planetesimals that accreted to form the Earth. It is to our advantage, as Earth scientists, that discoveries of this kind require the methodology and expertise of mineralogists, petrologists and geochemists (McSween 2011).

Other important research targets of the mineralogical sciences include specific chemical elements and important minerals: their various theoretical aspects and practical significance, e.g. diamond (E 1/2), zircon (and geochronology, E 3/1), phosphates (E 4/2), platinium-group elements (E 4/4), gold (E 5/5), sulphur (E 6/2), and iron (E 7/2).

A special area of interest of modern mineralogy, petrology and geochemistry remain, importantly, basic problems of the Earth and its geological evolution. Several such topics and recent achievements have also been comprehensively reviewed in a number of thematic volumes of Elements, e.g.: fluids in planetary systems (E 1/1), large igneous provinces (E 1/5), early Earth (E 2/4), supervolcanoes (E 4/1), deep Earth and mineral physics (E 4/3), mineral magnetism (E 5/4), fluids in metamorphism (E 6/3), and, in future issues: when the continental crust melts (E 7/4), and migmatites (E 7/6). Within that area, experimental petrology and mineral thermodynamics remain crucial.

Interdisciplinary fields of the natural sciences are among the most up-to-date research disciplines, concerning general problems such as the origin and evolution of life, the material and environmental conditions of human existence on Earth at present and in the future. It is well recognized that recent land-use impacts may appear as strong as those related to climate change. Among many intriguing challenges in these fields is the problem of sustainable soil remediation, including, e.g., immobilization of contaminants by sorption reactions, phytoextraction and bioremediation. The future habitability of the Earth depends, undoubtedly, on the understanding and proper management of its surface layers. Many thematic volumes of Elements concern these interdisciplinary areas: the geochemical origin of life (E 1/3), the critical zone – where rock meets life (E 3/5), medical mineralogy and geochemistry (E 3/6), phosphates and global sustainability (E 4/2), stable-isotope biogeochemistry (E 5/6), atmospheric particles (E 6/4), sustainable soil remediation (E 6/6), and in future volumes: global water sustainability (E 7/3) and mining wastes (E 7/6).

Yet another important field of modern mineralogical sciences is connected with the development of new technologies, nanogeoscience and geoengineering. These topics attract much public attention and have been addressed in several other special volumes of Elements: the nuclear fuel cycle (E 2/6), energy: a geoscience perspective (E 3/3), carbon dioxide sequestration (E 4/5), and nanogeoscince (E 4/6). Nanotechnology and geoengineering are closely connected with mineralogy and geochemistry, to mention for example new graphene-based technologies, or engineered nanomaterials used in the remediation of degraded soils.

The new research trends in geosciences are stimulating for the development of new analytical methods, including *in situ* microanalytical techniques. Reviews of selected current methodological issues are covered in a few further thematic issues of Elements, e.g.: user research facilities in the Earth sciences (E 2/1), frontiers in textural and microgeochemical analysis (E 3/4), and the last, but not least, teaching of mineralogy, petrology and geochemistry (E 3/2).

3. Concluding remarks

Although many among the general public still remain unconvinced by evidence of dramatic anthropogenic influence on natural processes on Earth (e.g. climate change), to many scientists it is obvious that we should make efforts to reduce the impact of human activities on the global climate and the natural environment. This should be supported by developing new technological fixes, such as the safe capture and storage of greenhouse gases, helping to solve the problem of low-emission energy forms (e.g. nuclear waste disposal), and geoengineering (e.g. disposing of CO_2 in deep sedimentary formations or through reaction with Ca and Mg in silicate rocks, or "engineering" of the atmosphere, sustainable soil remediation etc.; Vaughan 2010). Here is fertile ground for interdisciplinary approaches that not only bring together a great diversity of experimental and analytical methods, but also juxtapose fundamentally different ways of thinking (Vaughan 2010).

Mineralogical sciences, including geochemistry and petrology, apart from their classical basic interests, have also an important role in prospecting for new mineral resources, the issue recently spectacularly exemplified by the problems of shortage of the REE supply, almost entirely (97 %) controlled by China, and by controversies about ecologically safe mining and utilization of shale gas (currently a hot topic in Poland).

Proper research policies, supporting sound research targets and funding relevant projects, should be supported by adequate education programmes, at both basic and academic levels. Mineralogical sciences, within the Earth and environmental sciences, need also active promotion in society. It is important, however, that core areas and core skills should not be allowed to wither away. As stated by David Vaughan (2010), "the neglect of optical mineralogy and petrography in many modern university courses is a great mistake which should be rectified before these skills are lost. We need a balanced approach both to the funding of research and to the ways in which university teaching is organized, so as to take advantage of the great expertise available when several disciplines are brought together."

To conclude, the most important challenges for the mineralogical and related Earth and environmental sciences revolve around providing the knowledge and the resources (energy, minerals and water) to support the growing and developing world population and, at the same time, to prevent irreversible damage of the natural environment. To quote David Vaughan (2010) again: *"It is appropriate that we be "centre stage" when it comes to pushing ahead the interdisciplinary agenda, both through our own work and through lobbying those who control the funding for research and teaching"*. In this world-wide context, there certainly will be much work for mineralogists, petrologists and geochemists in Poland, within the framework of global co-operation.

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The use of laser-ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) in mineralogical and petrological studies

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The laser ablation was introduced to trace element determinations in solid samples in the eighties of the 20th century. This technique was first used with ICP-OES (Thomson et al. 1981) and then with ICP-MS (Gray, 1985). Laser-ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) has the capability of determining the concentrations of trace elements at ppb levels in geologic and biologic solid microsamples. There are several laser ablation systems (193, 213 and 266 nm) producing craters in the sample ranging in size from 2 to 1200 µm. However, the most common lasers used in LA-ICP-MS are solid state Nd:YAG (neodymium: yttrium-aluminum garnet) lasers with frequency quadrupled to ultraviolet (266 nm).

The mineral grains or plant tissues (e.g. tree rings) are viewed through a polarizing microscope in reflected or transmitting light and the sample surface is ablated (burned) with a fine pulsed laser beam. The beam focused on the sample surface is usually supported by a camera system. The sample is placed inside an enclosed ablation cell (connected to an XYZ motorized stage), which is purged by argon to prevent the laboratory air from entering the cell. The laser shots create the sample aerosol, which is then sent to the inductively coupled argon plasma (ICP). The plasma generates ions that are subsequently introduced to the mass spectrometer (MS), in which the ions are separated and collected according to mass to their charge (m/e) ratios. The laser is controlled by a computer that enables setting ablation parameters, such as energy level, frequency, burst shots, spot size, repetition rate and ablation mode. There are several ablation modes (patterns) depending on the system, e.g. single spot, depth profile, single line scan, single line raster, segmented line scan, scanning, and rastering.

The LA-ICP-MS found application in investigating element composition of tree rings (King, 1995), fluid inclusions (Guenther et al., 1998) or dating geologic materials using U-Pb ratios (Xia et al., 2004). Spry and coauthors (2007) studied the REE distribution pattern of garnet-rich rocks at the Paleoproterozoic Broken Hill Pb-Zn-Ag deposit (Australia) using the LA-ICP-MS technique. The results indicated that garnetite and quartz garnetite were metamorphosed sediments that had formed due to submarine hydrothermal activity.

The LA-ICP-MS has also been used in forensic science. A microscopic sample weighing even less than one microgram is more likely to be moved undetected by a criminal from a crime scene. The principal objective of forensic investigations is to match evidence, e.g. silver, paint, glass, to a crime scene (Devos et al., 1999; Bajic et al. 2005). The LA-ICP-MS was applied to archeological artifacts or works of art to confirm their authenticity, for example ancient silver coins. This technique was applied to ancient silver coins to check the presence of surface enrichment in this metal (Sarah et al. 2007). Concentration depth profiles for two major elements (Ag, Cu) and five minor elements (Zn, Sn, Au, Pb, Bi) at single points excluded plating.

This report presents the preliminary results derived from the study of the following samples: (i) Upper Jurassic striped cherts (flints) from Ożarów (northeastern Holy Cross Mountains), (ii) silicified wood from Włoszczowice–Karsy (25 km south of Kielce) and (iii) pyritic quartzite-quartz breccia from the abandoned Podwiśniówka quarry (4 km north of Kielce) using the CETAC LSX 500+ laser ablation module coupled with the Perkin Elmer ICP-MS/MS ELAN DRC II instrument. The CETAC laser ablation module was equipped with the Q-switched Nd:YAG laser, frequency quadrupoled to 266 nm. The single line raster LA method was used. Sample surfaces were ablated with 250 shots at pulse energy of 9 >mJ. The other optimized laser parameters included: a pulse repetition rate of 20 Hz, a delay between spots 2 min. and a spot diameter of 25 µm (pyrite) or 100 µm (silicified wood, striped chert). A time-resolved plot of signal for each element was integrated and concentrations computed using DigiLaz^{TM} II operating software by CETAC. Operating conditions for the Perkin Elmer ICP-MS/MS ELAN DRC II instrument were as follows: low resolution, power (~1600 W), and sample gas flow rate (415 ±7 kPa at 20 l/min. Ar) adjusted to maximize atomic ion signal. The matrix matched USGS Microanalytical Reference Materials, i.e. Glass BCR-2G, Basalt glass BHVO-2G and Polymetal sulfide MASS-1, were used for quantitative analysis. The samples were analyzed for 20 elements: Ag, Au, B, Ce, Co, Cu, Fe, K, La, Mn, Nd, Ni, Pb, Rb, Sr, Th, Ti, Tl, U and Y) (Table 1).

In general, there was a similar element spatial distribution pattern in gray and brown patches of the Włoszczowice–Karsy silicified wood, except for Cu, Fe, Ti and Yb which exhibited distinctly higher concentrations in gray patches. The Ożarów striped chert revealed in turn a slight variation in trace element concentrations. The surface band displayed somewhat raised levels of Fe and Pb. In contrast, the inner bands showed an excess of B, K and Rb.

The single line raster pattern of the pyritic quartzite-quartz breccias exhibited a spatial variation of As within the pyrite. The concentration of this element was in the range of 1.83 to 8.23%. In contrast, the content of Cd and Zn was stable varying from 24.99 to 25.23 ppm (mg/kg) and from 416.16 to 421.53 ppm, respectively. It is interesting to note that quartzite fragments of the tectonic breccias displayed the same levels of Cd and Zn. These results have indicated that the LA-ICP-MS technique has the superior element detection capability in the microscopic area to the electron microprobe technique.

Table 1. Concentrations of selected trace elements in the silicified wood and striped chert nodule from the Holy Cross Mts

Element	Silicified wood		Striped chert (flint)		
	Gray patch	Brown patch	Outer light gray band	Dark gray boundary band	Inner light gray band
			ppb (µg/kg)		
Ag	130	160	679	217	388
Au	14	15	19	1	9
B	7.106	2.413	8.536	29.721	22.480
Ce	297	339	68	40	212
Co	7.709	8.277	91	93	7
Cu	31.157	7.729	276	842	140
Fe	275.827	192.827	13.190	9.737	5.693
K	241.233	245.944	39.510	95.300	42.646
La	115	89	23	12	8
Mn	7.928	8.223	34	22	52
Nd	235	303	51	13	57
Ni	3.270	2.002	1.958	1.602	863
Pb	33.580	38.171	1.095	591	739
Rb	620	691	6	17	44
Sr	3.773	3.804	350	489	297
Th	116	50	16	8	5
Ti	33.875	23.560	2.642	3.705	2.791
Tl	25	21	3	5	1
U	179	103	47	82	75
Yb	21	7	1	2	0

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Current trends in clay science with emphasis on geological applications

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Clay science is an interdisciplinary field of research, defined not by the approach but by the object of the studies, which are clays and clay minerals. Historically clay science evolved as a branch of mineralogy, and still several national clay groups (including Polish) are affiliated to national mineralogical societies. However, from the very beginning clay science overlapped also with other disciplines, like geology, surface chemistry and variable technologies. As a result of this overlap, and the volume of research on clays, which constitute 37% of the mass of sedimentary rocks, clay research evolved into a separate discipline with its own international associations (AIPEA, ECGA), journals (CCM, CM, ACS) and conferences (ICC, EUROCLAY). Over years proportions between contributions to clay science from particular fields evolved gradually. The general trend, well illustrated by the data presented in Table 1, involves the expanding contributions from material sciences and shrinking contributions from natural sciences. This trend continues, so today only ca. 20% of clay papers can be classified as representing mineral sciences (crystallography, mineralogy, geochemistry).

Discipline	1995/1996		2005/2006	
Crystallography, mineralogy, geochemistry	22	Natural Sciences	22	Natural Sciences
Geology: recent and past	23	**46**	18	**40**
Surface chemistry and physical properties	34	Material Sciences	35	Material Sciences
Industrial applications	8	**54**	14	**54**
Non-clay fine-grained materials	12		11	
SUM	100	100	100	100

Fig. 1. Topics of clay science publications. Data (in %) from Applied Clay Science, Clay Minerals, and Clays and Clay Minerals for two 2-year periods

The applications of clay studies to solving geological problems benefit from the progress in two main areas of clay research:

1) Methods of clay quantification and measurement of their various characteristics;
2) Interpretation of clay characteristics as indicative of specific geological processes.

Over the past decade the first area experienced a major progress. For the first time the quantification of clay minerals in the bulk rock became an accurate measurement, which was demonstrated by international round robin competition named "Reynolds Cup", organized since 2002 every two years by the Clay Minerals Society (e.g. Omotoso et al. 2006). Both the techniques based on natural standards (e.g. Środoń et al. 2001) and on Rietveld refinement (e.g. Kleeberg 2009) can produce accurate results. Current progress in handling complex clays by Rietveld-based Autoquan program will probably lead to the domination of this approach in the future.

The accurate bulk rock quantification of clays opened new clay research opportunities, because the bulk rock chemical data can be interpreted now from the mineralogical perspective. The problem of representativeness, characteristic of older studies relying on separated clay fractions is irrelevant for this approach. Recent applications deal with the role of clays in diagenetic history of nitrogen and boron (Środoń 2010; Środoń, Paszkowski, in press), important for the geochemistry of oilfield waters and the origin of excess nitrogen in natural gas. This approach turned also very useful for the calibration of borehole geophysics, dramatically improving the correlations between geophysical and mineral data (e.g. Zorski et al. 2011). It can be anticipated that this will play an important role in the genetic interpretation of petrophysical properties of the shale gas rocks.

Another major methodical development of the last decade is an automated modeling of complex 1-dimensional XRD patterns of clay mixtures, based on the approach of Sakharov et al. (1999). Such modeling has been available since the NEWMOD program of R.C. Reynolds, but the manual operation made this technique prohibitively time-consuming for routine use. The application of genetic algorithms for fitting of the experimental patterns resulted in a tool for every day use. The method produces quite accurate quantitative data, as verified recently using independent, chemistry-based techniques (Zeelmaekers 2011). This approach has a potential for widespread geological applications, as it allows identification and quantification of clay fraction components much more accurately than older techniques. So far the applications have been restricted by the limited access to the program. The best known examples include studies of the diagenetic illite-smectite series, which reinterpreted their XRD patterns as representing two-component mixtures (McCarty et al. 2008; 2009), and call for the revision of illite-smectite as the paleotermometer. The technique can also be used for tracing ammonium substitution in illite, which records the level of hydrocarbon generation in the basin (Lindgreen et al. 2000).

Clays of illite-smectite group offer a unique chance of radiometric dating of several geological processes (glauconite: stratigraphy; celadonite: submarine basalt alteration; illite: diagenesis, metamorphism, hydrothermal alteration). New developments in this field include the introduction of dating ultra-fine submicron fractions, representing different classes of fundamental particles of illite and the interpretation of dates in terms of illite crystal growth (Środoń et al. 2002). This approach, when combined with illite-smectite paleothermometry, produces independent information on basin history (e.g. Środoń et al. 2006; 2009), consistent with the apatite fission track dating. Sequential acid dissolution allows checking if the K-Ar dates of glauconites represent true stratigraphic ages (Derkowski et al. 2009). New computerized approach to the interpretation of K-Ar dates of shale fractions allows to better constrain the end-member diagenetic and detrital ages (Szczerba et al. 2010).

Explanation of variable dehydroxylation temperatures of illite-smectites by their cis/trans occupancy of the octahedral sheet (Drits et al. 1998) has a potential for multiple applications in geological studies (K-Ar dating, stable isotope geothermometry, crystal shape and clay origin).

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Mineral evolution on Earth: from the Hadean to the Anthropocene

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1. Introduction

The Earth has shown a systematic increase in mineral species through its history, with three ‘eras’ identified by Robert Hazen and his colleagues (Hazen et al. 2008), associated with planetary accretion, crust and mantle reworking and the influence of life, respectively. We demonstrate here a further level in this form of evolution, where humans have engineered a large and extensive suite of novel minerals, some of which will leave a geologically significant signal in strata forming today.

2. From the early Solar System to plate tectonics

Hazen et al. (2008) and Hazen & Ferry (2010) have outlined this story admirably. Before the solar nebula, there was interstellar gas and dust, the latter expelled from dying stars and comprising some dozen minerals, most notably (and perhaps most commonly) diamond, but also including a few carbides, nitrides, oxides and silicates. As our own solar nebula formed - its gravitational collapse likely triggered by a nearby supernova explosion – the intense luminosity of the early Sun melted and recondensed the circling dust into primitive chondritic meteorites. This was the start of Earth’s first mineral era, even before the planet itself formed. Some 50 additional minerals now appeared, among them spinel and some of the pyroxene, feldspar and olivine family. The collision-driven growth of larger meteorites and planetesimals fuelled further mineral formation. Notably, the addition of water from cometary debris enabled low-temperature hydration and aqueous precipitation reactions: calcite, gypsum, halite and the first clay minerals appeared, and such minerals can be found in carbonaceous chondrites that fall to Earth (McCoy 2010). By now, some 250 minerals are present: they are the building blocks of an Earth-sized rocky planet.

The Earth’s second mineral era began as our planet formed, and differentiated into core, mantle and crust. The range of classical igneous processes, including fractional crystallization and various water-related reactions initially took the number of minerals to some 500 – roughly the same is as likely present on Mars. The Moon, being largely anhydrous, only has some 350 (Hazen & Ferry 2010).

Once the engine of plate tectonics started, the number of minerals climbed. Melting and remelting of crust drove the composition from basaltic to granitic to (locally) pegmatitic, concentrating rare and incompatible elements into a diverse range of new minerals. Metamorphism (both regional and contact) took place. On such a dynamic Earth, some 1500 minerals can be generated. The Earth, though, was still biologically dead. More was to come.

3. The impact of life

The Earth's third mineral era was driven by life. Not immediately: the earliest microbial life-forms (from >3 Ga) soon became abundant, certainly, and generated or mediated abundant and distinctive strata, notably banded iron formations and stromatolitic reefs. However, the number of new mineral species remained small. Then, at about 2.4 Ga, a biogeochemical innovation appeared: photosynthesis and the development of an oxygenated surface environment, in what is now termed the "Great Oxidation Event'. This phenomenon created a wide range of oxidised products of primary minerals, more than doubling the number of mineral species on Earth, to something in excess of 4000 (Hazen et al. 2008; Sverjensky & Lee 2010, for instance, describe the diversification of uranium minerals in an oxidised environment).

The later stages of this process, most notably the rise of metazoa – at first at sea, then on land – further modified this process, although arguably more in terms of pattern and distribution than substantial further increase in new minerals. The sophisticated and intricate patterns in biomineralized structures such as bivalve shells, diatom tests and echinoderm plates (Dove 2010), and the volume and complexity of, say, reef limestones, have made the strata of the last half-billion years of Earth history clearly distinctive. The next major development in the Earth's mineral storehouse was to await the emergence of organised societies in one recently-evolved primate species, *Homo sapiens*. This, current, phase of global mineralogical innovation is one part of the diverse phenomenon that is now termed the Anthropocene.

4. The Anthropocene

The concept of the Anthropocene – that humans have changed the geological processes operating on the Earth's surface sufficiently to justify a new geological time interval – is not new. Such ideas were suggested from over a century ago by such as George Perkins Marsh (1878), Antonio Stoppani (1873 – who proposed the 'Anthropozoic Era'), and Vladimir Vernadsky (1945). However, these early suggestions were largely discounted by the geological community (e.g. Berry 1925) which regarded human geological influence as trivial compared to the natural forces of volcanism, mountain building and so on.

The concept of the Anthropocene was re-stated in this millennium by Paul Crutzen (Crutzen, Stoermer 2000; Crutzen 2002). This time, the idea was suggested at a time when the scientific community was becoming aware of the significant nature of various types of anthropogenic change – in rising CO_2 levels and their likely effect, for instance, and in the transformation of large parts of the terrestrial surface and consequent biotic change. The term began to be used, almost immediately, in the serious scientific literature (e.g. Steffen et al. 2004; Syvitski et al. 2005). In view of this, the Anthropocene was analysed as a potential new, formal addition to the Geological Time Scale by the Stratigraphy Commission of the Geological Society of London (Zalasiewicz et al. 2008; see also 2011), which concluded that a case for formalization could be made. Evidence cited include changes that may be considered as lithostratigraphic (human changes to erosion and sedimentation, both direct and indirect), biostratigraphic (the current biodiversity changes involving extinctions, species invasions and biomass changes); and chemostratigraphic (notably changes to the Earth's carbon chemistry).

An Anthropocene Working Group of the Subcommission of Quaternary Stratigraphy, a constituent body of the International Commission on Stratigraphy, was subsequently set up to examine the question. A body of evidence has already been published (e.g. papers in Williams et al. 2011; Zalasiewicz et al. 2010; Ellis et al. 2010). There has been considerable interest in this concept in the wider community (e.g. Nature 2011; Steffen et al. 2011, in press), not least because of its significance for science - and indeed society - as a whole. We here consider a previously neglected aspect of this phenomenon: the increase in the Earth's range of mineral species as a direct product of human activity.

5. Human-made minerals

Humans have long modified the compositions of terrestrial minerals that they have exploited. One of the earliest examples is the production of native metals, generally something of a rarity on a pre-human Earth. At first these were those that occurred naturally, albeit in small amounts, such as copper and iron. Subsequently, humans learnt to separate metals that do not occur naturally in their native form, such as aluminium (first isolated in the late nineteenth century), titanium, vanadium, molybdenum and so on, and now do so on a large scale; annual world production of aluminium now exceeds 35 million tons, for instance, and of titanium 100 000 tons. Most metals have now been isolated, some in considerable quantities.

Other "synthetic minerals", for smaller-scale purposes, include novel forms of garnet for use in lasers and as artificial gems (Hazen et al. 2008), the new mineral borazon, harder than diamond, now a routinely used abrasive, various artificial zeolites (including synroc, manufactured to hold nuclear waste). There seem to be no inventories of new minerals - not least because the current regulations of the International Mineralogical Association, that validates such names, does not recognise minerals of anthropogenic origin. However, the combined novel mineral products of the world's laboratories likely now number in the thousands. Most will be rarities (as are, however, many of the recognised natural minerals); others are more widespread.

One might consider such substances as man-made glass and plastics as new minerals sensu lato. Although not strictly stoichiometric in composition, glass (>50 mT produced annually) and plastics have clearly become specific and widely visible parts of the Earth's surface – as have the minerals associated with, say, ceramics, concrete and brick production, and in mining and smelting wastes and slags, where the mineralogical and petrographic novelty is clear.

It seems, clear, therefore that a significant new epoch in the Earth's mineral evolution has begun, that may emerge as the most striking new development since the Great Oxidation Event of the Precambrian. It may, though, be short-lived, unlike the case with natural minerals (cf. Hazen et al. 2008). Many man-made minerals will become extinct (i.e. cease to form), either because they come to be obsolete for humans or, ultimately, with the extinction of humans. Nevertheless, there will undoubtedly be a distinctive mineralogical character (allowing for subsequent diagenetic effects) to the Anthropocene strata of the future.

6. Conclusions

The Earth has been host to an increasing diversity of minerals though geological time, mainly via a small number of step-like increases associated with significant global environmental changes. The latest of these increases has been associated with the human transformation of the Earth, and gives our present epoch a mineralogically novel and distinctive character.

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Garnet geochronology of high temperature metamorphism: example of migmatitic gneisses from the Day Nui Con Voi massif in N-Vietnam

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The application of Sm-Nd and Lu-Hf garnet geochronology offers a quantitative link between isotopic ages and metamorphic conditions. Most commonly, the link is established on the basis of major element zonation in garnet, textural relationships or by means of thermodynamic calculations. This approach is valuable for low temperature conditions, where major element distribution reflects growth conditions. Under high temperature conditions (>650-700 °C), where major element distributions can be partially or completely modified by diffusion, the interpretation of isotopic ages obtained by both geochronometers is a subject to a large degree of uncertainty. This is a result of the likely decoupling of Rare Earth Element (REE) and High Field Strength Element (HFSE) behaviour from that of the major elements. Although trace element analyses of garnets became fairly common, the interpretation of their record is often far from obvious. In this study, we investigate the potential influence of diffusion and resorption on Sm-Nd and Lu-Hf garnet geochronology in polymetamorphic migmatitic gneisses from the Day Nui Con Voi massif in northern Vietnam.

High-grade migmatitic and mylonitic gneisses from the Day Nui Con Voi massif in northern Vietnam record temperatures of 760-810 °C at pressures of 6-10 kbars. Such high temperature conditions have resulted in development of the major element diffusional profiles in garnet. The laser ablation ICP-MS analyses of trace elements indicate that REE and Hf closely followed Rayleigh-like fractionation trends but underwent significant post-crystallization modification. The Nd and Sm profiles show progressive flattening with the decreasing garnet size, reaching complete homogenization in the crystals smaller than 1.5 mm. This had a profound influence on the Sm-Nd dating and resulted in isochron ages ranging from 50 to 32 Ma. The youngest age was obtained for a sample, where all garnet crystals are smaller than 2 mm and recorded light REE profiles are completely or nearly completely reset. Thus, only the youngest age provides valuable information on the resetting episode caused by the early Oligocene metamorphism.

At the same time, we did not find any evidence for intracrystaline diffusion of heavy REE. Regardless of crystal size, the Lu zonation profiles show steep gradient from the core to the rim indicating preservation of growth signature. Similarly, Hf shows, typical for growth conditions, gentle content increase from the core to the rim. The Lu-Hf isotopic analyses of bulk garnet fractions despite yielding high isotopic ratios appeared very scattered and did not allow defining isochron ages. Instead, apparent ages defined by the whole rock and the individual garnet fractions range from c. 80 to 160 Ma. We propose that the high scatter is due to the mixing of older (Mesosoic), original garnet (preserving steep Lu zonation profiles) with its rim modified by resorption. We link the resorption process to the early Oligocene anatectic metamorphism, the same, which is also responsible for the partial to complete resetting of the Sm-Nd ages.

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Melt produced during anatexis of the continental crust: compositional constraints from experimental homogenization of melt inclusions in peritectic garnets of migmatites

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Recently, Cesare et al. (2009 and 2011) have shown that peritectic minerals in migmatites and granulites can trap droplets of anatectic melt formed by incongruent melting reactions during high-temperature metamorphism and granite formation. Detailed geochemical studies on these melt inclusions (MI) have shown that they can represent a window of information into the prograde history of partially melted rocks (Acosta-Vigil et al. 2010). However, the recovery of this information is not straightforward as remelting and homogenization of MI at ambient pressure with the routine igneous petrology technique produce inclusion decrepitation, interaction with a host mineral and volatile loss (Cesare et al. 2011).

To avoid these problems, we performed the experimental remelting of MI using a piston cylinder apparatus. MI are located within peritectic garnets, hosted in the metasedimentary migmatites from Ronda (Betic Cordillera, SE Spain). These garnets contain primary 2-10 µm MI that range from totally glassy to fully crystalline (*nanogranite*, Cesare et al. 2009). Partially crystallized MI are very common and generally contain quartz, biotite, muscovite and, more rarely, plagioclase, along with variable proportions of glass. Raman spectroscopy has documented the presence of liquid H_2O-filled micropores in nanogranites, in agreement with the presence of a micro- to nano-porosity observed by SEM investigation. The piston cylinder remelting experiments led to the complete rehomogenization of crystalline MI at conditions close to those inferred for anatexis (700 °C, 500 MPa). The remelted MI have peraluminous, granitic composition with high (up to 7.5 wt%) H_2O content; they overlap the composition of glassy MI, but differ from the composition of leucosomes in the host rock. Some CO_2 bubbles are present after remelting experiments, suggesting fluid present, $a_{H2O} < 1$ conditions, in agreement with the graphite occurrence in the protolith.

Our study shows that partially crystallized and nanogranite inclusions in peritectic minerals from migmatites can be successfully remelted and analyzed, and that this experimental approach may become an ordinary procedure for future studies on MI in the anatectic rocks worldwide. With the use of this method, we have identified the natural anatectic melt composition and fluid regime at the onset of crustal melting for this case study, which were unknown otherwise. Hence, MI in migmatites represent a unique tool for the *in situ* characterization of the anatexis in its early stages, and provide the only means of determining the volatile fluid content of anatectic melts.

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Dehydration and rehydration of biotite during anatexis: constraints from microstructurally-aided SIMS analysis of hydrogen

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The SIMS-based study of Ti-H relationships in biotite during the prograde and retrograde phases of HT metamorphism and anatexis (Cesare et al. 2008) has been expanded with the addition of three new case studies that help providing a coherent scenario for metapelitic rocks. Two of the three studied sample suites are enclaves or xenocrysts in lavas which have been demonstrated to be the ideal setting for the preservation of the primary composition of biotite from high-grade anatectic metapelites (Cesare et al. 2003).

In a Spl-Crd enclave from El Hoyazo, Spain (Alvarez-Valero et al. 2005), biotite shows TiO_2 content ranging from 2.5 to 7.5 wt.%. The Ti content is microstructurally controlled: small biotite inclusions in the core of garnets have the lowest Ti content, whereas the coarser grained crystals toward the garnet rims have the highest. Biotite in the matrix outside the garnet shows intermediate Ti content. Like in the samples of Grt-Bt-Sil enclaves from the same lavas, the measured H content is negatively correlated with Ti along a trend that provides further support to the Ti-oxy exchange. Furthermore, the decrease of H_2O content from 4 to 2.5 wt.% shows that biotite progressively dehydroxilates during the growth of garnet that records the development of partial melting of the rock with increasing temperature.

Biotite inclusions have been also studied in some garnet xenocrysts and in enclaves in the Crd-bearing lavas from Lipari (Aeolian arc, Italy; Di Martino et al. 2011). Here, the range of Ti content (5 to 11 wt% TiO_2) includes the highest values reported in the literature, whereas the analysed H content includes the lowest reported values (from 1.7 down to 0.3 wt.% H_2O). These data extend the occurrence of a Ti-oxy exchange to previously uninvestigated Ti contents. In addition, they suggest that the (OH+F+Cl) content of extremely Ti-rich biotite may decrease to almost zero.

The third case study is represented by the metapsammitic granulites (leptynites) of the Kerala Khondalite Belt (India), in which Cesare et al. (2008) had suggested the occurrence of retrograde hydroxylation and fluorination during the slow cooling of these regional anatectic rocks. SIMS profiles at high spatial resolution (1.8 μm spot size, 2-4 μm distance increments) combined with EMP traverses demonstrate that the H, Ti, Fe, Mg, and F diffusion profiles are preserved in the outermost 50 μm of biotite in contact with garnet. These patterns indicate an increase of H, F and X_{Mg}, and the simultaneous decrease of Ti, in accordance with an inverse Ti-X_{Mg} relationship and the Fe-F avoidance.

The new data integrate and confirm previous indications or inferences, showing that:

- Ti-oxy is the dominant exchange over the entire TiO_2 range so far investigated in biotite from metapelitic rocks;
- During prograde heating and continuous melting, biotite is progressively dehydroxylated via Ti uptake until it may eventually become OH-free;
- In most granulites and migmatites, the halogen and hydrogen content of micas is probably increased by retrograde diffusion, and biotite may preserve the evidence of such reequilibration in thin (a few tens of μm) rims in the contact with garnet.

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Microstructures and composition of anatectic melt inclusions in metasedimentary rocks

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Investigation of melt inclusions (MI) represents a widely used approach to gain information on a number of igneous processes on the Earth system. The recent finding of crystallized and glassy MI in high-grade, partially melted metapelites and metagraywackes opened up the possibility to investigate also the anatectic processes with the same method. The present work expands the study of Cesare et al. (2009; 2011) providing a detailed microstructural and microchemical investigation of three occurrences: Khondalites (India), Ronda migmatites (Spain) and Barun gneisses (Nepal). These are only part of a continuously-growing list of very recent findings, suggesting that these MI are widespread in migmatites, despite they went (almost) unnoticed until now.

So far, the anatectic MI are reported in peritectic garnet and ilmenite, although they may be expected in other peritectic phases, more likely in hardest minerals, e.g. spinel. They preferentially form clusters with a different degree of packing, a spatial arrangement that testifies for their primary entrapment, i.e. during host mineral growth. Inclusions are generally isometric, more rarely tubular, and very small in size, (mostly ≤15 μm, rarely up to 30 μm). In most cases inclusions are crystalline and contain a granitic phase assemblage with quartz, feldspars and one or two micas (depending on the case study), often along with accessory phases (usually zircon, apatite, rutile). Because of these features, these crystalline inclusions have been named "nanogranites" (Cesare et al. 2009). Besides the fully crystallized nanogranites, partially crystallized inclusions are locally abundant. Glassy inclusions, generally very small (≤8 μm) may occur in the same cluster.

After entrapment, inclusions underwent limited microstructural modifications, such as shape maturation and, locally, necking-down processes that, however, should not have modified their original bulk composition. Decrepitation evidence are present, locally very widespread (Barun gneisses), but also in this case no assemblage differences are recognizable between the decrepitated and the preserved inclusions.

Obviously, the most important aim of these research is to gain representative data of the original anatectic melt in the targeted rock, that is likely to be represented by the bulk composition of the anatectic MI. To obtain a larger and reliable dataset, nanogranites have been homogenized and analyzed by electron microprobe (EMP), since workable glassy inclusions, which would not need any treatment before analyses, are generally very rare. Several problems must be considered and overcome in order to obtain reliable analyses, such as: 1) Na migration, 2) the size of the melt droplets close to EMP analytical limits, 3) interaction with the host garnet during re-melting, 4) the possible occurrence of boundary layer effects.

The data obtained so far show leucogranitic and peraluminous composition, similar to those expected from literature and experiments on partial melting of natural rocks (Montel, Vielzeuf 1997; Stevens et al. 2007). When plotted in a ternary CIPW diagram, they are at variable distances from the minimum melt composition, consistently with the inferred partial melting T of each melt, e.g. more K-rich melt from Khondalites forms at T ≥ 900°C (Johannes, Holtz 1996).

The analysis of a bulk composition of anatectic MI may become in the future the strongest constraint to the composition of the anatectic melt pushing forward our understanding of how crustal rocks undergo partial melting.

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Relationship between migmatites, granites and deformation in the west-central part of the Paleoproterozoic Svecofennian orogen, Sweden

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The 1.95-1.75 Ga Svecofennian, or Svecokarelian, orogen of the Fennoscandian Shield is composed of a collage of rocks formed at different plate tectonic settings including the 1.86-1.84 Ga continental margin granitoids in the Ljusdal Domain (LjD) and the >1.88 Ga Bothnian Basin. Partial melting of this hot and slowly cooling orogen is related to LP-HT metamorphism.

A coherent granite and migmatite belt occur between the LjD and the Bothnian Basin. Regardless of crosscutting relationships between various types of migmatites and granites and differences in structural style zircon and monazite chronology shows that they are product of the same melt producing event at 1.87-1.86 Ga (Högdahl et al. 2008; 2011). The eastern part of the belt is tectonically emplaced on the LjD whereas the parts to the north of the LjD granitoids are less transposed and coincides with a gravity low and a co-linear magnetic anomaly pattern mimicking the mainly steep gneissic foliation of the migmatites. The granite and migmatite belt is dominated by melt depleted, mesocratic diatexites, and to the northwest by essentially undeformed coeval Kfs-megacryst bearing granitoids. Adjacent to the belt there are structurally controlled areas of lower grade metatexites and rocks of predominantly metasupracrustal origin that have escaped anatexis.

In the diatexite, syn-migmatite deformation is indicated by leucosome filled shear bands and bt-schlieren. The temporal relationship and emplacement sites of different types of granites indicate that syn-migmatite deformation facilitated melt transport. Kfs-megacryst bt-granites are emplaced in the diatexites whereas leucogranites (2-mica granites and ms-granites) and pegmatites are preferentially found in lower grade areas reflecting, respectively, in source and melt that has moved through the system. In the northwestern part of the belt the leucogranites and pegmatites have intruded in a dextral en echelon array. The intersection between this syn-emplacement deformation zone and a coeval conjugate sinistral zone has acted as a conduit for the melt that accumulated and formed a larger (c. 50 km) pluton hosting a kfs-megacryst bearing bt-granite. In addition to tiling of kfs-megacrysts at the margin of the intrusion syn-emplacement deformation is indicated in the adjacent diatexite by frozen channel ways within and parallel to the gneissic fabric. The location of the smaller 1.78 Ga, A-type Grötingen granite (Gorbatschev et al. 2004) at the same shear zone intersection suggests that it also served as a melt transfer system for this younger magmatism.

The thrust tectonics related to emplacement of the granite and migmatite belt on top of the LjD caused partial melting in the latter at 1.83-1.82 Ga. Migmatites of this generation are not present in the hanging-wall or to the north of the LjD. At least in the eastern part of the granite and diatexite belt this metamorphic event is expressed by growth of a second generation of garnet.

At the waning stage of the orogenic evolution, between 1.815-1.795 Ga, a large number of major strike-slip deformation zones were established due to localised shear, including the dextral Hassela Shear Zone (HSZ) and conjugate zones at the boundary between the LjD and the granite and migmatite belt. This shear episode has also facilitated melt transport, but to a lesser degree. Syn-kinematic emplacement of a 1.80 Ga granite within the HSZ is indicated by both geochronology and the compatibility of the magmatic and the sub-solidus shear fabrics.

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Microstructural evolution during solidification of silicate liquids

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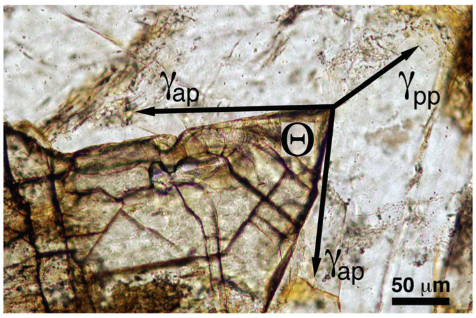
Understanding solidification is the key to understanding the evolution of igneous rocks and the differentiation of the Earth. It is also the key to decoding the microstructures in melt-bearing rocks. The development of microstructures during solidification is essentially dependent on cooling rate, although as solidification progresses and the remaining liquid pockets become smaller, pore size plays an increasingly important role. In this contribution I will focus on the dihedral angle – a relatively new addition to the array of microstructural parameters available to the petrographer.



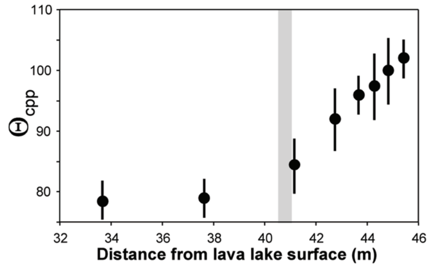
A plagioclase-plagioclase-augite junction, with the dihedral angle, Θ, formed by the balance between the energy of the plagioclase-plagioclase grain boundary, γ_{pp}, and that of the two augite-plagioclase boundaries, γ_{ap}.

