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The 2nd Conference organized by the Geochemical Group of the Mineralogical Society of Poland Kielce, Sept. 24–26, 2012





The 11th Geochronological Conference "Dating of Minerals and Rocks XI" Kielce, Sept. 26–27, 2012



Abstracts, excursion and field session guide

KIELCE, SEPTEMBER 24-27, 2012

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The 2nd International Conference "Contemporary Problems of Geochemistry"

&

The Conference "Dating of Minerals and Rocks XI"

organized by

Mineralogical Society of Poland

together with

Jan Kochanowski University in Kielce

Mass Spectrometry Laboratory of Maria Curie-Skłodowska University in Lublin



KIELCE, SEPTEMBER 24-27, 2012

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(2) Neolithic Flint Mine at Krzemionki

Dear Colleagues,

Welcome to the 2^{nd} International Conference on "Contemporary Problems of Geochemistry" and the 11^{th} Geochronological Conference "Dating of Minerals and Rocks XI"! The paired conferences are held in Kielce on $24^{th} - 26^{th}$ and $26^{th} - 27^{th}$ of September 2012, respectively.

Both these conferences are co-organized by the Geochemical Group of the Mineralogical Society of Poland, the youngest thematic group of the Society, but very active since being established in 2009. The 1st International Conference on "*Contemporary Problems of Geochemistry*" was organized by this Group also in Kielce in 2010 and represented a significant scientific event.

This year, according to the original schedule, we come back to hospitable Kielce for the 2^{nd} Conference of this cycle. The Conference is co-organized by the Geochemical Group of the MSP and the Jan Kochanowski University in Kielce. The planned three-days' oral and poster sessions are expected to cover a wide spectrum of research problems currently being undertaken within environmental geochemistry and related disciplines. The two conference field excursions are dedicated to geoeducation issues, and the mining and cultural heritage of the region.

The 11th Geochronological Conference "*Dating of Minerals and Rocks XI*" is coorganized by the Maria Curie-Skłodowska University in Lublin, the Jan Kochanowski University in Kielce and the Geochemical Group of the MSP. The previous ten conferences of this series were organized regularly in Lublin (six times) and also in several other research centres of Poland. The programme of this Meeting in Kielce (two days of oral and poster sessions) covers a broad scope of geochronological issues, such as various isotopic and non-isotopic dating methods, and stable-isotope techniques related to the dating of geological materials.

We are grateful to the Jan Kochanowski University in Kielce for their kind invitation and hospitality. Many thanks are due to the Organizers led by Zdzisław M. Migaszewski and Agnieszka Gałuszka (Geochemistry), and Stanisław Hałas (Geochronology), for all their organizational efforts and arrangements. Several supporting institutions are thanked for their help.

Let both the conferences be scientifically successful and let all the participants take the very best of impressions from Kielce 2012!

Ryszard Kryza

President of the Mineralogical Society of Poland

Invited lectures

Contemporary Problems of Geochemistry

MINERALOGIA - SPECIAL PAPERS, 39, 2012 www.Mineralogia.pl MINERALOGICAL SOCIETY OF POLAND



MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE

Black carbon and polycyclic aromatic hydrocarbon pollution in India

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The fuel such as gasoline, coal, biomass etc. is widely used for the energy production in central India. Their burnings produce several toxic compounds, such as black carbon (BC), hydrocarbons, CO, CO₂, NO_x, SO_x, polycyclic aromatic hydrocarbons (PAHs), metals, etc. in the environment. Among them, BC is a second culprit for the climate change after CO₂ (Ramanathan, Carmichael 2008). In addition, BC is a carrier of several toxic compounds including PAHs, heavy metals, etc. The BC size is in the nano order, and they penetrate lungs by dissolving toxic compounds in the blood (Donaldson et al. 2005). PAHs are toxic, carcinogenic and persistent organic compounds (Douben 2003).

Therefore, in the present work, distribution and sources of black carbon (BC), organic carbon (OC), carbonate carbon (CC) and polycyclic aromatic hydrocarbons (PAHs) in the ambient air (associated with PM), road dust and sediment of central India are described. Distribution of twelve toxic PAHs, i.e. phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (Baa), chrysene (Cry), benzo[b]fluoranthene (Bbf), benzo[k]fluoranthene (Bkf), benzo[a]pyrene (Bap), dibenz[a,h]anthracene (Dba), benzo[ghi]perylene (Bgh) and indeno[1,2,3-cd]pyrene (Ind) were investigated.

The BC, OC, CC and Σ PAHs content in the air (n = 24) ranged from 8.8 to 65.5, 7.2 to 55.4, 6.1 to 58.7, and from 0.04 to 0.17 µg/m³, with mean values of 28.8±6.8, 23.2±5.4, 22.7±6.8 and 0.09±0.02 µg/m³, respectively during 2007-2008. The concentration of the BC, OC, CC and PAHs in the PM₁₀ was in the range of 7.3 to 13.0%, 6.0 to 11.2%, 2.4 to 17.3% and 290 to 376 mg/kg, with mean values of 9.8±0.7%, 8.2±0.6%, 7.8±1.4% and 333±19 mg/kg, respectively. The contents of BC, OC and PAHs raised as the PM size decreased from PM₁₀ to PM_{2.5}.

Except for the atmospheric deposition, roads are impacted by air pollution, mainly from motor vehicles. The concentrations of BC, OC, CC and Σ PAHs in the road dusts (n = 8) of Raipur city ranged from 5.45 to 8.81%, 0.22 to 0.49%, 0.35 to 0.57% and from 8.69 to 21.69 mg/kg, with mean values of 6.87±0.83%, 0.39±0.06%, 0.49±0.04% and 12.74±2.81 mg/kg, respectively.

The pond sediments are sinks of diffused pollutants. The concentrations of BC, OC, CC and Σ PAHs in the sediments (n = 10) of Raipur city varied from 7.54 to 9.43%, 0.1 to

0.18%, 0.06 to 0.15%, 6.77 to 10.91 and 241 to 538 μ g/kg, with mean values of 8.74±0.38%, 0.15±0.02%, 0.12±0.01% and 9.17±0.82 mg/kg, respectively.