The dihedral angle is that angle formed between two inter-phase boundaries, either grain boundaries in the case of solid rocks, or fluid-solid interfaces in the case of fluid-bearing rocks. In textural equilibrium, the dihedral angle is a function of the relative magnitudes of the energies of the interfaces and grain boundaries involved, and is usually of the order 120°. However, in many igneous rocks the population of dihedral angles is not in equilibrium, but is a function of the cooling rate via the balance between grain growth and textural equilibration. The recognition that dihedral angles in many rocks are not in equilibrium has opened the way to using this as a proxy for thermal history.

The clearest idea of microstructural evolution during solidification can be gained by an examination of lava lakes. Drilling of the 130m deep Kiluaea Iki lava lake has produced a sequence of cores containing snapshots of progressive solidification (Helz 1980). Phases that nucleated and grew subsequent to eruption include plagioclase and pyroxene. These form interlinked monomineralic chains and loose frameworks in the early stages, with inter-phase grain boundaries developing later. Completely formed three-grain junctions are seen in appreciable numbers only once the melt fraction is reduced to ~20 vol.%.

The populations of dihedral angles at clinopyroxene-plagioclase-plagioclase junctions have a high median, Θ_{cpp}, in partially solidified rocks and this value decreases with progressive solidification, demonstrating that augite fills the wider pores before the narrower ones. This is most likely due to a combination of the effects of surface curvature on the required undercooling for crystal growth (meaning that crystallisation in smaller pores requires a greater undercooling compared to larger pores, Cahn (1980)) and on the difficulties of mass transport in confined spaces. The value of Θ_{cpp} in the fully solidified lava lake crust is 78 – 85°.

The margins of dolerite sills have similar values of Θ_{cpp} to the lava lakes, but higher values in the centre. The Θ_{cpp} varies smoothly and symmetrically across sills, correlating very closely with the time taken to cool from 1200°C to 1000°C (the interval over which the dihedral angles are forming). It shows no correlation with the average plagioclase grain size. This discrepancy is most likely due to the formation of large-scale segregations of silicic liquid in the upper parts of the sills due to relative movement of solids and liquid: plagioclase grows over an extended temperature range in these melt pools and attains a large size.



The variation of median dihedral angle variation as a function of depth in the Kiluaea Iki drill core. The grey line marks the base of the fully solidified crust. The median is determined from populations of 30-100 measurements and the error bars give the 95% confidence interval.

The microstructures in migmatites are fundamentally different to those in dolerites, as they undergo a period of up-temperature reaction (melting) before they solidify. The microstructures are a function of the duration of the heating and cooling events, with the long duration of many regional events resulting in the possibility that melt-bearing rocks can approach textural equilibrium (i.e. the melt topology is controlled by the dihedral angle and the volume fraction of melt): this is never the case with dolerites.

The microstructures in large pockets of melt in migmatites can essentially be interpreted in the same way as those in dolerites, albeit with slower cooling rates and smaller undercooling before crystallisation (Holness, Sawyer 2008). At the cooling rates typical of large contact aureoles, solidification begins to be affected by pore size for melt pockets < 200 μm across. For these smaller pockets, a greater undercooling is required for crystal nucleation and this leads to enhanced pre-solidification textural equilibration before the melt is pseudomorphed by single grains. The low dihedral angles formed during solidification are usually well-preserved, and are even identifiable in high-grade terrains. This is because sub-solidus modification of dihedral angles requires a long time at high temperatures, and is especially difficult in coarse-grained rocks. Further work is required to quantify the rate at which microstructures attain textural equilibrium in the sub-solidus.

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Migmatites of the Góry Sowie Massif (SW Poland): current state of knowledge and research prospects

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The Góry Sowie Massif (GSM) in SW Poland, a triangle-shaped tectonic unit near the NE edge of the Bohemian Massif, is composed of very high-grade metamorphic rocks, and surrounded by contrastingly lower-grade units (including the Central-Sudetic ophiolite) and younger clastic sedimentary successions. The massif, apart from its rather enigmatic tectonic position within the structural mosaic of this part of the Variscan orogen, includes many intriguing puzzles concerning, e.g., the origin of the rocks and their polyphase-metamorpic evolution (Kryza et al. 2004; Mazur et al. 2006). The massif is composed predominantly of high-grade gneisses and migmatites (with minor amphibolites and other lithologies), and subordinate, but particularly interesting, HP-HT granulites, associated with mantle-derived mafic and ultramafic bodies (Kryza et al. 1996; Brückner et al. 1996).

The Góry Sowie Massif is a well known classical migmatitic terrain that has attracted the attention of geologists since at least the 19th century, and the migmatites and partial melting of rocks are still of wide interest to modern petrology (Sayer et al. 2011). The first systematic mapping of the GSM area in the early 20th century revealed considerable textural and structural variation of the dominant rock types, and more recent studies (Grocholski 1967; Kryza 1981; Żelaźniewicz 1990) confirmed the presence of all the main textural types of migmatites defined by Mehnert (1968). It was in the GSM, where Scheumann (1937) introduced his term “metatexite” to petrology, to indicate a rock that experienced a moderate degree of partial melting.

The prolonged studies of the GSM gneisses, migmatites and associated rocks resulted in often controversial interpretations of their genesis, ages, metamorphic P-T-t paths, structural evolution and geodynamic models. A recent review of ideas and models concerning the GSM rock complex is given by Kryza & Fanning (2007). Here, in this paper, a few of the most important petrological and geodynamic issues are raised, that may help to define future research targets.

1. Protoliths and their ages

The protoliths of the GSM gneisses and migmatites have been a matter of controversy for decades. Recently, most authors have considered these rocks as derived from sedimentary precursors, and only minor lithologies, such as two-feldspar augen gneisses or some amphibolites, as representing meta-igneous rocks (e.g. Kryza, Pin 2002; Kryza, Fanning 2007, and refs. therein). However, there are also different opinions that regard the majority of the gneisses and migmatites as derived from granitoid protoliths (Kröner, Hegner 1998).

The protolith ages of the gneisses and migmatites are poorly constrained. Rather uncertain biostratigraphic evidence suggests a late Proterozoic age of the sedimentary precursors (Gunia 2000). Geochronological data show a wide scatter of ages, difficult for unequivocal interpretation. Recently published SHRIMP zircon ages indicate c. 580 Ma protolith ages for the granulites and, tentatively, a c. 500 Ma age for protolith material in the migmatites (Kryza, Fanning 2007).

Both the nature and ages of the protoliths of the GSM gneisses and migmatites would require further detailed investigations.

2. P-T-t metamorphic paths: granulite (and eclogite?) early metamorphism followed by MP-HT retrogression and anatexis

The P-T metamorphic paths for the gneisses and migmatites have been well constrained (Kryza 1981; Żelaźniewicz 1990; Kryza, Pin 2002). Also, the early granulite-facies event recorded in the falsic and Px-bearing granulites has been assigned to HP-HT conditions of c. 16-20 kbar, 900-1000°C (Kryza et al. 1996; Kryza, Pin 2002). An open question remains the extent of the early HP-HT event in the rock complex, whether it was generally limited to the granulites or (partly?) extended over the gneisses and migmatites (Kryza, Pin 2002; Kryza, Fanning 2007). Quite a few of the mafic rocks (amphibolites) bear clear evidence of early HP-HT metamorphism (e.g. Winchester et al. 1998; Kryza, Pin 2002); such evidence in metamafic rocks at Piława in the E part of the GSM has recently been interpreted to reflect eclogite-facies conditions (Ilnicki et al. 2010).

The timing of the metamorphic events in the GSM rocks is fairly well constrained, at c. 400 Ma for the granulites, and at c. 380-370 Ma for the subsequent amphibolite facies metamorphism and partial melting (Oliver et al. 1993; O'Brien et al. 1997; Bröcker et al. 1998; Kröner, Hegner 1998; Timmermann et al. 2000; Kryza, Fanning 2007).

3. Geodynamic interpretations

The metamorphic P-T conditions for the GSM garnulites demonstrate their deep-crustal provenance which is in accord with the close spatial link of these rocks with mantle-derived mafic and ultramafic rocks. Whether other rock types (e.g. the retrogaded amphibolites from Piława) represent an early HP-HT eclogite-facies event (similarly to the granulites of the Kutnă Hora Complex in the more internal part of the Bohemian Massif; Faryad et al. 2010) would require more detailed thermobarometric evaluation. Certainly, there are indications that some other rocks of the GSM have undergone relatively HP-HT conditions (mostly within the granulite-facies; Kryza, Pin 2002) but, in general, the gneisses and migmatites lack any signs of that early very high-grade metamorphism. The migmatites are strongly overprinted by the subsequent (at c. 380-370 Ma) amphibolite facies metamorphism and anatexis at mid-crustal levels. The latter event in the gneisses and migmatites corresponds to the decompressive retrogression well recognised in the granulites (Kryza, Pin 2002; Kryza, Fanning 2007).

The P-T-t paths of the granulites and migmatites clearly indicate a two-step exhumation process of the HP-HT rocks of the GSM from deep crustal levels (Kryza, Pin 2002; Gordon et al. 2005; Kryza, Fanning 2007).

Within a regional context, the GSM is interpreted as a deep-crustal fragment of the Variscan orogen, uplifted, in two steps, to shallow depths and exposed before the Late Devonian, as shown by geological field evidence and geochronological data (Kryza et al. 2004; Mazur et al. 2006, and refs. therein).

To conclude, the migmatites of the Góry Sowie Massif, together with the other associated very high-grade rocks, provide a unique object for petrological and geodynamic study. Future research targets could usefully cover such topics as: the nature, provenance and age of the protoliths; refinement of the P-T metamorphic paths and their timing for various types of rocks; and, finally, testing of geodynamic models of exhumation of deep-crustal blocks during orogenic processes.

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Formation of corundum megacrysts during partial melting of leucogabbro from the Skattøra Migmatite Complex, North-Norwegian Caledonides

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Corundum megacrysts and pseudomorphs of corundum megacrysts occur at two outcrops within the Skattøra Migmatite Complex (SMC) of the Nakkedal Nappe, North-Norwegian Caledonides. The corundum megacrysts are intimately associated with plagioclase-rich leucosomes (X_{An} = 0.47), suggesting that corundum formed during incongruent melting of plagioclase under water-saturated conditions. In this setting, aluminium was rapidly transported by the melt to surfaces of the growing corundum crystals, providing necessary nutrients for megacryst formation. Petrographic observations suggest that corundum formed together with melt, hornblende, biotite and plagioclase. Hornblende-plagioclase thermometry suggests temperatures in the range 790-810 °C at 10 Kbar pressure for the formation of the corundum bearing zones. PT pseudesections based on the average composition of corundum bearing zones indicate equlibrium PT at 750-825 °C at 9 kbar. Alteration of corundum occurred as a result of water infiltration during retrogression. Corundum reacted principally with plagioclase to form a zoned reaction corona with an inner zone composed of margarite, and an outer zone composed of paragonite, muscovite and clinozoisite. PT pseudosection modeling of margarite composition indicate cooling and decompression from the peak PT (750-825 °C at 9 kbar) to 600°C and 5 Kbar.

Geochemically, the corundum-bearing migmatite is most similar to the leucogabbroic component of the SMC. However, compared to the average composition of the leucogabbro, the corundum-bearing rock shows higher contents of Al, K, Rb and Ba, but lower contents of Fe, Mn, Mg and Ca. Mineralogically, the corundum-bearing rock contains abundant biotite, which is rare in the mafic components of SMC. Based on its geochemical and mineralogical compositions, we suggest that the corundum-bearing rock initially had a composition close to the average composition of the leucogabbro. Migmatization of the corundum-bearing rock was triggered by infiltration of a K-, Rb- and Ba-enriched hydrous fluid. Melting of muscovite and biotite in the pelitic components of the migmatite complex might be the source of the fluid. Probably, some Ca, and possible Fe, Mn and Mg were transported out of the rock by excess fluids, thus increasing the peraluminousity of the rock to grow corundum from the melt.

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Composition, structure and age of the Kamsak migmatites Southern Urals

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The Urals are characterized by a pronounced set of meridional-striking tectonic zones. Across strike, the Urals are subdivided into the Eastern-Uralian (mostly volcanic and volcanic sedimentary complexes) and the Western-Uralian (mostly Paleozoic sedimentary complexes) megazones by the Main Uralian Fault (MUF) or Uralian Suture. In turn, the megazones are subdivided into zones and subzones. Within the Eastern megazone of Southern Urals, the Prisakmarsko-Voznesensk and the Magnitogorsk zones are distinguished.

When geological mapping during the 50-60-years of XX century had been carried out, a large massif composed of migmatites, gneisses and amphibolites was fixed in the southern part of the Eastern-Magnitogorsk subzone, near its western boundary. In the early papers, the Magnitogorsk zone was interpreted as a synclinorium representing a relict of an eugeosynclinal (Perfiliev 1979; Peive et al. 1977 and others). Later, the Western-Magnitogorsk and Eastern-Magnitogorsk subzones were interpreted as relics of two ensimatic island arcs and the Central-Magnitogorsk subzone – as a relic of the intra-arc basin located between the arcs during the Devonian (Zonenshain et al. 1990; Maslennikov, Zaykov 1998). In Kazantsev et al. (1994) this massif was named as the Kamsak block and was described as an allochtonic block lying structurally on the Middle and Late Paleozoic nonmetamorphosed volcanic-sedimentary and sedimentary rocks .

Obviously, the existence of a large massif of metamorphosed silica rocks in the western part of the Eastern-Magnitogorsk subzone does not fit a simple tectonic “two island arcs” model. It seems, this is a reason why the Kamsak block is poorly known and was not taken into account for the tectonic reconstructions. On the recent geological maps, the Kamsak block is shown as a many-stages Late Paleozoic intrusion cutting the Devonian and Carboniferous units. The gneiss-like structure and obvious metamorphic nature of the rocks are ignored.

Our recent studies in the valley of Kamsak river confirmed a vast area of highly metamorphosed rocks (Kamsak block) composed of both high-alumina, and high-calcium (calcium-magnesium) metamorphic rocks. The high-alumina rocks are generally characterized by leucocratic appearance. They are often metapelites composed mostly of quartz, feldspar and mica. The high-calcium (calcium-magnesium) metamorphic rocks are generally melanocratic. They are often represented by amphibolites of different structural-textural types and compositions. Both leucocratic, and melanocratic rocks of the Kamsak metamorphic complex are abundantly intruded by granitoid bodies in the form of very thin veins, dyke-like bodies, irregular bodies and large stocks. The bodies of granitic pegmatites are often seen. Some parts of the Kamsak complex are migmatized. We did not watch the direct relations of the Kamsak metamorphic complex with the surrounding rocks. However, there is a reason to believe that the Kamsak complex has the highest position in the structure of the Epihercynian part of the Southern Urals. We dated several zircons from the Kamsak rocks. Three grains showed concordant ages ($^{206}Pb/^{238}U$) of 551.0±3.1, 552.9±3.4 and 569.4±2.5 Ma. We interpret those ages as a ~ time interval of the major stage of the metamorphism which was in the Late Ediacaran.

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Migmatites from Åreskutan Nappe – implications for granulite facies metamorphism in the Middle Allochthon of the Scandinavian Caledonides, Central Jämtland (Sweden)

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SIMS U/Pb dating of zircons from the Åreskutan Nappe in the central part of the Seve Nappe Complex of western central Jämtland provides new evidence for the timing of metamorphism of the granulite facies migmatitic paragneisses and amphibolites and associated leucogranites and pegmatites. The paragneiss (garnet migmatite) yielded an age for the peak metamorphism of ca. 442 Ma, very similar to that of the leucogranites of ca. 441 Ma. Within the mafic leucosome in the migmatitic amphibolites, felsic segregations crystallized at 436±2 Ma. Pegmatites, cross-cutting the dominant Caledonian foliation towards the base of the Nappe, yield 428±4 Ma and 430±3 Ma ages. Thus, this study provides confirmation of previous less precise geochronological data indicating that the high grade metamorphism of the Seve Nappes in this part of the mountain belt occurred in the Early Silurian (Llandovery) and that nappe emplacement continued through the Silurian, probably into the Early Devonian.

Peak metamorphism at 442-442 Ma is almost contemporary with Scandian deformation, therefore the Seve nappe could not have been completely cooled down and rigid and it was possibly sandwiched between relatively cold units of Köli (Laurentian) Nappe and Lower Allochthon. While the Upper Seve rocks were migmatised and buried deeper in the subduction zone reaching the granulite facies, underlying sedimentary rocks of weakly-metamorphosed Lower Seve were transported possibly at a high levels where they escaped the high temperature Scandian metamorphism.

Comparison with underlying and overlying nappes suggests that the Caledonian orogeny proceeded in a form of multiple events and it was not synchronous along the orogen. The thickening of the accretionary prism at that time and subduction related magmatism in possibly arc environment was located at the western part of the continental margin above the subducting wedge, while the turbidite deposition continued further east, in back-arc basins, closer to the continental Baltica. This evidence together with Laurentian fauna indicates that both continents where relatively close to each other already in early Silurian.

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Monazite dating in the Åreskutan migmatites (central Swedish Caledonides) unravels their earlier HP history

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The collisional Caledonide Orogen in Scandinavia comprises an assemblage of allochthonous units that were thrust onto the margin of Baltica mainly during the Silurian and Early Devonian. However, some of the nappes record an Ordovician history of subduction and thrusting. Recently, Majka and Janák (2011) reported a new finding of kyanite eclogite in the Seve Nappe Complex of northern Jämtland, in the Swedish Caledonides. This eclogite provides important information about the UHP metamorphism and subsequent granulite facies overprint. The calculated peak metamorphic P-T conditions, obtained from Grt-Omp-Ky-Phn geothermobarometry and thermodynamic modelling, are in range of 2.6-3.4 GPa and 720-850 ºC. The maximum pressure conditions fall within the coesite stability field. A granulite facies overprint at 0.8-1.2 GPa and 800-900 ºC is constrained by the calculated pseudosection and Sap-Spi geothermometry. Brueckner et al. (2004) and Brueckner & van Roermund (2007) reported c. 455Ma Sm-Nd mineral age on the (U)HP rocks from that area.

Interestingly, monazite dating of the same tectonic unit c. 300km farther south (Åreskutan, Jämtland), but comprising mostly migmatites and rare kyanite-bearing felsic granulites, reveals three different age peaks, one at c. 455Ma, another at c. 440Ma and yet another at c. 420Ma. Based on the monazite chemistry, it was concluded that the oldest monazite growth event is probably connected with high P metamorphism prior to 440Ma, which represents the peak of granulite facies migmatization. The youngest age is probably related to fluid activity contemporary with the hot nappe emplacement (thrusting), which is expressed by micro-fabric context and chemistry of the 420Ma domains. The oldest obtained monazite age corresponds well to the age of (U)HP metamorphism farther north. It may indicate that much more widespread parts of the Seve Nappe Complex could have been affected by that (U)HP metamorphism. Importantly, Ordovician (U)HP metamorphism of the Seve Nappe Complex in Jämtland has commenced c. 50Ma earlier than the main Scandian UHP event in the Scandinavian Caledonides.

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The orthogneiss-derived migmatites of the Variscan Ulten Zone, Northeastern Italy: limited magma movement through the lower crust

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Anatectic melt (or magma) created in migmatites, is potentially mobile (Sawyer 2008). The Variscan Ulten Zone, on the contrary, provides an example of limited melt transfer within a km-sized lower crust. In the southern side of the Maddalene, the mountain range that straddles the Ulten and Non Valleys of Northeastern Italy, the high-grade basement of the Ulten Zone is dominated by metapelite-derived stromatic to nebulitic migmatites with intercalated minor granitic orthogneisses. In this area we have successfully recognized different stages of partial melting within the orthogneisses. The source rock of the orthogneiss-derived migmatites is a leucocratic gneiss made of alkali-feldspar + quartz + plagioclase and white mica (up to 12 vol%), and accessory biotite, garnet and ilmenite. The migmatites are characterised by the occurrence of patch or layers of felsic and isotropic leucosome. In the migmatites, the residuum contains skeletal grains of white mica, suggesting that the breakdown of white mica controlled the partial melting process. Thermodynamic modelling indicates that the complete consumption of white mica produces a melt fraction of 5%. The major-element chemical composition of the orthogneiss-derived migmatites is similar to that of the orthogneiss source rock, thus supporting the hypothesis that the partial melting of the Ulten orthogneiss occurred without, or limited, removal of material. Correspondingly, the stromatic to nebulitic migmatites produced by 20-30% partial melting of the Ulten metapelites (Braga, Massonne in press) have a composition consistent with their source rocks.

The observations from the Variscan Ulten Zone suggest that the melt fraction in a deep crust is not always capable of migrating away from the source region. The occurrence of a melt-rich lower crust during orogenic evolution decreases the strength of the thickened crust thus favouring the gravitational collapse of mountain belts (Vanderhaeghe, Teyssier 2001).

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High to ultra-high temperature contact metamorphism and dry partial melting of the Tasiuyak paragneiss, Northern Labrador

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Contact aureoles of the anorthositic to granitic plutons of the Mesoproterozoic Nain Plutonic Suite (NPS), Labrador, are particularly well developed in the Paleoproterozoic, regionally metamorphosed, granulite-facies, migmatitic Tasiuyak paragneiss. Regional metamorphism formed the assemblage Qtz-Ksp-Pl-Grt-Sill-Bt-Leucosome. Partial melting during regional metamorphism was followed by a partial melt-loss event, leaving behind a relatively dry bulk composition. Phase equilibria modeling estimates the conditions of melt crystallization to be granulite-facies at ~8.3 kbars and ~850°C. Rocks within the NPS contact aureoles were overprinted by lower pressure, but high to ultra-high temperature mineral assemblages and by microstructures related to a second partial melting event. In general, the contact metamorphosed paragneisses are characterized by cordierite-spinel and cordierite-orthopyroxene intergrowths after sillimanite and garnet, respectively, within a cordierite-bearing quartzofeldspathic matrix.

The second melting event is significant because the Tasiuyak paragneiss was strongly dehydrated during the regional metamorphism and such rocks are not expected to remelt unless they experience UHT conditions. Evidence for UHT conditions observed in these contact aureoles include: (i) the presence of pseudomorphs after the UHT mineral osumilite; (ii) UHT temperatures of up to approximately 980°C estimated by Ti-in-Qtz thermobarometry and phase equilibria modeling; (iii) high-Al orthopyroxenes; (iv) the presence of Zn- and Cr-bearing spinel; and (v) other common UHT textures.

Microstructural evidence for the contact-metamorphism-related partial melting includes: (i) fine-grained monomineral pockets of xenomorphic K-feldspar, plagioclase or quartz; (ii) euhedral cordierite enclosed by xenomorphic K-feldspar; (iii) thin albitic rims on plagioclase; (iv) in-filling of fractures of K-feldspar by plagioclase, plagioclase-quartz symplectites and/or quartz; (v) biotite-quartz symplectite rims on biotite coronae around ilmenite; and (vi) very fine- to medium-grained geometric intergrowths of cordierite and quartz.

The UHT conditions and concomitant melting are attributed to the prolonged and pulsing intrusion of the very hot and generally dry, anorthositic to granitic plutons of the Nain Plutonic Suite, probably over several tens of millions of years.

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Constraining the P-T conditions of melting in stromatic migmatites from Ronda (S Spain)

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The objective of this research are fine-grained stromatic metatexites occurring c. 400 m below the contact with the Ronda peridotite (Ojén unit, Betic Cordillera, SE Spain). These rocks contain Qtz + Pl + Kfs + Bt + Fib + Grt + Ms + Ap + Gr ± Ilm and have a main foliation defined by alternating layers of biotite, fibrolite and thin (~ 0.5 cm) leucosomes. Garnet occurs in a very low modal amount (<1%). Muscovite is texturally retrograde or occurs as an armored inclusion.

The microstructural evidence of melting in the migmatites includes pseudomorphs after melt films, euhedral feldspars, and nanogranite inclusions in garnet. The remelted nanogranites show granitic compositions. The latter microstructure demonstrates that garnet crystallized in the presence of melt.

We have constructed two pseudosections: one for the bulk rock in the MnNCKFMASHT system, and the other for the composition of the remelted nanogranite inclusions in the NCKFMASH system. The calculated isopleths for the chemical parameters of garnet (X_{Mg}, X_{Grs}), biotite (X_{Mg}, X_{Ti}) and plagioclase (An content) in the Qtz-Pl-Kfs-Bt-Grt-Sil-melt field match the actual values in the rock. The P-T conditions of the equilibration were estimated at 4.5-4.8 kbar and 680-700 °C. These P-T conditions overlap with the low-T tip of the melt field in the pseudosection for the nanogranite composition. They are also consistent with the complete experimental remelting of the nanogranites at 700°C.

These results indicate that nanogranites represent the anatectic melt generated at, or soon after, muscovite melting, and that garnet is able to trap melt inclusions also at temperatures lower than these of biotite breakdown melting.

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Fluid regime during the formation of the continental crust

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The continental crust acquires its structure and composition through metamorphic episodes, linked either to compression (typically subduction of oceanic under continental lithosphere) or extension, in many cases caused by the detachment of the subducted slab. A good example is the Variscan crust of the French Massif Central, known from either exposed granitic middle crust or granulite lower crust brought to the surface by recent volcanoes as xenoliths (e.g. Touret 2009). In this case, the extension, dated at about 300 Ma (emplacement of Carboniferous granites), post-dates the Eohercynian compression by about 100 Ma. Both lead to continental accretion: lateral in the first case, through subduction-related volcanism, vertical in the second, through progressive accumulation at the base of the crust of mantle-derived, mainly gabbroic magmas. In both cases, metamorphic P-T conditions exceed minimum granite melting, leading to the widespread production of migmatites in the middle (granitic) as well as in the lower (granulitic) crust. Maximum conditions reach in both cases extreme metamorphic fields (eclogite and granulite), but with marked differences between the compressive and extensive episodes. P-T trajectories in the first case are clockwise, reaching firstly the eclogite field, followed by HP (High-Pressure) granulites. In the second case, magma stacking at the base of the crust leads more to anticlockwise trajectories, with a widespread occurrence of HT (High-Temperature) granulites. As temperature increases markedly during decompression, the field of UHT -granulites (Ultra-High Temperature, T about 1000°C) can be reached in both cases, much more commonly however for granulites related to extension (e.g. Pan-African orogen in former Gondwana; Touret, Huizenga, in press) than to compression (e.g. Limpopo Complex; Tsunogae, Van Reenen 2011). In both cases, the trajectory after peak temperature is quite similar: firstly a rather long segment of sub-isobaric cooling until temperature reaches about 400°C (Moho temperature in most stabilized cratons). Then, after a long emplacement at the base of the crust, a sudden decompression towards the surface when the crustal segment is reworked by a subsequent orogen.

The study of fluid remnants preserved in mineral inclusions provides much information on the fluid regimes during all phases of this complicated evolution. In the upper part of the crust, free fluids circulating in the rocks in open fissures or along intergranular mineral boundaries are dominantly (if not exclusively) aqueous. Crustal melting in the middle crust (dehydration melting = breakdown of OH-bearing mineral phases) releases large quantities of H_2O, immediately eliminated through dissolution in granitic melts: the migmatite crustal melting, which starts within the amphibolite facies field, at temperatures as low as (about) 700°C, acts as a water barrier, prohibiting the occurrence of free water at higher temperature. Low H_2O-activity fluids may however be created at this stage, notably by the reaction of liberated H_2O with former organic matter (graphite) or by gas release during the destruction of some mineral structures (e.g. N_2 in micas). Typical gases found in inclusions, always in relatively minor quantities, are impure CO_2, mixed with variable quantities of (notably) N_2 or hydrocarbons (CH_4).

But the fact that free water cannot survive crustal melting does not mean that the large remaining granulite segment at the base of the crust is fluid-free. Dehydration-melting continues, this time for lithologies (e.g. metagabbros, amphibolite) which had escaped melting at amphibolite conditions. But, at the same time, the amount of low-water activity fluids (first of all high-density CO_2 and highly saline aqueous brines) becomes so abundant that it is impossible to consider them only as by-products of dehydration melting. An external source is required: either remnants of former surface fluids (which, for this reason or another, had escaped the "migmatite barrier") or injection from upper mantle fluids at peak metamorphic conditions (at the time where the granulite lower crust has acquired its diagnostic, water-deficient mineral assemblage). Arguments for this "fluid-assisted granulite " model are notably (Touret, Huizenga in press; Touret, Nijland in press):

- The preservation, especially in UT- and UHT- granulites, of fluid inclusions (high-density, pure CO_2 and high-salinity brines) trapped at peak metamorphic conditions (synmetamorphic fluids).
- For purely physical reasons (similarity of high-density CO_2 isochores and retrograde granulite trajectories) CO_2 inclusions are much more abundant and better preserved than brines, which occur commonly in the form of minute cavities squeezed around remaining solids (collapsed inclusions). Their major importance is however documented by the traces that percolating brines have left at intergranular mineral boundaries (K-feldspar microveins, myrmekites around feldspars, amphibole coronas around pyroxene), as well as by a number of mineral transformations (feldspar to scapolite).
- "Incipient charnockites" at the amphibolite/granulite transition zone correspond to the metasomatic transformation of various lithologies into granulites or charnockites under the influence of fluid streaming. These are not the pathways by which fluids have entered the lower crustal reservoir, but have left it at the onset of retrogradation.
- The fluid amount at peak granulite conditions is further indicated by the massive traces left by granulite fluids when expelled of the lower crustal domain during ongoing retrogradation: (e.g.) regional-size albitisation or quartz-carbonate megashear zones, involving a great number of gold deposits worldwide.

In conclusion, it is proposed that fluid-assisted granulite metamorphism is a process of major importance for the formation of the continental crust. It stores massive quantities of "deep" fluids (high-density CO_2 and brines) in the lower crust, notably during the final stages of supercontinent amalgamation. These may cause large-scale climatic changes when they reach the atmosphere during supercontinent breaking-off.

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Abundant xenocrystic and rare juvenile zircons in rhyolitic ignimbrites: preliminary SHRIMP data from the Lower Permian of the Intra-Sudetic Basin (SW Poland)

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The Góry Suche Rhyolitic Tuffs (GSRT), a moderate-volume ignimbrite (c. 100 km^3 of tephra), is a regional stratigraphic marker in the Lower Permian Volcanic Complex of the Intra-Sudetic Basin, a late Palaeozoic intramontane trough at the NE margin of the Bohemian Massif. An ignimbrite sample from the northern-central part of the basin was tentatively dated at 300±4 Ma (Awdankiewicz, Kryza 2010). In the SE part of the basin, the rhyolitic tuffs correlated with the GSRT occur in isolated outcrops in tectonic grabens. To confirm the intra-basinal correlations and get further insights into the volcanic evolution of the area, two tuff samples have been selected for this SHRIMP study. The samples come from the most distal sections available: from Dzikowiec in the E (sample 805) and from Raszków in the SE (sample 814). Both samples are non-welded ignimbrites composed of altered glass shards and less abundant pumice, quartz and feldspar crystals, and lithic clasts.

Zircons separated using standard methods were analyzed at the Beijing SHRIMP Center, People's Republic of China. In both samples, the zircons are very diversified. Morphologies vary from rounded and subrounded, to subhedral and euhedral, normal-prismatic; a few are broken. All crystals are transparent and colourless, rarely with small inclusions, and vary from rather homogeneous, CL-dark, to CL-brighter, often with distinct magmatic zonation. The U and Th content ranges widely; sample 805: U 53-6377 ppm, Th 14-2921 ppm; sample 814: U 26-1054 ppm, Th 1-1550 ppm. The common lead is low to moderate, with a few spots higher, above 1 %. The ^{206}Pb/^{238}U ages are extremely widely dispersed:

Sample 805: around 2.76, 2.03 Ga, and 835, 560, 490, 390, and between 350-287 Ma.

Sample 814: around 2.70, 2.14, 1.75 Ga, and 602, 556, 478, and between 389-287 Ma.

Several magmatic zircons in both samples cluster between 298 and 302 Ma, suggesting the emplacement age of the tuffs in accord with the earlier obtained age of c. 300 Ma. Most zircons, however, represent xenocrysts, possibly inherited from the magma source and/or derived from the conduit/crater wall rocks or from the basin floor deposits upon the eruption and emplacement of pyroclastic flows. The different zircon assemblages in stratigraphically equivalent samples from different parts of the basin may also reflect a multiphase eruption and accumulation of the tuffs from several successive pyroclastic flows.

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Zoned dravite from Forshammar granitic pegmatite, central Bergslagen province, Sweden: EMPA, XRD and LA ICP-MS study

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Distinctly zoned green dravite occurs in a small pegmatite body in Forshammar, central Bergslagen province, Sweden. The pegmatite is product of the late Svecofennian granitoid magmatism which resulted in the emplacement of numerous 1840 to 1750 Ma old S- to A-type granites and 1820 to 1785 Ma old pegmatites (Romer, Smeds 1994; 1997).

The composition of tourmaline was established with a CAMECA SX100 electron microprobe (State Geological Institute of Dionýz Štúr, Bratislava), powder X-ray diffraction analyses were made using a BRUKER D8 Advance diffractometer (Comenius University in Bratislava, Department of Mineralogy and Petrology), and the trace-elements content was determined with a UP 213 laser ablation system and an Agilent 7500 CE ICP-MS spectrometer (Department of Chemistry, Masaryk University, Brno).

Tourmaline from Forshammar occurs as scattered in quartz, distinctly zoned crystals up to 10 cm in length and 2 cm in width. Tourmaline crystals consist of a green core and a greyish green rim. Moreover, there is a darker green zone in between the core and the rim, observable in the thin section. The optical zoning corresponds to the chemical zoning. Small euhedral inclusions of Hf-rich zircon and xenotime-(Y) are scattered in the tourmaline. Tourmaline is cut by veins of younger tourmaline and even younger veins of muscovite and hydroxylbastnäsite-(Ce).

Tourmaline from Forshammar belongs to the alkali subgroup (Fig. 3) and have a composition of dravite poor in Fe; XMg varies between 0.76 (intermediate zone between core) and 0.93 (rim). The crystal structure refinement of tourmaline from the rim gives the formula $(Na_{0.7}Ca_{0.1}\square_{0.2})(Mg_{1.5}Al_{1.2}Fe_{0.2}\square_{0.1})(Al_{5.3}Mg_{0.7})(BO_3)_3(Si_{6.0}O_{18})(OH)_3[(OH),O]$.

The chemical zoning of dravite from Forshammar is the best pronounced in the distribution of Fe, Mg, Al and Na. The core has the highest proportion of the *X*-site vacancy (0.34-0.43) and the content of Al (6.62-6.71 *apfu*), while the intermediate zone is the most enriched in Fe (0.44-0.54 *apfu*) and Na (0.69-0.75 *apfu*), although the Mg content is similar in both zones (1.74-1.89 *apfu*). The rim is slightly depleted in Al (6.46-6.47 *apfu*) and it has the lowest content of Fe (0.16-0.18 *apfu*) and the highest content of Mg (2.12-2.18 *apfu*) and Na (0.74-0.77 *apfu*) in comparison to the inner zones. The tourmaline vein has similar composition to the rim, but it is even more enriched in Na (0.79-0.84 *apfu*), Mg (2.40-2.49 *apfu*) and has the lowest content of Al (6.18-6.25 *apfu*). The chemical zoning of dravite from Forshammar causes only a slight change of the lattice parameters: a = 15.9252(7) Å, c = 7.1627(3) Å in the core (powder XRD data); a = 15.9223(6) Å, c = 7.1706(5) Å in the rim according to the powder XRD data or a = 15.921(1) Å, c = 7.175(1) Å in the rim from the crystal structure refinement. The variability in the chemical composition is the result of the $Al^{X}\square Mg_{-1}Na_{-1}$ and $AlOMg_{-1}(OH)_{-1}$ substitution.

Most of trace elements in tourmaline were below detection limit; only Li, Ti, Mn Zn, Ga and REE have significantly increased content. Zoning of tourmaline is also expressed in the distribution of trace elements. The content of Ti, Mn, Y and REE is generally increased in the rim while the content of Zn, Ga and Sn decreases from the core to the rim. Moreover, trace elements in the core display oscillatory zoning which is not pronounced in the content of major elements. Titanium, manganese and REE accumulate in the inner parts of the rim and decrease towards the outer parts. The intermediate zone expresses a similar content of trace elements to the inner part of the rim but it has the highest content of Zn and Ga. The REE chondrite normalized values show enrichment in LREE with the most abundant Ce. All zones of tourmaline display a very strong negative Eu anomaly. The content of REE increases from the core to the intermediate zone, reaching the highest values for the inner part of the rim, and then decreases to the outer part of the rim.

The dravite zoning suggests at least two different processes in the tourmaline evolution. The core is likely a product of a magmatic process as suggested by oscillatory zoning. The intermediate zone and the rim could have been formed during a late magmatic to a hydrothermal stage. The vein of tourmaline as well as hydroxylbastnäsite-(Ce) and muscovite are apparently products of hydrothermal processes.

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Degradation phenomena in historic lime mortars – the case of sacral buildings from NW Poland

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The ancient masonries on historical buildings suffer from the attack of air pollutants present in today's atmosphere. Particularly, the ancient mortars and plasters are strongly affected by degradation processes contributed by pollution. Therefore, the detection of the degradation process is essential for avoiding the significant damages and for planning the future restoration.

Different types of the ancient mortars and plasters were collected from historic buildings (churches) dated back to the period of XVII-XIX century, in various (urban, suburban and rural) locations of NW Poland. The aim of this research is to provide the identification of the formation products that were formed in the samples exposed to the atmospheric pollutants. The analyses were performed by means of optical microscopy, X-ray diffractometry, scanning electron microscopy and chemical analysis.

The optical observations and XRD data show that the mortars and plasters contain an inert aggregate consisting mainly of quartz with less common lithic fragments (magmatic rocks and sparse limestones) and accessory minerals: biotite, opaques, amphibole and glauconite. Calcite (in the form of micrite) is the main constituent forming a binder of all mortars.

The results of the chemical analysis exhibit a significant presence of water-soluble salts. The sulfates are the most abundant alongside chlorides which occur typically in smaller quantities. Moreover, some of the analyzed samples contain traces of nitrates. The total amount of soluble salts can reach up to 5.2 wt. % of a sample.

The characterization of the finest particle size fraction (<0.063 mm) performed by XRD detected the presence of different crystalline phases connected with the occurrence of the water-soluble salts. The XRD analysis confirmed a different content of sulfates species in the crystalline form of gypsum ($CaSO_4 \times 2H_2O$) and uncommon hannebachite ($2CaSO_3 \times H_2O$). Halite ($NaCl$) and niter (KNO_3) occur in individual samples only.

The sulfates detected by means of chemical analysis and XRD occur as numerous plates well visible in the SEM image as pseudo-hexagonal lamellar crystals. Typically, they form polycrystalline aggregates located inside cavities and fractures, or rims around aggregate's grains. Their euhedral form and position suggest that these have not crystallized as a constituent of the paste, but they have been formed later, within rigid and hardened material. Thus, gypsum and hannebachite are secondary phases, formed as a consequence of the sulfating process of primordial calcium carbonate. They occur within the zones sheltered from water but attacked by an SOx-polluted atmosphere. The sulfation processes and the crystallization of gypsum and hannebachite give rise to expansion, stress and cracking of the external parts of the samples, promoting progress of the sulfation.

Halite and niter, identified in the particular mortars, are connected to the land-pollution. The former one could originate from the defrosting salts, used throughout decades for the snow clean-up of the pavement surface encircling churches. The presence of nitrates can be commonly associated with the graveyards localized in the nearest neighborhoods.

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Detrital high-pyrope garnet in quartz-rich Turonian sandstones from the North Sudetic Basin: interpretation and open questions

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This study concerns Upper Cretaceous (Turonian) sandstones which are exposed at Jerzmanice Zdrój, North Sudetic Basin, in an old disused quarry being currently a natural reserve. The sandstones are coarse-grained subarkosic to quartz arenites and were deposited in a shallow marine environment. The siliciclastic material came from the weathered Sudetic highs that emerged from a vast Late Cretaceous shelf sea. The aim of the study was to constrain the provenance of the Late Cretaceous sandstones because their mature composition as well as the widespread Late Cretaceous erosion effectively blurred the palaeogeographic situation.

Although the 30 m thick section seems at first homogenous, the detail mineralogical observations allowed to distinguish two parts: the lower and the upper. The lower one consists of subarkosic arenites and contains abundant garnet grains in the heavy fraction. The composition of detrital garnet is diverse and can be categorize into several groups (based on approx. 500 microprobe analyses):

- Cr-pyrope ($\mathrm{Prp_{66\text{-}72}Alm_{14\text{-}20}Grs_{1\text{-}8}Uvr_{4\text{-}12}}$) and pyrope ($\mathrm{Prp_{44\text{-}68}Alm_{15\text{-}34}Grs_{10\text{-}34}}$; $\mathrm{Cr_2O_3}$ < 0.03 wt%)
- high-pyrope high-grossular almandine ($\mathrm{Alm_{36\text{-}52}Prp_{18\text{-}43}Grs_{10\text{-}37}Sps_{<1}}$)
- high-pyrope low-grossular almandine ($\mathrm{Alm_{48\text{-}70}Prp_{20\text{-}48}Grs_{1\text{-}7}Sps_{<1}}$); this group is the most abundant
- spessartine ($\mathrm{Sps_{45\text{-}88}Grs_{2\text{-}34}Alm_{3\text{-}24}Prp_{0\text{-}29}}$; various solid solutions) and high-spessartine almandine ($\mathrm{Alm_{40\text{-}60}Sps_{20\text{-}44}Grs_{0\text{-}22}Prp_{2\text{-}16}}$)
- almandine ($\mathrm{Alm_{>80}}$); a rare group.

The sandstones from the upper part of the section contain less feldspar (partly may be classified as quartz arenites) and far less garnet (0.5-2%) in the heavy fraction than the sandstones from the lower part. The composition of garnet is highly restricted. Individual samples contain exclusively either Cr-pyrope or spessartine. Between these two extremes a 1:1 mixture of both garnet types was found.

Interpretation

The (a) and (b) garnet groups reflect a high pressure assemblage of garnet peridotites, garnet pyroxenites, eclogites and felsic granulites, which is typical of the European

Variscides and occurs in several places in the Bohemian Massif. Medium- to low-pressure granulites (garnet group c) as well as various calc-silicate rocks (possibly indicated by the grossular-rich spessartine from the group d) – in a broader sense – also fit this category of the lower crust (and mantle) origin. Thus, the garnet assemblage from the lower sandstones is internally consistent. The ultimate origin of this assemblage may have been from the Góry Sowie Massif (e.g., Biernacka, Józefiak 2009) or, alternatively, from the Saxothuringian or Moldanubian high-pressure rocks redeposited into the Sudetic area. Both scenarios show some weaknesses, however the composition of detrital pyrope (n = 119 grains) highly resembles that of the Góry Sowie Massif (taking into account minor chemical components like TiO_2 or Na_2O) and differs slightly from the Moldanubian pyrope (Medaris et al. 2005).

The composition of the detrital garnet in the upper sandstones is somewhat inconsistent. The occurrence of Cr-bearing pyrope along with the lack of any other high-pyrope garnet or the wide spectrum of spessartine solid solutions in one sample (sps-grs, sps-prp, sps-alm) are difficult to interpret. Moreover, the high-grossular and high-pyrope spessartine has not been reported from the Bohemian Massif so far. Tentatively, the unusual composition of the detrital garnet from the upper sandstones might be explained as the effect of selective weathering.

Open questions

(1) Presumably, the garnet group minerals show various resistance to weathering. The observations from the Jerzmanice site suggest that pyrope and spessartine may be the most metastable under weathering conditions. However, there is lack of experimental data concerning this problem.

(2) A compelling argument for the origin of the Upper Cretaceous sandstones directly from crystalline or sedimentary precursors is still lacking.

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Devonian/Missisipian I-type granitic magmatism in the Western Carpathian sector of the Variscan Orogen (Slovakia)

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Zircon U-Pb data obtained from 120 single grains in eight Variscan granitoids of the Western Carpathians indicate origin of I-type granitoids during a magmatic event between 365-355 Ma, older than majority of other European Variscan granitic occurrences. Two age groups may be recognised: the older biotite tonalites with their differentiates from the Tribeč Mts. (ca. 362 Ma) and all other biotite tonalites and granodiorites from Nízke Tatry, the Čierna Hora Mts. and the Veporic Unit (ca. 356 Ma). Based on the presented SIMS dating, we re-interpreted older ideas about the genesis of I-type granitoids in the Western Carpathians during the Middle/Upper Carboniferous obtained by conventional U-Pb dating and TIMS method.

The supposed scenario of formation of the I-type West-Carpathian granitoids places them (in sense of Stampfli and Borel 2002) to an arc-related environment, where magmatic activity was activated by beginning of subduction of the Paleotethys Ocean below the European Hunic Terrane (a fragment of Gondwana). A part of the Hunic Terrane, where the early I-type granitoids appeared during Devonian/Missispian was named Proto-Slovakides. Subduction of the Rhenohercynian Ocean from opposite side of Proto-Slovakides resulted in closure of the ocean and amalgamation of Proto-Slovakides with Laurussia by oblique collision, which afterward, triggered north-eastward drift on Laurussia through the transpression faulting. The Variscan drift reactivated during the Alpine orogenesis led to the present eastern position of the crystalline cores within the arc of the Western Carpathians.

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Lu-Hf and Sm-Nd timing constraints on metamorphism in the inverted Barrovian sequence, Sikkim Himalayas, India

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The lower Himalayas in Sikkim (NE India) expose well developed and complete Barrovian sequence in metapelitic rocks. Because the sequence is inverted, the higher grade rocks come out at the progressively higher structural levels, from chlorite to sillimanite + K-feldspar zone. To the north, the higher Himalayan crystallines (HHC) are made mainly of gneisses and migmatites of pelitic composition, and minor quartzites, calc-silicate rocks, metabasites and small granitic bodies (Dasgupta et al. 2004, 2009). The boundary between the lower and higher Himalayas has been considered either as the Main Central Thrust (MCT) or as a zone of ductile deformation named the Main Central Thrust Zone (MCTZ) (Dasgupta et al. 2009 and references therein). Essentially, the inverted metamorphic sequence (IMS) belongs to the MCTZ, which relation and origin still remains as a matter of discussions.

This study demonstrates application of the Lu-Hf and Sm-Nd dating of garnet using multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) to constrain timing of metamorphism recorded in gneisses and amphibolites from the west Sikkim IMS. The sample preparation included acid leaching of garnet fractions with H_2SO_4 (Anczkiewicz, Thirlwall 2003) to eliminate inclusions of phosphate minerals that commonly contain high amounts of Sm and Nd in the gneisses.

The oldest Lu-Hf isochron age of 21.0 ± 0.8 Ma (MSWD = 2.4) defined by garnet and the whole rock was obtained for sillimanite- and kyanite-bearing gneiss. Two amphibolites yielded Lu-Hf isochron ages of 18.3 ± 0.3 Ma (MSWD = 0.45) defined by garnet and hornblende, and 18.8 ± 0.4 (MSWD = 2.5) Ma defined by garnet, hornblende and the whole rock. The data are characterized by a small age error and good fit of individual data points on the regression line.

Significantly younger ages were provided by the Sm-Nd geochronology. Dating of garnet and the whole rock from sillimanite-bearing gneiss gave 11.2 ± 2.1 Ma (MSWD = 0.8) isochron age. Age of 9.0 ± 1.4 Ma (MSWD = 1.6) defined by garnet and the whole rock was obtained for the other sillimanite-bearing gneiss.

The results from this study are consistent with previous monazite dating, indicating that the MCTZ in Sikkim was active at ca. 22, 15-14 and 12-10 Ma (Catlos et al. 2004). The Lu-Hf ca. 21-18 Ma ages obtained for the sillimanite- and kyanite-bearing gneiss and the amphibolites are interpreted as possibly reflecting age of the peak of a high grade metamorphism. Conditions of metamorphic peak may correspond to those from recent thermobarometry study of the sillimanite-muscovite grade metapelites that constrained P-T conditions to 7.5-8.1 kbar and 670-706°C in east Sikkim, and 6-6.8 kbar and 610-711°C in north Sikkim (Dasgupta et al. 2009). Interpretation of the discordance between the Lu-Hf and Sm-Nd ages requires further analyses, including distribution of rare earth elements within garnet.

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High temperature synthesis of chlorapatite and manganese chlorapatite

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The objective of the project is development of experimental techniques for controlled synthesis of chlorapatite $Ca_5(PO_4)_3Cl$ which would be utilized for studies of isomorphic substitutions in the mineral structure, particularly substitutions of Mn for Ca. It is hypothesized here, that relatively high content of Mn in chlorapatites occurring in some pegmatites (up to 18 wt. % or even up to 32 wt. % of MnO, A. Pieczka, personal communication) results not only from Mn substitution for Ca but partly from MnO_4 substitution for PO_4.

Chlorapatite does not precipitate from aqueous solutions or the precipitate is poorly crystalline witch admixtures of hydroxylapatite. Therefore, high temperature synthesis in furnace is utilized. The syntheses are conducted in quartz crucibles by firing synthetic hydroxylapatite mixed with $CaCl_2$ (in stoichiometric proportions or with the excess of $CaCl_2$) in the temperatures between 800-1040°C for 16 to 24 hours. The products of the synthesis are washed with water to remove CaO, and air dried. Hydroxylapatite used here is prepared by wet synthesis from solutions: stoichiometric proportions of $Ca(NO_3)_2$ and K_2HPO_4 are mixed at alkaline pH. The precipitate is aged for several days, washed on the filter and air dried. In-lab synthesis of hydroxylapatite is performed because, for unknown reasons, the use of commercial hydroxylapatite (Merc) in high temperature synthesis of chlorapatite does not give positive results.

The best results are observed in synthesis at 1040°C for 24 hours when 10 times molar excess of CaCl over hydroxylapatite is used. The product of the reaction is crystalline chlorapatite. The XRD pattern fits the chlorapatite JCPDS standard and no impurities are detected within the detection limit of the method. SEM/EDS analysis reveals elongated hexagonal rods up to 0.2 mm long with elemental composition of chlorapatite.

The synthesis of Mn-substituted chlorapatite was attempted using the very same experimental conditions. In these runs, $MnCl_2$ was added at various proportions. Unfortunately, oxidation of $MnCl_2$ is fast resulting in formation of black powder of pyrolusite, which does not react with hydroxylapatite. Therefore, large excess of KCl was added to create a melt preventing the contact of reactants with oxygen. The products of the synthesis were washed with water to remove CaO and KCl, and air dried. The results are inconclusive. The experiments resulted in blue precipitate the XRD pattern of which fits the pattern of chlorapatite with minor shifts observed on some peaks. However, no Mn is observed in EDS spectra. This means that Mn substitution, if any, is below ca. 0.5 wt. % MnO. Microprobe analysis will be used to quantify the results. The attempts to synthesize high Mn chlorapatite (at least up to 18 wt. % of MnO) by substitution of K_2HPO_4 by manganese phosphate are in progress.

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Plumbogummite series minerals in deformed High Tatra granitoid rocks

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During the study of samples from deformed granitoid rocks from the High Tatra shear zones, plumbogummite series minerals were noted. These relatively rare minerals belong to the APS minerals (aluminum – phosphates and sulphates from the alunite supergroup), with a general formula of the series $AB_3(XO_4)_2(OH)_6$ (A – Ca, Sr, REE, Pb, Ca, Ba, H; B – Al, Fe^{3+}; X – P, As, S, Si).

The samples were collected from two ca. 35/85 oriented High Tatra tectonic zones: in the Karb pass and on the Zawratowa Turnia mountain (near the Zawrat pass). Samples from the Karb pass represent highly mylonitized granite with K – feldspar and plagioclase porphyroclasts. The granite from the Zawratowa Turnia mountain contains almost completely sericitized feldspars, quartz, biotite and muscovite; high amount of apatite was also noted. Epidote, chlorite and quartz coating flat surfaces of shear planes occur in both samples. Plumbogummite ($PbHAl_3(PO_4)_2(OH)_6$) identification was based on the chemical composition determined using SEM-EDS method.

The average chemical composition of plumbogummite from both localizations determined using SEM – EDS method are presented in Table 1.

Table 1. Average chemical composition of plumbogummite minerals from EDS analysis (wt%)

	Plumbogummite – Karb pass mylonite	Plumbogummite – Zawratowa Turnia mountain
P_2O_5	32.38	27.93
SiO_2	1.81	2.81
ThO_2	n.d.	2.68
As_2O_5	0.21	n.d.
Al_2O_3	21.68	23.01
Fe_2O_3	0.08	1.12
CaO	12.47	4.93
PbO	30.91	37.22
Na_2O	0.15	n.d.
K_2O	n.d.	0.17
Cl	0.26	0.15
Total	99.95	100.02

Plumbogummite occurs in two characteristic associations. In the Karb pass mylonite, plumbogummite occurs as irregular veins or accumulations at margins, and inside strongly cataclased apatite, epidote and K – feldspar grains. Plumbogummite from Zawratowa Turnia mountain occurs in clusters within REE bearing epidote and apatite along with thorite. It is worthy to mention, that in one sample collected on the Zawratowa Turnia, close to the sample containing plumbogummite, small inclusion of galena inside K-feldspar was noticed.

The plumbogummite minerals were characterized by deficiency of cations in the B position and by admixture of chlorine. There are differences in chemical composition between minerals from the Karb pass and the Zawratowa Turnia mountain. Plumbogummite from the first localization exhibits a higher content of phosphorus and calcium, while the later lead, aluminium and silica. Iron occurs sporadically. In one analytical spot, arsenic was detected. Low amounts of sodium, potassium and thorium as well as irregularities in chemical composition might be related to the analytical inaccuracy caused by small crystal size.

The Karb pass plubmogummite origin is probably related to the reaction between components originating from apatite and K – feldspar dissolution. Plumbogummite associated with thorite and REE bearing epidote can be interpreted as a product of the monazite breakdown. In both cases, the process of plumbogummite formation was facilitated by intense circulation of fluids in the shear zone.

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Epsomite efflorescences on the surface of the Ediacaran Lausitz Greywackes in Włosień outcrop

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The Lausitz greywackes belong to the Izera-Karkonosze Block (Lausitz-Izera unit) which is a part of the West Sudetes (Żelaźniewicz et al. 2003). The greywackes were a product of the turbidites sedimentation from a deep-sea fan, which was sourced from the erosion of granitoides and volcanic rocks of an active continental margin. The greywackes have intercalations of metavolcanics (tuffogeneous), as well as cherts and black shales (Kemnitz, Budzinski 1991). A tuff intercalated with the greywackes was dated using a Pb-Pb-zircon method at 562 Ma age (Gehmlich et al. 1997). In the Lausitz (Saxothuringian Zone), Cambrian granodiorites (at 541±7 Ma) intruded into Proterozoic greywackes (Oberc-Dziedzic 2009) which was the upper age limit of the Neoproterozoic sedimentation (Dörr et al. 2002).

In Poland, the Lausitz greywackes outcrop in Zgorzelec, Platerówka and Włosień (Żelaźniewicz et al. 2003). During field trip to Włosień village, some weathering efflorescence was observed on the surface and between shaly disintegrated rock fragments. The weathering zone was present only in the limited vertical area. The observation yielded no connection between the position of the weathering area and the topography of rock layers in the outcrop. Secondary minerals in form of the white, soft powder were sampled with their base rock. The greywackes are fine grained and in some part have greenish tint. White encrustations were observed under the 10x magnification using a binocular microscope. The minute, isometric crystals achieve up to 0,3mm size and are white to transparent. After the preliminary observation, the material was taken for further analyzes.

In the mineralogical investigation, the XRD spectrum was obtained and the SEM-EDS analyzes were made. A sample for the X-Ray Powder Diffraction was powdered both from the greywacke fragments and from the secondary white powder minerals. On the spectrum obtained, the following minerals were identified in the rock mass: epsomite (36-0419) (Fig. 1), gypsum (36-0432) and probably mascagnite (44-1413) as the weathering products; muscovite (46-1409), chlorite (probably clinochlor) (29-0701), feldspar (probably albite) (31-1480) and quartz (46-1045).

The results of the EDS analyzes clearly confirmed the presence of the epsomite with Mg/S ratio counted between 0,95 to 1,05. Also some additional minerals from the alunogen group were found on a diffraction pattern and interpreted likely as mascagnite.

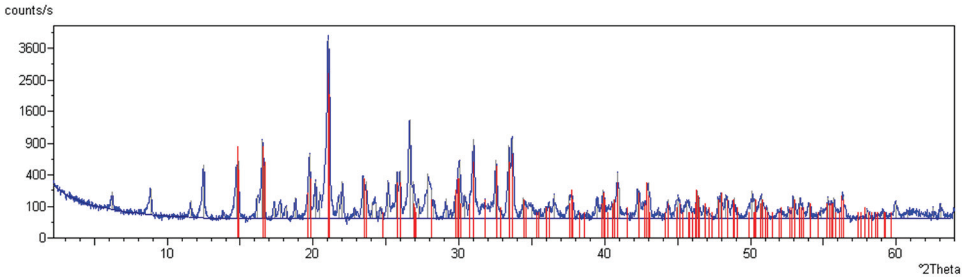

Fig. 1. X-ray powder diffraction spectrum with lines of epsomite (36-0419) for 2theta CuKα radiation.

The mineral from the chlorite group is a source of magnesium for epsomite, however a source of sulfur is not so obvious. The feldspars are likely a source of calcium for gypsum. Oxidation of sulfur, and increasing of the acidity of the chemical environment connected with sulfates anions is necessary for the Magnesium activation from the rock. Because of the numerous conventional (using brown coal) electric plants, the acid rains commonly occur in the West Poland, which can explain the process of weathering. The second possible Sulfur source might be connected with a presence of the dispersed sulfides in the greywackes.

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Geochemistry and Petrogenesis of the Neoproterozoic mafic rocks of the Allaqi area, southeastern desert, Egypt

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The Neoproterozoic mafic rocks of the Allaqi area in southeastern desert, Egypt comprise of two gabbroic varieties. The Type 1 gabbro exhibits tholeiitic nature characterized by the Fe and Mg-enrichment (11.48 and 12.05 on average, respectively), Zr/Y < 4 (2.57 on average), Ti/Zr > 70 (144 on average) and Nb/Y < 0.2. On the other hand, the type 2 gabbro defines a calc-alkaline evolutionary trend on the AFM diagram, exhibits LILE enrichment and HFSE depletion, and has a negative Nb-anomaly along with high Zr/Y ratios. These features are characteristics of the arc magmatism. The trace elements concentrations in the type 2 gabbros are transitional between island arc and MORB, which suggests that the type 2 gabbros do not represent a mid-ocean ridge environment, but most probably have developed in a back-arc tectonic setting. The difference in the slopes of the variation trends suggests that the mineralogical composition of the fractionating assemblage in each gabbroic type is not similar. The rapid decrease and curvilinear trends of Cr, Ni and CaO indicate extensive olivine, clinopyroxene and plagioclase fractionation. The predicted fractionation history for the type 2 gabbros is: Ol, Ol + CPx and Ol + Cpx + Pl and for the type 1 gabbros is: Cpx + Ol and Cpx + Ol + Pl. The mafic rocks of the Allaqi area may have been formed in a back-arc environment and tectonically transported onto the old continental crust during the closure of the late-Proterozoic ocean basin. Consequently, the oceanic assemblage had been intruded by the type 2 gabbros.

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Major and trace elements distribution in lamprophyres from SW Spitsbergen

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The samples for this study have been collected from Chambelindalen valley situated in the NW part of Wedel Jarlsberg Land at the southern cost of Bellsund fiord, SW Spitsbergen. Upper Precambrian basement rocks which outcrop there were affected by Caledonian Orogeny. This area consists of diamictites, dolostones, various slates, greenstones and greenschists (metabasalts to metatrachites) cut by several mafic and ultramafic intrusions. All rocks belong to Recherchefjorden Sequence. Monchiquite, scyelite and cortlandite were distinguished among lamprophyre intrusions.

Biotite-bearing monchiquite (ouachitite) dyke, up to 1 m wide, cuts foliation of the host rocks, and is inferred to be post-metamorphic. Scyelite forms large (up to 200m in size) irregular lenses which are cut by thin (ca. 0.5m thick) veins of younger cortlandites. Both rocks differ distinctly in terms of fractionation of olivines and pyroxenes. They belong to the appinite suite, together with numerous diabase sills apparent in Chamberlindalen. All rocks of the suite as well as surrounding slates are affected by Caledonian metamorphism. The objective of the project is determination of the relation between pre- and post-metamorphic types of lamprophyres: their age, geotectonic setting and the origin of magmas.

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The effects of siderophores on microbial dissolution of pyromorphite by a *Pseudomonas mendocina* bacterium and preliminary observations of a potential link between siderophore release and biofilm architecture

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Siderophores are organic ligands produced by aerobic organisms to acquire nutrient Fe; in addition to binding Fe(III) strongly, they may also bind other metals such as Pb(II). Previous research by our group (Manecki, Maurice, 2008) showed that siderophores may enhance dissolution of the Pb-bearing mineral pyromorphite ($Pb_5(PO_4)_3Cl$) that forms when apatite is used to remediate Pb-contaminated soils. This enhanced dissolution releases nutrient phosphate to solution. Hence, it is possible that in addition to their primary role in Fe acquisition, siderophores may affect the bioavailability of phosphorous to aerobic bacteria. This research compared growth of a siderophore-producing wild type (WT) *Pseudomonas mendocina* bacterium to that of an engineered Δ- pmhA-lacZ mutant (Δ; Dehner et al. 2010) incapable of producing siderophores. Growth conditions were replete with Fe as FeEDTA, which *P. mendocina* can easily access without the need for siderophores. Pyromorphite was the only source of phosphate. Microbial growth experiments were conducted for 50 h. A biosensor (the β-galactosidase activity assay) was used as a means to sense upregulation of siderophore production in both WT and Δ strains as a response to Fe deprivation, even though the mutant could not actually produce siderophores. Epifluorescence microscopy was used to characterize biofilm architecture. In one experiment, the bacteria were physically separated from the pyromorphite by a dialysis membrane that allowed siderophores and phosphate to pass through but prevented bacteria from directly colonizing mineral surfaces.

Both the Δ and the WT strains enhanced pyromorphite dissolution and obtained phosphate from pyromorphite. Two as yet not fully explained phenomena were observed. First, results of epifluorescence microscopy revealed different biofilm architectures for the WT-versus Δ-strains in association with pyromorphite. The WT biofilms were dense and concentric, whereas the bacteria of the Δ strain were sparsely and irregularly arranged around pyromorphite crystals. Second, the mutant showed far more up-regulation of the siderophore production pathway (even though it could not ultimately produce and release siderophores) than the WT strain when the bacteria were grown under conditions in which they could freely attach to pyromorphite. However, this enhanced upregulation was not observed for either WT or Δ in experiments in which bacteria were physically separated from crystals by a dialysis membrane. These observations raise questions about whether siderophore production, attachment to mineral surfaces, and biofilm formation pathways or processes are somehow linked, opening the door for future research.

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Bacterially enhanced dissolution of pyromorphite $Pb_5(PO_4)_3Cl$ by *Pseudomonas putida* strain grown on glucose

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Pyromorphite $Pb_5(PO_4)_3Cl$ is the most stable, mineral form of lead phosphate, which can be found in soils as a product of the *in-situ* phosphate-induced remediation method of Pb-contaminated areas. A recent study by Flis et al. (2010) indicated that the activity of *Psudomonas putida*, which is a common soil bacterium, can significantly enhance pyromorphite dissolution resulting in release of Pb_{aq} to the environment. The enhanced dissolution of the mineral forms of phosphates by the gluconic acid has been reported e.g. by Lin et al. (2005). Some bacteria can live in symbiosis with plants that supply glucose to a symbiotic strain: as a result of the microbial metabolism of the glucose, a gluconic acid is expelled to the environment. The objective of this study is quantification of the effect of glucose as an organic carbon source on the efficiency of bacteria-mediated mineral dissolution. The *P.putida* IBPRS KKP 1136 strain was grown in a glucose-rich medium in presence of pyromorphite serving as a sole source (P-deficient medium) or additional source (P-rich) of phosphates for the bacteria. The experiments were carried out for 160h; the experimental media were periodically sampled and analyzed for pH, [Pb], [P] and gluconic acid. The optical density of the bacterial suspensions was determined by the absorbance measurement at 600nm.

The bacteria have successfully acquired phosphorous from dissolving pyromorphite. The highest Pb concentration was found in a solution in which pyromorphite was the only source of phosphates for the bacteria (5 times higher than in the corresponding P-rich medium). The pH of the solutions inoculated with *P.putida* decreased with time from 7 ± 0.5 at the starting point to 3.6 ± 0.2 at 32h of the experiment; after this time, the pH remained constant. This is probably due to gluconic acid production by *P.putida*. The acid has been detected in bacterial suspensions amended with pyromorphite at the concentrations of 1 mM and 0.4 mM in the P-rich and the P-deficient medium, respectively.

The use of glucose as an organic carbon source for *P. putida* bacterium growth led to the gluconic acid production which enhanced a solubility and a dissolution rate of pyromorphite significantly increasing the release of Pb to the solution.

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Mineral chemistry of the As-bearing ore minerals from Złoty Stok nephrites – preliminary results

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The As-bearing minerals from the contact aureole of Kłodzko-Złoty Stok granitoid Intrusion Unit (Sudetes Mts) are known since medieval ages. The main As-ore bearing minerals in this deposit are arsenopyrite and löllingite (Jędrzejewska, Sałaciński 1997). Nephrite occurs there occasionally, forming thin veins within pyroxenites. The microprobe study of the As-ore minerals from the Złoty Stok nephrites was the main goal of this research.

After the field sampling, the conventional petrographic studies were made and some samples were marked out for microprobe analysis . The 18 electron microprobe analyses of the As-ore bearing minerals were carried out using the Cameca SX 100 microprobe analyzer in the Microscopy and Microprobe Laboratory at the Warsaw University,.

The obtained results showed that the As-ore bearing minerals from Złoty Stok nephrites contain of 0,697-3,359 wt% S; 67,573-70,525 wt% As; 27,960-29,134 wt% Fe; 0,178-0,317 wt% Se; respectively – 1,481-6,832 at% S; 59,680-64,064 at% As; 33,897-34,269 at% Fe; 0,149-0,270 at% Se. Other elements occur in trace quantities.

For the comparison, the chemical composition of the major As-ore minerals from selected Au-bearing arsenic deposits and experimentally synthetized minerals are presented below:

- Arsenopyrite from Fäboliden deposit, northern Sweden, analyses after Bark (2008): 17,31-18,40 wt% S; 47,19-48,71 wt% As; 33,80-34,63 wt% Fe.
- Arsenopyrite from eastern Kazakhstan Au deposits (Kovalev et al. 2011): 18,34-22,19 wt% S; 42,45-47,85 wt% As; 32,59-34,67 wt% Fe; respectively – 32,73-36,71 at% S; 30,34-34,43 at% As; 32,51-32,94 at% Fe.
- Arsenopyrite experimentally synthetized (Fleet, Mumin 1997): 14,70-39,90 wt% S; 24,20-53,50 wt% As; 30,40-35,20 wt% Fe; respectively – 26,60-3,20 at% S; 27,70-51,50 at% As; 31,60-32,70 at% Fe; results depending on synthesis temperature.
- Löllingite from Fäboliden deposit, northern Sweden (Bark 2008): 2,98-3,18 wt% S; 67,59-68,06 wt% As; 27,17-27,38 wt% Fe; 0,74-1,06 wt% Ni, Se absent in all analyses.
- Löllingite experimentally synthetized (Fleet, Mumin 1997): 2,00 wt% S; 70,40 wt% As; 27,40 wt% Fe; respectively – 4,20 at% S; 62,90 at% As; 32,80 at% Fe.

The composition of the analyzed As-ore minerals from the Złoty Stok nephrites is typical for löllingite and similar to e.g. cases from northern Sweden. Some samples have chemical composition similar to synthetic löllingite. Crystals with the highest amount of S (and adequately the lowest As values) probably represent the solid solutions between major löllingite and minor marcasite, because of their structural similarity (O'Day 2006). Some samples with the highest Fe and lower As content, can be an effect of the As substitution by Fe (Radcliffe, Berry 1968). The occurrence of löllingite, arsenopyrite, pyrrhotite and native gold mineral paragenesis indicates the crystallization at the temperature of 525 to 650°C and the pressure between 3 to 4 kbar (0,3-0,4 GPa) (Bark, Weihed 2007). In the experiments on FeAs-NaCl-H_2O system, löllingite occurs at the temperature range from 500 to 600°C. Below granulite facie conditions, the most common As-bearing ore mineral is arsenopyrite, usually occurring with pyrrhotite or pyrite (Barnicoat et al. 1991, vide Bark, Weihed 2007). During the progressive metamorphism, the desulfidation of arsenopyrite takes place, resulting in formation of löllingite and pyrrhotite (Bark, Weihed 2007). The process can be illustrated by the chemical reaction:

$$\begin{array}{ccccccc} 4\,FeAsS & \rightarrow & 2\,FeAs_2 & + & 2\,FeS & + & S_2 \\ \textit{4} \times \textit{arsenopyrite} & \rightarrow & \textit{2} \times \textit{löllingite} & + & \textit{2} \times \textit{pyrrhotite} & + & \textit{sulphur} \end{array}$$

The occurrence of löllingite and the absence of arsenopyrite and pyrite are the arguments for the ore mineralization in pyroxenite and nephrite at a temperature of 500 to 650°C , which is probably higher than in other rocks from Złoty Stok deposit. This can also be a temperature of the whole rock formation – higher than in the major parts of the deposit, however, more study is needed to prove or deny this argument. The absence of other sulfide minerals is unexplained; perhaps it is related to the specific conditions during the mineralization in studied rocks or it may be a result of too small number of studied samples. The abundance of Se in löllingite is difficult to explain and gives the opportunity for further study.

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Clinopyroxene phenocrysts variation in the Księginki nephelinite

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The Miocene Księginki nephelinite consists of clinopyroxene + nepheline + opaques groundmass containing phenocrysts of clinopyroxene and olivine plus megacrysts of clinopyroxene. The groundmass clinopyroxene has the composition of subsilicic titanian diopside (mg# 0.69 – 0.79). Two populations of groundmass grains of different size (<20 µm and >20 µm) occur, the latter showing Ti and Al zonation (Puziewicz et al. submitted).

The sub- to euhedral phenocrysts are up to few mm in diameter. They typically consist of diopsidic cores (mg# 0.78 – 0.83) surrounded by oscillatory-zoned rims of subsilicic diopside composition and by outermost margin which composition is identical to that of groundmass clinopyroxene.

Some of the phenocrysts have cores compositionally similar to the megacrysts, which come from the mantle pegmatitic cumulates of nephelinite magma (Puziewicz et al. submitted). These phenocrysts supposedly originated at mantle depths. The composition of others spread between that of megacrysts and that of groundmass, suggesting that they record the host nephelinite eruptive history.

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New data on weathering of bismuth sulfotellurides at Rędziny, Lower Silesia, Southwestern Poland

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In the middle part of the Rudawy Janowickie Range near Czarnów, there is a large dolomite quarry at Rędziny located within the Czarnów schist series of the eastern metamorphic envelope of the Variscan Karkonosze pluton. A NNW–SSE trending schist belt, that focused migration of hydrothermal solutions derived from the nearby granite, intersects the exploited lens of dolomite marble. Ores disseminated in schist and in contact zones with dolomite include arsenopyrite, cassiterite and pyrite, and subordinate base metal sulfides, bismuth sulfides, bismuth sulfoselenides and sulfotellurides, Ag(Cu)-Pb-Bi(Sb) sulfosalts, Sn-bearing sulfides and many others (Pieczka, Gołębiowska 1997; Parafiniuk, Domańska 2002; Parafiniuk 2003; Gołębiowska 2003; Gołębiowska et al. 2006; Pieczka et al. 2009).

In the southwestern part of the schist belt, an association of bismuth sulfotellurides was recognized, composed mainly of joséite-A, Bi_4TeS_2, joséite-B, Bi_4Te_2S and so called protojoseite $Bi_3(Te,S)_2$, sometimes containing numerous inclusions of native bismuth, bismuthinite, pavonite, benjaminite, Ni-bearing arsenopyrite and rammelsbergite. In the northern part of the belt, Bi sulfotellurides are represented mainly by subordinate inclusions of tetradymite, Bi_2Te_2S, and still less frequently by inclusions of ingodite, Bi(S,Te) and kawazulite, $Bi_2(Te,Se,S)$, commonly occurring within bismuthinite associated with pyrrhotite, cubanite, sphalerite, stannite, arsenopyrite, chalcopyrite, pyrite, matildite, native gold and bismuth.

Pingguite, $Bi_6Te_2O_{13}$ and montanite, $Bi_2TeO_6 \cdot 2H_2O$ are rare secondary tellurate phases forming during oxidation of the above-mentioned bismuth sulfotellurides. Pingguite contains 72.4 wt.% Bi and 12.4 wt.% Te on average, whereas montanite only 63.8 wt.% Bi and up to 18.1 wt.% Te. Both minerals sometimes show a distinct enrichment in As and S; pingguite contains about of 1.0 wt.% As and variable S content reaching 4.50 wt.%, while montanite shows only traces of As and 2.00–2.20 wt.% S. Bismuth tellurates form rims on the surface of sulphotelluride plates and tiny inclusions along cleavage planes suggesting their formation during an initial weathering stage, but later than formation of bismite. Besides pingguite and montanite, main products of oxidation of the primary Bi-rich sulfotellurides are bismite, Bi_2O_3, eulytite, $Bi_4(SiO_4)_3$, bismutite, $(BiO)_2CO_3$, and beyerite, $CaBi_2(CO_3)_2O_2$, a rare Bi carbonate mineral. Accumulations of the latter mineral, snow-white in color and fluffy, reaching to 1.5 cm, clearly distinguish this carbonate from other Bi-containing secondary phases. Beyerite most often is surrounded by bismutite, pale-grey to yellowish in color, and by green eulytite. Bismuth silicate and carbonates can be accompanied by white needles of tellurite, TeO_2. In addition, within the primary Bi sulfotellurides, lenses of a unrecognized secondary Bi-rich phase containing to 5.0 wt.% As were detected. Small grains of gold have been sometimes observed within the oxidized Bi- and Te-bearing mineralization as well as within plates of partly altered Bi sulfotellurides. They form irregular inclusions with sizes reaching few tens of micrometers across and with composition (73.5 wt.% Au and 26.2 wt.% Ag as the mean content) corresponding to a natural alloy with Ag (*electrum*).

Pieczka et al. (2009) have evaluated the conditions of formation of the primary mineralization at Rędziny, established from textural relationships and compositions of main ore-forming minerals. Based on these data it is inferred that the Bi sulfotellurides have crystallized below the formation temperature of bismuthinite and native bismuth, probably at temperatures not exceeding 220°C.

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New results of monazite dating from the metamorphic envelope of Karkonosze granite, Poland

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Fifteen samples of mica-schists from two transects in the metamorphic envelope of Karkonosze granite were collected for the elemental electron microprobe analysis (EMPA) of petrographic thin sections to obtain total-Pb monazite ages in an effort to determine the thermal effects of post-tectonic magmatism on the main metamorphic signature. The northern transect in Izera Mountains is parallel to, but 10 km away from, the Karkonosze granite contact (samples IZ08 1 to 10 in Fig. 1). The southern transect in the region of Rudawy Janowickie (samples MS1 – MS13 in Fig. 1) is perpendicular to the granite contact, beginning directly in the hornfels zone and extending to > 2 km south-east from the granite.

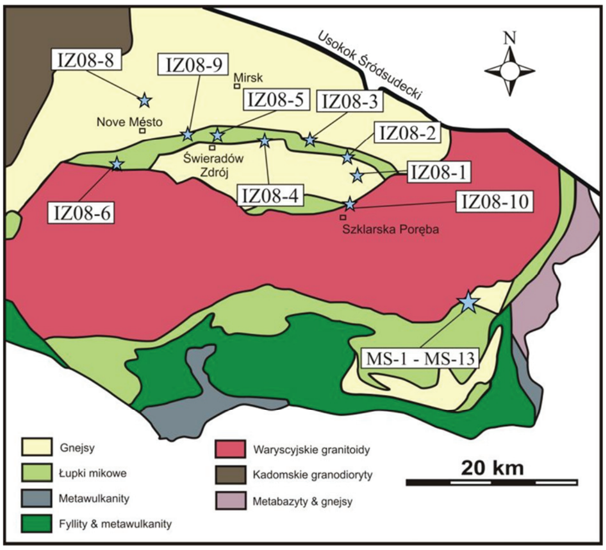

Fig. 1. Simplified geological map of the study area with sample locations.

The rocks consist predominately of medium grained, well-foliated, garnet-bearing mica schists with some garnets showing a rotated (i.e. syn-tectonic) paragenesis. Unfortunately, monazites occur only in few samples. They form small, mostly homogeneous laths (~15 µm) occurring dominantly in the matrix although some occur as inclusions in garnet. Monazites suitable for dating are often associated with grains low in Th and U.

Age calculations follow the protocol of Montel et al. 1996, modified by Konečný (2004). Over two hundred eighty single spot analyses yielded a range of total-Pb dates from 428 Ma to 247 Ma (Fig. 2), with single spot errors of about ±10 Ma. Surprisingly, the intrusion of Karkonosze granite had less effect on the monazite ages than it was expected, even in the samples which were taken in the close vicinity (within one kilometer) to the contact. Therefore, the older metamorphic signature is clearly apparent. The distribution of main population of dates is consistent with the results from previous studies. The dates in the range of 306-318 Ma are interpreted as the age of thermal overprint resulting from the intrusion. Geological significance of the youngest (ca. 251 Ma) and the oldest (ca. 425 Ma) dates is unclear. The age population around 377 Ma is consistent with the proposed age of high-pressure metamorphism of the nearby blueschist facies rocks, the 341-351 Ma dates correspond to the greenshist facies overprint widely recognized in the region, and 326 Ma corresponds to the major thrust displacement and Karkonosze granite cooling.