The concentration variations and sources of BC, OC, CC and PAHs in three environmental compartments, i.e. air, dust and sediments are discussed.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Using ICP-MS to decipher biogeochemical processes: speciation and isotope doping case studies

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This talk will illustrate the use of modern quadrupole ICP-MS instrumentation using collision/reaction cells to study biogeochemical processes using two case studies.

Case 1: Speciation of arsenic, selenium, and chromium in ash, soils, and simulated biological fluids using HPLC-DRC-ICP-MS

In 2007-2009, the state of California experienced several large wildfires that damaged large areas of forest and destroyed many homes and buildings. The U.S. Geological Survey collected samples from several fire impacted areas for testing to identify any possible characteristics of the ashes and soils from burned areas that may be of concern for their impact on water quality, human health, endangered species, and debris-flow hazards. The samples collected were subjected to analysis for bulk chemical composition for 44 elements by inductively coupled plasma mass spectrometry (ICP-MS) after acid digestion. Water leach tests generated leachate solutions ranging from pH 10-12, suggesting that ashes can generate caustic alkalinity in contact with rain water or body fluids (e.g., sweat and fluids in the respiratory tract). Samples from burned residential areas in the 2007 fires had elevated levels for several metals, including: As, Pb, Sb, Cu, Zn, and Cr (Plumlee et al. 2007). In some cases, the levels of As, Pb, Sb, and Cr were above the U.S. EPA preliminary remediation goals (PRG) for soils.

Speciation analyses were also conducted on the de-ionized water and simulated lung fluid leachates for As(III), As(V), Se(IV), Se(VI), Cr(III), and Cr(VI). All species were determined simultaneously under the same chromatographic conditions using an ion-pairing HPLC-ICP-MS method (Wolf et al. 2007). In general, it was found that for de-ionized water leachates containing high levels of total Cr, the majority of the chromium was present in the hexavalent, Cr(VI), form. Higher total and hexavalent chromium levels were observed for samples taken from burned residential areas. Arsenic was also generally present in the more oxidized, As(V), form. As(V) and Cr(VI) levels were significantly higher in simulated lung fluid leachates. Selenium(IV) and (VI) were present, but typically at levels below 2 ppb for most samples. The presence of the oxidized forms of As and Cr is not surprising, given the oxidizing conditions of a fire; however, the presence of Cr(VI) has potential health implications from exposure during fire-fighting and clean-up efforts. In addition, the high pH solutions generated from interaction of the fire-impacted soils and ashes with water, indicate the potential for stabilization of Cr(VI) in the environment as the soils and ashes interact with natural precipitation (Wolf et al. 2011).

Health and safety regulations should ideally be based on effects resulting from contact with the element or compound being regulated, generally from inhalation, ingestion, or absorption by the body. However, there is limited data available as to the stability of Cr(VI), in particular, in sample and standard solutions or in various fluids in the human body. In order to assess the potential fate and stability of Cr(VI) through various exposure routes, we have conducted a study examining the stability and rates of interconversion between Cr(VI) and Cr(III) in tap water as a function of pH and in simulated lung, gastric, and intestinal fluids at various concentrations of Cr(VI). These studies indicate that Cr(VI) is rapidly and completely reduced to Cr(III) in the simulated gastric fluid (pH \sim 1.5) at concentrations $\leq 200 \ \mu$ g/L. At concentrations between 200 and 1000 μ g/L, 75% or more of the Cr(VI) is reduced to Cr(III) and remains stable for up to 24 hours. In simulated intestinal fluid (pH \sim 4.8), reduction of Cr(VI) to Cr(III) happens at a reduced rate and is concentration dependent, resulting in only 25% conversion after 6 hours in the lowest concentrations tested. It was also found that Cr(VI) is extremely stable in the simulated lung fluid (pH \sim 7.4) with less than 10% reduction after 6 hours at all concentrations tested up to 1 mg/L and only 15-25% reduction after a full 24 hours. Finally, in tap water, it was found that the addition of a small amount of ascorbic acid (from lemon juice) could rapidly reduce up to 200 μ g/L Cr(VI) to Cr(III). Additional studies have been performed on the stability of Cr(VI) and Cr(III) in standard solutions and in spiked reference waters at different storage temperatures and these results will also be presented and discussed. Results indicate the Cr(VI) stability should always be evaluated in the matrix of interest as effects due to concomitant species have been observed.

Case 2: Use of stable Zn isotopes to evaluate zinc uptake in fish gills

This study used stable zinc isotopes in a toxicity study to measure zinc uptake in the gills of brown trout (*Salmo trutta*), rainbow trout (*Oncorhynchus mykiss*) and brook trout (*Salvelinus fontinalis*). Preliminary studies indicated that the ${}^{67}Zn/{}^{66}Zn$ ratio could be measured in digested fish gill samples with no significant interference effects from sulfur and phosphorus using a quadrupole ICP-MS system (Wolf et al. 2009). The long-term (96-hour) precision obtained was 0.7% RSD for fish gill laboratory control samples and the accuracy as relative standard error achieved over the same time period was 0.3%. ${}^{67}Zn/{}^{66}Zn$ ratios were measured using brown trout for 3-hour and 24-hour exposures in ${}^{67}Zn$ -enriched waters. Significant differences (p>0.05) in the measured ${}^{67}Zn/{}^{66}Zn$ ratios were observed between the control fish (unexposed) and both the 3-hour and 24-hour exposed groups of fish. A significant difference was also observed in the ${}^{67}Zn/{}^{66}Zn$ ratios between the 3-hour and 24-hour exposure groups.

A full-scale exposure study was performed on rainbow trout. Exposures were carried out in 67 Zn-enriched waters at various concentrations in both hard and soft waters in order to evaluate the effect of competing cations, such as Ca²⁺ and Mg²⁺, on zinc uptake by the gills. The measured 67 Zn/ 66 Zn ratios were used, along with total Zn measurements, to calculate the amount of zinc accumulated in the fish gills during the exposures. Differences were observed in the amount of accumulated zinc between groups of fish exposed to the same concentration of 67 Zn-enriched water at different water hardness levels. This indicates that water quality parameters, such as hardness, are important when evaluating the impact of exposure to zinc on fish toxicity. The information obtained was used to update coefficients used in the Biotic Ligand Model used by the U. S. EPA to establish water quality criteria levels for Zn (Todd et al. 2009).