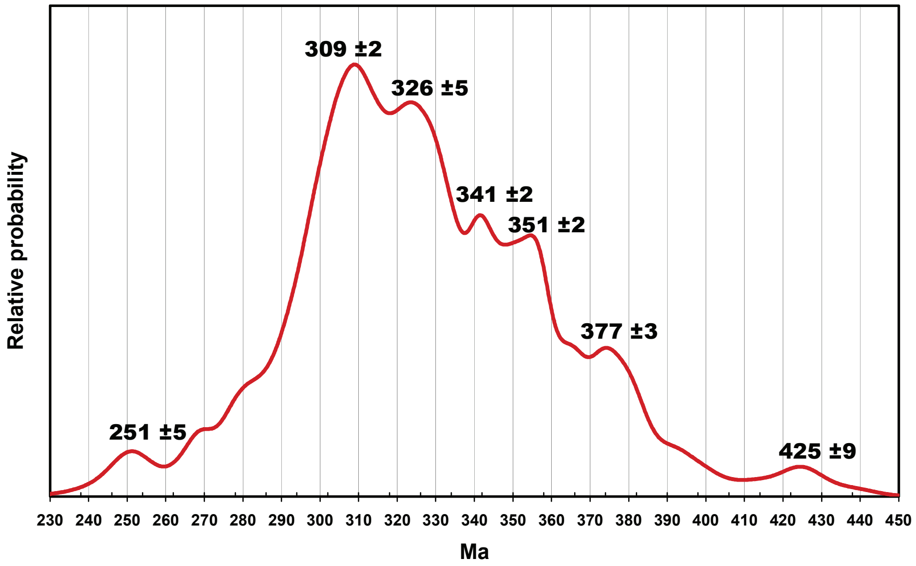

Fig. 2. ISOPLOT cumulative frequency diagram and the results of unmixing of the superimposed populations of ages.

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Weathering-associated bacteria in the forefield of Werenskiold glacier, W Spitsbergen – preliminary results

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Chemical weathering and soil forming processes associated with retreating glaciers contribute to a surprisingly high chemical denudation observed in Polar regions. The area of the study is the foreland of the Werenskiold glacier (SW Spitsbergen). This glacier has been continuously retreating in the last century by several meters a year. The objective of this study is correlation of microbial diversity with the advancement of weathering processes increasing with the distance from the glacier front. The samples were collected at three localities: 50m, 1000m, and 1700m from the front of the glacier. The sampling site closest to the glacier was uncovered from underneath the glacier within last 10 years while the furthermost – over 70 years ago.

Werenskiold glacier basin is eroded in metamorphic rocks which belong to Precambrian Hecla Hoek Succession. The soils are almost entirely composed of primary minerals: rock-forming minerals coming from phyllites, quartzites, carbonate-mica schists, chlorite schists, conglomerates, amphibolites, greenschists and marbles. Alterations of minerals include dissolution of carbonates and oxidation of pyrite accompanied with formation of clays. Secondary minerals resulting from weathering include kaolinite, vermiculite, illite, smectite, and goethite. Secondary clays were identified only in the oldest (the furthermost) soil sample. The correlation between the composition of the waters and the distance of the glacier front is also observed: they evolve from carbonate-dominated to sulfate-dominated. The pH decreases from 8.6 to 7.7 while TDS increases from 133 to 748 mg/L.

The number of bacteria in each soil sample was estimated by total direct count (TDC) method following DAPI (4,6-diamidino-2-phenylindole) staining and microscopic enumeration. Soil DNA extraction, PCR of the highly variable V3 region of the 16S rRNA gene and then denaturing gradient gel electrophoresis (DGGE) for estimation bacterial community composition were performed. Along the Werenskiold glacier forefield total bacteria number was relatively high and varied in the range 1.75 – 2.93 x 10^8 cells g^{-1} soil. Molecular assessment of bacterial diversity of soil DNA revealed that the composition and succession of bacterial populations on the studied stations were different. Comparison of Shannon diversity index values indicated that all sampled populations were significantly different ($p < 0.05$). The results indicated that diverse of number and structure of bacteria between the three stations vary from youngest to oldest soil and depend on the distance to the front of the glacier. The most interesting is high abundance but the lowest heterogeneity of bacteria in the station situated near to the front of glacier. The highest heterogeneity of population (28 OTU), the smallest number and the largest cell sizes (average 0.3 μm^3) are apparent in the middle station.

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The mineral chemistry of Imbramowice metaophiolite suite (Fore–Sudetic block) - petrologic implications

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The Lower Palaeozoic Imbramowice Metaophiolite Complex consists of several steeply dipping tectonic blocks and is located in the central part of the Fore-Sudetic block in the contact zone with the Strzegom-Sobótka granitoids Massif. It includes the altered ultramafic rocks (with tremolite and chlorite) (Majerowicz 1965), the strongly tectonically deformed metagabbros (with plagioclases and Ca amphiboles) and the greenschists (primary basic lavas or vulcanoclastics). All of them previously underwent a low-grade regional metamorphism and a later hornfels contact metamorphism event with emplacement and dismembering. As previously reported (Majerowicz, Pin 1994), the subsequent mantle-derived ultrabasics and basic intrusives of IMC are comparable with remnants of the Lower Palaeozoic oceanic crust known later as the Sudetic Ophiolite (in the sense of: Cwojdziński, Żelaźniewicz 1995), whilst the rocks of the primary basic volcanic members are inhomogeneous. Their composition varies from the typical MORB through the transitional to alkaline basalts, and thus they were interpreted as melange of fragments of oceanic and seamount basalts. (Majerowicz, Pin 1994). The purpose of this paper, is to present new data on the chemical composition of selected minerals from the ultrabasites, gabbros and greenschists of IMC with an attempt to clarify their ophiolitic or un-ophio-litic provenience.

After the field sampling, the conventional petrographic studies were conductedto select samples for the microprobe analysis. About 80 analyses of minerals were carried out using a Cameca SX 100 microprobe in the Microscopy and Microprobe Laboratory at the University of Warsaw.

The analysed minerals of altered ultramafic rock are from a small outcrop near Imbramowice village. The analysis allowed to recognize : forsteritic-chrysolite olivine relics with $Fo_{87,8-89,4}$ content and low abundances of CaO (0,04-0,17wt.%), and NiO ranged from 0,28 to 0,37 wt.%, low-Al diopsidic clinopyroxenes $Wo_{25,76-28,46}En_{66,11-68,78}Fs_{4,73-5,55}$ and secondary penninitic Mg-ortochlorites $(Mg_{9,26-9,50}, Fe_{0,77-0,88})_3Al_2SiO_5(OH)_4$.

The strongly sheared metagabro? (amphibolite?) specimen was collected from the loose rock debris North-West from Imbramowice village. In the sample analyzed, the presence of feldspars with $Ab_{69,71-70}$ content as well as felted fibres of Ca-amphiboles with composition of $Ca_{1,92-1,95}Mg_{2,12-2,22}[(OH_2]/Si_8O_{22}]$ were ascertained. Relics of pyroxenes have not been found in the studied metabasics.

In the greenschists from abandoned quarry at the Pyszczyńska Góra hill, the relics of clinopyroxenes $Wo_{28.20-29.50}En_{52.95-55.13}Fs_{15.93-17.55}$ were found as well as strongly albitized feldspars ($Ab_{99.62-99.74}$). The most widespread phases are there also epidotes and chlorites. First of these can be characterized by following formula $Ca_{4.011-4.063}Al_{4.269-5.283}Fe_{0.690-1.734}$. Chlorites represent rich Fe septechlorites (oxidize chlorites) comparable with chamosite–thuringite group (ripidolite-pycnochlorite subspecies) with formula $Mg_{6.244-6.511}Fe_{2.954-3.133}Al_{4.696-5.005}Si_2O_5(OH)_4$.

The obtained IMC mineral chemistry results do not give a definite answer to question about the ophiolitic provenience of the studied suite. However, the composition of olivines and pyroxenes in the IMC intrusive unit cis comparable with chemistry of ultramafic and mafic cumulate components of ancient oceanic crust formed by slow crystallisation at the shallow levels of magma chamber (Coleman 1977).

The pyroxenes relics from a basic volcanic member differ significantly in composition from the pyroxenes typical for an ophiolitic sheeted dykes complex. Most probably they represented remnants of pyroxenes from hipabyssal dykes formed in continental environment.

It should also be noted, that many of the primary, original minerals of IMC have been replaced by secondary phases during metamorphism events. Therefore, an accurate determination of the geotectonic regime (continental or oceanic?) of IMC using only a mineral chemistry microprobe method is impossible. The explanation of geotectonic position and magmatic evolution of IMC (in the context of complicated geology of Foresudetic part of Lower Silesia region) requires further studies applying the advanced methods of petrological analysis.

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Metamorphic record of retrogressed eclogites from the Piława Górna (Sowie Góry block, SW Poland)

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Migmatitic gneisses exposed in the Piława Górna quarry comprise amphibolites with variably retrogressed eclogite bodies. The least retrograded eclogite samples are dominated by garnet, clinopyroxe+plagioclase and spinel + plagioclase symplectites (Fig. 1), but also contain minor ilmenite, calcic amphibole, orthopyroxene and apatite.

Microstructural features of the rocks suggest that the eclogite stage assemblage (garnet, omphacite X_{jd} up to 0.39, kyanite, rutile and quartz) was overprinted by symplectitic breakdown of omphacite to clinopyroxene and plagioclase, followed by a corona stage (replacement of garnet by amphibole + plagioclase), growth of orthopyroxene and formation of spinel + plagioclase symplectite at the expense of kyanite.

The metamorphic evolution of the eclogites has been constrained using conventional geothermobarometry coupled with phase equilibrium modelling. P-T pseudosections in the system MnNCFMASTH were calculated using Theriak-Domino (DeCapitani and Brown 1987) and the Holland and Powell (1998) thermodynamic database.

The calculated phase equilibrium models for the eclogite stage of metamorphic evolution indicate conditions of 700-750°C and 2.6-2.7 GPa. Conventional geothermobarometers yielded similar pressures (2.1-2.6 GPa), however, at higher temperatures (770-830°C). The subsequent, post-eclogitic events appeared in response to nearly isothermal, probably rapid, decompression. The symplectite stage (formation of clinopyroxene + plagioclase) took place at 770-680°C at pressures 1.7-1.4 GPa. The following corona stage is constrained by phase diagram sections to 1.2-0.6 GPa at 600-700°C, while applied geothermobarometers yielded more precise values of 0.7-0.8 GPa at temperatures 660-700°C. Appearance of orthopyroxene as well as late re-equilibration of clinopyroxene and plagioclase were also due to further pressure decrease (0.7-0.5 GPa).

The phase diagram models predict the stability of spinel (present in symplectite spinel + plagioclase) at pressures < 0.5-0.6 GPa.

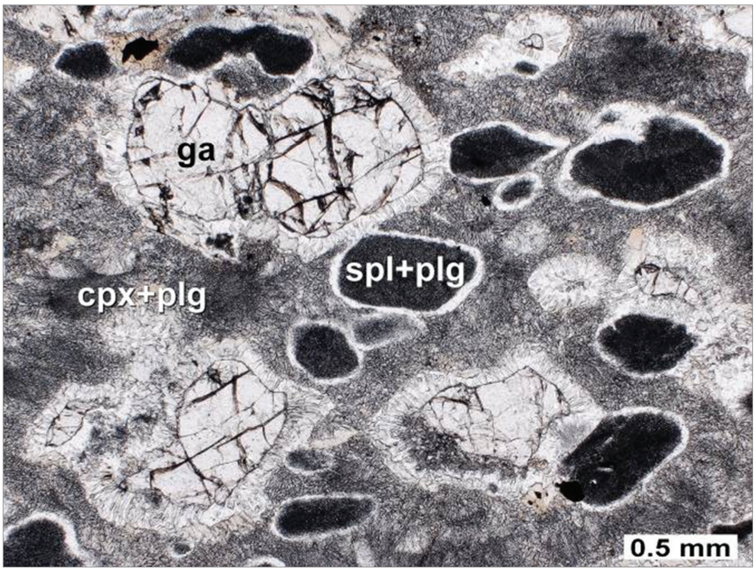

Fig. 1. Microphotograph showing the studied retrogressed eclogites (PPL). Abbreviations: ga – garnet, cpx – clinopyroxene, plg – plagioclase, spl – spinel.

The phase equilibrium modelling suggests that stability and composition of mineral assemblages observed in the studied rocks were very sensitive to the amount of water available in the system and presumably its local fluctuations. However, the overall conditions of metamorphism were relatively dry, particularly at late stages, and eclogite domains remained effectively isolated from the influence of external fluids throughout their P-T path.

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Timing of the polyphase tectonometamorphic evolution the Staré Město Belt, NE Bohemian Massif

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The Staré Město Belt (SMB) is a narrow suture zone located at the northern continuation of the Moldanubian Thrust Zone. The SMB forms an east-verging thrust stack consisting of three NNE-trending narrow lithotectonic units. Two marginal units are dominated by metasedimentary rocks whereas the middle unit comprises NNE-elongated body of the MORB amphibolites (Don et al. 2003). Scattered inlayers of migmatites and mica schists, and an elongated body of the Carboniferous granitoids occur within the amphibolites (e.g. Štípská et al. 2004). All units contain dispersed small-scale leucocratic patches and veins. The structural architecture of the Staré Město Belt is the result of the polyphase Variscan evolution that includes the collision between Saxothuringian or Moldanubian terrane of the Bohemian Massif and Brunovistulia terrane (D1 stage), partial uplift resulted from the continuous underthrusting of the Brunovistulia terrane (D2 stage) and the subsequent mutual displacements between the terranes along the WNW-dipping suture zone (D3 stage) (Jastrzębski in prep.). The transition from D1 to D2 stages was concurrent with the regional metamorphism up to upper amphibolite facies metamorphism that finished with a partial melting at the peak temperature conditions (late-D2). The D3 dextral (top-to-the-NNE) shearing was concurrent with locally superimposed contact metamorphism phenomena, related to the emplacement of NNE-trending, Carboniferous tonalite sill in the axial part of the Staré Město Belt.

To recognize the timing of the metamorphic progression concurrent with the WNW-ESE directed continental collision (D1), a chemical U-Th-Pb dating of monazites included in garnet cores and forming older metamorphic overgrowths of composite monazite grain was undertaken. The timing of the peak metamorphic conditions was established by dating of zircons coming from the leucosome patches and veins resulted from partial melting of the adjacent metamorphic rocks (late D2). The timing of the dextral (top-to-the-N) regional shearing was established using chemical dating of younger metamorphic overgrowths of monazites and those monazites that define the composite S2-S3 foliation in the matrix (D3).

Monazite in the upper unit yielded three distinct ages of 368±6Ma, 355±5Ma and 342±7Ma. The oldest age was obtained on the low-Y metamorphic rim of composite monazite grain exhibiting detrital core and two metamorphic overgrowths. The low Y content in the internal rim suggests that this zone was presumably growing in presence of stable garnet. The external rim of this composite grain yielded an age of c. 340 Ma and that particular zone seems to be dating D3 dextral shearing (since the zone itself is a kinematic indicator). The c. 340 Ma age was also obtained on several other grains. Monazite of this age occurs both as inclusions in garnet and in the matrix. Notably, one of the c. 340Ma grains co-existing with xenotime yielded minimum crystallization temperature of c. 625°C based on the Y-saturation thermometer of Pyle et al. (2001). Importantly, one grain from the upper unit yielded an age of 355±5Ma. This grain forms an elongated prism enclosed in garnet and is characterized by relatively low-Y content. Generally, there is no correlation between the age and the microtextural context of monazite in regard to garnet. This might be simply an effect of fluid flow connected with re-heating events. It is quite possible, since all of the dated monazites enclosed in garnet are connected via cracks with the matrix. Monazite in the middle unit (both, matrix- and garnet-located) yielded only an uniform age of 336±4Ma. It cannot be excluded, however, that some older monazites have also preserved in the rock.

The local in-situ partial melting of metamorphic rocks and the development of associated melt patches and veins could be coeval with the termination of the D1-D2 eastward thrusting. The SHRIMP zircon dating of a leucocratic patch developed at the boundary between the upper and the middle unit yielded the concordia age of 356±2Ma. We interpret this age as age of their crystallization from anatectic melt formed during the Variscan thermal metamorphic peak concurrent with the eastward thrusting. The MS-ICPMS zircon dating of a leucocratic vein from the middle unit yielded the zircon crystallization age of 359±3Ma. Similarly, this age determines the timing of the peak metamorphic temperatures to which rocks of the middle unit of the SMB were subjected at the end of the D2 piling up of the SMB units.

In conclusion, the referencing of the geochronology studies and the tectono-metamorphic record of rocks of the Staré Město Belt reveal multistage tectonic evolution of this zone. The sequence of Variscan events may be described as follows: the Famenian continent-continent collision and related eastward thrusting that led to the tectonic burial and regional metamorphism presumably ending with the Famenian/Tournasian partial melting of the metamorphic rocks, and the Visean subhorizontal dextral (top-to-the-NNE) strike-slip movements.

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Zircon U-Pb dating of Himalayan foreland basin rocks – Himachal Pradesh, NW India

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The geochronology of detrital minerals deposited in the foreland basins provides an important insight into the evolution of the rising orogen. The Sub-Himalayan foreland basin in the Himachal Pradesh region of the Western Himalaya bears a very well developed stratigraphic record of collisional and post-collisional Himalayan history. One of the main obstacles in using the full potential of this record is a highly complicated structure of the foreland basin. More recently, Mukhopadhyay & Mishra (2007) provided detailed balanced cross-section in the Nahan region, which enabled to obtain good control on stratigraphic position of the collected samples. Those samples are currently subjected to the *in situ* LA-ICP-MS U-Pb zircon dating as well as apatite fission track analyses. The main goal of the ongoing work is to restore the uplift and exhumation history of the Himalaya.

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Formation of secondary REE-bearing minerals during grusification of Karkonosze granite

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The Variscan pluton of Karkonosze granite is located in the Western Sudetes (SW Poland – N Czech Republic). It forms an east-west elongated body extending for *circa* 70 km. It is composed of three main types of granites: porphyritic granites, equigranular granite and granophyric granite.

The samples of fresh and grusified porphyritic Karkonosze granite were examined. The REE bearing minerals were studied using SEM-EDS method. Because a standardless method of quantification of the EDS results was applied, the content of water in the REE-bearing minerals was not determine. Thus, a distinction between monazite and rhabdophane is based mainly on the crystals habit and their relationships with other minerals in the rock.

In the unaltered Karkonosze granite (from the quarry at Szklarska Poręba – Osiedle Huty), monazite is the only identified carrier of LREE. In the grusified granites (Głębock, Miłków, Kowary Średnie), primary monazite nearly completely disappears, and secondary phosphates: rhabdophane-(Ce) (Miłków, Głębock) or florencite-(Ce) (Kowary Średnie) were formed.

The primary igneous monazite in the unaltered granite from the Szklarska Poręba – Osiedle Huty quarry is usually present as about 100μm crystals. The monazite grains were observed mainly within quartz, plagioclase and biotite. Their composition is characterized by a high content of light REE (about 0.6 apfu LREE) and Th (about 0.1 apfu Th). The average chemical formula (based on SEM EDS analysis) is: $(Ce,La,Nd,Ca,Th)_{0.7}(PO_4)$.

The altered monazite from Głębock is rather scarce – only two crystals were found in studied samples. Monazite is nearly completely replaced by muscovite – only the rims of large crystals (500 μm, 1 mm) are present. It occurs together with xenomorphic crystals of thorite ($ThSiO_4$), rutile (TiO_2) and Fe oxides. Remains after the monazite crystals were observed mainly in K-feldspar and their composition were characterized by a large amount of light REE (about 0.8 apfu LREE) and trace of Th (about 0.05 apfu Th). The chemical formula of monazite from Głębock is: $(Ce,La,Nd,Th,Pr)_{0.8}(PO_4)$. More common LREE-bearing mineral is rhabdophane-(Ce). It occurs in strongly serecitized K-feldspar. It forms 5-10 μm tabular and needle shaped crystals. They usually group together along fractures or cleavage planes of feldspar. The average chemical formula of rhabdophane from Głębock is: $(Ce,La,Nd,Ca)_{0.9}[(P,S)_{1.1}O_4]\cdot H_2O$. About 0.02 apfu of phosphorus is replaced by sulfur.

The occurrence of rhabdophane –(Ce) in Miłków is related to the hydrothermally altered granites (cointaining a high volume of secondary chlorite, albite, sericite and quartz veins). Rhabdophane-(Ce) from Miłków is not as common as in Głębock, but it occurs in similarly altered feldspars, forming elongated 5 – 10μm crystals in serecitized K-feldspar. Very common are radial clusters of rhabdophane crystals. In Miłków, there are two types of rhabdophan-(Ce): with a higher content of La than Nd: $(Ce,Nd,La,Ca)_{0.8}[(P,S)_{1.1}O_4]\cdot H_2O$, and with a higher amount of Nd than La: $(Ce,La,Nd,Ca)_{0.7}[(P,S)_{1.1}O_4]\cdot H_2O$. There are no other differences between those two types of rhabdophan. About 0.03 – 0.04 apfu of sulfur occurs.

Florencite-(Ce) from Kowary Średnie were found in almost completely sericitized K-feldspars as 5-10μm skeletal crystals. The examined minerals are square-shaped in cross-sections. They occur in clusters along fractures and cleavage planes of feldspar. Florencite is characterized by the presence of a small amount of arsenic (about 0.2 apfu of As). The average chemical formula of florencite-(Ce) from Kowary Średnie is: $(Ce,La,Nd,Ca)_{0.9}(Al,Fe)_{2.9}[(P,As,S)_{1.8}O_8)|(OH)_6]$.

Both rhabdophane-(Ce) and florencite-(Ce) occurs in only few samples. Most of the examined samples from Głębock, Miłków and Kowary Średnie are devoid of LREE-bearing minerals. The absence of Th and other actinides, which are present in primary monazites, is characteristic for secondary REE-bearing phosphates present in the grussified granite. The Si, Mg and alkali content measured in these minerals can be related to the background influence in SEM-EDS analysis of tiny crystals of rhabdophane and florencite.

The hydrothermal alteration of granite in Miłków (not so evident in other localizations) and strong sericitization of feldspars which contain the secondary REE minerals can indicate its hydrothermal origin, but according to Sawka et al. (1986) the formation of secondary REE minerals (e.g. rhabdophane and florencite) can be related to the weathering processes. Decomposed primary monazite is the main donor of elements forming the secondary REE minerals, but sericitized feldspars should be also considered as the source of Al, P (Deer et al. 1997) and REE (Słaby et al. 2007; Dostal, Chatterjee 2010).

The differences in the REE-bearing secondary minerals from Głębock, Miłków and from Kowary Średnie can be explained by a different path of geochemical alteration between decomposition of monazite and formation of rhabdophane or florencite, and a release of different amounts of Al during the alteration of granite.

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Mineral-microbe interaction in the natural gas reservoirs (Altmark, North Germany) exposed to CO_2

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Within the CO_2 Largescale EGR in the Altmark Natural gas field (CLEAN) project, the microbial community of the natural gas field was investigated in saline fluid samples from former production wells taken by downhole sampling. The Altmark reservoir located at the depth of approximately 3500 m, consists mostly of aeolian sandstones and siltstones, and is characterized by high salinity (up to 420 g/l) and temperatures between 120°C and 130°C. Changes in reservoir conditions can increase microbial activity which, as a consequence, may influence dissolution and/or precipitation of minerals. Microbial community of the reservoir fluid samples was dominated by different H_2-oxidising, thiosulfate-oxidising and biocorrosive thermophilic bacteria as well as microorganisms similar to representatives from other deep environments, which have not previously been cultivated. Due to the hyperthermophilic reservoir conditions, cell numbers and activities were below detection limits (Morozova et al. 2011). In addition long term experiments are carried out with sandstones from the Rotliegend Altmark gas field and reservoir fluids.

The interactions between minerals and microorganisms and the changes in the microbial communities are monitored during CO_2 exposure in experimental conditions. In order to stimulate microbial growth, rock core samples from the core deposit were grinded and milled to the size of 0,5 mm, three times autoclaved, and incubated with fresh reservoir fluids as inoculum for indigenous microorganisms in a $N_2/CH_4/H_2$-atmosphere in high pressure vessels at a temperature of 80°C and pressure of 40 bars to simulate microbial growth. After about three months of incubation seven samples out of eight were exposed to high CO_2 concentrations by insufflating it into the vessels, and one sample was exposed to pure N_2 as a controller. First sampling of rock material was executed 10 months after start of the experiment.

Characterization of samples before and after long-term experiments was carried out and compared to samples incubated with N_2 atmosphere to obtain reliable results and give detailed interpretation of mineral-microbe interaction during CO_2 exposure. Different methods (XRD, SEM-EDS) were applied to characterize changes in mineral composition and morphology. Molecular biological techniques like DGGE, PCR SSCP, and molecular cloning will be used to characterize the microbial community composition and the changes due to CO_2 exposure.

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Modeling of ettringite reaction with CO_2 in mineral carbonatization

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Production of electricity at power plants using coal or lignite is associated with the formation of solid waste: fly ash and slag. Energy industry annually produces over 20 million Mg of waste, which constitutes about 17% of the total quantity of waste generated in Poland. Only fraction of this waste is further used in the industry, but much of it remains on the dumps of waste (Sikora et al. 1999). Recently, the potential for use of fly ash in mineral carbonatization of CO_2 is broadly investigated (Uliasz-Bocheńczyk 2009). However, the storage results in certain changes in the structure as well in the chemical and mineral composition of ash. Ettringite is a hydrous calcium aluminum sulfate $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$ frequently formed as secondary phase. Its occurrence negatively affects further use of stored fly ash in the construction industry and affects potential use for production of synthetic zeolites or for mineral carbonatization of CO_2.

The objective of this study is modeling of the effect of ettringite presence on the mechanisms of mineral carbonatization of CO_2 using fly ash. It is proposed here that recycling of fly ash resulting from lignite combustion by complementary application of carbonatization procedures followed by synthesis of zeolites may positively influence effectiveness of both processes. Modeling was carried out using hydro-chemical model PHREEQC. Mineral composition of the ash used in the model is assumed to be similar to the products of lignite combustion in power plants. The role of ettringite in carbonatization stems from its solubility. Calcium ions released to the solution improve the process by formation of calcite. This reaction, however, is competing with potential Ca-sulphate formation of anhydrite and gypsum. On the other hand, the release of aluminum species may positively affect formation of synthetic zeolites. An important element in the model is a control of pH. Therefore, the model was divided into segments allowing for assessment of pH effect on all the mineral phases involved. The results of modeling will be verified experimentally.

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The Goryczkowa granitic type – SHRIMP dating of an original granodiorite-tonalite variety

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The Goryczkowa granite type was described a hundred years ago as a dark grey coarse-grained partly-foliated granite, representing a more basic counterpart to the common felsic (acid) Tatra granite type from Koszysta area (Morozewicz 1909; 1914). Frequent presence of veins and nests filled by fine- to coarse-grained granites & pegmatites rich in pink Kfs within the Goryczkowa granite inspired Michalik (1951) to introduce a process of "metasomathosis" there. Since this time, it become popular to denote this granite as pinkish porphyric "autometamorphosed" type, belonging to a group of so called the Prašivá granite type in the Central Western Carpathians (CWC). Noteworthy, that analogues of this red-pinkish coarse-grained and porphyric granite (Prašivá-type) were described nearly in all Core Mountains granitic massifs in the CWC during the creation of the General geological map of Czechoslovakia in a scale of 1 : 200 000 in the sixties of the XXth Century. The basic geological mapping of the Tatra Mts. for this General geological map was done by Gorek (1959), indeed, he never linked the Goryczkowa granite with the Prašivá type. However, in the Explanations to this General geological map, the authors like: V. Zoubek and L. Kamenický (Maheľ 1967) allocated this type to a family of the Prašivá alkaline granite type. This paradigm was so well-established, that survived nearly to present (e.g. Nemčok et al. 1994; Kohút, Janák 1994; Burda, Klötzli 2007).

A recent field and laboratory study forced us to confront our findings with historical knowledge about this territory. Dominance of a more basic (granodiorite to tonalite) variety in the central part of the body, close to Goryczkowa Czuba, and extensive penetration by pinkish Kfs-bearing pegmatitic and granitic material in the marginal parts were in contrast to the "valid specification" of this granitic type. Informations from Burchart (1970) led us to study the original works of Morozewicz (1909, 1914), where the primal description of the Goryczkowa granite type was in sound to our observations, and in published reappraisal (Kohút et al. 2009) we returned more or less to the original opinion. In a description of the Goryczkowa granite type, we recommend to use: a) the main (core) type as a biotite partly sheared granodiorite to tonalite and b) the marginal type as Kfs-bearing granodiorite to granite variety. The main ridge between Ľaliové sedlo (saddle) and Kondratova Kopa is build by a granitic cupola body intruding into gneissic-amphibolitic rocks of the metamorphic mantle. The central part of this granitic body is dominated by a coarse- to medium-grained sheared biotite granodiorite to tonalite so called Goryczkowa type s.s. However, in the marginal parts of the cupola, these granitic rocks are vastly injected by veins and nests filled by fine- to coarse-grained granites & pegmatites rich in pink Kfs often porphyric in habit. It is obvious that during synkinematic intrusion of the biotite granodiorites to tonalites, the host metamorphic rocks made a carapace. This inhibited an escape of fluids from residual fractionated melt that attacked partly solidified basic Goryczkowa type s.s. close to RCMP (rheological critical melt percentage) Arzi (1978), whereby a Kfs-rich marginal variety originated. We do not exclude an existence of limited metasomatism up to 10 cm in diameter induced by the internal fluids within a late stage of the Variscan magmatic process. The representative sample of the Goryczkowa s.s. type – biotite granodiorite to tonalite was collected for dating. The U-Th-Pb zircon dating by means of SHRIMP was carried out at the All-Russian Geological Research Institute (VSEGEI) in St.-Petersburg. A detailed CL and BSE zircon study exhibits presence of magmatic homogeneous and oscillatory-zoned grains typical for the I-type granitic rocks without restite cores. The zircons SHRIMP spot ages vary in the interval 370 ~ 344 Ma (core – rim) with dominance of the ages between 365 ~ 353 Ma and the concordia age 358 Ma. Noteworthy, this age is in a good correlation to the age 356 ± 8,4 Ma obtained by Burda, Klötzli (2007) from the marginal Kfs-bearing variety. However, presence of the restitic cores (1800 & 560 Ma) within studied zircons (Burda, Klötzli l.c.) indicates not only an attack of residual fractionated melt, but a limited input of different S-type granite melt, and/or participation of mixing & mingling (hybridisation) processes at the origin of the Goryczkowa marginal Kfs-bearing variety. Generally, this dating is compatible to the recent dating from other CWC areas published by Kohút et al. (2010) and Majka et al. (2010).

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Hydrothermal Ni-Co-As mineralization from the Khovu-Aksy ore deposit, south Siberia

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The Khovu-Aksy ore deposit is situated in Tuva Republic, Russia, in the south Siberia. It is a part of the Uvs-Nuur-Khovu-Aksy cobalt-bearing zone which extends along the deep fault zone and has a northeastern strike. The Ag-Au-Bi-Ni-Co arsenide hydrothermal-metasomatic mineralization is connected with the Late Paleozoic-Early Mesosoic rifting between the East Tannu-Ola uplift and the West Tannu-Ola basin, where the mineralized zone is observed (Lebedev 2003).

The Khovu-Aksy ore formation system is generally divided into a skarn stage and hydrothermal vein mineralization stages. The hydrothermal mineralization is hosted by skarns which are formed after Silurian terrigenous-carbonate rocks and Lower Cambrian sedimentary-volcanogenic rocks. The skarns are mainly pyroxene and garnet-pyroxene. The hydrothermal vein mineralization was separated from the skarn stage by a movement of dikes which caused the formation of a new system of faults used by migrating fluids. The formed ore veins were rich in Ni, Co and Fe arsenides, sulfides, sulfosalts and native Bi, Ag, Au and As (Borisenko, Lebedev 2009).

The samples, which have been examined, were taken in July 2010 from the dumps in the Khovu-Aksy inoperative mine. The skarns with the ore mineralization were collected from Severnyi and Yuzhnyi ore field districts.

During the macroscopic studies, pyroxene and garnet-pyroxene skarns were distinguished. Among the ore minerals, nickeline, pyrite, arsenopyrite, chalcopyrite and Ni-Co mineral parageneses were pre-identified. The secondary minerals such as tyrolite, erythrite, azurite were also observed.

Using the optical microscopy in polarized light, the hosted rocks were examined. The minerals which form the skarns are pyroxenes, metasomatically altered feldspars, carbonates, epidotes, chlorites and garnets. The identified garnets are of two types: isotropic and anisotropic ones.

The ore minerals were recognized using the optical microscopy in reflected light. Ni arsenides such as nickeline, rammelsbergite, Co-arsenide such as safflorite and skutterudite commonly occur in samples. Safflorite forms the characteristic stars-like intergrowths. Many mineral microstructures were found. They are connected with the zonal growth of arsenides. These are colloform-zonal structures, cocarde structures, zonal spherulites and breccias. Rammelsbergite is usually overgrown by skutterudite, safflorite, calcite with rims of löllingite, probably. Chalcopyrite, pyrite, hamatite, tennantite-tetrahedrite were also identified.

The zonal arsenide structures were studied with Scanning Electron Microscopy (SEM-EDS). The chemical data and diffraction patterns indicated Ni, Co, Fe arsenides, Ni, Co, Ca arsenates as well as the existence of the uranium-bearing arsenates.

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LA-ICP-MS U-Pb zircon dating of granitic dykes, Sikkim Himalaya (NE India)

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The origin of the inverted Barrovian metamorphic sequence, recognized throughout most of the Himalaya, remains one of the most debated problems not only in the Himalayan geology. The Sikkim region of NE India exposes a complete inverted Barrovian sequence with relatively little tectonic disturbance, which is exceptional on the scale of the entire orogen. Thus, Sikkim Himalaya gives an excellent opportunity to investigate relationship between the inverted metamorphism and the main tectonic structure of the Himalaya. Of particular interest is the Main Central Thrust, which is believed to have played a crucial role in genesis in metamorphic inversion. Granitic intrusions within the MCT zone, as well as these structurally below and above this discontinuity, show a clear syn- to post-kinematic relative emplacement time. This gives an opportunity to provide time constraints on the MCT movement, which combined with direct dating of the metamorphism should help to explain the relationship between these events.

The obvious method of choice in granitoids geochronology is a U-Pb zircon dating technique. However, most of the zircons reveal a very complex internal structure. In the zircons analysed so far, the CL imaging have exposed several zones. The typical for the magmatic crystallization and very reproducible pattern is represented by a partially resorbed core with well-developed oscillatory zoning . The core is surrounded by two successive rims: (1) a homogenous, bright overgrowth of irregular shape, probably linked to the dissolution-reprecipitation process and (2) a weak band of dark CL emission with a high U content, which is interpreted as reflecting the younger metamorphic episode. An *in situ* LA ICP-MS U-Pb dating of each zone is attempted.

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Transformation of cerrusite into lead phosphates and arsenates at various pH

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Bioavailability of Pb and As depends strongly on thermodynamic stability of crystalline species controlling their concentration in solutions. However, the mechanisms of transformation of more soluble cerrusite $PbCO_3$ into less soluble lead apatites are not well undersood (Zhang, Ryan 1999). In this study, the soluble Pb concentration and formation of hydroxylpyromorphite $Pb_5(PO_4)_3OH$ and hydroxylmimetite $Pb_5(AsO_4)_3OH$ were monitored during the reaction of cerrusite $PbCO_3$ and dipotassium phosphate $K_2HPO_4{\cdot}7H_2O$ or dibasic sodium arsenate $NaHAsO_4{\cdot}7H_2O$ at various pH. The phosphate (or arsenate) was added in slight excess with respect to stoichiometric amounts needed for complete transformation of Pb from cerrusite to lead apatite.

At alkaline pH, the dissolution of cerrusite in the presence of $K_2HPO_4{\cdot}7H_2O$ or $NaHAsO_4{\cdot}7H_2O$ is relatively rapid, and complete conversion of cerrusite to hydroxylpyromorphite or hydroksylmimetite is observed within 20h. The final concentration of aqueous Pb is controlled by the solubility of hydroxylpyromorphite/ hydroksylmimetite. XRD and SEM/EDS analyses indicate that hydroxylpyromorphite $Pb_5(PO_4)_3OH$ and hydroxylmimetite $Pb_5(AsO_4)_3OH$ are the only reaction products. The observed reaction mechanism is dissolution of cerrusite accompanied with precipitation of lead apatite, which is driven by the difference in solubility constants of these crystalline phases. A CO_3^{2-} substitution in the structure of precipitating lead apatites is possible. This will be the objective of a separate study.

At acidic pH, lead apatites are not the exclusive products of cerrusite reaction with phosphate or arsenate ions. Hydroxylpyromorphite associated with $PbHPO_4$ precipitate in the reaction of cerrusite with phosphates at pH 3. Similarly, hydroxylmimetite associated with $PbHAsO_4$ (shultenite) form in the reaction of cerrusite with arsenates at pH 3. This might be a combination of kinetics and thermodynamics of the reaction as well as crystal-chemical effect of carbonate ions:

1) kinetics: $PbHPO_4$ and $PbHAsO_4$ are possibly precursors of hydroxylpyromorphite/ hydroksylmimetite formation;
2) thermodynamics: a result of solution speciation at the acidic pH;

3) crystal-chemical effects of carbonate CO_3^{2-} ion presence in the solution resulting in inhibition of precipitation of lead apatite and/or decrease in solubility constant due to the substitution of CO_3^{2-} in the crystalline structure of apatites.

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Synthesis of zeolitic materials from fly ash received from co-firing coal and biomass

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The fly ashes are highly regarded and widely used for the production of synthetic zeolites. The fly ashes are formed during combustion of ground coal in a furnace for pulverized coal in power plants (Quant 1997). Due to the need for obtaining energy from renewable sources, an addition of few percent of co-combusted biomass is increasingly used (Pyssa 2005). This changes the chemical and mineral composition of the burned fuel altering also the parameters of the received fly ash (Wilczyńska-Michalik et al. 2009).

The goal of this research was to investigate the possibility of synthesis of zeolites from the fly ash generated by co-firing coal (~ 95%) and biomass (~ 5%). The main purpose of transformation was synthesis of a good sorbent. The experimental studies were carried on using the fly ash captured by electrostatic filters in the power plant "Kraków" S.A.

The addition of biomass does not affect the mineral composition of the fly ash significantly: small amounts of lime and periclase are present in the sample. However, the changes of chemical composition are more pronounced: the content of CaO, MgO, alkalies, and Fe_2O_3 increases (Wilczyńska-Michalik et al. 2009).

The fly ash was transformed to zeolitic material by a two-stage and by a hydrothermal methods of synthesis (at temperatures of 50 and 70°C, with 0.5, 3 and 5M NaOH). The zeolitic material was more diversed and a greater number of zeolite phases was formed in comparison with the zeolite materials derived from fly ash generated from the same power plant with no co-combustion of biomass (Derkowski, Michalik, 2007). The product of the synthesis was a mixture of several phases of zeolites which were usually fine-crystalline. Seven zeolitic phases were formed: zeolite A, Na-X, cancrinite, sodalite, faujasite, NaP1 and chabazite. The zeolite phases synthesized by the hydrothermal method were most often A and Na-X zeolites, while the material obtained by the two step method consisted of Na-X zeolites and cancrinite.

The experiments allow to demonstrate that it is possible to synthesize zeolite phases even at 50°C. The low temperature requires a longer reaction time. With increasing temperature, longer reaction time and higher concentration of NaOH, the zeolites crystallized in order:

Na-X zeolite A, NaP1 → chabazite → faujasite → cancrinite → sodalite.

The adsorption of lead from aqueous solution was carried out to compare the sorption properties of various products of synthesis with raw fly ash. The concentration of Pb was measured with ICP-OES. Synthesized zeolites adsorbed up to 80 mg Pb on 0.180 g of sorbent which is two times higher than sorption on raw ash. The two-step method of synthesis allows to obtain 15% better absorbent material than the hydrothermal method. The adsorption is relatively fast: after 30 minutes the adsorption level varied between 80 to 90% of the adsorption capacity. The highest adsorption on the zeolite materials was observed after 120 minutes.

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Mineral composition of cave sediments

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The aim of the project is to verify if porous sediments collected in Zygmunt Cave, (Będkowska Valley, S Poland) were formed in place or transported before their deposition. The Zygmunt Cave is formed in Upper Jurassic marine series of bedded limestone. It has been discovered recently and human impact or anthropogenic air pollution is minimal there. Geomorphology and the cave system of the local area have been described. A sample of 50 kg of sediment has been collected from the bottom of the cave and parted to two types. The "upper" type is a top layer, which covers the whole sediment matter named the "lower" type. Grain fractions were separated by sedimentation in water suspension. Primary structure and mineral composition were determined with the use of optical microscopy and X-ray diffraction.

The differences between the sediments are significant. The "upper" type is partly washed and more massive. The "lower" one is darker, porous and with more diverse mineral composition. Quartz, calcite, iron oxides nodules (mainly hematite), plagioclase, potassium-feldspar and clay minerals were identified in the sediment. However iron compounds have been found only in the "lower" type.

Unusual sediment structure is a result of rare way of direct deposition in caves when no transport in suspension, perturbing the sediment, is involved. The water infiltrating and percolating through the walls of the cave dissolve the limestone while accumulating the insoluble mineral matter in situ. Finally, the accumulated substance falls to the cave ground and forms the porous sediment (Ford, Williams 2007). When no flowing water perturbs or destroys that sediment neither the structure nor mineral composition are altered since deposition. More research is planned on the role of bacteria in the process of mineral formation, presence of cosmic matter, and detailed mechanism of formation.

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Hydrothermal copper-bismuth mineralization from the Joremeny adit, Dobšiná, Slovak Republic – preliminary report

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The hydrothermal Cu-Bi mineralization is associated with carbonate veins in the Joremeny adit in Dobšiná (Slovak Republic). The Dobšiná region is located in the Spiš-Gemer Ore Mountains, central part of the Slovak Ore Mountains in the Inner Western Carpathians. The area is situated on the boundary of three tectonic elements: the North Gemeric syncline, the Hnilec anticline and the contact of Veporic and Gemeric Superunit. Due to such geological position the complicated metalogenic processes occurred (Koděra 1986). The hydrothermal carbonate-quartz-sulfide veins in the Dobšiná region are hosted by phyllites, acid metavolcanics and metasedimentary rocks of the Gemeric Superunit (Grecula et al. 1995; Turecký, Števko 2010).

The ore mineral assemblage includes tennantite [$(Cu,Ag,Fe,Zn)_{12}As_4S_{13}$], enargite ($Cu_3AsS_4$), luzonite ($Cu_3AsS_4$), chalcopyrite ($CuFeS_2$) and bornite ($Cu_5FeS_4$), with minor amounts of digenite (Cu_9S_5), pyrite (FeS_2), tetrahedrite [$(Cu,Fe,Ag,Zn)_{12}Sb_4S_{13}$], gersdorffite (NiAsS), arsenopyrite (FeAsS), wittichenite (Cu_3BiS_3), galena (PbS), and Se-, Pb- and Ag-bearing minerals. Ore minerals are present as small veinlets at the borders of carbonate veins forming contact between carbonates and host rocks. Occasionally, enargite, luzonite and arsenopyrite form individual pristine crystals in the carbonate veins.

The textural features indicate presence of two types of chalcopyrite. The first type forms cracked grains associated with bornite and digenite and is partially replaced by tennantite. The cracks in chalcopyrite are filled by tennantite. This suggests that chalcopyrite crystals were formed during the oldest recorded hydrothermal processes. The second type of chalcopyrite forms tiny inclusions and small veinlets in tennantite crystals.

Enargite-luzonite group minerals form main part of carbonate veins. These minerals form intergrown and twinned crystals. Chemical composition of enargite and luzonite is similar, with Sb content of 2 to 7 wt.%.

Four types of tennantite were distinguished based on textural features and chemical composition. The first type (Tnt-I) forms massive and irregular crystals. The second type of tennantite (Tnt-II) fills cracks in luzonite and enargite crystals or replaces both minerals indicating the earlier crystallization of the minerals from enargite-luzonite join. Fine crystals of bornite and digenite form inclusions in tennantite veins. The third type of tennantite (Tnt-III) shows distinct zoning in the BSE imaging. The zoned crystals, veinlets and irregular forms of Tnt-III are enriched in Bi (1.93-11.05 wt.%). Occasionally, the Tnt-III crystals are cut by younger type of tennantite (Tnt-IV) veinlets. The Tnt-IV is depleted in Bi (ca. 1.00 wt.%) with respect to Tnt-III.

The zoned crystals and veinlets of Tnt-III are concentrated in areas where Bi-, Se-, Ag-, and Pb-bearing minerals occur. Small crystals (<5 μm in size) of mineral with composition similar to clausthalite (PbSe), bohdanowiczite ($AgBiSe_2$) and crystals of wittichenite occur in these veinlets. Additionally, the wittichenite forms individual crystals with small inclusions (<5 μm in size) of mineral reflecting composition similar to bohdanowiczite, clausthalite and naumannite (Ag_2Se) with elevated contents of S and Cu. The inclusions of galena are observed in tennantite, enargite and luzonite.

The textural features and chemical characteristics of ore minerals provide insights to the reconstruction of the hydrothermal processes recorded in the Cu-Bi mineralization from the Dobšiná region. The oldest minerals forming this assemblage are chalcopyrite, bornite, tetrahedrite and digenite. The textural position of Tnt-I and enargite-luzonite group minerals indicate that they were formed during younger hydrothermal event. The Tnt-II is texturally younger than Tnt-I, however, their similar chemical composition suggests that both types crystallized from similar hydrothermal fluids. The Bi-enriched Tnt-III, as well as clausthalite, bohdanowiczite, naumannite and wittichenite were most probably formed during circulation recurrence of hydrothermal fluids. The Tnt-IV was formed during the youngest hydrothermal event, possibly at the culmination of the one that formed Tnt-III.

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Evolution of Variscan Orogenic Popiel Ultramafic Rock (SW Poland)

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A small (few hundred metres in diameter) outcrop of ultramafic rock (peridotite/pyroxenite) occurs in the western part of the Sudetes (SW Poland) at the Intra-Sudetic Fault Zone, close to the NE margin of the Karkonosze granite, which is one of the main tectonic lines in NE Bohemian Massif.

The rock consists of olivine (Fo_{84-88}, NiO 0.17 – 0.36 wt %), orthopyroxene (mg# 0.84 – 0.88, Al_2O_3 0,71 –- 4,69 wt. %) and spinel (typically $Mg_{0,68}Fe_{0,31}Ni_{0,01}Al_{1,79}Fe_{0,13}Cr_{0,08}O_4$) + chromiferous magnetite ($Fe_{0,99}Mg_{0,02}Mn_{0,01}Ni_{0,01}Fe_{1,68}Cr_{0,19}Al_{0,06}Ti_{0,03}O_4$) + very scarce ilmenite. The composition of the minerals varies from sample to sample. The primary mineral assemblage is overprinted by tremolite (Si = 7.95 atoms pfu) overgrown by magnesiohornblende (Si = 6.78 a pfu). The serpentine is texturally later than the amphibole.

The major elements content of: SiO_2 39 – 43, Al_2O_3 4 – 7, CaO 3 – 6 wt %, MgO 24 – 32 wt % and Fe_2O_3 11 – 13 wt % suggests a primary clinopyroxene-rich modal composition. The whole rock trace-element and REE patterns are flat with weak Zr and Eu negative anomalies, and slightly (1 – 10 times) enriched relatively to the primitive mantle. The rock has been affected by metasomatism and later metamorphism under oxidizing conditions. It was altered by the low-grade metamorphism producing tremolite, followed by the contact metamorphism in the Karkonosze granite aureole (hornblende crystallization). Supposedly, it is the unique in Sudetes (NW margin of the Bohemian Massif) example of a small orogenic ultramafic body affected by the metasomatic and metamorphic conditions.

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Thermodynamic stability of fluorpyromorphite $Pb_5(PO_4)_3F$ at 5, 25, 45, and 65°C

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The purpose of this study was experimental determination of solubility dependence on temperature for F variety of pyromorphite: $Pb_5(PO_4)_3F$ (fluorpyromorphite FPY). 300mg of synthetic FPY was dissolved for over 3 months in 500mL of 0.05M KNO_3, pH between 2 and 3, at temperatures of 5, 25, 45, and 65°C. Experiments were run open to the air. Solutions were periodically syringe-sampled and analyzed for Pb using AAS. The experiment was run in triplicates.

The equilibrium was attained after 3 months. Solubility of FPY measured with [Pb] increases with temperature. The results indicate that dissolution of FPY according to the reaction:

$$Pb_5(PO_4)_3F \ <=> 5Pb^{2+} + 3PO_4^{3-} + F^-$$

is endothermic. For the first time apparent solubility constants at 5, 25, 45, and 65°C were determined using experimental results: measured [Pb] recalculated to activity was used as input. $[PO_4]$ and [F] were calculated assuming stoichiometric dissolution and using speciation modeled with PHREEQC computer code with the thermodynamic database from Lawrence Livermore National Laboratory. In the range of 25 to 65 °C, the dependence of $\log(K_{sp})$ on the inverse temperature can be approached with linear function suggesting that the enthalpy of dissolution reaction is constant over this temperature range. The enthalpy and entropy of the dissolution reaction was estimated from linear fit of the experimental results to the function

$$\log(K_{sp}) = A \cdot 1/T + B$$

where $A = -\Delta H^o_{rxn}/\ln(10) \cdot R$; $B = \Delta S^o_{rxn}/\ln(10) \cdot R$; R = gas constant.

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CO_2 sequestration by mineralisation using ultramafic rocks – insights into the processes

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Anthropogenic release of CO_2 into the atmosphere from burning fossil fuel and deforestation adds substantially to the natural greenhouse effect, causing warming of the Earth. As a consequence the atmospheric CO_2 concentration has risen from 280 ppm during the pre-industrial times to 393 ppm today (NOAA-ESRL 2011).

One of the proposed solutions for removing CO_2 from the atmosphere is its permanent fixation into minerals stable on the Earth`s surface, such as carbonates, through processes commonly known as CO_2 sequestration by mineralisation (CCSM). The principal concept of this solution is to *turn silicate into carbonate*. Mg-rich silicates, such as serpentine and/or olivine are the suggested minerals for use in the process. Two models for CCSM are being presently considered worldwide: *in situ* and *ex situ.* The *in situ* model involves direct injection of CO_2 into ultramafic rock-dominated sites (e.g. ophiolite complexes). It is assumed that the CO_2 – rich fluids will react directly with the fractured host rock to form carbonates. The *ex situ* model is the focus of our study and it comprises quarrying of feed rock, transport to a processing plant, chemical and physical pre-treatment and carbonation; finally disposal of the CO_2 - rich solids. The great advantage of the latter over both *in situ* and underground geological storage is that it offers permanent safe carbon storage (Maroto-Valer 2010). The costs of post-sequestration monitoring are therefore anticipated to be negligible. Nevertheless, the high energy penalty that all the carbon capture and storage (CCS) processes introduce is one of the main concerns, and the reduction of costs is being investigated worldwide.

The implementation of CCSM on an industrial scale is dependent on the development of low energy intensive processes with high reaction conversion and reaction kinetics (ETI Team, 2011, unpublished). Such kinetics is achieved through a series of physical, chemical and thermal pre-treatment processes of the feed rock prior to its carbonation. The pre-treated substrate, magnesium ions or magnesium oxide, is reacted with dissociated CO_2 to form magnesite - a phase stable over geological time (millions of years).

Previous studies showed that the rate of reaction varies greatly depending on the feed rock material. One of the solutions to overcome high energy penalties is to identify the most effective reaction pre-treatment (enhancement) processes for a specific feed rock. This includes investigating the optimal temperature and pressure as well as the reactants that catalyse the processes. Our study envisages a detailed petrographical analysis of the feed rock and a series of subsequent laboratory experiments reacting a range of ultramafic and mafic rocks collected from various target localities within the United Kingdom. The rocks selected display a wide compositional and textural diversity from massive and sheared serpentinite, serpentinised harzburgite, pyroxenite and melatroctolite.

The CCSM process, despite being first suggested in 1990 (Seifritz 1990), is still a novel solution; thus it introduces uncertainty and causes a strong debate between scientists. The most effective technology for a specific feed rock is a topic of current research. However, CCSM potentially offers a viable alternative for countries that do not have appropriate geological formations suitable for underground geological storage as well as for areas where the storage sites are located far from the emitters (Maroto-Valer 2010).

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Carbonate substitutions in hydroxymimetite $Pb_5(AsO_4)_3OH$

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Due to their relatively high environmental stability, mimetites have gained a considerable attention as metal sequestration agents in water treatment and remediation of contaminated soil. Hydroxymimetite $Pb_5(AsO_4)_3OH$ is a mineral isostructural with hydroxylapatite $Ca_5(PO_4)_3OH$. Carbonate CO_3^{2-} substitutions in hydroxylapatite have been studied in details for years. Carbonate substitution in mimetite, however, has been ignored. It is hypothesized here that carbonate CO_3^{2-} ion can be incorporated in the structure of hydroxymimetite affecting its solubility and other thermodynamic properties.

Hydroxymimetite was synthesized from aqueous solutions in the presence of carbonate ions. Aliquots of $Na_2HAsO_4{\cdot}7H_2O$ and $Pb(NO_3)_2$ were dissolved in 300mL of redistilled water and gradually mixed into a large 3-L beaker filled with 1.5 L of continuously stirred redistilled water containing dissolved NH_4 HCO_3 at 22°C. The concentration of carbonates was limited by the solubility of cerussite $PbCO_3$ so that carbonate content was kept below cerussite saturation. The pH was kept at 9 during the synthesis with the use of NH_4OH. After the addition of solutions was complete, the suspension was allowed to age for at least 48 h, decanted, filtered, washed with redistilled water and air dried. In the control experiments, hydroxymimetite was synthesized in the absence of NH_4 HCO_3. No attempt to avoid the presence of dissolved CO_2 from air was made.

The solids were examined with the use of X-ray powder diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM/EDS). The product of both syntheses is crystalline hydroxymimetite free of any impurities. Shift of certain diffraction peaks with respect to JCPDS standards was observed in both samples. These standards, however, provide no information about the potential carbonate content. Therefore, computer modeling will be used to verify the potential effect of CO_3^{2-} substitution on diffraction patterns. Calculation of unit cell parameters a = 10.2622 Å, c = 7.5015 Å indicate an increase of "a" unit-cell edge which is attributed to the dilation of the apatite channel (Fleet et al. 2004). In the FTIR spectra of both synthetic mimetites, two characteristic bands are apparent: at 1385 and 1420 cm^{-1}. The absorption bands in this area are indicative of B-type CO_3^{2-} substitution in hydroxylapatite (Regnier et al. 1994; Fleet et al. 2004). These results suggest that, similarly to hydroxylapatite, carbonate ion can be incorporated into hydroxymimetite structure. The effect of substitution on stability and thermodynamic properties of this mineral phase are to be determined.

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Gahnite inclusions in beryl in pegmatites of the Sowie Mts. Block, the Strzegom-Sobótka Massif and the Hruby Jesenik Massif, Sudety Mts.

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The paragenesis of gahnite with beryl was described, among others, by Jeremenko et al. (1988) and recently by Downes, Bewan (2002). None example of the paragenesis have been found in Poland yet, except for a note of Szuszkiewicz and Łobos (2004), who described one beryl crystal with gahnite inclusion from a granitic pegmatite at Siedlimowice.

We recognized gahnite inclusions representing the Fe-rich member, so-called ‘kreittonite’, in some beryl crystals from pegmatites of Sudety Mts. It is worth to underline, the gahnite inclusions were found only in some from several dozen of analysed beryl crystals (Łodziński 2007), however, in abundant quantities they have been found only in crystals from the Sowie Mts. Block, the Strzegom-Sobótka Massif and the Hruby Jesenik Massif. Gahnite in a pegmatite from the Sowie Mts. Block has been described earlier by Pieczka et al. (2004) and from the Hruby Jesenik Massif by Stanek (1960) and by Novak et al. (2003).

The presence of gahnite was identified in beryl crystals from muscovite zone, feldspar zone and quartz core in such localities like Piława Górna in the Sowie Mts Block, Branna, Maršikov, Petrov nad Desnou, Šumperk and Velké Losiny (all the localities in the Hruby Jesenik Massif), and Siedlimowice in the Strzegom-Sobótka Massif. At Piława, gahnite was found in ‘Subtrio’ vein cutting migmatitic gneisses, eclogites and amphibolites where it co-occurred with schörl, beryl, bavenite, bityite, clinochlore, phenakite, zeolite-group minerals (laumontite). At Branna, gahnite occurs in pegmatite veins in two-mica gneisses and quartzite along with Fe-Mn garnet, schörl, columbite, apatite, zircon, uraninite, native Bi; at Maršikov in pegmatite veins in gneisses along with schörl, Fe-Mn garnet, chrysoberyl, columbite, zircon, native Bi; at Petrov nad Desnou in veins in migmatized biotite gneisses, together with Fe-Mn garnet, bavenite, columbite, zircon, apatite, bismutine, epidote, goethite, hematite; at Šumperk in veins in gneisses with Fe-Mn garnet, bavenite, schörl, columbite, triplite, zircon, bertrandite, bismutine, pyrite, arsenopyrite, magnetite, whereas at Velke Losiny in pegmatite veins in gneisses with Fe-Mn garnet and columbite. At Siedlimowice gahnite occurs in pegmatite veins within two-mica granite and is associated with Fe-Mn garnet, beryl, columbite, apatite, zircon, monazite, rutile, galena and sphalerite.

The gahnite inclusions form always euhedral crystals from 3 up to 70 μm long (10-20 μm on average), very often with an atypical elongated habit with a width to length ratio close to 1:25. They often occure in the form of streaks parallel to column walls of the beryl crystals and are located perpendicularly in relation to inclusions of other minerals. The inclusions, very often closed inside a thin quartz ‘bubble’, predominate in the outer zone of beryl, however, they are present in whole beryl crystals. In beryl from the Sowie Mts Block, gahnite coexists with inclusions of feldspars, apatite, muscovite, tourmaline-, columbite- and pyrochlore-group minerals; in crystals from the Hruby Jesenik Massif with inclusions of K-feldspar, albite, Mn-apatite, muscovite, biotite, zircon, magnetite, Fe-Mn garnets, andalusite, columbite-group minerals, whereas in crystals from the eastern part of the Strzegom-Sobótka Massif with K-feldspar, Fe-Mn garnets, muscovite, zircon, monazite, rutile, Mn-apatite, pyrite, sphalerite, galena, tourmaline- and columbite-group minerals.

The gahnite inclusions are commonly homogeneous in composition. Crystals from the Sowie Mts Block contain (54.79-56.08) wt% Al_2O_3, (32.87-36.83) wt% ZnO, (6.35-9.27) wt% FeO, (0.00-1.19) wt% Fe_2O_3, (0.15-0.35) wt% MnO and (0.07-0.20) wt% MgO, whereas the contents of Cr, Ti and Ca are always below the respective detection limits. An average chemical formula is $(Zn_{6.26}Fe^{2+}_{1.60}Mn_{0.05}Mg_{0.04})(Al_{15.97}Fe^{3+}_{0.07})O_{32}$. Analysis of gahnite inclusions from other then SMB localities are difficult due to very small sizes and extremely elongated crystals. The Chemical formula for gahnite from Velke Losiny in the Hruby Jesenik Massif is $(Zn_{4.73}Fe^{2+}_{3.17}Mn_{0.11})(Al_{14.83}Fe^{3+}_{1.17})O_{32}$.

The Zn-bearing gahnite plots in a field of magmatic pegmatites, and those richer in Fe in a field of metamorphosed pegmatites in the Batchelor`s and Kinnaird`s (1984) diagram. Gahnites from the Strzegom-Sobótka Massif (Zn/Fe_{total}=2.95) and from the vein ‘Subtrio’ (Piława Górna, Sowie Mts. Block) (Zn/Fe_{total}=2.94-5.26) correspond to magmatic pegmatites. The gahnites from Gilów (Zn/Fe_{total}=1.09) in the Sowie Mts. Block (Pieczka et al., 2004), from Branna (Zn/Fe_{total}=1.00) (Novak et al., 2003) and Velke Losiny (Zn/Fe_{total}=0.96-1.35) all in the Hruby Jesenik Massif represent highly evolved metamorphic pegmatites.

The chemical composition of gahnite with a low MgO content below 0.12 wt% allows to classify the pegmatite from Siedlimowice and the pegmatite ‘Subtrio’ from Piława Górna as typical rare-element granitic pegmatite in the classification of Černý and Ercit (2005). A high MgO content of up to 0.78 wt% in gahnite from Gilów in Sowie Mts Block (Pieczka et al. 2004) and from Branna in the Hruby Jesenik massif (Novak et al. 2003) indicates that these pegmatites are the most influenced by metamorphism and the most fractionated.

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Calcite-fluorite paragenesis in Zechstein rocks of the Kłodawa Salt Dome – preliminary data

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Fluorite in marine evaporites is regarded as a sedimentary or diagenetic mineral that precipitates either from sea water or from pore brines, but it may also originate from hydrothermal fluids after burial of sediments (Warren 1999). Its origin is particularly enigmatic in highly deformed, deeply buried evaporites which could be flushed by pore fluids at various stages of tectonic deformation. The occurrence of fluorite in Zechstein evaporites was evidenced by Bereś et al. (1971) at the Fore-Sudetic Homocline. However, there is no published information on its occurrence in salt diapirs in central part of the Polish Zechstein Basin. The only finding of fluorite in the Kłodawa salt mine by Ł. Karwowski is quoted as "personal information" by Wachowiak (1998). This study presents first data on occurrence and origin of fluorite in the Kłodawa Salt Structure (KSS).

The KSS is a diapiric salt ridge situated in central Poland. It is built of Zechstein evaporitic-terrigeneous rocks accumulated during four Zechstein cycles: PZ1, PZ2, PZ3 and PZ4. These sequences were deformed due to salt flow between the Zechstein and present. The more competent beds (shale-, carbonate- and sulphate-rich) became fractured and locally sealed by a variety of epigenetic minerals. Our investigations focused on fluorite-bearing veins which were evidenced in Stinking Shale – Main Dolomite succession of the second Zechstein cycle in several locations within the Kłodawa salt mine.

The Stinking Shale and Main Dolomite in the KSS are built of laminated clay-carbonate and carbonate-sulphate successions, respectively. They are separated by Upper Anhydrite sulphate deposits from the Oldest Halite rock salt and by Basal Anhydrite sulphate deposits from the Older Halite rock salt. These beds are cut perpendicularly and/or obliquely to layering by arrays of extensional veins. The thickness of veins varies between 1 mm and about 10 cm, whereas their length is up to several metres.

Calcite is the dominant mineral in fluorite bearing veins. Most commonly it is colourless and translucent or whitish. The crystal size varies between 0.1 mm at vein contacts with host rocks to several millimetres in vein centres. The largest crystals exceed 1.5 cm in diameter. Majority of crystals have xeno- or hypautomorphic shapes, however the largest crystals are rhomboedric. Fluorite is either violet or depicts zonal, violet-to-colourless structure. It is dominantly xeno- and hypautomorphic with crystals of 1-2 mm in size which occur in aggregates of 3-5 mm in diameter. The size of largest crystals exceeds 3 cm and their aggregates exceed 5 cm in diameters. Fluorite has overgrown smaller calcite crystals and locally it contains calcite inclusions. Larger crystals seem to have grown coevally with larger crystals of calcite. Intercrystal pores are filled with solid bitumens and central parts of thicker veins are built of anhydrite and halite. X-ray analysis evidenced local occurrence of celestite. Cathodoluminescent analysis indicates that there is only one generation of calcite crystals.

The analyses of isotope composition of carbon and oxygen in calcite indicate that it contains $\delta^{13}C$ = -10.19‰ and $\delta\,^{18}O$ = +2.07‰, respectively. Based on isotope fractionation curves and obtained data, crystallization temperatures for calcite were evaluated. These varied between 6°C according to equation by O'Neil et al. (1969) and 18°C if equation by Zheng (1999) is applied.

Geometry, composition and structure of veins occurring in Stinking Shale and Main dolomite beds in the KSS indicate that these are extensional syntaxial veins which were originally built of calcite and fluorite. Some veins re-opened at later stage of bed extension and were sealed with anhydrite-halite phases, as well as with bitumens. Such a sequence of mineralization points to crystallization of calcite and fluorite prior to fracturing of anhydrite beds, which enabled circulation of brines between rock salt beds and Stinking Shale – Main Dolomite complex. This conclusion is supported by temperature of calcite crystallization interpreted on the basis of its isotope composition. Lower than 20°C temperature implies that deformation of shale-carbonate succession of the second Zechstein cycle started after shallow burial of sediments (evaluated for 200 m to 600 m of sediment overlay), still in the Zechstein or in early Triassic. Therefore, the low temperature calcite-fluorite paragenesis most probably crystallized from original sea brine entrapped in pores. It started to develop after sediment cementation due to bed extension, brittle fracturing and progressive compaction of sediments, thus, it probably records the earliest deformation in horizontally layered Zechstein sequence. Sea water provenance of this mineral paragenesis is also supported by isotopic data.

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^{222}Rn and ^{220}Rn emanations from metamict minerals

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Metamict minerals contain radioactive elements that degrade their crystal structures over geologic time. The degradation occurs primarily through progressive overlapping recoil nuclei collision cascades from α-decays of ^{238}U, ^{232}Th, ^{235}U and their daughter products. We have measured ^{222}Rn and ^{220}Rn emanations from metamict minerals comprised of nine oxides (brannerite, davidite, fergusonites, pyrochlores,samarskites and uraninite), two phosphates (monazites), and eight silicates (cerite, gadolinites, perrierite, rinkite, thorite, turkestanite and vesuvianite). Total absorbed α-doses for these minerals ranged from 1.4 x 10^{15} to 4.6 x 10^{18} α-decay/mg for cerite and uraninite, respectively. The ^{222}Rn emanation coefficients varied from 1 x 10^{-6}% (uraninite) to 1.2 x 10^{-2}% (monazite Petaca). The ^{220}Rn emanation coefficients varied from 1.1 x 10^{-4}% (gadolinite Ytterby) to 0.1% (gadolinite Marysin). The ^{222}Rn emanation coefficients are lowest for metamict minerals with the highest concentrations of ^{238}U i.e., uraninite, samarskites and brannerite. The results of our study indicate that both ^{222}Rn and ^{220}Rn emanation coefficients are significantly lower than those reported previously.

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Phenomenon of decolouration (bleaching) of Dębnik limestone (S Poland) – a case study

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Black limestone from the Dębnik quarry near Cracow (S Poland) was widely used in the Polish architecture of the 17th and 18th centuries. Upon exposition to the atmospheric conditions outdoors, the stone changes the original black colour to grey or even white. These effects can be widely seen in both architectonic elements and outcrops. Superficial whitening of the Dębnik limestone exposed to the polluted, urban atmosphere is combined with deposition of anthropogenic particulates on the stone surfaces, which makes any plausible explanation of the phenomenon more difficult.

The study was carried out on samples of fresh and weathered stones from the Dębnik quarry. The analyses included colorimetric measurements and a range of mineralogical and chemical methods: optical microscopy, scanning electron microscopy with energy dispersive spectrometry, X-ray diffraction, infrared spectroscopy, Rock-Eval pyrolysis, gas chromatography combined with mass spectroscopy, and X-ray fluorescence.

The variety of Dębnik limestone used widely in the Baroque period in the minor architecture in Poland is a black, homogenous, micritic rock with fossils and white calcite veins and nests (Bromowicz 2001; Niemcewicz 2005). Except for calcite, the limestone contains subordinate feldspars, clays, pyrite, organic matter of the kerogen type, and traces of quartz and hydromuscovite. Of the components present within the rock, its black colour is imparted by pyrite and organic matter (Marszałek 2007; Marszałek, Skowroński 2010). Weathering of these two is commonly blamed for decolouration of the black limestones but no new mineral phases have been observed in the rocks exposed in the Dębnik quarry. This should rather exclude pyrite and suggest that the changes could be associated with alterations of the organic compounds. However, the superficial microstructural changes, expressed mainly by roughing the outer layer and resulting in surface optical phenomena, cannot be excluded. They may include scattering of the light on rough rock surface, i.e. on the grain boundaries, with simultaneous lowering of the light absorption. Additionally, one of the decorating technique of Dębnik limestone (‘manière criblée’, ‘graining’) seems to confirm this last reason of bleaching these stone.

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Challenges and frontiers in modern analytical mineralogy and geochemistry: accuracy vs. precision, reproducibility vs. traceability

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The role of mineralogy as a separate and significant science has recently been questioned by many mineralogists worldwide (http://www.mindat.org/forum.php). Wrongful categorization of mineralogy as a dying-out museum-custodian profession draws our attention away from its huge role in material sciences and economic geology. Interdisciplinary profile of a modern mineralogist including chemistry, physics, biology, environmental science, laboratory skills and recently economics makes him a unique and valuable asset in many branches of so-called high-tech industry dealing with thin wafers, micro-computer chips and synthetic HP-HT phases, quality control management, large-scale and urban mining operations and development of existing and emerging microanalytical techniques.

Modern world's demand for highly reliable data is not only dictated by the new standards in measurement protocols set by the scientific society (e.g. clean labs) or improved capabilities of new analytical equipment (e.g. high resolution probes) but also by the necessity of founding political decisions regarding environmental, human health and food hazard norms on something tangible. In the time of depleted resources (such as REE, refractory metals, PGE and metalloids) certain authorities more than ever must base their feasibility studies on very accurate numbers since concentrations falling in the μg/g range may decide on the viability of mining. A measurement value becomes not only a proof of some scientist's theory; it becomes money, lives and life standards.

With the advent of the new, highly precise and spatially resolved microanalytical *in situ* methods (e.g. nSIMS, S-μXRF) obtaining a satisfying value is no longer an issue. The question is whether the value, nevertheless precise, is accurate. How far does it fall from a true value? Several recent studies showed that using the same high-resolution mass spectrometers, however employing different measurement protocols, yields significant biases and discrepancies between precision and accuracy of the measurements (Vocke, Mann 2010). Such differences may originate from several factors including systematic errors and inappropriate calibration routines (Kirkup, Frenkel 2006). A reasonable choice of a reference material (RM) for calibrating analytical instruments may result in the accuracy of the measurement being very close to the precision of the instrument. Unfortunately, the choice of a RM gives rise to a whole series of new issues such as traceability and reproducibility of the values obtained in the measurement.

Many of the so-called in-house RMs (either well-described natural samples or fit for purpose synthetics) meet inner-laboratory accuracy requirements especially when both are used to calibrate the instrument and calculate the composition of the unknown analyte (e.g. in comparative methods) but fail to satisfy traceability requirements (like in the study of Ballhaus 2000) because they lack the documentation (or it is incomplete) or the link to a primary standard is missing. The use of uncertified RMs also leads to, recently widely recognized, poor reproducibility and comparability between different laboratories and methods.

In comparative methods such as SIMS or EPMA where matrix effects are of central importance, certified RMs (CRMs) are used not only for calibration of the instrument but also for quantification of the analyte. It is widely recognized that most of the available CRMs fail to satisfy the matrix-matching criteria and hence contribute to the production of incorrect data. They are usually amorphous (glasses, pressed pellets) and thus (1) interact with the beam (ions, laser, x-rays) differently compared to natural samples (Kuhn 2010), (2) frequently have exotic compositions or (3) contain dopants that are not certified (Jochum 2010) and in the end, (4) none of them has homogeneity assured at the sub-µg sampling scale making them useless for high-resolution analysis (Kane 1997; Wiedenbeck 2010).

Several attempts have been made worldwide to produce and certify RMs appropriate for analysis of crystalline phases. The authors of this presentation are involved in one of such activities. Problems of modern geo-microanalysis and its link to mineralogy were only mentioned here and will be addressed and presented in detail.

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Preliminary results of SHRIMP zircon study of granite from the Kudowa-Olešnice granitoid massif (Sudetes)

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The Kudowa granite massif occurs in the western part of the Orlica-Śnieżnik Dome in Sudetes. It is composed mostly of peraluminous, sometimes metaluminous igneous rocks, classified as monzogranite, granodiorite and tonalite (Borkowska 1957; Żelaźniewicz 1977). These rocks are grey or reddish in colour, coarse to medium grained. They contain biotite with intensive pleochroism, plagioclase euhedral crystals (reaching 0.5 cm in diameter),

K-feldspar, quartz, biotite and muscovite. Accessory minerals are represented by Fe-oxides (mainly hematite), epidotes, titanite, apatite and zircon. The latter occurs as euhedral, colourless to yellowish-brown, normal to long prismatic crystals. The most frequent crystallographic forms are {110} and {101}. BSE imaging reveals oscillatory zoning typical of magmatic growth and ubiquitous inherited cores. The zircons are rich in UO_2 and ThO_2 which contents are up to 0.89 and 0.49 wt%, respectively. Increase of U and Th contents is coupled with grow of metamictisation degree reflected by lower totals of chemical analyses and presence of Fe, Ca, Al – elements not typical for zircon composition.

The Rb-Sr isochron data of Kudowa-Olešnice granitoids yielded the value of 331±11 Ma (Bachliński 2002). K-Ar dating of biotite presented the wide spectrum of age values from ca. 275.4 to 338.2 Ma (Bachliński, Hałas 2002).

Looking for the best quality zircon for dating purposes, the coarse grained granite sample was collected from small outcrop close to Lewin Kłodzki (50° 24’ 25”N and 16° 18’ 16” E. Fourteen zircon grains (100 – 200 μm in length) were analysed by SHRIMP II at the Research School of Earth Sciences, Australian National University (Canberra). Six results were rejected from further consideration due to their high discordance (>10%) and high content of common Pb (>1%). The youngest, statistically homogeneous group of nearly concordant ages, yielded 329.1±4.5 Ma (n=4) which is interpreted to be the best estimate of Kudowa-Olešnice granite emplacement.

The remaining ages represent inherited component with two $^{206}Pb/^{238}U$ ages at ca. 560 Ma and two individual results at 399.1±3.2 Ma (1σ) Ma and 361.2±4.2 Ma (1σ).

Similar ages were previously documented in metamorphic rocks of Orlica-Śnieżnik Dome (Jastrzębski 2010; Bröcker et al. 2009; Anczkiewicz et al. 2007).

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Low temperature synthesis of libethenite Cu_2PO_4OH and olivenite Cu_2AsO_4OH solid solutions

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Historical mine tailings in Ľubietová, Slovak Republic, are well known to mineral collectors primarily as a type locality of libethenite Cu_2PO_4OH. The tailings and abandoned excavations result from XIX century mining activity for gold, iron and copper. Primary copper minerals (e.g. chalcopyrite, tetrahedrite) and secondary copper minerals (including malachite, langite, azurite, libethenite, reichenbachite, olivenite, and covellite) were identified in the deposit. Optical microscopy reveals that the secondary copper minerals are often a result of transformation of chalcopyrite. The objective of this project is low temperature aqueous synthesis of libethenite Cu_2PO_4OH, olivenite Cu_2AsO_4OH and their solid solutions. It is hypothesized that some occurrences of libethenite and olivenite found in mine tailings around Lubietova result from post-excavation weathering. It is interesting also that libethenite does not coexist with olivenite at Lubietova and seldom traces of As are found in Cu_2PO_4OH or traces of P in Cu_2AsO_4OH.

All syntheses were run by mixing solutions of $Cu(NO_3)_2$, K_2HPO_4 and $Na_2HAsO_4 \cdot 7H_2O$ in stoichiometric proportions and aging at 25, 45 and 65°C at acidic conditions (pH 2, 3, 4, 5). The solids were characterized with the use of X-ray diffraction and scanning electron microscopy with chemical microanalysis SEM/EDS. The results indicate that libethenite, olivenite and their solid solutions can precipitate from aqueous solutions. A strong effect of temperature on the reaction kinetics was observed: the reaction takes several month at 25°C and only several hours at 65°C. In all cases formation of metastable precursor precipitates of various compositions was observed which recrystalized with time into stable form of libethenite, olivenite or their solid solution.

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Petrographic analysis of historic pavement stones from Vilnius, Lithuania

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The Old Town of Vilnius, the capital city of Lithuania, is marked by old streets paved with stones. In 2002, when one of the authors visited Vilnius, in some streets, e.g. Maironio Gatve in the Gothic Quarter, near the beautiful St Anne's church, the historic pavements were substantially deteriorated; naturally and/or due to municipal works. Most of these pavement stones represented red or grey-reddish crystalline rocks; granitoids and syenitoids. Some of them were relatively small, naturally rounded pebbles, from 2-3 cm to a dozen cm in diameter.

Lithuania is covered with a thick envelope of Quaternary, glacial sediments, without natural outcrops nor quarries of local basement rocks. On the other hand, the Pleistocene, glacial sediments contain abundant gravels and bigger eratic blocks, which could have been used for historic pavements.

The petrographic analysis was made for several pavement stones collected in 2002 from deteriorated pavements at the street Maironio Gatve and some adjacent streets in the Gothic Quarter of Vilnius. Most of the sampled stones represented phanerocrystalline igneous rocks, only one sample exhibited laminated texture pointing on its metamorphic origin.

The reddish, coarse-grained pebbles consisted of predominating rose, tabular feldspars, accompanied by pale, whitish feldspars, quartz, and biotite. Microscopic analysis demonstrated that the largest crystals represented orthoclase perthites, other feldspars being microcline and acid plagioclases. In some samples feldspars and quartz formed myrmekite-type intergrowths. The remaining mineral components were biotite and accessory zircon, apatite, sphene, and opaque phases. Feldspars and biotite exhibited more or less advanced weathering processes, however, taking into account the glacial and more recent history of the analysed pebbles, they turned to be relatively little altered.

Darker, grey-reddish pebbles represented medium- and even fine-crystalline rocks, consisting of various feldspars (perthite, microcline, plagioclases), quartz, biotite, and (in some specimens) hornblende. In these samples plagioclases prevailed over K-feldspars and the weathering processes (sericitization, chloritization, opaque pseudomorphs after sphene) were more advanced.

Quantitative microscopic analysis demonstrated that the five analysed samples represented alkali-feldspar granite, and quartz varieties of intermediate rocks; quartz syenite and quartz monzonite.

The analysed materials represent a relatively large spectrum of feldspar-rich, acid and intermediate igneous rocks, apparently coming from the Fennoscandian shield. Some of them yield excellent examples of typical mineral intergrowths (perthite, myrmekite) and weathering processes. Their connection with parent massifs would require broader and more systematic studies, not only petrographic, but also historic, concerning the origin of the material for paving the Vilnius streets in historic times.