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ORAL AND POSTER Contributions

Contemporary Problems of Geochemistry

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Origin of saline waters in the vicinity of Rzeszów in the light of isotope ($\delta^{18}O$, δD , $\delta^{13}C$, $\delta^{37}CI$) and hydrochemical studies

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Several decades ago during exploration for additional resources of tap water, a saline water deposit (Cl-Na, J, Fe, B type) was discovered in the area of the Rzeszów hospital park. Nowadays, this water is extracted for balneological purposes. Within the scope of this study the following stable isotopes: δ^{18} O, δ D, δ^{13} C, δ^{37} Cl and radiocarbon were determined for the first time in order to elucidate the origin of water, its mineralization and quality. Oxygen and hydrogen isotope data lead to conclusion that these waters were formed in a warm pre-Pleistocene period or they are a mixture of Miocene seawater with Pleistocene infiltration waters. The carbon isotopic composition (δ^{13} C=-8.65‰) of bicarbonate is characteristic of deep pore waters that occur in sedimentary rocks, whereas positive δ^{37} Cl value rather excludes chlorine ion from an open sea basin.

The absence of radiocarbon in borehole Rzeszów indicates no admixture of recent infiltration waters. This suggests that these waters are well isolated from anthropogenic pollution sources. This is further confirmed by a very low concentration of nitrate.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Preliminary results of neutralization of AMD waters from selected reservoirs in the Muskau Arch near Łęknica, W Poland

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The study was conducted in selected two reservoirs at the southern tip of the geological structure called the Muskau Arch (Fig. 1). The Muskau Arch is a large horseshoe-shaped glaciotectonic belt formed during the Mid-Polish Glaciation. Neogene lignite deposits containing pyrite were excavated there till the '80s of the 20th century. The abandoned mine pits are filled up with water forming a set of about 110 reservoirs called "anthropogenic lakeland".



Fig. 1. Geological sketch map of the research area (after M. Kupetz)

Oxidation of sulfide-containing lignite, exposed to atmospheric oxygen and water leads to formation of acidic waters. The waters are characterized by relatively high Fe and SO_4^{2-} contents. This chemical association and predominantly low pH values of the water represent main environmental waste problem in this region, which is typical for AMD environments. The objective of this study is to compare the effects of various neutralization treatments potentially applied to two selected reservoirs. The largest reservoir called Africa (Fig. 2) is a meromictic lake with permanent stratification: (i) mixolimnion at the top (down to ca. 10 m in depth), in which the water is well mixed and saturated with oxygen, and (ii)

monimolimnion in the deeper part, which is oxygen-depleted and not mixed with upper water. The pH and concentration of major ions in this reservoir are strongly controlled by the stratification. The low pH (pH = 2.75) and ion concentrations (average TDS amount 1400 mg/L) in the upper layer and a higher pH equal 4.75 and salinity (average TDS reach 5500 mg/L) in the bottom one. The other pond is chemically homogeneous and does not reveal any stratification. The pH of this pond water is approximately 4.0 and the average TDS reaches 350 mg/L.



Fig. 2. Sampling points in the study area

In the set of model experiments, the lakes water was mixed with various materials commonly used for neutralization of AMD water (lacustrine limestone, dolomite, hydrated lime). The treatment results in a rapid increase of pH to about neutral (6-7) or even alkaline (11-12 in case of lime) and precipitation of various secondary phases, mostly gypsum and iron oxides and hydroxides. This caused the removal of ferric and ferrous ions and reduction of sulfate content by 50%.

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The effect of water activity on the eutectic point in natural granitic system

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The water activity except for pressure is known to be the most important parameter affecting the eutectic point in granitic systems. Water saturated magmas have lower solidus temperatures than water undersaturated magmas (Johannes, Holtz 1996). Water activity influences also Ab-Or relation in granitic systems (Holtz et al. 1992). Mineral phases present in water saturated conditions differ from those present in water poor conditions (Dall'Agnol et al. 1999).

This effect of water activity on the granitic system has so far been analyzed on synthetic materials. Other parameters which would affect the eutectic point might exist in a natural granitic system. Therefore, two natural samples of Wangrah granites from Australia were taken to analyze their crystallization path. They were chosen so they had very similar composition in terms of Qz-Ab-Or, but different in terms of Ca and Fe contents. The homogenous glass powder was used as a starting material. The water was added to reach water saturated conditions. The water and silver oxalate were added to reach water undersaturated conditions. Crystallization experiments with both samples were performed in cold seal pressure vessel (CSPV) in the temperature range of 680-720°C for water saturated conditions and 765-815°C for water undersaturated conditions. The pressure of 2 kbar and oxygen buffer NNO were established for 15 days. The phases were identified and glass composition was determined by an electron microprobe. The water content of glass was measured with the use of near infrared spectroscopy.

The results were plotted on the Qz-Ab-Or diagram with application of Blundy and Cashman corrections (Blundy, Cashman 2001) for the An content. Two very similar compositions in terms of Qz-Ab-Or show a different position of their cotectic lines for water saturated conditions. One possible explanation of this fact is that the projection of Blundy and Cashman does not account accurately for the effect of Ca. The alternative explanation is that there must be other parameters controlling the position of the cotectic line, one of them may be Fe. In any case, one cannot simply project natural granite or rhyolites on the Qz-Ab-Or diagram to extract quantitative information on pressure or water activity of granites or rhyolites. A new set of experiments should be performed to clarify this problem.

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Application of selected modified halloysite adsorbents for ammonia adsorption determined by capillary electrophoresis method

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Halloysite is a layered silicate (Fig. 1) used for obtaining mineral sorbents. This raw material $(Al_2[(OH)_4|Si_2O_5]\cdot 2H_2O)$ is composed of silica, aluminum and iron. In contrast to other minerals of kaolinite group, it has a greater surface area and the ability to exchange ions. It consists of two layers: tetrahedral and octahedral. The tetrahedral layer is built of tetrahedrons, in which a central cation is Si⁴⁺ surrounded by four oxygen anions O²⁻. The octahedral layer, called metal-oxygen-hydroxide, is built of octahedrons with an Al³⁺ ion, in the centre of this structure, coordinated by OH⁻ and O²⁻ anions. The O²⁻ anions are common for both tetrahedral and octahedral layers. These layers form a block structure (Stoch 1974).



Fig. 1. Schematic imaging of halloysite layer structure (Yelleswarapu et al. 2010)

In the microscope image it usually forms nanotubes with a diameter of about several dozen nanometers and averaging several micrometers in length. They are significantly cheaper and more easily available than the carbon nanotubes. The Polish halloysite clay is mined in the Dunino quarry near Legnica. The Polish deposit belongs to the largest in the world containing about 10-12 million tons of this raw material.

Ammonia is a toxic gas for people and animals, responsible for the water and soil pollution, causing forests deterioration, and also contributing to eutrophication of land ecosystems and surface waters (Bouwman et al. 1997; Sutton et al. 1998; Hyde et al. 2003). The main source of the ammonia emission is a farm output, especially animal breeding. In the last decade many methods of limiting the occurrence of this gaseous pollutant in farms and inventory buildings with intensive animal production have been tested (McCrory,

Hobbs 2001; Makles, Galwas-Zakrzewska 2005; Kolacz, Dobrzański 2006). There are more and more information on possibilities of use of different mineral materials assigned to this group of aluminosilicates (Kozak, Domka 2004) for reducing chemical air pollution, including odors.

The principal aim of this work was to examine ammonia adsorptive properties on a modified halloysite adsorbent using the capillary electrophoresis method. The halloysite was subjected to acidic activation (Garnuszek et al. 2011) and then it was added to ammonia solution. After adsorption of ammonia on a halloysite surface, the solution was analyzed by capillary electrophoresis to check the amount of ammonia present in the solution.

Capillary electrophoresis is an analytical method which can be used for ions determination in water solutions. In traditional electrophoresis, electrically charged analytes move in a conductive liquid medium under the influence of an electric field. The results of the analysis are presented on electropherogram (Fig. 2).



Fig. 2. Electropherogram of solution analysis after adsorption on halloysite; peak 1 is from ammonia, peaks 2-5 are unidentified

Mineral sorbents received from halloysite can be applied to sorb ammonia from the air.

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Cavity Ring Down Spectrometry: an alternative to Isotope Ratio Mass Spectrometry

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Stable isotope ratios measurements of water (D/H and ¹⁸O/¹⁶O) are extremely important in studies of hydrologic cycles. The isotope data provide valuable information about the direction of water flow, mixing processes, evapotranspiration, identification of origin/adulteration of food (e.g. beverages), or in criminology. Isotopic water composition is a marker of processes, typical for areas that generate differences in the isotopic ratio. The most important factors determining the isotopic composition of water, include the hydrogeological and climatic conditions.

Stable isotope abundance measurements in water and other materials have so far been a domain of stable isotope ratio mass spectrometry (IRMS). To determine the variability of small deuterium amounts in natural samples, measurement precision must be better than 0.15 ppm (~1‰ in delta notation). Even precision better than 0.1‰ (in delta notation) is needed when measuring ¹⁸O/¹⁶O due to the low natural ratio and smaller isotopic fractionation. So far IRMS has failed to develop a high-precision reliable method that would provide isotopic analysis directly from water. Chemical conversion of water to H₂, O₂ or more often to CO₂ is a limiting factor of the attained precision (Żuk 1980; de Groot 2004).

However, a new technique called Cavity Ring-Down Spectroscopy (CRDS) has been developed to overcome some inconveniences of IRMS. This method consists in light absorption by water molecules on circulating light pulses in an optical cavity. The decay time is called the cavity ring-down time and it is conversely proportional to all losses inside the cavity. In an empty cavity, the losses arise only by not ideal reflectivity of the cavity mirrors. Injecting an absorbing sample inside the cavity leads to a faster decay of light pulse in the cavity, and consequently, to a shorter ring-down time. Mathematical fit to the shape of that absorption line is what is actually used to calculate the isotope ratio (Godoy et al. 2012; Brand et al. 2009).

The Cavity Ring Down Spectrometry (CRDS) represents an alternative to the Isotopic Ratio Mass Spectrometry (IRMS), in determination of δD and $\delta^{18}O$ in water samples, allowing for direct detection without any sample preparation. Moreover, this technique may achieve a precision of 0.038‰ and 0.011‰ for δD and $\delta^{18}O$, respectively.

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Anomalous concentrations of rare earth elements in mosses and soils from the Kielce region (south-central Poland)

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Rare earth elements (REEs) include the lanthanide elements from lanthanum (Z=57) to lutetium (Z=71) plus Sc and Y (by IUPAC). They are widely spread in the environment and occur in trace amounts. The mean abundance of rare earth elements in the earth's crust is about 215 ppm and it ranges from 0.5 ppm for Tm to 66 ppm for Ce, but the elements with an even atomic number (e.g. Ce, Nd, Sm) are more common than the elements with an odd atomic number (e.g. La, Pr, Eu) (Wyttenbach et al. 1998; Chiarenzelli et al. 2001; Lawrence et al. 2006).

REE are useful in environmental studies because: (1) they are tracers of geochemical processes in geochemistry, mineralogy, petrology and sedimentology, (2) they can be used as indicators of geogenic pollution sources. However, to compare graphically REE abundance for environmental samples, it is necessary to eliminate the Oddo-Harkins effect by normalizing concentrations of individual REE to their concentration standards: Post-Archean Australian Shales and North American Shale Composite (Market et al. 1989; Pourmand et al. 2011).

The biogeochemical studies were carried out in the Kielce region in 2011 (Fig. 1). A total of 60 samples including: 20 samples of moss *Pleurozium schreberi*, 20 soil samples from the subhorizon Ofh and 20 soil samples from the mixed horizon AE were collected at 20 sampling sites. The moss and soil samples from the subhorizon Ofh were digested with a mixture of nitric acid (1:1) and hydrogen peroxide (1 ml). The soil samples from the horizon AE were digested in *aqua regia* in a closed microwave system (Multiwave 3000). In the last stage 14 rare elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb) were determined using the ICP-MS technique (ELAN DRC II Perkin Elmer).