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Petrological criteria for quality evaluation of a Badenian-aged tuff (Babczyn-2 core, Polish Carpathian Foredeep) used in ^{40}Ar/^{39}Ar geochronological studies

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A Badenian-aged tuff (3 cm thick) was recently recovered from the Babczyn-2 borehole in the NE Polish Carpathian Foredeep (east of Lubaczów) and radiometrically dated using the ^{40}Ar/^{39}Ar method (Nejbert et al. 2010). We present the results of quality evaluation of this same tuff in the context of petrological test criteria used for similar pyroclastic materials in such geochronological studies. Petrological studies (i) constrain tuff provenance and degree of alteration, (ii) help resolve the problems brought about by redeposition which leads to the accumulation of mixed pyroclastic horizons with different age populations, and (iii) are of great value for regional stratigraphic correlations across the Carpathian Foredeep. Stratigraphically, the Babczyn tuff lies ca. 3.4 m above the gypsum deposits of the Badenian Salinity Crisis. Radiometric ^{40}Ar/^{39}Ar dating of biotite and glass fragments revealed consistent multi-sample average ages of 13.06 ± 0.10 Ma and 13.06 ± 0.12 Ma, respectively (Nejbert et al. 2010), resulting in the highest quality and most precise radiometric ages currently available for the Miocene of Carpathian Foredeep (13.06 ± 0.11 Ma, age of Pecten Beds deposition).

The Babczyn tuff consists of well preserved volcanic components within a primary grain-supported fabric (Fig. 1), without admixture of non-pyroclastic sedimentary material nor microfossils such as foraminifers which are common in the hosting marly Pecten Beds. It is dominated by fresh, unaltered volcanic glass shards (>90 vol.%) showing platy and cuspate morphologies and by subordinate amounts of pumice fragments. The phenocryst assemblage consists of biotite, plagioclase, Na-K-feldspars, apatite and Fe-Ti oxides, which are accompanied by tiny porphyritic volcanic lithoclasts. Based on the relative proportions of glass, phenocrysts and lithoclasts, this tuff is best classified as vitric. Major oxide contents of the volcanic glass are as follows: SiO_2: 73.39-75.71 wt.%, Al_2O_3: 11.71-12.28 wt.%, Na_2O: 0.84-2.24 wt.%, and K_2O: 2.5-3.97 wt.%. Feldspars are dominated by plagioclase ($An_{83-63}Ab_{63-16}Or_{1-0}$) with only minor amounts of K-feldspar ($Or_{69-67}Ab_{29-28}An_{4-2}$). Biotite, with no traces of chloritization, contains between 48.61 and 50.57 mol.% of the phlogopite end-member.

Projection of both the whole-rock and volcanic glass geochemical data on a TAS diagram reveals a composition corresponding to that of a rhyolitic melt, comparable to the composition of similar-aged tuffs common throughout the Polish Carpathian Foredeep. Both the age and petrological characteristics of the Babczyn tuff suggest that its origin can be ascribed to magmatic activity in the Western and/or Central Segment of the Carpathian-Pannonian volcanic province.

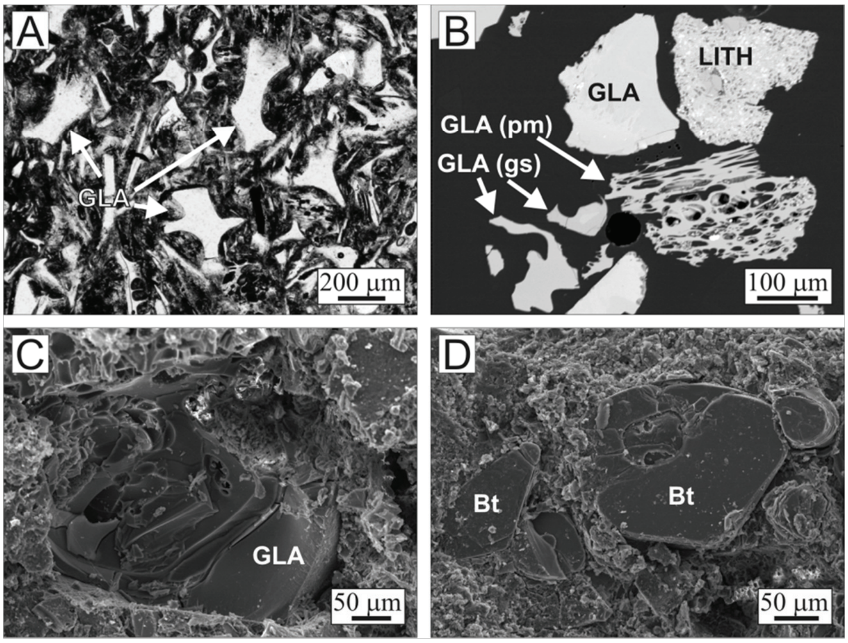

Fig. 1. Tuff petrography (Babczyn-2 core). A) grain-supported fabric dominated by platy and cuspate glass shards; transmitted light. B) BSE image showing the textural and compositional variability of pyroclastic grains within the tuff. C) SEM image of pumice fragment surrounded by a clayey matrix. D) SEM image of biotite microphenocryst within the tuff's clayey matrix. Bt – biotite, GLA – glass, GLA (gs) - glass shards, GLA (pm) – pumice glass, LITH – lithoclast.

Petrological test criteria for assessing the quality and suitability of such pyroclastic material for $^{40}Ar/^{39}Ar$ geochronological studies can be summarized as follows: (i) lack of non-pyroclastic detrital material, including microfossils and fragments of macrofossils in particular; (ii) relatively simple tuff composition, dominated by only 1-2 pyroclastic components (*e.g.* glass, volcanic rock groundmass, phenocrysts) whose mineralogical compositions corresponds to common volcanic rock types; (iii) similar or only narrowly variable chemical compositions of like pyroclastic components (*e.g.* phenocrysts, volcanic glass); (iv) similar ratios of radiogenic isotopes (*e.g.* $^{87}Sr/^{86}Sr$ or $^{143}Nd/^{144}Nd$) within the different pyroclastic grain types; and (v) comparable $^{40}Ar/^{39}Ar$ ages (within analytical error) obtained from two or more unaltered pyroclastic phases.

The Babczyn tuff satisfies most of the above petrological criteria. Its overall high quality is particularly confirmed by consistent $^{40}Ar/^{39}Ar$ ages obtained from both phenocrystic biotite and volcanic glass, permitting the acceptance of the obtained age of tuff deposition as realistic.

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Petrographic and microstructural data on ultramafic xenoliths from the Muchowskie Hills (Lower Silesia – SW Poland)

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The Muchowskie Hills (Muchowskie Wzgórza, MH) are one of over 300 field examples of Cenozoic volcanic activity in Silesia, SW Poland (Badura et al. 2006). They are located near Muchów village, 20 km SW from Złotoryja and 15 km SE from Jawor. The Muchowskie Hills consist of three elevations: Obłoga, Mszana and NW-situated nameless one with the top at 462 m asl. The volcanic body was described as a neck with lava-flow remnants (Jerzmański 1968). The MH volcanic rocks were initially classified as phonolitic basanites (Kozłowska-Koch 1987), but based on the geochemical studies, they were renamed to basalts (Badura et al. 2006) or basanites (Nowak et al. *this issue*). This is the first publication focused on the ultramafic xenoliths found in this occurrence.

Almost all the xenoliths were found in an abandoned quarry at the SW slope of the nameless, 462 m asl hill. The collected ultramafic samples were identified as (1) upper-mantle peridotites (harzburgites, dunites), (2) pyroxenites (clinopyroxenites) and (3) ultramafic cumulates (consist mostly of olivine and clinopyroxene). The xenoliths are characterized by small size, up to 4cm, with the cross-section shapes changing from rounded, through triangular, to rectangular. There are no sharp contacts between the xenoliths and their host rocks. All of them display ~0,1 mm reaction rims (selvages) and in individual cases contain also internal reaction zones.

To characterize the microstructures of the xenoliths, the qualitative classification by Mercier, Nicolas (1975) has been used. Tabor et al. (2005) using statistical methods based on quantitative measurements have indicated, that there are continuous transitions between the basic microstructural types conventionally recognized in peridotites. As the part of the MH samples cannot be simply classified as porphyroclastic, equi- or protogranular, we additionally distinguished intermediate microstructural classes. Consequently, out of 18 analysed samples, 3 xenoliths are protogranular, 3 protogranular/porphyroclastic, 6 porphyroclastic/protogranular, 3 porphyroclastic and 3 equigranular. For the chosen samples, the quantitative measurements of grain geometry using GIS software and PolyLX toolbox in Matlab (Lexa 2011) have been conducted. The axial ratio of olivine (Ol) grains varies between the samples from 1,54 to 1,68. In case of orthopyroxenes (Opx) its value is analogical, ranging from 1,47 to 1,68. The mean area of the Ol grains changes from 0,25 mm^2 in equigranular sample MW4_1, to 1,25 mm^2 in protogranular MW2_2. Mean lengths of the longer axes of Ol vary from 0,65 mm in the porphyroclastic/protogranular 2B to

1,54mm in protogranular MW2_2. These differences are considered to be the evidence for consecutive deformation stages from the protogranular to equigranular type (e.g. Tabor et al. 2005). Although most of the xenoliths under the micro-diascope and in the optical scan images appear to be randomly structured, the Ol grains in all samples reveal quite clear shape preferred orientation of longer axes, when projected on rose diagrams with PolyLX.

The parallel zoning, visible under crossed polarizers in the olivine grains, caused by presence of kink bands/subgrains within the crystals, is more frequently observed in the protogranular/porphyroclastic, porphyroclastic/protogranular and porphyroclastic samples. The equigranular samples show distinctly poorer parallel zoning and contain only few weakly zoned grains. In the non-protogranular xenoliths, more profound kinking-related zoning is observed in the bigger Ol grains rather than in small ones. It seems to be related to the deformation of olivines by the mechanism of dynamic recrystallization under deviatoric stress (Karato 2008), which produces the smaller-size grains by affecting the lattice, causing diffusion and dislocations within the larger crystals.

The chemical composition of the minerals in the MH ultramafites is highly variable regarding different types of the xenoliths. In the peridotites, the forsterite (Fo) content in the olivines is ~91 with two exceptions: ~86 in MW2_2, and in the selvages where it drops to 75 (with simultaneous increase of Ca content up to 4000 ppm). Opx are represented by enstatites with mg# value ~92 (exception: mg#=87 in MW2_2). Clinopyroxenes occur only in the reaction zones and melt pockets; in the reaction zones they have diopsidic to augitic composition (mg#=93-94), in the melt pockets they are diopsidic (mg#=89-95). At the contacts with the host rock, mg# decreases to 80. Spinels show transitional composition, closest to magnesio-chromite with cr# value up to 78. In the ultramafic cumulates, the Fo content of Ol equals ~80; Cpx occur in two types: larger, up to 2 mm (diopside, mg#~85 in cores, and 75 at spongy rims), and smaller in melt pockets, ~0,2 mm (diopside, mg#~80-75). The pyroxenites are fine-grained (max. 1,5 mm) and contain mostly Cpx (diopside). Usually, the crystals have spongy rims (mg# varies from ~66 in cores to 74-80 at rims). Olivines (Fo~75), feldspars, feldspathoids and apatites were identified in their melt pockets.

The peridotitic xenoliths from the Muchowskie Hills represent cold, depleted lithospheric mantle, with no clear evidence of modal or cryptic mantle metasomatism (except sample MW2_2). Based on the Ca in Opx thermometer by Brey and Köhler (1990), the temperatures in the MH upper mantle xenoliths range from 784° to 898°C. All the investigated xenoliths show strong interactions with host rocks, which suggest longer period of contact with magma, not constrained exclusively to their transport to the Earth surface. As the Muchowskie Hills xenoliths represent the upper mantle sampled by volcanics ca. 31 Ma ago (Badura et al. 2006), up to date they are the oldest xenoliths described in the Cenozoic volcanic rocks in Poland.

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Geochemical and isotopic variability of selected Cenozoic volcanic rocks from the North Sudetic Basin (SW Poland)

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Cenozoic volcanic activity occurred over a large part of Europe, including Lower Silesia (SW Poland) (Lustrino, Wilson 2007; Ladenberger et al. 2006). Volcanic rocks in Poland are concentrated in two large, and several smaller, fields (Badura et al. 2006; Matusiak-Małek et al. 2010). In this paper we present new geochemical, petrological and isotopic data from seven occurrences: Wilcza Góra, Kozia Góra, Jeziorna, Muchowskie Wzgórza, Czartowska Skała, Owczarek and Wołek Hill. All are located in the North Sudetic Basin and are a part of the Legnica-Jawor-Złotoryja "volcanic field" (Badura et al. 2006; Matusiak-Małek et al. 2010).

The analyses include 18 whole-rock analyses (ICP-MS, ACME Laboratories, Canada, repeated on 10 samples by MC-ICP-MS), about 350 EPMA analyses (Inter-Institute Analytical Complex for Minerals and Synthetic Substances in Warsaw), Nd and Sr isotopic measurements on 12 samples (TIMS at the UAM Isotopic Laboratory in Poznań), and Pb isotopic ratios on 10 samples (MC-ICP-MS, ACME Laboratories, Canada).

The rocks in question have been variously classified as phonolite-tephrite, basanite, alkali basalt, trachyandesite, etc. (Birkanmajer et al. 1970; Kozłowska-Koch 1987). The latest available geochemical data indicate that most of Cenozoic volcanic rocks in SW Poland are basanites (Ladenberger et al. 2006). Based on TAS classification, we confirm this classification for five of the outcrops: Wołek Hill, Wilcza Góra, Kozia Góra, Muchowskie Hills and Owczarek. The rocks from Jeziorna are classified as basalts while these from Kozia Góra and one sample from Wilcza Góra are basanites/nephelinites.

The rocks are grey to dark grey, some showing a thin light grey weathering crust. Sunburn (*Sonnenbrand*) was recognized only in samples from Wołek Hill and Wilcza Góra. The rocks are porphyritic to glomeroporphyritic. Olivine (Ol) and clinopyroxene (Cpx) occur as phenocrysts and are the dominant phases in the groundmass. Xenocrysts have been recognized only at Wołek Hill (Napieralska, Muszyńki 2006). In several thin sections, especially from the Muchowskie Hills and Owczarek, olivine phenocryst show orange to red weathering rims. Clinopyroxenes display sector zoning.

Ol shows variable Fo content (87-70); values below 70 (even to 60) are characteristic of crystals with weathering rims. Some phenocrysts from Wołek Hill show reverse zoning. Ol xenocrysts contain ca. 91 Fo and show rims where Fo decreases to ca. 82. Cpx occurs as diopside (cores – mg# up to 87) to Ti-diopside (rims – mg# min. 69), also with increasing content of Tschermak's molecule on rims.

The rocks represent primitive magmas (MgO >10 wt%, Na_2O+K_2O – 3.7-5.2 wt%). We noted positive (Ti, Ca, Na, P) and negative (Al, Mg) correlations with decrease of SiO_2 content, from ca. 46 wt% (Jeziorna) to ca. 40 wt% (Wilcza Góra, Wołek Hill). Incompatible trace elements normalized to primitive mantle show negative Rb, K, Zr, Pb anomalies and positive Nd anomalies. The Wołek Hill basanites differ from other samples in having positive Pb anomalies and a strong positive Cs anomaly. Negative K anomalies suggest the presence of residual amphibole in the magma source(s), as noted by Ladenberger (2006). The positive Cs and Pb anomalies suggest crustal contamination and are related to the presence of numerous small quartz grains which could not be removed during sample preparation. On the other hand, K, Th, La and Ta content do not support the assumption of crustal contamination.

The REE patterns of these rocks are similar to OIB basalts. The samples from Muchowskie Hills, Owczarek, Czartowska Skała and Jeziorna are comparable with rocks containing spinel-bearing lherzolites from the magma source, and samples from Wilcza Góra, Wołek Hill and Kozia Góra are comparable with garnet-bearing lherzolites in the source.

$^{87}Sr/^{86}Sr$ (0.70311-0.70352) and $^{143}Nd/^{144}Nd$ (0.51290-0.51283) isotopic ratios are in agreement with the previous results. Unfortunately, Pb isotopes ratios do not provide unequivocal evidence as to the magma source.

In summary, there are some distinct differences between studied rocks. On the other hand, our results are similar to the data reported elsewhere (Blusztajn, Hart 1989, Ladenberger et al. 2004; Lustrino, Wilson 2007). We propose that the geochemical and isotopic variability is related to the heterogeneity of the lithospheric mantle.

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Krystyna Oleksynowa (1912-1998) – a chemist in the world of Earth science

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Krystyna Maria Oleksynowa, née Dajewska, was born in Lwów. She started her studies in chemistry at the Ioannes-Casimirus University in Lwów (1938-1940), and after the interruption, caused by the German occupation, she continued them at the Jagiellonian University in Kraków. Her MSc thesis, defended in 1949, was based on typically physico-chemical experiments carried out under the supervision of prof. Bohdan Kamieński.

On September 1st, 1949, she began to work at the Soil Science Department at the Agriculture-Forestry Faculty of the Jagiellonian University. Since that time, she did not change her place of employment although its name was modified many times (now it is Agricultural University of Cracow). Under the supervision of prof. dr Julian Tokarski, well known geologist and mineralogist, she published several papers in the field of soil science and mineralogy and prepared her PhD dissertation on Polish phoshates from Chalupki (Oleksynowa 1959).

The further scientific fascination of Krystyna Oleksynowa spanned many aspects of Earth science: from hydrochemistry with special interest in carst phenomena (e. g. Ek C. et al. 1969) to soil science with some stress on clay minerals (e.g. Komornicki et al. 1965).

Her habilitation (Oleksynowa 1970), which was a result of systematic many-years' studies of hydrochemistry of the waters in the Tatra Mountains, based on hundreds of analyses, became a kind of a reference paper for the investigations of the environmental changes in the Tatra National Park.

She took a very substantial part in preparation of the soil map of the Tatra Mountains and was the main author of the hydrochemical map; both maps were published in the "Atlas of Tatra National Park" in 1985.

Her last papers concerned new problems, almost non-explored then from a chemical viewpoint, i.e. the chemistry of sub-Tatra waters (Oleksynowa 1993) and the distribution of heavy metals in the Tatra soils and its relation to that in the rocks (Oleksynowa, Barszcz 1996).

Krystyna Oleksynowa liked to share her enthusiasm for soil science, geochemistry, hydrochemistry and mineralogy with her students and many of them took it over.

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Thermodynamic stability of hydroxylpyromorphite $Pb_5(PO_4)_3OH$ at 5, 25, 45, and 65°C

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The purpose of this study was experimental determination of solubility dependence on temperature for OH variety of pyromorphite: $Pb_5(PO_4)_3OH$ (hydroxylpyromorphite HPY). 300mg of synthetic HPY was dissolved for over 3 months in 500mL of 0.05M KNO_3, pH between 2 and 3, at temperatures of 5, 25, 45, and 65°C. Experiments were run open to the air. Solutions were periodically syringe-sampled and analyzed for Pb using AAS. The experiment was run in triplicates.

The equilibrium was attained after 3 months. Solubility of HPY measured with [Pb] increases with temperature. The results indicate that dissolution of HPY according to the reaction:

$$Pb_5(PO_4)_3OH \iff 5Pb^{2+} + 3PO_4^{3-} + OH^-$$

is endothermic. For the first time apparent solubility constants at 5, 25, 45, and 65°C were determined using experimental results: measured [Pb] recalculated to activity was used as input. [PO_4] and [OH] were calculated assuming stoichiometric dissolution and using speciation modeled with PHREEQC computer code with the thermodynamic database from Lawrence Livermore National Laboratory. In the range of 25 to 65°C, the dependence of $\log(K_{sp})$ on the inverse temperature can be approached with linear function suggesting that the enthalpy of dissolution reaction is constant over this temperature range. The enthalpy and entropy of the dissolution reaction was estimated from linear fit of the experimental results to the function:

$$\log(K_{sp}) = A \cdot 1/T + B,$$

where $A = -\Delta H^o_{rxn}/\ln(10) \cdot R$; $B = \Delta S^o_{rxn}/\ln(10) \cdot R$; R = gas constant.

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Mobility of metals from historical Cu slags present in the Rudawy Janowickie Mts. (SW Poland)

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The area of the Rudawy Janowickie Mountains located in south-western Poland represents a historical mining and smelting site. One example of metal ores exploitation in the area is in the vicinity of Janowice Wielkie and Miedzianka. In XIV century, studied area was the largest center for mining and smelting of metals such as Cu, As and Ag. The exploitation in Janowice Wielkie and Miedzianka involved dumping large amounts of mine tailings and slags in the area close to the villages. The slags contain elevated amounts of heavy metals, which might be released to surrounding environment thus they represent a potential source of pollution for the studied area.

In this study we present the analysis of the distribution of selected metallic elements in soils, stream sediments and surface water. Furthermore, on the basis of leaching experiments, simulating various environmental conditions, we attempt to identify major factors controlling heavy metal release from slags deposited in the studied area.

Chemical analyses of soils, stream sediments and surface water indicate that some elements reach extremely high concentrations and distinctly exceed environmental permissible norms (especially in soils: Cu ca. 400 ppm, Zn ca. 1000 ppm, As ca. 200 ppm).

Three types of metallurgical slags (porous slag and two massive slags having different phase composition) occurring in the studied area were submitted to a 24-hour leaching experiment. Three different solutions (distilled water, stream water, citric acid solution) were used to determine heavy metal mobility. The results of leaching experiments revealed that heavy metals content in stream water solution (pH=7.3) and distilled water (pH=5.9) were low (< 0.1%). The highest concentration of heavy metals were leached by citric acid solution (pH=2.68) simulating rhizospheric conditions. Furthermore, leaching tests performed on each type of slag show that the heavy metal release is higher from porous slags than from these having massive texture.

Geochemical analyses of soils, sediments and surface waters indicate a deleterious environmental effects of the former industrial activities in the area of the Rudawy Janowckie Mountains. On the basis of leaching tests it was pointed out that the most unfavorable environment for slag storage is soil rich in organic matter. The present study indicates that the most important factors controlling metal release from slags are: environmental conditions (e.g. pH, organic matter content) and physical characteristics of the waste material (e.g. texture, permeability).

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Deterioration of sandstones: a case study from St. Elizabeth Church in Wrocław (preliminary results)

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The monumental gothic St. Elizabeth Church in the centre of the city of Wrocław (SW Poland) is built predominantly of bricks, but it contains also considerable amount of natural stones in architectural details and decoration: mainly sandstones, subordinately granites, marbles and limestones. The location in the city centre is the reason why the St. Elizabeth Church is exposed to a destructive influence of the atmospheric pollution of the city. The lithological variety of the stones enables to assess the susceptibility of various rocks to deterioration processes which are also controlled by several other factors, e.g. exposition in relation to the geographic directions and climatic agents (sunshine, wind, rain).

Small samples for petrographic investigations have been collected (with permission of the Historical Monument Protection Office) from variously deteriorated stone details in the façade of the church, from a number of sites of various exposition. The samples were thin-sectioned and investigated under a polarizing microscope. A range of mineralogical and petrographic instrumental methods have been applied. The thin sections were studied by an electron microprobe (EDS) technique. Dark incrustations of the samples were separated and investigated by the X-ray diffraction (XRD) method.

The research focused on sandstones which are the most common rocks in the façade of the church. The majority of sandstones are covered with dark tarnish which locally takes the form of incrustations, thus demonstrating variable degree of weathering. For this study, fifteen sandstone samples were collected. The samples show significant mutual petrographical similarities. They are yellow and whitish quartz arenites of various grain size. The grain framework is built mainly of mono- and polycrystalline quartz, a small amount of feldspars and lithic fragments. The framework components are moderately sorted and variably rounded. The intergranular space is filled with microcrystalline quartz and clayish substance.

In the weathering subsurface zones of the majority of samples, dark incrustations penetrate the rock up to a few mm. A common phenomenon observed in the samples is an increase in the number of cracks in grains of the framework towards the surface of sample.

The XRD studies showed, beside the main primary components of the rocks, the common presence of gypsum in the black weathering incrustations. The BSE images obtained with the electron microprobe showed a detailed structure of the weathering zones and gradual transition inwards, to the unchanged sample interior. The EDS investigations indicated the presence of sparite, gypsum, phosphate and other phases of variegated composition. The EDS X-ray element mapping indicated also an increased content of sulphur, calcium and phosphorus in the weathering layers, compared with sample interiors. In the weathering zones, the amount of aluminum decreases, indicating that the primary clay-mineral cement has been removed away and replaced by secondary weathering materials.

The research is being continued and the results of the petrographic investigations of the deterioration of the stone materials in historical monuments will be useful for future renovation and conservation works.

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Fe-metasomatism in lithospheric mantle beneath SW Poland

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Mantle metasomatism is preceding alkaline volcanism at initial stages of continental rifting. The complete example of its various effects is offered by xenolith suite occurring in the Miocene Księginki nephelinite (SW Poland). It is located at the NE termination of the Eger Rift, the easternmost of the rifts forming the European Cenozoic Rift System.

The lithospheric mantle was infiltrated by alkaline silica-undersaturated magma resembling the Księginki nephelinite. Olivine clinopyroxenites originated by crystal accumulation in channelized magma flow. The “Fe-metasomatism” operated in mantle harzburgites subjected to pervasive magma flow. It lowered olivine Fo (down to 86 %) and resulted in REE patterns of clinopyroxene identical to those ocurring in olivine clinopyroxenites. The mg# of clinopyroxene is also lowered to smilar values (Puziewicz et al. submitted).

The Fe-metasomatism effects occur also in the Krzeniów and Wilcza Góra basanites (Matusiak-Małek 2010). However, lack of bulk rock Ca enrichment suggests low fraction carbonated-eclogite-derived melts (Dasgupta et al. 2006) to be a metasomatic agent in the sites.

The peridotites affected by Fe-metasomatism occur in the Miocene lavas occurring to the north of the Intra-Sudetic Fault Zone (IFZ), whereas they have not been found in young Pliocene lavas to the south of IFZ (Lądek Zdrój: Matusiak-Małek et al. 2010; Kozákov: Ackerman et al. 2008) . This suggests that the IFZ, which is one of the major dislocation zones in the region, is reaching the lithospheric mantle depths.

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Application of sequential chemical extractions and Mössbauer spectroscopy for identification of iron distribution in the weathering crust on the Flysch Carpathians' sandstones

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In the Foothill of the Polish Flysch Carpathians numerous sandstone tors occur. The outer, exposed parts of the rocks are often covered by crust which is up to several centimeters thick. This crust, usually laminated, forms as a result of weathering processes. The laminae run parallel to the surface and differ from the internal part of the rocks in colour and composition. The hue and intensity of the colour can vary significantly. The objective of this study was to determine the types of iron compounds, which are probably responsible for the variable colouration and cementation of the weathering crust.

Based on results of earlier works, 6 sampling locations were chosen including tors build of Istebna and Ciężkowice sandstones. A total of 31 samples were selected for laboratory analyses. Because of quite low total Fe contents in the studied samples, sequential chemical extractions and Mössbauer spectroscopy were applied besides standard mineralogical analyses (data not presented here). The sequential chemical analysis included five extractants (Rzepa et. al. 2006): (1) distilled water; (2) acetate buffer (1 M CH_3COONa + conc. CH_3COOH, pH 5); (3) oxalate buffer (0.2 M $(COONH_4)_2$ + 0.2 M $(COOH)_2$, pH 3, extraction in darkness); (4) buffered sodium dithionite (0.3 M $C_6H_5Na_3O_7$ + 1 M $NaHCO_3$ + solid $Na_2S_2O_4$, 85°C) and (5) concentrated mineral acids ($HF + HClO_4 + HCl$). After each extraction stage, the sample was centrifuged and the concentration of Fe was determined in supernatant using AAS (Philips PU9100X spectrometer). The Mössbauer spectroscopic analyses were performed by transmission method at room temperature and 77 K, using Wissel 360 spectrometer and ^{57}Co placed in Rh matrix as a source.

The studied sandstones are composed of quartz, rock fragments, feldspars, micas and accessory heavy minerals. The cement is formed by matrix, carbonate minerals and ferruginous phases (Alexandrowicz et al. 2011). Iron (oxyhydr)oxides concentrate in intergranular spaces, comprise pigment in clay minerals, occur in fractures in detrital minerals and sometimes appear as single grains of various morphology.

The results of sequential chemical extractions show a significantly higher total Fe content in the darker parts of the crusts. The majority of iron (up to 95% of the total amount) is extracted by dithionite, therefore is bound in 'crystalline' oxides. The content of these phases in darker layers is higher. Essential portion of Fe is also bound in chemically resistant minerals (mainly silicates). There is again more iron in the darker layers. The amount of iron soluble in the oxalate buffer is usually below 10% of the total content, indicating minor contribution of ‘amorphous’ oxides (like ferrihydrite) to Fe speciation. Moreover, although the oxalate buffer should not affect the structures of minerals with better crystallinity, it may actually leach out some iron from the lepidocrocite and magnetite as well as from iron-bearing phases containing Fe(II). Therefore, it is not necessarily ferrihydrite which could be responsible for the concentration of iron soluble in the oxalate buffer. The proportion of Fe soluble in H_2O and acetate buffer hardly ever exceed 1% of the total quantity.

Mössbauer spectra recorded at 77 K provide much more information about the nature of iron compounds than these recorded in room temperature and for this reason are presented here. The studied sandstones may be divided into two groups. The samples belonging to the first one comprise zones of the crusts exhibiting yellow(ish) or brown(ish) colours. Their spectra are characterized by the presence of sextets with the values of isomer shift (IS) ca. 0.45–0.49 mm/s, quadrupole splitting (QS) ca. –0,2 to –0,3 mm/s and hyperfine fields (Hf) 40–48 T. These parameters correspond to goethite. The low values of Hf intensity compared to the reference value ~50 T (Cornell, Schwertmann, 2003) and the phenomenon of superparamagnetism observed at room temperature, indicate the poor ordering of the structure of this oxyhydroxide. Goethite binds ca. 55–80% of the total Fe occurring in these rocks. The remaining part is the Fe(III) occurring in octahedral coordination probably in silicate structures (IS ~ 0.3–0.5 mm/s and QS ~ 0.5–0.9 mm/s), and Fe(II) showing much higher values of IS (1.3–1.8 mm/s) and QS (> 2 mm/s) possibly also associated with (alumino)silicates. The proportion of the latter does not exceed the level of a few percent of the total quantity of Fe. The samples belonging to the second group comprise zones of the crusts showing red(dish) or pink(ish) colours. Their spectra exhibit slightly different parameters – lower QS (~ –0.17 to –0.21 mm/s) and Hf > 50 T. These characteristics point at hematite as the phase responsible for magnetic splitting. The fact that it does not undergo Morin transition i.e. the reorientation of magnetic moments, in combination with the intensity of Hf lower than that typical of hematite (Murad 2010), are indicative of structural imperfections and/or the fine-crystallinity of this oxide. Hematite carries 60–70% of the total quantity of Fe present in these samples. The remaining part occurs as Fe(II) and Fe(III) bound in silicates, in similar proportions of these forms as in the first group.

The results indicate that the major factors controlling coloration of the weathering crusts are not only total Fe content but mineral character of iron compounds as well, with goethite and hematite being the most important. The former is present in yellow and brown-coloured zones, whilst the latter is responsible for red and pink hues. These phases usually do not coexist within particular laminae and in many cases hematite occurs in the most external zone whereas goethite often appears in a distance from the surface. This may suggest that hematite is not a direct product of weathering of primary minerals, but is a product of goethite transformation.

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Adsorption of phosphate by clinoptilolite exchanged with Pb

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Among natural and synthetic microporous materials, zeolites constitute a major group with unique physicochemical properties. Due to these properties, zeolites have been widely applied as molecular sieves, ion-exchange units, adsorbents and catalysts in industry and environment protection. I this research, clinoptilolite modified by Pb-exchange was used to remove phosphate ions from solution. The aim of experiments was comparison of phosphate removal by Pb-sorbed and unmodified clinoptilolite.

The zeolite used in this study is clinoptilolite separated from the claystone from Winston in New Mexico (Haggerty, Bowman 1994). Exchanged forms of clinoptilolite were prepared by sorption of 10 mM Pb on the zeolite sample. For reaction with phosphate ions, samples of unmodified and Pb-exchanged zeolite were treated with solution containing PO_4^{3-} anions.

After modification of clinoptilolite with Pb cations, the mineral was found to remove a considerable amount of the phosphate anion from the solution. The amount of adsorbed PO_4^{3-} was higher for Pb-exchanged zeolite than for unmodified zeolite. The reaction resulted in the precipitation of lead phosphates. New mineral phase crystallized on the surface of zeolite. Phosphates were removed by precipitation with metals desorbed from exchange sites of the zeolite or adsorbed on the surface of clinoptilolite. Phosphates immobilization was proportional to the K_{sp} of the metal phosphate precipitating in the reaction and the amount of the exchangeable cation.

The loss of phosphate ions from solution was also observed in the control experiment with unmodified zeolite. Since zeolite surface itself shows weak affinity for adsorption of anions, observed decrease in PO_4^{3-} concentration in solution results most probably from the reaction of phosphate ions with Ca and Mg desorbed from natural clinoptilolite. Therefore, it can be expected that reaction of phosphates with unmodified zeolite (which has ion exchange sites partly filled with transition metals), may result in precipitation of various phosphate phases and their solid solutions. \

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Mineral suspension and hydrochemical stratification in AMD reservoirs of the Muskau Arch near Łęknica, W Poland

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The Muskau Arc is a large horseshoe-shaped glaciotectonic belt formed during the Mid Polish Glaciation. Neogene lignite deposits containing pyrite were excavated there till the 80-ties of the 20th century. The abandoned mining pits filled up with water forming set of reservoirs called "anthropogenic lakeland". Oxidation of sulfide-containing lignite, exposed to atmospheric oxygen and water leads to formation of acidic waters and precipitation of ochreous sediments. The waters are characterized by relatively high Fe and SO_4 content. The precipitates consist usually of schwertmannite, goethite, jarosite and gypsum. Such chemical and mineral association are typical for AMD environments: sulphate concentrations and pH determine the composition of mineral phases.

The aim of this study is to correlate hydrochemical stratification of AMD reservoirs with the variability of mineral precipitants in suspension. Water and sediment were sampled in June 2011. Two selected reservoirs with contrasting chemical characteristics were sampled by pumping water in the profile from surface to bottom in 2 meters interval. Water was filtered by 0.2 μm PC membrane. Sediment on the filter and sampled water were analyzed.

Concentration of Ca^{2+} and SO_4^{2-} is closely linked with precipitation and dissolution of gypsum. Surprisingly, iron and sulfate concentrations are often negatively correlated. On the other hand, sulfate and calcium activities are correlated positively. Abundant gypsum precipitation is observed in dry months while in humid periods this mineral partly dissolves. Therefore, sulfate concentration in water is probably controlled partly by pyrite oxidation and partly by gypsum dissolution equilibrium.

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Probabilistic trace element concentration-gradient models – a potentially effective tool for tracking the mixing and replenishment process on a micro-scale

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Alkali feldspars from Karkonosze pluton derived by mixing of crustal and mantle-lamprophyric magmas have been collected. A three-dimensional depiction of trace-element distribution in a cross-cut of mineral zones, formed during intensive stirring of two magmas of contrasting compositions, shows a complex pattern of micro-domains. New tools, probabilistic models, for the in-depth interpretation of trace-element distributions permits the pattern correlation with progressive equilibration as heterogeneous domains become more coherent due to magma homogenization (Słaby et al. 2011). The models based directly on the data collected by LA ICP MS and constructed 3D, not interpolated, depiction of element distribution. Thus the 'probabilistic' approach can introduce measurement errors into the model but is free of uncertainties caused by interpolation. The approach was used to search accordant and discordant element behavior during crystallization. Though these features make the 'probabilistic' approach more reliable, they do not fully encompass the spatial relationships of the data as only data from discrete collection points is involved in the comparison. The models, concentration and gradient ones, provide a tool for tracking at two levels of precision, geochemical heterogeneity in growing crystals. At both levels, the characteristics of a chaotic system are evident. Concentration models and gradient models reveal similar patterns of accordance-discordance in element behavior, though the latter provide a more detailed level of information.

Whole rock composition synthesizing the temporal and chemical evolution of Karkonosze granitic magma indicate at least three stages of replenishment, each involving different end-member magma compositions (Słaby, Martin 2008). The process is reflected in a succession comprising hybridized porphyritic granite, hybridised granodiorites, intermediate enclaves in granite and subsequent composite- and late mafic dykes. Such a sequence implies a long-lived mafic magma source coexisting with a granitic chamber and argues for a deep-seated mafic magma chamber rather than for continuous mantle melting. Geochronology of the pluton confirms the order of the recognized sequence. Comparison of micro-scale and macro-scale models give complementary and more precise data on pluton development. Similarly to the models based on whole rock composition the probabilistic models show that the replenishment process proceeds from mantle-derived magma of distinctly different composition. These models, however, provide many more pieces of information and point to much more complicated picture of the chamber replenishment. They indicate that at the last stage of pluton evolution mafic magma was supplied via mafic chamber as well as via direct injection into the granitic chamber without passing through the mafic chamber. Thus crystal geochemical heterogeneity and output models interpreting this heterogeneities in term of changes of the magmatic field composition can be useful giving more precise insight into granitic magma evolution process than that yielded by whole rock composition.

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Heavy metals content in marine sediments of the Southern Baltic Sea and their mineral association

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Core samples of sediment were collected from the Gulf of Gdańsk (1-4), Bornholm Deep (5-7) and the Odra Bank (8).. The horizons at depth of 0-3cm (horizon A), 25-28cm (horizon B) and 35-38cm (horizon C) were analyzed separately for mineral (XRD, SEM-EDS) and chemical (ICP-MS and ICP-AES) composition. Sequential extraction of sediments was also carried out followed by chemical analysis of the leachates.

The higest value of heavy metals (especially Cd, Hg, As and Mo) is present in the sediments from Gulf of Gdańsk. Geoaccumulation index (defined as $I_{geo}= \ln(C_n/1.5 \cdot B_n)$, where C_n – measured concentration in µg/g and B_n – geochemical background value in µg/g) indicates strong to very strong Cd pollution in surface samples from Gulf of Gdańsk. Significant variation of heavy metals concentration in profiles is often noted (Fig. 1).

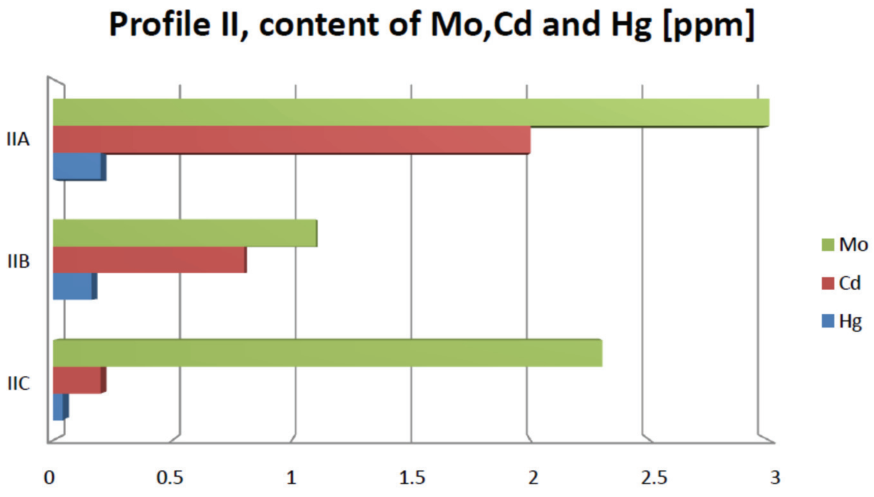

Fig. 1. Example of Cd and Hg distribution in horizons at Deep of Gdańsk.