The principal objectives of this study were as follows: (1) to determine REE concentrations in moss and soil samples, (2) to normalize measured values against Post-Archean Australian Shales and North American Shale Composite and find anomalous concentrations of REEs.

The distribution of REEs in the mosses-soil profile system differs considerably. The horizon AE was enriched in all the elements determined (G.M. 1.087 mg/kg) compared to the subhorizon Ofh (G.M. 0.511 mg/kg) and the moss samples (G.M. 0.081 mg/kg). The lowest concentrations were noted in mosses that accumulate elements from rainfall and solid particles adsorbed onto their tissues. The REE concentrations follow the order:

- Ce>La>Nd>Pr>Gd>Sm>Dy>Er>Yb>Eu>Ho,Tb>Tm,Lu for *Pleurozium schreberi*;
- Ce>La>Nd>Pr>Gd>Sm>Dy>Er>Eu>Yb>Tb,Ho>Tm,Lu for the subhorizon Ofh;
- Ce>La>Nd>Pr>Sm>Gd>Dy>Er>Yb>Eu>Tb,Ho>Tm,Lu for the mixed horizon AE.



Fig. 1. Localization of investigation sites in the Kielce region

All the examined samples showed LREE enrichment and HREE depletion.

The shale-normalized curves are shown in Fig. 2a,b. Both the subhorizon Ofh and horizon AE are slightly enriched in Gd. The moss samples showed significant positive Eu and Gd anomalies. The same trend was observed for moss samples from Sweden (Rühling, Tyler 2004), Norway (Berg, Steinnes 1995) and Canada (Chiarenzelli et. al. 2001).



Fig. 2. Shale-normalized patterns of REEs in a) soil and moss samples; b) moss samples

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Stable isotope record of carbonates from the Poznań Formation

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The Poznań Formation had been formed from Miocene to Pliocene (Piwocki et al. 2004). This formation consists of clays, silts and subordinate sands, with lignite intercalations and beds in the central-western part of Poland. The uppermost part of the Poznań Formation is represented by the youngest succession of sedimentary rocks, informally named as "Poznań clays". They are widespread on the Polish Lowland and occur as massive horizontal layers (up to 200 meters in thickness) overlain by Quaternary deposits, or slices of glacitectonic origin (up to dozen meters in thickness), cropping out at the surface (Wichrowski 1981; Kaczyński, Grabowska-Olszewska 1997; Piwocki et al. 2004).

Mineralogy and chemistry of the Poznań Formation were studied in detail due to their use for ceramic industry (Wyrwicki, Maliszewska 1974; Wichrowski 1981; Piwocki et al. 2004). These studies showed that sedimentary rocks in the southern Wielkopolska region are of terrestrial origin and were formed as paleosols, which is evidenced by textures typical for paleosols and microfabric, e.g. horizonation, slickensides, gypsum levels and petrocalcic levels: calcrete horizons (Duczmal-Czernikiewicz 2010, 2011). These structures and textures give valuable information on the moisture regime and paleoclimatic conditions of sedimentary rocks that were formed under terrestrial conditions during their deposition and also weathering and diagenesis. The aim of this study was to characterize the isotopic record of the Poznań clays, especially calcretes that occur in the upper part of the Poznań Formation. Sampling encompassed nodules from the drill core Leszno-Zaborowo and clay concretions from the Dymaczewo Stare deposit near Poznań. The results obtained provided new information about the physical and chemical conditions during the Miocene and the Miocene-Pliocene transition in this part of Europe.

Isotopic analysis was carried out using a dual inlet and triple collector mass spectrometer (modified and modernized MI1305 model). Carbonate samples were analyzed on CO₂ produced by reaction with 100% H₃PO₄ in a glass vacuum-line connected to the inlet system of the mass spectrometer. The reaction proceeded at electronically controlled temperature of 25°C ± 0.2 °C to achieve δ^{18} O in the PDB scale. For normalization of both δ^{13} C and δ^{18} O values the international standard NBS-19 was analyzed for each series of samples. The analytical uncertainty of both delta values in terms of standard deviation was better than 0.06‰.

The calcretes from drill-core consist of nodules varying from 1 to 3 cm in diameter. They are irregularly elongated or ellipsoidal in shape. Moreover, these nodules consist of $CaCO_3$ which was formed from micritic or subordinate sparitic matrix with microscopically-sized root remnants which are also composed of calcite. In some places

 $CaCO_3$ incorporates trace amounts of Mg, Fe and Mn, as shown by the microprobe analysis (Duczmal-Czernikiewicz 2010). The nodules locally comprise siderite (in inner part) and calcite (in outer part). Calcareous levels have been found at four different depths: 76, 85, 93 and 98.5 m below the surface.

The calcretes from the open-pit occur at two separate levels at a depth of 0.75 m and 2.5 m below the contemporary earth surface. They are elongated reaching up to 1.5 m accross. The calcretes consist of calcite (sparite or micrite), commonly intercalated with Fe oxides (mainly hematite). Some nodules contain septarian druses (or honeycomb cracks) that narrow from the central part of the nodule outward. These structures originated at the later stages during nodule formation, compaction processes and recrystallization of carbonates. They are filled with two distinct carbonate generation. In the outer concretion rims and/or in a carbonate breccia cement, gypsum crystals were found reaching 1-2 mm in length in the brecciated parts of nodules or 10 cm in the outward rims of nodules.

The level of carbonate accumulation from the interval of 93-85.5 m is characterized by the δ^{13} C and δ^{18} O values in the range of -12.03 to -11.4‰ and -4.80 to -4.24‰, respectively. They correspond to the Miocene-Pliocene boundary in Spain (Domingo et al. 2009) derived from the tooth enamel of prehistoric mammal genus *Hipparion* in the Iberian Range (mean δ^{13} C and δ^{18} O values of -11.6 and -6.4‰, respectively). The isotope record at the lowest level (depth of 98 m) is characterized by the least negative delta values (δ^{13} C varies from -7.9 to -6.7‰ and δ^{18} O from -2.7 to -1.6‰) and they could correspond to the highest temperature during growing of concretions (Dworkin et al. 2005), and/or diagenetic alteration of sediments. The carbonates from the upper level (at a depth of 76.5 m) exhibit higher δ^{13} C values than those from the open-pit, which in turn, are strongly depleted in ¹³C. This isotopic record suggests drying and wetting cycles that allowed formation of slickensides by infiltration of carbon compounds through opened cracks and slits. The isotope records may also be altered by vegetation as a result of contemporary weathering processes.