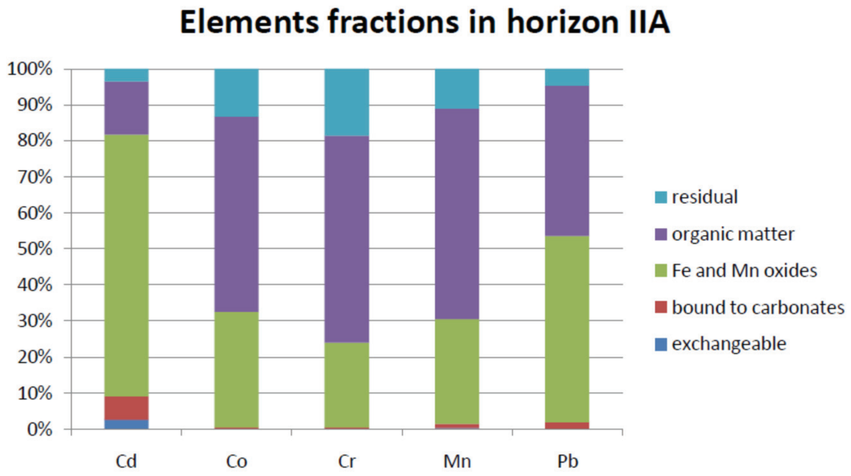

Fig. 2. Element fractions compiled based on sequential extraction.

The results of sequential extraction shows that heavy metals are bound in large amounts to Fe and Mn oxides or organic matter and Fe sulfides (Fig. 2).

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Variscan thrusting, crustal scale folding and exhumation recorded by metasediments from the Bystrzyckie Mts Crystalline Massif (Orlica-Śnieżnik Dome, Central Sudetes, Poland)

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The Bystrzyckie Mts. Crystalline Massif (BMCM) forming the western flank of the Orlica-Śnieżnik Dome (OSD) are composed of large orthogneiss bodies that are mantled by the metamorphosed volcano-sedimentary series comprising mainly mica schists, paragneisses, basic and acid metavolcanics and marbles. The protolith age of paragneisses and mica schists is believed to be either of Latest Neoproterozoic–Early Palaeozoic (on the basis of micropaleontological findings) or middle Cambrian–early Ordovician (based on detrital zircons ages). Results of structural and petrological investigations carried out in the BMCM allow recognizing three main tectonic units, bearing record of contrasting metamorphic paths. From bottom to top they are: Poręba, Młoty and Niemojów Units. Four deformation events were documented in the rocks of the study area. The oldest D_1 structures are represented by the S_1 foliation preserved as inclusion trails mainly within plagioclase blasts. In the investigated area there are no traces of the D_1 structures in the orthogneiss bodies. Therefore, it appears that the D_1 event was older or simultaneous with intrusion of the orthogneiss protolith. Two successive stages of deformation are a record of the Variscan evolution of the Central Sudetes. During the D_2 stage the S_1 foliation was folded into the F_2 folds with the S_2 cleavage developed in their axial planes. The S_2 planes bear the L_2 lineation developed due to intersection of the S_1 and S_2 planes. During the D_2 event crystalline nappes were emplaced and folded. Consequently, the structurally lowest Poręba Unit represents an antiform located above the Młoty Unit representing a synform. The structurally highest Niemojów Unit is not folded. The metamorphic record M_2 simultaneous with the D_2 deformation documents increase of temperature and pressure. The maximum pressures were recognized in the structurally highest Niemojów Unit, whereas the lowest - in the structurally lowermost Poręba Unit. The following D_3 deformation phase was associated with reactivation of the older S_2 foliation. The newly formed complex S_{2+3} foliation dips steeply to W or SW. On the S_{2+3} planes the N-S trending L_3 mineral lineation is developed. The analysis of quartz microfabric suggests that the D_3 event was characterized by two components: dextral non-coaxial shearing and coaxial extension. A non-coaxial component of the D_3 final strain is gradually increasing in the SW direction. The D_3 deformation was possibly associated with the dextral strike-slip shearing along the contact of the Teplá-Barrandian and Moldanubian terranes at 340 Ma. The final phases of this event involved gravitational collapse of the previously thickened nappe pile resulting in the development of asymmetric west-vergent F_3 folds. The M_3 phase of metamorphism is characterized by a zonal pattern with isograds trending generally parallel to the border between the Nové Město Unit and Orlica-Śnieżnik Dome. The metamorphic grade decreases outwards from the central part of the Bystrzyckie Mts. The last D_4 deformation stage was brittle-ductile and could be linked to the Alpine orogeny.

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Microfabric of the Jeglowa date-quartzite (Strzelin Crystalline Massif, East Sudetes, Poland)

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The shape preferred orientation (SPO) and crystallographic fabric are investigated in a deformed quartz-pebble metaconglomerate cropping out near Jegłowa (40 km south of Wrocław) in the Strzelin Crystalline Massif. The Taylor-Bishop-Hill model (TBHm) is used to simulate the development of the lattice preferred orientation (LPO) in a quartzite. A comparison between the simulation results and the measured LPO patterns allows to infer a relative critical resolved shear stresses (CRSS) of the slip systems.

The most conspicuous features of the investigated date-quartzite are pebbles which are up to 4 cm in size and exhibit a prolate shape resembling of dates that float in a fine-grained matrix. This peculiar appearance was already appreciated by Wolfgang Goethe during his visit in the area in 1790. The pebbles are composed of quartz grains reaching up to 1.5 mm in diameter, while quartz grains in the matrix rarely exceed 0.5 mm in diameter. The grains are rather uniform in size within domains and their boundaries are straight suggesting that the main recrystallization mechanism was subgrain rotation recrystallization. The measurements of the quartz optical axes are performed using a computer-aided microscopic technique with AVA Generator and StereoNett software and the manual U-Stage method.

The investigated metaconglomerate is characterized by a domainal fabric. Matrix grains exhibit a strong c-axis maximum centred near the Y axis of the finite strain ellipsoid. A secondary maximum is observed at an intermediate orientation between the Y and Z. The c-axes of quartz crystals in the pebbles are predominantly spread in the X-Z plane with a maximum close to Z axis and between X and Z.

The simulations of the LPO pattern were carried out using a TBHm for constriction and combination of constriction and simple shear using CRSS of 1 for both basal<a> and rhomb<a> slip systems. During the simulations CRSS for +rhomb<a+c> and prism<a> slip systems were varied in the range from 0 to 1 and 0 to 1.3, respectively. The choice of velocity gradient in the far field is justified by the shape of pebbles resembling flattened cigars and quartz-c axis patterns which in many cases are similar to II type crossed girdles. Moreover, most of the obtained LPOs show significant asymmetry suggesting a non-coaxial component of deformation.

The following conclusions can be drawn from the results: (1) both the SPO and LPO fabrics differ between the pebbles and the matrix in the studied metaconglomerate, (2) the mean size of recrystallized grains in the matrix is three times smaller than in the pebbles, (3) the pebble rims are decorated by a subordinate phase, which could have acted as a lubricant and effectively shielded the pebbles against the deformation, (4) a non-negligible contribution of diffusion creep could explain a higher effective viscosity in the pebbles than in the matrix due to the effects related to grain size. Thus, matrix and pebbles though composed exclusively of quartz could behave as rheologically different phases.

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The age of rhyolitic volcanism in the North-Sudetic Basin, SW Poland: preliminary SHRIMP zircon results

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The North-Sudetic Basin is a large intramontane trough in the eastern part of the European Variscan Belt, at the NE edge of the Bohemian Massif. In latest Carboniferous – Permian times, the basin was the site of continental, alluvial and lacustrine sedimentation and intense, late-orogenic bimodal volcanism. Zechstein shallow-marine transgression and subsequent Triassic and Cretaceous continental and shallow-marine sedimentation completed the Mesozoic evolution of the basin. A similar succession in the Fore-Sudetic Monocline to the north, concealed underneath the Cenozoic cover, is the host of world-class Kupferschiefer-type Cu-Ag ore deposits.

Volcanic rocks of the North-Sudetic Basin have not been dated by isotopic methods so far. Two samples selected for this study represent major rhyolitic complexes in the central part of the basin, north of the town of Świerzawa. Sample 775 is collected from a 30 m thick section of rhyolite flow(s) exposed at Dynowice. Sample 2 is from the well-known ‘Organy Wielisławskie’ site, where a columnar-jointed lava dome, or laccolith, is exposed. Both samples are strongly porphyritic rhyolites, with up to 30% of phenocryst, less than 3 mm in size. The most abundant phenocrysts are K-feldspar (in sample 2: Or_{72}, over- and inter-grown by Or_{99}), rounded and often embayed quartz, and albitized plagioclase. Less abundant biotite phenocrysts are variably altered, in sample 2 replaced by chlorite, close to diabantite in composition. The groundmass in both samples is felsitic, flow-laminated (sample 2) or locally spherulitic (sample 775).

Zircons were separated using standard methods and were analyzed at the Beijing SHRIMP Center, Chinese Academy of Geological Sciences, People’s Republic of China. Zircons in both samples are very similar: mostly normal-prismatic, euhedral, rarely subhedral or rounded; quite many are broken. Small vacuoles, and less frequently other inclusions, are found in many crystals. In CL images, they display variable brightness and often distinct “magmatic” zonation. Some grains have oval or irregular, usually CL-darker interiors; distinct cores are rare.

SHRIMP data for sample 2 reveal a single coherent age group, with a mean $^{206}Pb/^{238}U$ age of 293±2 Ma (1σ). The data for sample 775 (excluding one inherited grain of c. 1.4 Ga and three other outliers) yield a mean age of 294±3 Ma.

The age of sample 775 is in accord with the geological position of the Dynowice rhyolitic lava flows, within the Lower Permian sedimentary succession. The age of sample

2, indistinguishable within the analytical errors, proves an Early Permian age of the "Organy Wielisławskie" (sub)volcanic body and, together with geological evidence, strongly suggests that this can be part of the feeder system for the overlying Dynowice flows. The new SHRIMP data constrain exactly the age of the rhyolitic volcanism in that part of the North-Sudetic Basin.

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Garnets from pegmatites and granites of the eastern part of the Strzegom-Sobótka granitic massif (Lower Silesia, SW Poland)

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Accessory garnet is a valuable monitor of fractionation trends in peraluminous granites and granitic pegmatites (London 2008). This reconnaissance study focused on garnet from pegmatites as well as biotite granodiorite and two-mica monzogranite, the rock varieties building the eastern part of the Late-Variscan Strzegom-Sobótka massif. Characteristics of the rocks and previous reports on the garnet are given by Majerowicz (1972) and Janeczek, Sachanbiński (1989).

Bt-granodiorite was obtained from Strzeblów. Samples of two-mica granite come from Gogołów, Sobótka-Górka (alkali leucogranite regarded as the intrusion's marginal facies) and Gołaszyce. The latter crops out together with the associated pegmatitic vein close to a contact of granodiorite with the metamorphic cover. Character of the contact between the two granites is unknown due to a poor state of the exposure. Primitive pegmatites were sampled in Strzeblów and Gołaszyce. Garnet from a pegmatite of beryl-columbite type, rare-element class was obtained from Siedlimowice. BSE imaging and electron microprobe analyses (EPMA) were conducted using Cameca SX100 in the Inter-Institute Analytical Complex for Minerals and Synthetic Substances at Warsaw University. Ca, Ti, Sc, Na, Si, Y, Al, Mg, Fe and Mn were measured. U, Th, Nb, Zr, Cr and V were not detected. The molar ratio of $Mn^*=Mn/(Mn+Fe^{2+})$ was used as a fractionation indicator.

Granitic garnets from Strzeblów and Sobótka-Górka show similar magmatic features. They are up to 2-3 mm large, eu- to subhedral and almost inclusion-free. In fine-crystalline Gołaszyce garnet, euhedral segments coexist with parts anhedral against quartz and K-feldspar. Inclusions and embayments filled by rock-forming minerals are common. In contrast to other granitic garnets, distributed homogeneously within the rocks, Gogołów crystals form two clusters that consist of several up to 5 mm large sub- to anhedral rounded grains. Within the pegmatites, up to 15 mm large euhedral garnet crystals are ubiquitous. Sometimes they are aligned along edges of large K-feldspar crystals. Pegmatitic garnet is enclosed in beryl and contains inclusions of accessory minerals: apatite, gahnite and Nb-Ta oxides.

BSE imaging of granitic garnets reveals no zoning in samples from Gogołów and faint concentric zoning with irregular patches in crystals from Gołaszyce. Several generations were recognized in crystals from Strzeblów and Sobótka-Górka. Small

(<50 µm) slightly rounded sub- to anhedral cores (GrtI) are embedded in sector-zoned euhedral GrtII with delicate hourglass pattern and overgrown by concentrically-zoned euhedral GrtIII. GrtI and GrtII generations partly dissolved and overgrown by GrtIII were also observed.

Crystals from Strzeblów, Sobótka-Górka and Gogołów are compositionally very similar and consist of the end-members almandine (0.53-0.59, 0.53-0.58, 0.51-0.56), spessartine (0.37-0.41, 0.37-0.42, 0.37-0.41), pyrope (≤0.02, 0.03, 0.03-0.05), grossular (≤0.03, ≤0.01, ≤0.02) and andradite (≤0.04, ≤0.01, ≤0.02). Other calculated components are skiagite (≤0.04), majorite (≤0.01) and yttrogarnet (≤0.01). GrtI is enriched in Ca (≤0.12apfu), relative to the other generations (<0.05apfu). Zoning observed in BSE seems to correlate with Y concentration. In the Y-enriched sectors, Y_2O_3 content reaches 1.06 and 0.47wt% in Strzeblów and Sobótka-Górka samples, respectively. In Gogołów garnet Y_2O_3 rarely exceeds 0.1wt%. In core-to-rim profiles of the garnets from Strzeblów, Sobótka-Górka and Gogołów, Mn* increases in the ranges of 0.38-0.42, 0.39-0.43 and 0.40-0.42, respectively. Mg displays flat pattern in Strzeblów garnet, decreases from core to rim in Sobótka-Górka crystals and increases in Gogołów samples. Ca is constant in Sobótka-Górka garnet but grows in crystals from Gogołów.

Garnet from Gołaszyce is relatively Fe- and Mg-enriched and Mn-depleted with 0.58-0.65 of almandine, 0.29-0.35 of spessartine and 0.04-0.05 of pyrope, the other components being similar to other granitic garnets. Y is below the detection limit. Core-to-rim profiles reveal a decrease of Mn* from 0.31 to 0.36. Ca and Mg display rather flat patterns.

Internal structure of pegmatitic garnet revealed by BSE imaging ranges from unzoned crystals from Siedlimowice through weak concentric and/or sector zoning in Strzeblów samples to a complex patchy, sector and oscillatory pattern in garnet from Gołaszyce. The chemical composition of pegmatitic garnets is diversified. The cores become progressively Fe-enriched and Mn-depleted in the order of Strzeblów-Gołaszyce-Siedlimowice. The crystals consist of the end-members almandine (0.28-0.41, 0.44-0.52, 0.46-0.75, respectively), spessartine (0.52-0.62, 0.40-0.49, 0.22-0.50) with negligible amounts of pyrope (≤0.02, 0.03-0.04, ≤0.02), grossular (≤0.01, ≤0.06, ≤0.01), andradite (≤0.02, ≤0.02, ≤0.01) and skiagite (0.01-0.07, ≤0.01, ≤0.01). Other calculated end-members do not exceed 0.01. Mn* decreases from core to rims within the ranges of 0.62-0.53, 0.51-0.44 and 0.41-0.29 for Strzeblów, Gołaszyce and Siedlimowice, respectively. In the outermost parts, a slight increase of Ca and Mg in Strzeblów garnet and an increase of Mg coupled by decrease of Ca in Gołaszyce crystals were noted. Mg tends to increase also in garnet from Siedlimowice. Y_2O_3 and Sc_2O_3 contents are higher in Strzeblów samples (0.18-0.56 and ≤0.26wt%, respectively), lower in Gołaszyce crystals (≤0.33 and ≤0.13wt%) and below detection limits in Siedlimowice garnet.

A consequent increase of Mn* from core to rims in granitic garnets from Strzeblów, Sobótka-Górka and Gogołów is regarded as a “normal” magmatic trend, commonly observed in peraluminous granites. Mn* of the melt is controlled mostly by other more abundant mafic minerals (e.g. biotite). Mn* values for crystals from the three localities overlap suggesting a similar mechanism and extent of fractionation in the parental magmas.

Pegmatitic garnets show a “reverse” trend of decreasing Mn*. This indicates that garnet was a dominant phase responsible for Mn* of the melt. It is consistent with biotite restricted to the outermost pegmatitic parts and lack of tourmaline. Comparable Mn* values in the cores of Gołaszyce and Siedlimowice garnets suggest similar concentrations of Mn and Fe in the parental melts. Lower Mn* in the margins of Siedlimowice crystals indicates more prolonged garnet-controlled fractionation. Higher Mn* in the cores of Strzeblów garnet suggests relatively Mn-enriched and Fe-depleted melt. If all the pegmatites have the same source, the one from Strzeblów should be considered as the most primitive of the three.

A "reverse" trend of Mn* observed in granitic garnet from Gołaszyce together with its partly anhedral shapes and inclusions of rock-forming minerals may suggest that the garnet formed as a late phase in the crystallization order and probably post-dated biotite.

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Monazite from the eastern part of the Strzegom-Sobótka massif: chemical composition and CHIME ages

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Eastern part of the Strzegom-Sobótka massif (Fore-Sudetic block, SW Poland) is composed biotite granodiorites and two-mica granites with minor tonalite (Majerowicz 1972). The latter, cropping out in a quarry close to Łażany village, is accompanied by probably genetically related biotite granodiorite.

Chemical composition of monazite was investigated using Cameca SX-100 electron microprobe at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances, University of Warsaw. Ages were calculated by "AgeFinder" (Appel 2010) from Th, U and Pb concentrations following Chemical Isochron Method (CHIME) proposed by Suzuki and Adachi (1991).

Monazite in SSM biotite granodiorites from Pagórki Zachodnie, Chwałków and Łażany quarries forms yellowish prismatic or tabular, mostly euhedral or subhedral crystals up to c.a. 200-300μm in length with sector and/or oscillatory compositional zoning. Usually sharp boundaries separate chemically distinct domains. Some grains are altered to various extent. Alteration results in: replacements of primary compositionally zoned monazite by a more homogenous one, cracks, spongy texture and sometimes inclusions of secondary minerals e.g. galena and Th-rich minerals. Monazite grains (up to ~300 μm) in the two-mica granite occurs mostly within biotite, xenotime and high-uranium zircon.

All monazites in the biotite granodiorites are of similar composition. They can be classified as monazite-(Ce) with Ce ranging from 0.238 to 0.426 apfu. The other REE elements present in lattice in significant amount are: Nd (0.128-0.210 apfu), La (0.088-0.232), Sm (0.024-0.107 apfu), Pr (0.031-0.053 apfu) and Gd (0.017-0.086 apfu). Thorium content varies in a wide range from 0.032 to 0.332 apfu and replaces LREE mostly by huttonite substitution: $Th^{4+}+Si^{4+} \leftrightarrow REE^{3+}+P^{5+}$. Uranium is a minor constituent reaching up to 0.01 apfu.

On the other hand, in monazite-(Ce) from two-mica monzogranite and related pegmatite (Siedlimowice quarry) , Th is incorporated mainly according to the $Th^{4+}+Ca^{2+} \leftrightarrow 2REE^{3+}$ (cheralite) substitution. The level of Th in the monazite of monzogranite varies from 0.043 to 0.079 apfu and U content – from 0.002 to 0.030 apfu. Ca and P concentrations are higher than in monazite from biotite granodiorites - 0.047-0.095 apfu and 0.976-1.028 apfu, respectively. Monazite from the associated pegmatite shows more evolved chemical composition. It is enriched in Th (0.114-0.157 apfu), U (0.039-0.051 apfu) and Ca (0.152-0.205 apfu) and is simultaneously REE depleted.

An isochron ages obtained for samples from Chwałków quarry (300.2±11.2Ma, MSWD=0.9, y-intercept at 0.0046±0.0038) and Łażany quarry (300.4±13.5 Ma, MSWD=0.6, y-intercept at 0.0040±0.0047) are interpreted as ages of monazite formation in biotite granodiorites. They overlap within error limits with U-Pb SHRIMP results obtained for zircon (e.g. Turniak, this volume). Small variation in Th and U concentrations in monazite from Siedlimowice pegmatite precluded age calculation from an isochrone. Instead, using the weighted-histogram method of Montel (1996) the age of 312.6±1.7 Ma was calculated. The result seems to be slightly overestimated comparing to ID-TIMS U-Pb age of 309.1±0.8 Ma obtained by Turniak and Bröcker (2002) for monazite from two-mica granite. Similarities in chemical composition and obtained CHIME age point to a conclusion that pegmatites and hosting granite, exposed in Siedlimowice quarry, are genetically related.

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Perovskite from Dobšiná metaperidotite and Vysoká – Zlatno skarn (Western Carpathians, Slovakia): compositional variations and evolution

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Perovskite ($CaTiO_3$) represents an accessory mineral of silica-undersaturated, Ca- and Ti-rich, high-temperature conditions, especially in ultramafic and alkaline magmatic rocks as well as in some Ca-Mg skarns. The first findings of perovskite in Slovakia have been identified in perovskite-clinopyroxene-grossular bearing rock fragments in serpentinized metaperidotites at Danková near Dobšiná (Radvanec 2009). We describe here perovskite composition by EMPA and LA-ICP-MS methods from two new contrasting occurrences: Dobšiná metaperidotite and Vysoká – Zlatno skarn.

The Dobšiná town quarry metaperidotite represents serpentinized and segmented lherzolite body with jadeite-talc-glaucophane blue schist in the tectonic mélange of the Meliata Unit. Perovskite forms very rare disseminated euhedral crystals (up to 300 μm across) in hydrated orthopyroxene (enstatite) phenocrysts in association with remnants of olivine (forsterite) and Cr-rich spinel. Locally, perovskite contains tiny inclusions of millerite (NiS), and irregular overgrowths of pyrophanite at the rim of perovskite grains. The perovskite crystals show distinct sector zoning with sectors enriched/depleted in REE`s. Perovskite reveals a near end-member composition (ca. 98 mol. % $CaTiO_3$) with small amount of Fe (ca. 1 wt. %) and REE`s (2 wt. % in average). The chondrite normalized REE diagram shows smooth patterns with LREE > HREE (aver. $La_N/Yb_N = 59$) and regular decreasing of REE`s from La to Lu, but with distinct positive Ce anomaly ($Ce/Ce^* = 1.7$-2.2) and slightly negative Eu anomaly ($Eu/Eu^* = 0.7$-1.0). Chromium and tungsten reveal relatively increased concentrations (around 2200 ppm Cr and 600 ppm W), whereas contents of other trace elements (Zr, Hf, V, Nb, Ta, Na, Sr, Ba, Pb, Th, U, etc.) are low (up to 300 ppm).

The Vysoká – Zlatno near Banská Štiavnica (central Slovakia) represents Ca-Mg skarn at the contact between Miocene granodiorite porphyry intrusion with Cu-Au skarn-porphyry deposit (the Štiavnica stratovolcano) and Middle Triassic dolomites in the R-1 borehole. Perovskite euhedral crystals (up to 200 μm in size) are disseminated in monticellite, clintonite, andradite, magnetite and calcite, locally they contain inclusions of spinel. The perovskite crystals show 94 to 98 mol. % of $CaTiO_3$ and regular oscillatory zoning or irregular domains enriched in Fe, REE`s, and Th (up to 2.8 wt. % $Fe_2O_3$, ≤6 wt. % $(La+Ce+Nd)_2O_3$, ≤5.5 wt. % $ThO_2$). Average content of REE`s attains 1.5 wt. %. The chondrite normalized REE patterns show apparent dominancy of LREE over HREE (aver. La_N/Yb_N = 142) and regular decreasing of REE`s from La to Lu, with exceptions of slight positive Ce anomaly (Ce/Ce* = 1.0-1.7) and negative Eu anomaly (Eu/Eu* = 0.6-0.9). Perovskite contains increased average concentrations of Zr (ca. 5000 ppm), Nb (1200 ppm), Th (1000 ppm), U (790 ppm), Sr (390 ppm), Hf (230 ppm), Ta (100 ppm) and Sn (100 ppm); contents of other measured trace elements (Na, Ba, Cr, V, Pb, etc.) are negligible (below 100 ppm).

Textural relationships, internal zoning and compositional data indicate a primary magmatic, pre-metamorphic origin of perovskite in the Dobšiná metaperidotite. Regular normalized REE patterns are comparable with other magmatic perovskites (e.g., Jones, Wyllie 1984; Ulrych et al. 1988, 1996) and subchondritic weight Zr/Hf ratio (13.4) is comparable to mantle peridotites where the extremely low Zr/Hf ratios (10 to 26) are caused by partial melting processes and controlled by melting of clinopyroxene (Weyer et al. 2000).

On the other hand, perovskite from Vysoká – Zlatno precipitated during a contact metamorphism of dolomites by granodiorite intrusion. Association with monticellite, spinel and other metamorphic phases, as well as regular REE pattern indicate a high-temperature (above 600°C) origin of perovskite. Analogous perovskite-bearing contact metamorphic skarn assemblages are known worldwide (e.g., Marincea et al. 2001; Rosa, Martin 2010).

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Lower Silesian jaspers – their mineralogical variability and gemmological properties – preliminary results

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The neogene Pilce gravels and sands deposit is situated about 50 km south of Wrocław at the Foresudetic Block area (Lower Silesia region). This site is well known by mineral collectors as an interesting outcrop where multicoloured jaspers occur. Most of them represent small well rounded pebbles (boulders, often up to 0,2 m in diameter) with beautiful "colour game" especially well apparent on their polished surfaces. On the basis of preliminary observations and field investigation we can focus on the presence of colourful horn stones, black lydites and fossilized parts of stalks and boles of the trees as a main components of these silica-bearing decorative rocks (Badura et al, 1998).

55 specimens were collected from Pilce area. Gemmological properties and possibilities of usage for jewelry were determined. Samples were cut into slabs (approx. 2cm thick) and polished on one side. Additionally, the mineral composition was determined in thin sections using petrographic microscopy.

The results indicate that decorative rocks from Pilce have different colours: chocolate, orange, red, touch of green, brown or black. The majority of studied pebbles are smooth and well rounded. Only larger boulders are sporadically sharp-edged. Sharp edges of smaller specimens are secondary, resulting from technological processes (belt conveyor flight, hitting itself and other stones).

Besides the black lydites, the horn stones with homogeneous colouration are rare. Usually, the samples are characterized by zoned colour changes with gentle transition from one colour to another. Multicolouration usually involves shades of one colour. Among colourful horn stones the strongly cleaved as well as non cleaved pebbles occur.

Several variants of different colouration and different surface drawings can be distinguished in described specimens. Five typical specimens from the active gravel and sand mine in Pilce can be used for classification on account of the drawing or colouration of their polished surfaces.

The appearance of sample Pil/1 is worn smooth with visible smudged and spotted areas. The colouration is diversified and kept in light grey, light beige, light brown colours. Macroscopic observations and observations with the use of stereoscopic microscope reveal a web of small cracks. These features allow using this type as valuable jewellery and decorative material.

Sample Pil/2 is represented by sharp-edged fragments in the background with russet - brown colour, with numerous breccia zones. In these areas, the lighter colouration and numerous cracks and corrosion traces on the surface are common. This type can be used only as facing material.

Sample Pil/5 was identified as a dull black coloured lydite characterized by external smoothing showing small cracks in a big intervals of distance without thin white quartz veins. This can be utilized for facing and/or as a material for jewellery.

The most characteristic feature of Pil/6 sample of Pilce silica rocks is presence of sharp-edged fragments forming the "baleyage" of irregular areas filled with green, brown and grey colours. The most of these fragments display also the granoblastic pattern with large greenish areas**.** This incredibly interesting drawing and rare colouration is disturbed by presence of numerous cracks on the surface. Therefore, this can be used only as a good material for mineral collectors (Zenz 2009).

The last type for Pilce jaspers specimen (Pil/9) represents slightly rounded pebble with colouration kept in dark grey, beige and brown tones. On their surfaces the secondary brecciation in the healed posttectonic zones as well as minor crack systems are also well marked. These features limit the use of this type either for mineral collections or, in rare cases, for jewellery.

In summary, the obtained results of preliminary studies of Pilce silica pebbles indicate that they are represented by jaspers, breccias, lydites, fossilized parts of stalks and boles of the trees or cherts (hornstones). Colourfull horn stones represent mostly the varieties rich in black and chocolate colours. The most perspective are multicoloured varieties of horn stones, which can be used in the artcraft, accessories, souvenirs, and facing materials. The most valuable from gemmological point of view are stones with red colouration, black patches or with banded and brecciated appearance which can be compared with worldwide tumbled jaspers, breccia jaspers and lydites (Helfik 1989; Sachanbiński 1979).

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Chemical and mineralogical composition of biomass and biomass combustion products

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Biomass is considered as an important non-fossil renewable energy source. Potential biomass resources in Poland are estimated to be around 30 millions Mg per year and the share of biomass in electricity production and other applications is increasing systematically. Lack of complex life cycle assessment studies is the reason that real environmental value of biomass usage as fuel is not fully understood. Also environmental impact of biomass combustion is poorly studied. There is a common opinion that, unlike coal ash, the biomass ash does not contain toxic metals. Chemical composition of biomass is related to many factors, e.g.: type of biomass, age of plant, growth process, fertilizers and pesticides used, soils composition and contamination, atmospheric pollution of plantation area, harvesting, transportation and storage. The content of mineral component is low. Mineral particles in biomass can be considered as detrital (i.e. introduced by water or wind during plant growth) and anthropogenic (introduced during harvesting, transportation, storage and processing).

The study is based on chemical analyses of eight samples of biomass used in power-plants in southern Poland and products of biomass ashing at 475^{o}C as well as mineralogical (optical and electron microscopy, XRD) study of biomass and ashes obtained at 475 and 800^{o}C. We analyzed wood and woody biomass, agricultural straw, and agricultural biomass.

Moisture content in studied biomass is within ranges of 5.4-26.2wt% and 1.2-1.6wt% (as-received and air dried, respectively). Ash yield (dry basis, 550^{o}C) varies from 0.8 to 10.6wt%. Volatile matter (dry basis) content is between 72.3-84.8wt%.

The C content in biomass is within the range 49.04-54.51wt% (daf – dry, ash-free basis); O content calculated by difference varies in the interval 37.32-43.26wt% (daf); H within the range of 5.58-6.35wt% (daf); N content is from 0.29 to 2.93wt% (daf); S content varies from 0.01 to 0.23wt% (daf). The Cl content measured in dry material varies from 0.017 to 0.253wt%.

Chemical variation of studied samples of biomass is significant (e.g. Ca from 0.1 to 1.1wt%; P from 0.2 to 0.89wt%; Al from <0.01 to 0.09wt%; Na from <0.001 to 0.106wt%; K from 0.05 to 2.4wt%; S from <0.01 to 0.22wt% and for selected trace elements: Mn from

7 to 333 ppm; Pb from 2.9 to 25.6 ppm; Zn from 8.3 to 79.4 ppm; Cu from 2.2 to 25.2 ppm; Mo from 0.03 to 0.72 ppm; Hg from <1 to 21 ppb). The content of several trace elements (e.g. Mn, Cr, Cu, Ni, Pb, Zn) is within the range comparable with Polish coals.

The content of mineral matter in biomass is usually very low. In several samples quartz was determined using XRD method. Small quartz grains, probably originating from soil are apparent in optical microscopy.

Biomass was ashed at 475°C and the yield of ash was from 0.5wt% (sawdust) to 10.8 wt% (olive residue). Ash is usually rich in Ca (highest content ca. 16wt% in sawdust ash; content above 10wt% in three other samples; and the lowest ca. 1.9wt% in corn bran biomass ash), K (six samples with content above 10wt%, the lowest value for beech bark biomass), and P (two samples with content above 5wt% and the lowest content ca 0.5wt%).

Content of trace elements in studied samples of ash in often higher compared with typical coal ash, e.g. Mn from 321 to >10 000 ppm; Ag from 0.02 to 5.3 ppm; Cd from 0.13 to 71.3 ppm; Cr from 3.8 to 988 ppm; Cu from 18 to 588 ppm; Mo from 2 to 14.7 ppm; Zn 106 to 1923 ppm and Hg from <5 to 35 ppb.

Ash is usually enriched in metals compared with biomass samples. Highest enrichment (measured as ratio of content of element in ash/content of element in biomass) is observed for sawdust ash (e.g. Mo – 150; Cu - 193; Zn – 196; Ag – 143; Ni – 91; Co – 287; Mn – 156, Fe - 270; Cd – 230; Bi – 250; Cr – 177; Ba – 198; B – 464).

Mineral composition of ashes obtained after ashing at 475 and 800°C is highly variable. Variability reflects strong differences in chemical composition of ashes. Quartz and carbonates (calcite and fairchildite) are relatively common in low temperature ashes (obtained at 475°C). Sulphates are represented by arcanite and roemerite. Other minerals identified in low temperature ashes are: corundum, bayerite, bustamite, microcline and several types of phosphates and chlorides. Minerals determined in high temperature ashes are quartz, tridimite, cristobalite, lime, periclase, monticellite, spinel, anhydrite, arcanite, sylvite, tephroite, clinoenstatite, apatite, whitelockite?, graftonite?.

Significant differences in chemical composition of various types of biomass suggest that it is possible to expect different behaviour during combustion and different environmental impact. It also suggest that careful blending of biomass might be important.

These results indicate that both the chemical composition of low temperature biomass ash and the degree of enrichment in selected elements during ashing varies within broad range and mineral composition of ashes is very complex and variable. It indicates that systematic study is necessary to predict the influence of biomass co-combustion on properties of ash and possible environmental impact.

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Accessory minerals from enclaves of Karkonosze granite – mineral chemistry and petrologic implications

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The occurrence of different enclaves in Karkonosze Granite Intrusion was a subject of debate in many publications e.g. Słaby et al. (2008); Słaby, Martin (2008). The enclaves and their biotite-bearing porphiritic host granite are interpreted to be an evidence of interaction, mixing/mingling of the different, coexisting magmas. The aim of this work is to show new data of mineral chemistry of selected accessory minerals from the enclaves. On this basis, the assessment of the importance of the chemistry of minerals for the reconstruction of petrogenetic processes was also attempted.

The studied enclaves reach approximately 15 cm in size although these exceeding 80 cm can also be found. The samples were collected from two lokalities: to the east from Mysłakowice and from a quarry situated nearby Michałowice. The enclaves are of fine to medium-grained structure and consist of: biotite, amphibole, plagioclase, K-feldspar, quartz, chloride, and mica in various proportions. Some are abundant in porphyrocrystals of plagioclase and occellar quartz. The altered enclaves are rich in accessory minerals such as: apatite, zircon, epidote, and titanite.

Chemical analyses of minerals were performed at Faculty of Geology, Warsaw University (Inter-Institute Analytical Complex for Minerals and Synthetic Substances) on Cameca SX-100 microprobe.

There are two types of epidote (17 analyses): 1) allanite – low in Al_2O_3 (11.32 wt. %), CaO (10.17 wt. %), while rich in MgO (0.31 – 0.75 wt. %) and LREE such as: Th, La, Ce, Pr, Nd, and 2) epidotes rich in Al_2O_3 (21.84 wt. %) and poor in MgO (up to 0.3 wt. %) and LREE. This variability probably reflects different conditions of crystallization in the magma chamber. First group can be connected with melting at shallow levels. Second type of epidote indicates their hydrothermal or magmatic origin. However, more precise determination of their origin requires additional studies.

In titanite, TiO_2 content ranges from 19.11 to 32.15 wt. % (except for one – 0.2 wt. %), CaO = 26.45 – 29 wt. %t and SiO_2 = 30.31 – 36.84 wt. %. Composition of titanite is typical for accessory titanium silicates found in enclaves of magmatic origin.

The rare zircone grains show approximate content of ZrO_2 of about 66 wt. %t and SiO_2 values near 32 wt. %, which can reflect reducive conditions of their crystallization.

The composition of apatite is comparable with fluoroapatites which crystallize at high temperature in acidic magma. This can reflect a reheating event recorded during transition of deeper to shallower part of magma chamber.

The results of microprobe analyses of accessory minerals from enclaves of Karkonosze intrusion didn't provide much petrogenetic information. Most probably their crystallization event at shallow part of magma chamber as well as reheating of enclaves during migration from the bottom parts of intrusion were recorded. Precise reconstruction of conditions of these processes requires more detailed studies of unaltered material.

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Primary phosphate mineralization in a granitic pegmatite at Lutomia (Sowie Mts block, SW Poland)

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A granitic pegmatite from Lutomia, hosted by amphibolites of the Sowie Mts block, represents an interesting example of pegmatites with an abundant phosphate mineralization, relatively rare and little known from Poland. The most important data about phosphates from this region were given by German scientists, including Websky's information about occurrence of sarcopside from Michałkowa (Websky 1868). After almost 150 years break, Pieczka described phosphate mineralization from Góry Sowie block, including graftonite, sarcopside, ferrisicklerite, Ca-beusite, stanekite (wolfeite), alluaudite, hagendorfite, merrilyite (whitlockite), melonjosephite, fairfieldite, whitmoreite, earlshannonite, jahnsite, fosfoferrite – kryzhanovskite and apatite (Pieczka 2002; Pieczka et al. 2003). In this study, we present preliminary analytical WDS data on primary phosphates forming nodules in the Lutomia pegmatite. Two associations of primary phosphate minerals were found there: (1) lamellar intergrowths of graftonite, ferrisiclerite and sarcopside, and (2) concentrations of alluaudite, hagendorfite, stanekite (or wolfeite), sarcopside, Ca-graftonite (or Ca-beusite) and whitlockite in veinlets cutting the lamellar intergrowths. The compositions of and textures among the minerals forming lamellar intergrowths prove the partition of an initial P-bearing melt into a melt enriched in P, Fe, Mn, Li and Mg, *i.e.*, a part forming ferrisiclerite with inclusions of an early sarcopside with a low Mn/(Mn+Fe) ratio, and a melt enriched in P, Fe, Mn and Ca, *i.e.*, a part crystallized as graftonite. The crystallization of the second association in a later stage of evolution of pegmatite can be related to the filling of cracks in the phosphates of the first generation by a Ca-, Na- and probably Fe^{3+}-enriched melt as a precursor for crystallization of alluaudite, stanekite, a younger sarcopside with higher Mn/(Mn+Fe) ratio, whitlockite and Ca-graftonite or Ca-beusite. The simultaneous crystallization of ferrisicklerite and the early sarcopside on the one hand and stanekite with alluaudite, on the other, is proved by similar values of the Mn/(Fe+Mn) ratio for these minerals. The presence of Fe^{3+} in ferrisicklerite, alluaudite and stanekite and lackof hydrated phosphates (except for whitlockite that occurs in central parts of the veinlets) suggest a consolidation of this pegmatite under conditions of a medium to a high oxygen activity and a low activity of water.

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Primary phases in peridotites of the Ślęża ophiolite (SW Poland)

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The peridotitic members of the Variscan Ślęża Ophiolite (SW Poland) are part of the complete ophiolitic sequence. WR trace element and REE patterns of gabbroic/basaltic ophiolite member show MORB affinity (Pin et al. 1988).

The peridotites are serpentinized but aggregates of olivine ± clinopyroxene ± spinel are preserved in the central part of the outcrop (Radunia Hill). Olivine ($Fo_{91.8-92.6}$) contains 0.2 – 0.4 wt % NiO. Clinopyroxene (mg# 0.92 – 0.94, Cr_2O_3 0.9 – 1.2, Al_2O_3 2.7 – 3.4, Na_2O <0.03 wt %) is in places altered into clinopyroxene II (mg# 0.96 – 0.97), chromian magnetite (Cr usually between 0.10 and 0.80 atoms pfu, C=3). Isolated grains of olivine and chromian magnetite occuring in serpentine groundmass are less magnesian ($Fo_{89.3-90.5}$), and rich in Cr, respectively. The whole-rock REE contents are below detection limits of ICP-MS method.

We interpret most of the aggregates to be the remnants of primary MORB phase assemblage. However, the complicated HP metamorphic history was suggested by Dubińska et al. (2010).

The mineral composition of the aggregates suggests dunitic composition of the protolith. Highly magnesian content of olivine is probably the record of depletion typical for MORB mantle. Clinopyroxene possibly is the result of late melt infiltration. Serpentinization obviously decreases forsterite content in olivine, thus the chemical composition of phases occuring in relics may be not representative for primary mineral composition.

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Diamond prospecting using till geochemistry in remote areas of Finnish Lapland

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The most common diamond prospecting method in till-covered terrains uses indicator minerals such as pyrope garnet, picroilmenite, chromite and chromian diopside (Fipke et al. 1995; Lehtonen, Marmo 2002; Lehtonen et al. 2005). However, this method requires very large sample sizes (up to 80 kg; Lehtonen, Marmo 2002) and is therefore relatively expensive. Furthermore, collection and transport of large heavy samples has its own inherent logistical difficulties, particularly in remote areas. Another method in common usage worldwide utilizes till geochemistry (e.g. McClenaghan et al. 2000; McClenaghan, Kjarsgaard 2001). This method, however, has largely been abandoned in Finland due to a belief that it is not effective (e.g. Lehtonen et al. 2005). As exploration budgets are generally relatively small and the potential benefits great, we feel a strict reassessment of the effectiveness of till geochemistry prospecting in Finland is in order.

Diamonds exist within the upper mantle in unique host rocks that include eclogite and some peridotite varieties, mostly garnet- and chromite-harzburgite. At present, kimberlites and lamproites are the only commercially viable source of diamonds, however diamonds have been found in other mantle-sourced rock types including ultramafic lamprophyres and even carbonatites (e.g. Simandl 2004; Moore et al. 2009). These magmas are generated at very high pressure (> 3 GPa) from a mantle source enriched via carbonatite metasomatism (e.g. Mitchell 1986). Diamonds occur in these rocks as xenocrysts and/or in xenoliths that have been transported from the upper mantle by the magma during ascent. Common to all these potential source rock types are characteristic enrichments in HFSE, LILE, REE and some first-order transition elements. Many of these elements (e.g. Ti, Nb, Ta, Ba, Cr) are also generally immobile with respect to surface processes and therefore should result in detectable anomalies in till samples from within the glacial dispersal fan.

The first reported diamonds from Norway were found in alluvial sediments from the Pasvik River valley (Reusch 1895; Strnad 1991). However, the bedrock source of these diamonds remains undiscovered. The Finnish portion of the Pasvik River catchment area is located both upstream and "up-ice" from the location the diamondiferous sands were collected. A group of small anomalies can be seen in aeromagnetic maps of this area (Geological Survey of Finland 2011). Although these anomalies have been mapped as amphibolites, field investigations showed that actual outcrops of amphibolites in the area do not strictly correspond to the locations of the anomalies. Further field investigation into the anomalies revealed that they did correspond to relatively low-lying, typically rounded and often swampy areas lacking outcrops. Till samples were collected from around these anomalies and fine fractions (>0.074 mm) have been sent to Acme Analytical Laboratories, Canada, for analysis by Li-Tetraborate fusion. For comparison, control samples were collected from areas difinitively within and outside of the dispersal fans around known kimberlites in the Kaavi-Kuopio Kimberlite Province, Eastern Finland. This strict spatial control, particularly for the local background samples, will allow for more effective evaluation of potential soil anomalies in comparison with the regional till average used as background in the study by Lehtonen et al. (2005).

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Geochemical characterization of the altered Strzeblów granite (Strzegom-Sobótka Massif)

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The Variscian granitoid massif Strzegom Sobótka is situated in Fore Sudetic Block and consists of four types of granitoids: biotite monzogranite, biotite granodiorite, hornblende-biotite granite and two-mica monzogranite representing individual intrusions (Pin et al. 1989; Puziewicz 1990).

The studied Strzeblów biotite granodiorite is strongly altered due to metasomatic processes related to activity of postintrusive hydrotermal solutions. The granite from Strzeblów was subjected to albitizatization, which is a dominant alteration process, episyenitization and locally to chloritization, sericitization, kaolinization and arenitization.

Albitization process is related to reduction in amounts of Ca-Na plagioclase and K-feldspar and crystallization of secondary, almost pure albite (~97,5% Ab). Chemical composition of granites indicates significatnt enrichment in Na_2O and Al_2O_3 and depletion in K_2O and SiO_2 what is related to crystallization of secondary albite and removal of primary quartz. As albitization usually involves episyenitization (Davisson, Criss 1995), quartz is scarce or absent in the studied samples.

Based on isocon method (Grant 1986) it is possible to observe mobility of elements which have long been regarded to be immobile during alteration of igneous rocks, like Zr, Hf, Th or Ti. In all studied samples enrichment in REE was observed (mainly HREE with regard to LREE) relative to the sample which was considered to only slightly altered. Changes in content of REE are related to the dissolution of monazite and formation of cheralite and secondary xenotime.

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FIELD –TRIP GUIDE

The Tatra Mts. typical „core mountains“ of the Western Carpathians – their structure and evolution of the crystalline basement

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1. Introduction

The Western Carpathians as a part of the extensive Alpine–Himalayan equatorial, orogenic system extending from the Atlas in Morocco, through the Alps, Dinarides, Pontides, Zagros, Hindukush to the Himalayas and to China represent a typical collisional orogen. The Western Carpathians are the northernmost, E–W trending branch of this Alpine belt, linked to the Eastern Alps in the west and to the Eastern Carpathians in the east. Recent structure of the Alps, and Carpathians originated from the subduction–collision (convergence) processes of the African plate fragments (Adria - Apulia) with Eurasia mainly from the Cretaceous to the present. The Western Carpathians are divided into two belts: the Outer Western Carpathians (OWC), consisting mostly of Neo-Alpine nappes (dominated by Tertiary deformation), and the Inner Western Carpathians (IWC) with essentially a Paleo-Alpine structure (dominated by Mesozoic deformation) overlain by Tertiary post-nappe deposits. However, there has been proposed a concept of triple division into the Outer, Central and Inner Western Carpathians (Mahel, 1986), and/or External, Central and Internal Western Carpathians (EWC, CWC and IWC - Fig. 1), respectively (Plašienka 1998).

The CWC consist of three main crustal-scale superunits which are, from north to south: the Tatricum, Veporicum and Gemericum as well as several cover-nappe systems: the Fatricum, Hronicum and Silicicum (Plašienka et al. 1997). The basement units together with the Mesozoic cover and nappe complexes were tectonically juxtaposed through north-directed thrusting during the Upper Cretaceous.

The Tatric Superunit (Tatricum) represents the most external and lowermost component of the Slovakocarpathian tectonic system, cropping out in the form of so-called “core mountains” in western and northern Slovakia. The pre-Alpine crystalline basement complexes dominate internal structure of the Tatricum, though the Mesozoic cover rocks are widespread at the surface. As revealed by deep seismic transects, the Tatric sheet forms a tabular, slightly convex, more than 10 km thick upper-crustal body, rooted in the lower crust below the Veporic wedge (Tomek 1993; Bielik et al. 2004). At deeper levels, the Tatric sheet presumably overrides the Penninic-Vahic oceanic complexes (Putiš et al. 2008a), being overlain by thin-skinned Fatric and Hronic nappes, as well as by overstepping Tertiary sediments and volcanics. The Tatric Superunit is internally less differentiated compared to the overlying Veporic basement sheet. It creates a subautochthonous substratum for the cover nappes in majority of the core mountains. However, major overthrusts are present at the northern edge of the Tatric sheet, where Tatric partial nappe units overthrust fairly differing complexes of the so-called Infratatricum. The Malé Karpaty Mts. are such place where e.g. the Tatric Bratislava Nappe overrides the Infratatric Borinka Unit – Plašienka (1990), Polák et al. (2011). Upper Palaeozoic rocks are mostly present in the Infratatric units. The Tatric crystalline basement was only slightly affected by Alpine deformation and metamorphism; it commonly retains Variscan structures and isotopic ages. The Tatric sedimentary cover is autochthonous to parautochthonous with respect to the crystalline basement. Generally, these core mountains are Late Tertiary (Danišík et al. 2004; 2008; 2009; 2010) transtensional horst structures usually bounded by normal faults, comprising from bottom to top:

- the Tatric pre-Alpine crystalline basement and its Late Paleozoic – Mesozoic sedimentary cover;
- the Krížna Mesozoic cover nappe system (Fatricum);
- the Choc cover nappe system (Hronicum);
- the Upper Cretaceous and Tertiary post-nappe sedimentary and volcanic cover.

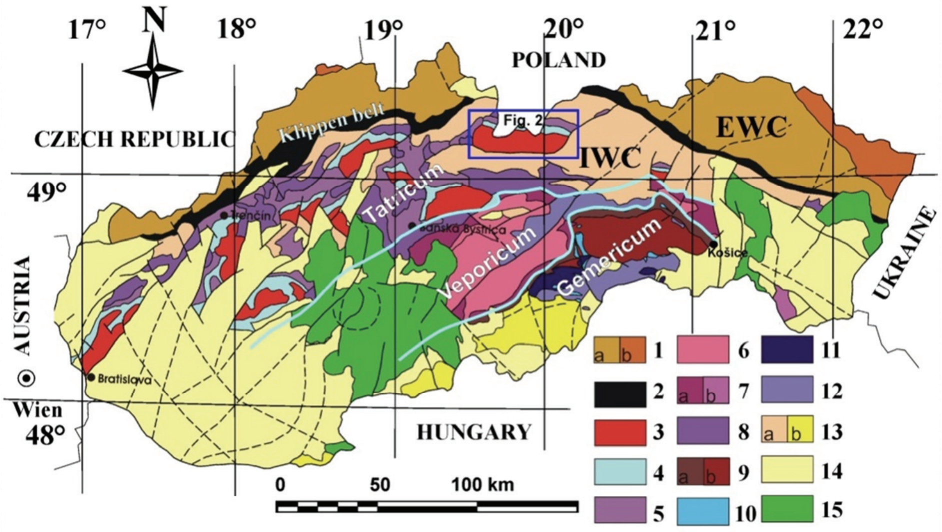

Fig. 1 Tectonic sketch of the Slovakian part of the Western Carpathians (simplified from Biely et al. 1996). Explanations: EWC – External Western Carpathians, IWC – Internal Western Carpathians 1) Flysch belt, *a*- Krosno zone, b- Magura zone; 2) Pieniny Klippen belt; 3) Tatricum Unit basement; 4) Tatricum Unit cover sequence; 5) Fatricum Unit; 6) Veporicum Unit basement; 7) *a*- Veporicum Unit cover sequence, *b*- Zemplinicum Unit cover sequence; 8) Hronicum Unit; 9) Gemericum Units basement and its cover sequence: *a*- Northern Gemericum Unit, *b*- Southern Gemericum Unit; 10) Meliaticum Unit; 11) Turnaicum Unit; 12) Silicicum Unit; 13) Post-Nappe sequences of the Inner Western Carpathians, *a*- Inner Carpathian Paleogene, *b*- Buda basin; 14) Neogene sediments; 15) Neogene volcanites.

2. Tatric crystalline basement

The pre-Mesozoic basement of the Western Carpathians is supposed to derive from the south-eastern-European Variscides (Matte 1991), which were in part incorporated into the Alpine orogenic belt. The basement complexes of the Central Western Carpathians are part of the Cretaceous Tatric, Veporic and Gemeric structural superunits (Plašienka et al. 1997), analogous to the Austroalpine realm in the Eastern Alps (Putiš 1992; 2002; Gebauer 1993; von Raumer, Neubauer 1993; Dallmeyer et al. 1996). The pre Alpine crystalline basement of the Tatricum forms backbone of core mountains, usually dominated by the Variscan granitic rocks and complicated puzzle of metamorphic rocks that mirrored polyorogenic evolution since Cambrian-Ordovician rifting of Gondwana continental margin to Carboniferous continental collision (Putiš et al. 2008b; 2009; Kohút et al. 2007; 2008). The Variscan nappe-stack is southeast-vergent (Putiš 1992; Putiš et al. 2008b) and despite Alpine tectonics, is still recognizable in domains outside the Cretaceous shear zones, namely in the Tatric basement. In general, the CWC basement can be subdivided into two large structural and/or lithostratigraphic levels from the view-point of main periods of its evolution.

The **Lower structural level** is related to evolution of the Rheic and South-Armorican Ocean at northern margin of Gondwana and is built by metamorphosed igneous and sedimentary products that originated during the older (Cambrian to Silurian) period. The 40 metamorphic settings of these rocks are variegated indeed, mainly reflecting medium- to high-grade conditions. However, it is suggested that part of these rocks experienced HP conditions (Janák et al. 1996; 2007; Faryad et al. 2005) during northward subduction of the South-Armorican Ocean crust under the Armorica before 420 – 390 Ma.

The **Upper structural level** is related to Devonian extension of the South Armorican margin, locally leading to the opening of smaller oceanic backarc basins, and their amalgamation during the Upper Devonian – Lower Carboniferous subduction/collisional processes (Putiš et al. 2008b). Volcano-sedimentary successions of these riftogeneous basin domains, including those resembling the Lahn-Dill type (Kohút et al. 2006), were metamorphosed mostly in lower amphibolite to greenschist facies conditions. Mutual relation of the Lower and Upper structural levels in respect of Variscan tectonics is dominantly in normal position, albeit inverted stacking is possible. However, the Variscan HT/MP metamorphism with concomitant widespread granitic magmatism has heavily overprinted these basement precursors, and masked their polyorogenic history.

Origin of vast felsic magmatic – granitic rocks related to the Variscan orogeny was connected to long lasting progradation of orogenic processes (Petrík, Kohút 1997; Broska, Uher 2001; Putiš et al. 2009; Kohút 2007). The proper collisional tectonics marked by lithospheric thickening with the formation of crustal scale nappe structures and large transcurrent faults during Meso-Variscan phase, which followed after subduction and amalgamation of oceanic lithosphere and/or convergence of microcontinents during Eo-Variscan period; continued to lithosphere delamination (slab breakoff) resulting in rapid postcollisional uplift and/or extensional tectonics in Neo-Variscan period. Two principal families of granitic rocks that mirrored distinct tectonic setting and/or different source of rock were identified in the Tatricum yet. The Early Carboniferous (Meso-Variscan) calk-alkaline I-type granites spatially come with subsequent type of granites but in less volume.

Generally, they are rather metaluminous to subaluminous, dominated by biotite tonalite to granodiorite with scarce hornblende, whereas muscovite-biotite granodiorite to granite are less frequent. Magmatic intrusion ages of this I-type granite group vary between 365 – 355 Ma. Peraluminous S-type granitic rocks (dominated by two-mica granites and granodiorites, while biotite granodiorites to tonalites are less common) represent contemporaneous or slightly younger – Meso-Variscan family of granitic rocks, having magmatic emplacement ages among 360 – 345 Ma. Besides these two principal groups of granitic rocks there were locally documented small Permian leucocratic granite veins (Poller et al., 2005). Though beyond these two principal Variscan granitic groups there were described the Permian A-type and ore-bearing specialised Ss-type granites in Veporicum and Gemericum superunits (Uher, Broska 1996; Broska, Uher 2001; Uher et al. 2008).

The Upper Paleozoic complexes of Carboniferous – Permian age have predominantly a continental character, only locally have deltaic-marine origin (Vozárová, Vozár 1988). Generally, are characterized by the prevalence of coarse-detrital clastic material derived from the vicinity rock complexes surround the original sedimentary basin. The Permian sedimentary complexes have prevailingly cyclic setting, and numerous thick sedimentary cycles in the sedimentary succession were distinguished. Each of them is formed at the base with the complex of polymict conglomerates, whereas toward the upper part are alternating with fine-grained sediments.

3. Basic features of the Tatra Mountains crystalline basement

The Tatra Mountains are situated in the northern part of Slovakia and southern Poland just at their border (Fig. 1, 2). The crystalline basement of the Tatra Mountains is composed of pre-Mesozoic metamorphic rocks and granitoids, which are overlain by Mesozoic sediments – Tatric cover. Two allochthonous Mesozoic units: the Fatricum – Krížna and the Hronicum – Choc nappes occur in a tectonically higher position. The crystalline basement together with its Mesozoic cover and the nappe complexes were juxtaposed through northdirected thrusting during the Upper Cretaceous. The Tatra Mts. form a typical horst structure and were finally exhumed during the Alpine orogeny in the Oligocene - Miocene period (Kovac et al. 1994; Kohút, Sherlock 2003; Jurewicz 2005). Metamorphic rocks are most abundant in the western part (Western Tatra Mountains), whereas the granites are more common in the eastern part (High Tatra Mountains). The basement is divided into two tectonic units, which differ in metamorphic grade and lithology (Kahan 1969; Janák 1994). The "*Upper Unit*" contains ortho- + para-gneisses, migmatites, granitoids, and some amphibolites whereas the "*Lower Unit*" consists mainly of metasediments (micaschists, metaquartzites). The two units show inverted metamorphism due to tectonic movements in the Variscan time (Fritz et al. 1992).

The Lower Unit is only exposed in the Western Tatra Mountains (Fig. 2) and comprises exclusively medium-grade micaschists. A kyanite-staurolite zone and a kyanite-sillimanite zone have been distinguished (Janák 1994; Janák et al. 1988; Gawęda, Kozłowski 1996; Kohút et al. 2008). P-T estimates indicate lower amphibolite facies conditions in the Lower Unit (ca 570 – 650°C, and 600 – 800 MPa; e.g. Janák 1994; Gurk 1999).

The Upper Unit shows high-grade metamorphism and migmatization due to partial melting. Its lower part is formed by older granites (orthogneisses), kyanite-bearing paragneisses and banded amphibolites with garnet and clinopyroxene-bearing eclogite relics (Janák et al. 1996), indicating HP (1.0 – 1.4 GPa) / HT (700 – 800°C) conditions. Higher levels, belong to the sillimanite zone and contain sillimanite, K-feldspar, and cordieritebearing migmatites, which indicate medium to low pressure - high temperature conditions (400 – 600 MPa, 750 – 800°C; Janák et al. 1999; Burda, Gawęda 1999; 2009; Gawęda et al. 2000; Gawęda; Burda 2005). The Upper Unit was intruded by a sheet-like granitoid pluton, with a compositional range from muscovite-biotite granite to biotite tonalite and hornblende diorite (Kohút, Janák 1994). Muscovite–biotite granites to granodiorites (younger granites) are most abundant intrusive rocks.

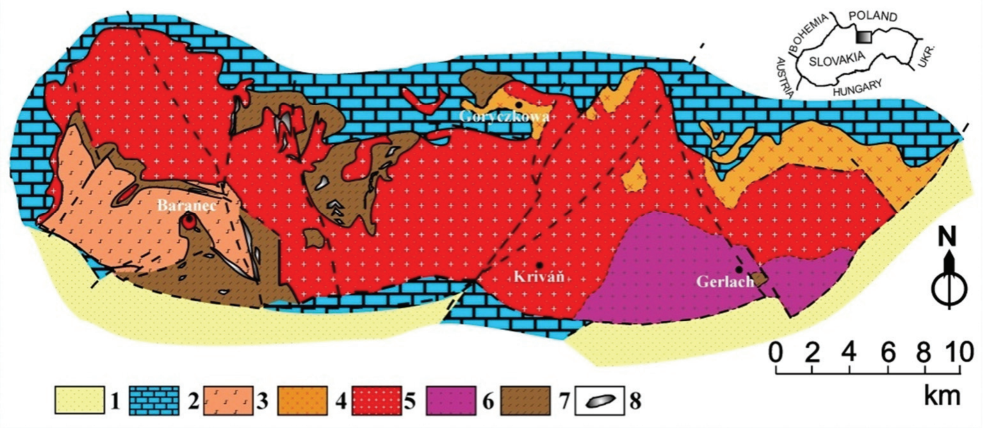

Fig. 2. Simplified geological map of the Tatra Mts. (Kohút, Janák 1994).
Explanations: 1) Paleogene; 2) Mesozoic en bloc; Lower Unit - 3) micaschists + metaquartzites; Upper Unit - 4) Goryczkowa granite; 5) Common Tatra granodiorite; 6) High Tatra tonalite; 7) gneisses (ortho- & para-), migmatites; 8) amphibolites.

Deformation and metamorphism in the crystalline basement Tatra Mts. are the remnant of a multi-stage evolution, during Variscan and Alpine orogeny. However, the Alpine overprint seems to be of a low grade, restricted to the local deformation. This allows to elucidate the pre-Alpine history of the basement and make some implications for the Variscan orogeny in the Western Carpathians. The Tatra Mountains has been affected by Variscan and Alpine deformations (Kahan 1969; Fritz et al. 1992; Jurewicz 2005; Jurewicz, Bagiński 2005). The first of two Variscan deformation phases (D1) is related to south-eastward thrusting of the Upper Unit onto the Lower Unit, whereas D2 deformation was related to EW extension (Fig. 3). Reliable age constrains on the Variscan P-T and tectonometamorphic evolutions in the Tatra Mountains are still lacking.

The Alpine influence is documented by mostly brittle deformation (D3) at lower P-T conditions; indicating northwest-directed shearing during Late Cretaceous compression. Magnetic fabrics (Hrouda, Kahan 1991) record this shear sense. D4 is related to updoming during Tertiary extension and uplift.

4. Geochronological data

First modern age determinations for the granitoids in the Western Tatra Mountains resulted in a Silurian age (406 Ma – Poller et al. 2000) for the precursor of the orthogneisses (older granites); indeed majority of the Western Carpathians orthogneisses gave protomagmatic ages close to 500 Ma (Putiš et al. 2009). Similarly detrital zircons from the Lower unit metasediments suggest for their Cambrian – Lower Ordovician igneous source (Kohút et al. 2008). This was followed by the metamorphic overprint of these orthogneisses around 365 Ma, and the intrusions of the Western Tatra granitoids 360 – 355 Ma ago (Poller et al. 2000, Burda & Klötzli, 2007, Burda & Gawęda, 2009; Kohút & Siman 2011-this volume). The Lower Carboniferous age of felsic – granitic magmatism was confirmed recently there by Re-Os molybdenite dating (from pegmatite) indicating 350 ± 1 Ma period of its crystallization from residual melt (Mikulski et al. 2011). This is in accordance to previous WR Rb-Sr pegmatite dating (Gawęda 1995). In the High Tatra Mts. the main phase of (younger) granitoid-emplacement occurred before 315 Ma (Poller, Todt 2000), respectively rather comparable as in the Western Tatras at 363 – 352 Ma (Kohút et al. 2010). Cooling ages of micas from the granitoids and migmatites obtained by the $^{40}Ar/^{39}Ar$ method range between 330 and 300 Ma (Maluski et al. 1993; Janák 1994; Kohút, Sherlock 2003). Apatite fission track data record the final uplift of the Tatra Mountains in Tertiary time, 15 – 10 Ma ago (Kovác et al. 1994).

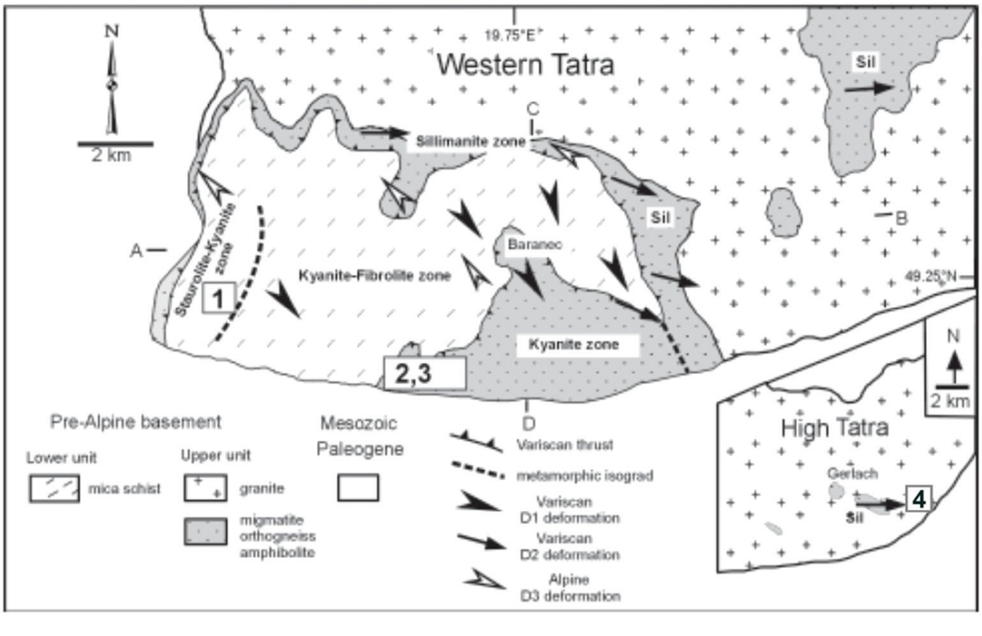

Fig. 3. Generalised tectono-metamorphic map of the Tatra Mountains with excursion stops; taken from Janák et al. (2001).

5. Metamorphism

5.1. Lower Unit

Metapelites in the lower unit contain the assemblages: kyanite ± staurolite + fibrolitic sillimanite + garnet + biotite + muscovite1 ± chlorite1 + plagioclase + quartz. Relics of rutile are sporadically present and ilmenite is more abundant. Staurolite is abundant in the staurolite-kyanite zone, exposed in the westernmost part of the Tatra Mts. (Fig. 3, 4). Kyanite and fibrolitic sillimanite are diagnostic minerals of the kyanite-sillimanite (fibrolite) zone where staurolite relics appear only sporadically. As inferred from metamorphic textures, fibrolitic sillimanite is a relatively younger phase than staurolite and kyanite. Later retrograde overprint is demonstrated by the formation of chlorite2, chloritoid, margarite and muscovite2 in the microfractures and pseudomorphs after staurolite, kyanite and garnet. Metamorphic *P*-*T* conditions from about 550 – 620°C and 0.5 – 0.6 GPa in the staurolite-kyanite zone to 620 – 660 °C and 0.6 – 0.8 GPa in the kyanite-sillimanite (fibrolite) zone have been calculated (Janák et al. 1988; Janák 1994; Ludhová 1999).

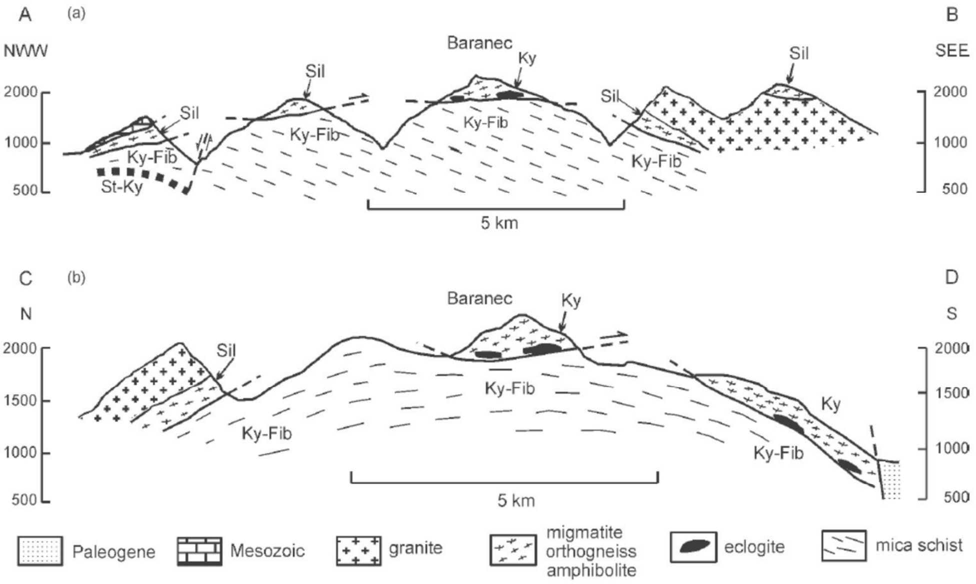

Fig. 4. Schematic profiles across the western part of the Tatra Mountains; taken from Janák et al. (2001).

5.2. Upper Unit

Metapelites in the upper unit show the following mineral assemblages: garnet + kyanite ± sillimanite + biotite + plagioclase ± K-feldspar ± muscovite with staurolite relics, and garnet + sillimanite + biotite + quartz + plagioclase ± K-feldspar ± muscovite; or biotite + sillimanite + cordierite ± garnet + quartz + plagioclase ± K-feldspar ± muscovite in the sillimanite zone. Ilmenite, rutile and magnetite represent Fe-Ti oxides. Minor and accessory minerals include orthoamphibole (gedrite, anthophyllite), chlorite, epidote, carbonates (calcite, siderite), zircon, monazite and apatite. Retrogression led locally to the origin of chloritoid, muscovite, margarite and chlorite in late fractures. The leucosome formation in the metapelitic migmatites resulted from the dehydration-melting of muscovite and biotite (Janák et al. 1999). Decompression from a high-pressure stage (1.2 – 1.4 GPa) led to the transformation of kyanite to sillimanite. Locally (area of Ježová), cordierite have been formed at ca. 0.4 – 0.5 GPa (Ludhová, Janák 1999). The CO_2 – rich fluid was generated during the interaction of melt-derived water with metapelite graphite (Janák et al. 1999; Hurai et al. 2000). Consequently, peak metamorphism high-grade assemblages have been strongly obliterated by retrogression at subsolidus conditions. Metabasites with garnet and clinopyroxene occur in the kyanite zone, showing symplectitic (diopside + plagioclase) and kelyphitic (amphibole + plagioclase) textures. Thermobarometric calculations from mineral inclusions in the garnet cores yield 670 – 700°C and 1.5 – 1.0 GPa, recording the initial path from amphibolite to eclogite facies conditions (Janák et al. 1996). The symplectites have formed by breakdown of inferred omphacite (Jd36), suggesting extensive re-equilibration of eclogites in the amphibolite/granulite facies conditions (650 – 750°C; 0.8 – 1.2 GPa) during their exhumation. Several generations of amphibole (pargasite, hornblende, cummingtonite, actinolite) are evidence of a transformation down to greenschist facies conditions. The fluid inclusions (Janák et al. 1996; Hurai et al. 2000) contain nitrogen–dominated, water-absent fluid similar to that reported from typical high-pressure eclogites. Presence of tonalitic and trondhjemitic veins suggests partial melting in metabasites. In the sillimanite zone metabasites, high-pressure relics are lacking. As inferred from spatial distribution of metamorphic zones and mineral assemblages in the upper unit, the highest-pressure conditions have been attained at the base of the unit, while the upper levels reveal metamorphic recrystallization at lower pressure conditions.

6. Description of stops

Stop No. 1

Topics: micaschists of the staurolite-kyanite zone in the Lower unit

Location: Western Tatra Mts., Jalovecká Valley.

Geographical coordinates: N 49°10.05`; E 19°39.51`

Outcrops along the path in the middle part of valley near Jalovcianka brook (Fig. 3). The outcrops show the micaschists of the lower structural unit. These contain staurolite and kyanite porphyroblasts attaining the size of several mm, almandine garnet, fibrolitic sillimanite, muscovite, biotite and chlorite. Retrograde chloritoid, margarite and sericite are sometimes present. Staurolite is a diagnostic mineral of the apparent staurolite-kyanite zone exposed in this area. Peak metamorphic conditions reached about 550 – 580°C and 0.5 – 0.7 GPa. Detailed geochemistry and detrital zircon dating is presented in Kohút et al. (2008). Geochemical data suggest derivation of the protolith – magmatogenic greywackes and claystones from the recycled continental island arc source. $^{87}Sr/^{86}Sr_{(350)}$ isotopic ratios between 0.713 and 0.723 together with low $\varepsilon Nd_{(350)}$ values of –9.5 to –11.1 and/or Pb isotope composition indicate a crustal origin of the investigated rocks. Detrital zircons from the metasediments often display homogeneous magmatic zoning with $^{207}Pb/^{206}Pb$ ages from 660 to 515 Ma and/or inherited components, with old cores displaying ages from ca. 1980 to 1800 Ma. These late Paleo Proterozoic detrital source ages are similar to the Nd model ages of the studied metasedimentary rocks with $t_{(DM2st)}$ ca. 1960 ~ 1830 Ma. The Late Cambrian (ca 500 Ma) age represents the last magmatic activity of the precursor rocks and/or it defines the maximum age for sedimentation of the present day metasediments. A possible source for the clastic material of the Lower Unit from the Western Tatra Mountains was the peri-Gondwanan continentals margin alike the eastern border of the Bohemian Massif – Moravo- Silesian zone or Sudetic block.

Stop No. 2

Topics: micaschists of the kyanite-sillimanite (fibrolite zone) in the Lower tectonic unit, close to the contact with the Upper unit.

Location: Western Tatra Mts., Žiarska Valley – middle part, exposures ca. 1500 m on the road towards the Žiarska challet (Fig. 3).

Geographical coordinates: N 49°08.78`; E 19°42.36`

Outcrops in the Žiarska Valley expose the micaschists of the kyanite-sillimanite (fibrolite) zone beneath the thrust contact. Mineral assemblage in metapelites contain kyanite, garnet, fibrolitic sillimanite, biotite, muscovite, plagioclase, rutile, ilmenite and quartz. P-T conditions of metamorphism reached 620 – 640°C and 0.6 – 0.7 GPa.

Stop No. 3

Topics: banded amphibolites and orthogneisses, HP-HT metamorphism and deformation at the base of the Upper unit.

Location: Western Tatra Mts., Žiarska Valley – lower part, rock exposures ca 30–50 m above the road to Žiarska challet (Fig. 3).

Geographical coordinates: N 49°09.11`; E 19°39.51`

Banded amphibolites are a characteristic lithology, marking the detachment plane of the upper (overthrust) unit. Mafic layers consist of amphibole (hornblende to pargasite) and plagioclase, with minor quartz, ilmenite, rutile and sphene. Leucocratic bands are composed predominantly of plagioclase (oligoclase) and quartz, almandine garnet is also present by breakdown of garnets in coronal textures. Orthogneisses are coarse-grained with augen-like K-feldspars of 1–2 cm size, or fine-grained, foliated, with distinctive mylonitic fabric. Quartz is platy and ribbon-textured; K-feldspar is perthitic, often with microcline twinning and signs of dynamic recrystallization. Plagioclase is albite to oligoclase, locally, myrmekite has developed. The micas form a “mica-fish” texture. Biotite is Fe-rich, often replaced by chlorite. Muscovite is slightly phengitic; some $^{40}Ar/^{39}Ar$ spectra are discordant due to an Alpine overprint. Garnet is almandine and spessartine-rich, partly replaced by biotite and chlorite. Accessory minerals are apatite, zircon and monazite. Cathodoluminescence study of zircons (Poller et al. 2000) revealed the cores overgrown by magmatic rims. U-Pb dating of these zircons (Poller et al. 2000) provided the lower intercept age of 406 ± 5 Ma, recording magmatic zircon crystallization, whereas the upper intercept of 1980 ± 37 Ma age indicates an inherited material in the zircons.

Stop No. 4

Topics: granitic rocks of the Tatra Mts.

Locality: Starý Smokovec, Hrebienok, High Tatra Mts.

Geographical coordinates: N 49°10.05`; E 20°13.10`

Key words: Tatra Mts., granitic rocks, pseudotachylyte, rock-forming and accessory minerals, geochemistry, geochronological dating.

Position: the High Tatra Mountains are the smallest high mountains, probably the smallest Alpine-type Mountain in the world. The Hrebienok near Starý Smokovec village where granite crops out is a touristic point accessible by a funicular train. The granitic rocks belong to the Paleozoic basement of the Tatric Superunit of the Central Western Carpathians. Granitic rocks: granite is medium to coarse-grained with local phenocrysts of pinkish K-feldspar. Biotite and muscovite-biotite granodiorite to granite slightly porphyric: so-called the "Common Tatra type" is cropping out at the locality Hrebienok at the destination of the cogged-railway. Predominance of biotite granodiorite named "High Tatra type" (Kohút, Janák 1994) to tonalite to muscovite-biotite granodiorite is typical for the eastern part of Tatra Mts. Single-crystal zircon age is 314 Ma but occurrence of a diorite with ~340 Ma age is also known (Poller, Todt 2001; Poller et al. 2001) However, last unpublished Poller´s results suggest for older age of metamorphic (migmatization) and magmatic activity around 335 Ma (CLC single zircon dating by TIMS) in the Tatra Mts. East from Hrebienok is the Gerlach peak - the highest summit in Slovakia where occurrences of phosphorus enriched enclaves dated by zircon (LA ICP MS) giving age between 361 ± 8Ma and 345 ± 5 Ma (Gawęda 2008) has been found. These age data are more or less comparable to zircon SHRIMP dating with concordia 363 ± 5 Ma indeed "youngest spot" shows age 346 ± 5 Ma for granodiorites from Velická Valley (Kohút et al. 2010). Noteworthy, that the first SHRIMP Tatra Mts. data indicated an older magmatic age ca 350 Ma, albeit authors (Poller et al. 2001; Poller, Todt 2001) preferred younger magmatic emplacement age (314 ± 4 Ma) obtained by CLC single zircon TIMS method this time. In mineral composition of granodiorite, is: plagioclase ca. 50 vol. %, quartz (ca. 30 vol. %), K-feldspar (6 vol. %), biotite (10 vol. %) ± muscovite, accessory minerals comprise mainly apatite, zircon, monazite, magnetite and ilmenite. Plagioclase I with An_{35-45} is enclosed in twinned phenocrysts of plagioclase II of An_{15-30}. Albite commonly occurs in interstitial position between older plagioclase. Petrographically, the „Common Tatra granite" represents a crustal anatectic rock with magmatic muscovite. The dominance of Na_2O over K_2O is typical. The Rb/Sr ratios are around 0.05-0.35 and initial strontium ratios are around I_{Sr} = 0.705 - 0.706; these data indicate an inhomogeneous, weakly differentiated lower crustal source or possibly a mantle input. The Mississippian Variscan emplacement & cooling at 330 ± 3 Ma (Maluski et al. 1993), respectively 331 ± 4 Ma (Kohút, Sherlock 2003) age was documented by ^{40}Ar/^{39}Ar dating of biotite from granitic rocks of the High Tatra Mts.

The Tatra granitic rocks form sheet-like intrusions (Kahan 1969) and they are located in the hanging wall of the Variscan nappe system preserving the inverted metamorphic zonation (Janák 1994). Metamorphic conditions in wall rock of the granite show 700 – 750°C temperatures and 400 – 600 MPa pressure (Janák et al. 1988; Janák 1994) indicating synkinematic emplacement of the granitic pluton in middle crustal level during the Variscan uplift.

North from the Hrebienok in the valley of the Batizovské Lake, pseudotachylyte veinlets occur. They originated by frictional melting of the granite during ancient the Oligocene 33 – 28 Ma (Kohút, Sherlock 2003) earthquakes when the Tatra Mts. began uplifted, indeed their final exhumation occurred later in the Miocene (15 – 10 Ma). The earthquakes were located in depth of 10-12 km. The pseudotachylyte is a Fe-rich rock with hematite content up to 26 vol. % (Petrík et al. 2003).

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