The carbon isotope composition of pedogenic carbonate can be influenced by many factors, e.g. type of vegetation, soil respiration and a depth of carbonate formation. The fourth calcrete level from the drill core displays at least three different isotopic values that could correspond to changes of climatic and paleoenvironmental conditions. The isotope signature indicates both climatic features during sedimentation (e.g. cooling and increase of humidity) and weathering or diagenesis.

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Arsenic in waters of the Podwiśniówka area: geochemical and environmental considerations

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Arsenic is a metalloid that ranks 20th among the most abundant elements in the Earth's crust (Cheng et al. 2009) and 47th among 88 naturally occurring elements (Vaughan 2006). This element occurs mostly in inorganic forms in surface and groundwater reservoirs and it is commonly associated with acid mine drainage (AMD). Arsenic mobility is governed by pH, redox conditions, EC, temperature and biological factors. The typical range of As concentrations in unpolluted surface water is 1-10 ppb, whereas in AMD and thermal waters these concentrations may reach several tens and even hundreds ppm (Henke 2009).

The study area is located about 5 km north of Kielce at the Podwiśniówka Mt. (Holy Cross Mts, south-central Poland). Twenty five water samples were collected in 6 series from three ponds: the Podwiśniówka (Pw) acid pit pond, the Marczakowe Doły (MD) acid pond and the MD fish pond. The chemistry of these ponds has been a subject of detailed geochemical studies and was described in several papers (e.g. Migaszewski et al. 2007, 2008, 2010). Additionally, water samples were collected from 8 farmer's wells located close to the AMD area. Arsenic was determined in filtrated samples (0.45 μ m syringe filters) by an ICP-MS method. The method detection limit was 0.2 ppb. Perkin-Elmer multielement standard solution was used for calibration and a certified reference material (NIST 1643e) was analyzed in parallel with the samples for quality control.

The Pw pit pond of 1.5 m deep has a direct contact with a pyrite zone that crops out at the western wall of the abandoned quartzite quarry. The pyrite is prone to weathering because of its crypto- and microcrystalline structure. The MD acid pond is located about 0.5 km east of the Pw acid pond. This small water body (of about 15 m in diameter and 1.6 m deep) shows typical features of AMD (low pH, high metal and sulfate ion concentrations, the presence of yellow-to-brown precipitates of iron oxyhydroxides and oxyhydrosulfates). The MD fish pond located about 150 m north of the MD acid pond reveals low concentrations of ions, which are characteristic of natural surface waters.

The preliminary LA-ICP-MS analyses of pyrite from the Pw quarry showed a heavy enrichment in arsenic (average 2.7%, in places up to 8.8%, unpubl. data). Sediments of the Pw pit pond have also high As concentrations (about 0.1%) (Migaszewski et al. 2007), creating a potential risk of water contamination with this toxic element. The major objectives of this study were: (i) determination of As in water samples collected from three ponds to find seasonal changes in As concentrations; (ii) evaluation of its geochemical background range; and (iii) comparison of As levels in ponds with those found in farmer's wells.

Concentrations of As in the Pw acid pit pond and the MD fish pond were similar (mean of 48 ppb, range of 6-106 ppb in the Pw acid pit pond and mean of 44 ppb, range of 17-105

ppb in the MD fish pond). These concentrations were about six times lower than those found in the MD acid pond (mean of 280 ppb, range of 68-589 ppb). Boxplots in Fig. 1 present variability of As concentrations in the waters of the three ponds examined. A distinct enrichment in As and the highest seasonal variability of As concentrations were found in the MD acid pit pond. It may be explained by seasonal changes in pH, temperature and redox conditions as well as generation of schwertmannite and transformation of this mineral into ferrihydrite and goethite that influence geochemical behavior of As in a sediment-water system.



samples from the three ponds examined

Geochemical background range of As in surface waters of the study area calculated with the use of iterative 2- σ technique (Matschullat et al. 2000), varies from 6 to 412 ppb. The two water samples of the MD acid pond collected in January and February of 2012, exhibited higher concentrations of As (511 ppb and 589 ppb) than the geochemical background upper limit value. The threshold value for this element, recommended for surface waters of good quality (I and II class), according to the regulation of the minister of the environment on the classification of surface water quality (Journal of the Acts of November 9, 2011, No. 257, item 1545), is 50 ppb. None of the As contents for MD acid pond is below this value and, moreover, this is not met for 23% of the results recorded for the Pw acid pit pond and 17% for the MD fish pond. The mean value of As concentrations in home wells is 1.1 ppb and all of the results obtained (0.6 to 2.4 ppb) are lower than the maximum allowable level for As in drinking water (10 ppb), according to the regulation of the minister of the minister of health on the drinking water quality (Journal of the Acts of April 20, 2010, No. 72, item 6333).

Of the three ponds examined, only the MD acid pond waters were heavily enriched in As. Despite very high concentrations of As in pyrite and in the Pw acid pit pond sediments, As concentrations in the water collected at this site were much lower than those in the MD acid pond.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Simultaneous preparation of N₂ and CO₂ for stable isotope analysis from nitrate samples

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The δ^{18} O and δ^{15} N values of nitrates dissolved in waters are very important markers applied in hydrology and geochemistry. They are one of the tools used for monitoring water quality and identifying sources (Piatek et al. 2005) of anthropogenic nitrate contamination (Vitousek et al. 1997). The stable N and O isotope analysis also allows us to observe changes in the isotopic ratios of nitrogen compounds that form at different stages of biogeochemical cycles (Delwiche 1981; Jaffe 1992; Granger et al. 2010; Casciotti 2009). Therefore, we wanted to develop a new nitrate preparation method that enables measurements of the δ^{18} O and δ^{15} N values with sufficiently high precision, and with low time consumption and sample preparation cost.

Our method is based on the thermal nitrate conversion of AgNO₃ form to CO₂ and N₂ gases in a vacuum system, in which the released gases do not come into contact with hot oxidized surfaces. Silver nitrate at high temperatures decomposes into gaseous NO₂ and O₂ and metallic silver. The reaction is carried out in a platinum boat at temperature of 800°C in the presence of graphite as a reducing agent, where Pt catalyzes the reaction. According to our study, a 60 minute reaction time is sufficient to yield gaseous end-products, predominantly CO₂ and N₂. These products are then separated cryogenically in the temperature of liquid nitrogen: CO₂ is collected in a glass ampoule and N₂ is collected in an ampoule containing activated charcoal as it is difficult to condense N₂ otherwise. The obtained CO₂ and N₂ gases are then analyzed on a dual inlet and triple collector isotope ratio mass spectrometer (δ^{18} O and δ^{15} N).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Micro ion selective electrodes – an alternative for nitrate/nitrite precision concentration measurements

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An excessive amount of nitrates in water affects both humans and most living organisms. NO_3^- and NO_2^- present in drinking water can cause methemoglobinemia, a disease associated with a decreased ability of transporting oxygen in the body (Price 1998). The progressive eutrophication of some reservoirs is now one of the major environmental problems (O'Neill 1993). Risks resulting from inappropriate levels of nitrate in all types of water reservoirs have been a basis for detailed water quality monitoring. Except for traditional methods of determining concentrations of NO_3^- and NO_2^- ions in water samples, i.e. colorimetry (Ellis et al. 1998; Xu et al. 2000) and more precise High Performance Liquid Chromatography (Torrentó et al. 2010), also attempts at using of ion selective electrodes were made (Badea et al. 2001).

We have tested a new nitric oxide measurement system (Model ISM-146NOXM NO₃⁻ and NO₂⁻ measurement system, Lazar Research Laboratories, Inc., USA) on laboratory samples. With this analyzer it is possible to determine nitrate concentrations in a wide pH range of 2 to 11 with a minimum 7 μ M NO₃⁻ content. Nitrite can be measured with a minimum 5 μ M sample content in a much narrower pH range of 4 to 8 (Lazar Research Laboratories, Inc. – specifications). Precise measurements of NO₃⁻ and NO₂⁻ concentrations in water samples provide information on the source and rate of nitrification/denitrification processes, which is a valuable supplement to traditional isotopic analysis.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



One-year spatial and temporal monitoring of concentration and carbon isotopic composition of atmospheric CO_2 and CH_4 in urban area (Wrocław, SW Poland)

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The aim of this study was to assess the anthropogenic impact on the urban atmosphere in Wrocław (city of ca. 630,000 inhabitants and an area of 293 km²). The study was based on the combined use of quantitative (analysis of concentrations) and qualitative analysis (analysis of stable carbon isotopic compositions) of the main greenhouse gases (CO_2 and CH_4). Traffic and industrial emissions were expected to influence carbon dioxide concentrations and characteristics, whereas methane emission from sewage irrigation fields (localized in north-central part of Wrocław) was expected to be dominant.

Samples of ambient air were collected at 15 points which were evenly distributed over the city area. Sampling was done in 3-week intervals during the period from 21^{st} January of 2011 to 22^{nd} December of 2011 (255 samples), always at the same time of day (10 a.m.). The samples were analyzed for CO₂ concentration (12 ml vials), CO₂ isotopic composition (12 ml vials) and for CH₄ isotopic composition (100 ml ampules) using mass spectrometry (CF-IRMS Delta V Advantage with Gasbench II and Precon). The concentration of CH₄ (100 ml vials) was measured using gas chromatography (Shimadzu GC-2014F with FID detector). The annual average results are as follows: (i) methane concentration: 2096 ± 609 ppb, (ii) carbon dioxide concentration: 469±71 ppm, (iii) carbon isotopic composition of methane $\delta^{13}C(CH_4)$: -48.1±4‰, (iv) carbon isotopic composition of carbon dioxide $\delta^{13}C(CO_2)$: -10.8±1‰.

The data were used to prepare detailed maps of the spatial distribution of the parameters analyzed and to observe the seasonal variations during the calendar year. Both CH_4 and CO_2 show seasonal variations. However, the urban character of the majority of the sampling points clearly influences final concentration and carbon isotopic signal. The analysis of temporal and spatial variability allows locating and characterizing local pollution sources as well as determination of their plumes.

Anthropogenic CO_2 accumulated in the vicinity of main roads, and the impact of industrial areas on CO_2 concentrations is also notable. In 2011 the highway city ring road (AOW/A8) was completed (31st August), causing a change of the main transit route. Surprisingly, we observed a significant increase of CO_2 concentrations at many sampling points thereafter, in spite of reduced traffic on the old main roads (5/E261 and 8/E67) in Wrocław. We believe that the dominant W and SW winds in the region create a plume of pollutants (e.g. CO_2) originating from A8 highway, which is situated in the western part of

Wrocław. The apparent accumulation of pollutants in some other areas of the city and lack of dependence of their plumes on the prevailing meteorological conditions indicate a rather poor ventilation of the city. Moreover, limited spread of pollutants is also related to assimilation by the terrestrial biosphere. This was confirmed at sampling points in the vicinity of green areas, which exhibit lower concentrations and higher $\delta^{13}C(CO_2)$ values.

In contrast to CO_2 , the dominant CH_4 source was biogenic, namely the methane produced at the sewage irrigation fields, which was spreading during the growing season at considerable distances, depending on the prevailing meteorological conditions. During the cold period biological input was negligible and anthropogenic background sources of methane could be observed.

Using discriminate plots (Keeling plots) for CO_2 , we determined anthropogenic end members of CO_2 , and based on these data, the isotopic compositions of dominant fuels were determined from Widory's equation. The obtained δ values are characteristic for coal during the first heating season and for gasoline/diesel during the second heating season. This difference between the two heating seasons was most likely caused by the abnormally warm November and December of 2011. Using Keeling plots we did not observe any systematic patterns for CH₄ or any correlations (quality and quantity) between CO₂ and CH₄.

The study confirmed our hypothesis, that there are different sources of methane and carbon dioxide in Wrocław city atmosphere: CO_2 was produced predominantly from fossil fuels, but CH_4 sources were mainly biogenic.

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Lithium isotope analysis in waters and sediments

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Lithium isotopes are of great interest for their geological and geochemical implications because of their unique chemical characteristics including large isotopic fractionation and high magmatic incompatibility. Lithium has only two natural stable isotopes ⁶Li and ⁷Li whose abundances are 7.59% and 92.41%, respectively. During weathering the lighter isotope ⁶Li preferentially retains in the solid phase, but ⁷Li⁺ preferentially dissolves in a solution. Thus river waters are enriched in heavy Li isotope compared to the original bedrock.

The purpose of the present study was to elaborate a lithium extraction method from water solutions on cation exchange column and to determine its isotope ratio by thermal ionization mass spectrometry. Water samples were loaded onto a AG 50W-X8 Bio-Rad 200-400 mesh resin column and then eluated with a mixture of $1N \text{ HNO}_3 - 80\%$ methanol. This mixed acid-methanol eluent ensures a good separation of Li from Na. To minimalize isotopic fractionation during the measurements, we applied a double filament technique and lithium phosphate as the loading material.

This method of lithium isotope determination does not require a complicated chemical sample preparation nor a large amount of material, and for this reason appears to belong to the simplest methods available so far.

The following samples have been investigated using this method: seawater from Mediterranean Sea, mineral water from borehole Zuber I in Krynica Spa (Fore-Carpatian region) and a sediment sample of this water (Hałas et al. 2011). The values of δ^7 Li for all the samples examined were achieved with reproducibility in order of 1‰. The obtained results for L-SVEC and for seawater (32.2‰±1.9‰) fall into the range known from literature. We have determined delta values of an archival sample of Zuber I mineral water and the sediment precipitated from this water. Isotope analysis of freshly sampled mineral water from Zuber I and Zuber II boreholes is in progress.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Ore minerals characterization and stable sulfur isotopes from Broken Hammer, Sudbury

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The Sudbury intrusion is a polymetallic, impact type, Proterozoic intrusion dated at 1.85 Ga age (Hecht et al. 2010; Ames, Farrow 2007). The mineralization of platinum group elements (PGE) occurs predominantly in the margin of the ore body, which is abundant in breccias with various sulfide minerals (Kjarsgaard, Ames 2010). The Broken Hammer PGE deposit is located in the northern part of this intrusion.

For the purpose of this study selected sulfide samples were analyzed with optical and electron microscopy (Hitachi SU6600 with EDS attachment) in the Electron and Optical Microscopy Laboratory Maria Curie-Skłodowska University in Lublin (total number of analyses was 488), whereas the δ^{34} S of sulfides and the δ^{13} C and δ^{18} O values of carbonates were determined in the Mass Spectrometry Laboratory, Maria Curie-Skłodowska University in Lublin.

The rocks studied belong to metamorphosed diabases, sediments and granitoides, which were fissured and cemented by Fe, Cu, Ni sulfides. The microscopic study of thin sections has indicated that the mineral paragenesis is characteristic for an epidote-amphibole facies. The next alteration stage of these rocks was their cementation by sulfides at a temperature of about of 400°C (Péntek et al. 2008; Dare et al. 2012). The most commonly distributed sulfides are pyrite, chalcopyrite and pentlandite. In these sulfides such minerals as cubanite (CuFe₂S₃), magnetite (Fe₃O₄), cassiterite (SnO₂) with PGE mineralization occur. The subsequent generation is iron oxides and hydroxides (hematite, goethite) with carbonates, being low-temperature (100-200°C) hydrothermal products (Péntek et al. 2008).

The minerals listed above are Pt and Pd tellurides and bismuthides. Of the tellurides, sperrylite grains several centimeters across occur. These minerals are associated with Ag tellurides, galena and sphalerite.

The sulfur isotope composition of sulfides studied shows positive $\delta^{34}S$ values varying from 3.41 to 10.26‰ in chalcopyrite, and from 2.82 to 3.00‰ in pyrite and pentlandite. Majority of these sulfides contain sulfur with slightly positive $\delta^{34}S$ values, which is typical for basic primordial igneous rocks (Thode et al. 1962; Schwarcz 1973; Hecht et al. 2010; Darling et al. 2010), whereas those with more positive delta values (ca. 10‰), are characteristic for igneous and sedimentary rocks. This suggests mixing of sulfur from these two sources.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Distribution and bioavailability of Ni and Cr in serpentine soils from Lower Silesia – preliminary results

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Weathering of ultrabasic rocks naturally enriched in some trace elements, such as nickel and chromium, leads to the formation of a specific type of soils called "serpentine soils". These soils have distinctive properties caused primarily by specific chemical composition of parent rocks.

Outcrops of ultramafic rocks and associated serpentine soils in Poland are located only in the Lower Silesia region (south-western Poland). Ultrabasic rocks occur as large massifs in the Fore-Sudetic Block and as small bodies in the Sudetes.

For the present study we have analysed ultrabasic rocks and soils from three localities: (1) Szklary massif situated on the Fore-Sudetic Block, (2) Popiel Hill and (3) Śnieżnik Mt., both located in the Sudetes. The parent rocks exhibit large diversity. The ultrabasic rock from the Szklary Massif was classified as a partially serpentinized peridotite, the parent rock from Popiel Hill was a hornblende peridotite, whereas the ultrabasite from Śnieżnik Mt. corresponded to a serpentinite. In order to eliminate factors other than the ultramafic parent rock type, the serpentine soils examined were sampled at a similar position in a toposequence and they were all classified as Leptosols (WRBSR-FAO classification). The concentration of Ni in the studied ultrabasic rocks ranges from 1300 ppm to 1800 ppm and is lower for serpentinites than for peridotites. The concentration of Cr varies from 1900 ppm in seprentinites to 4200 ppm in peridotites. The Ni and Cr concentrations in soils decrease upwards in analysed pedons and are in the range of 72 to 2350 ppm for Ni and 160 to 3500 ppm for Cr.

The bioavailability of Ni and Cr in the soils examined was estimated using the EDTA extraction method (Quevauviller 1998). Ni is distincly more bioavailable than Cr in the studied serpentine soils. Proportions of Ni present in a bioavailable fraction range from 5% in endopedons (B and C horizons) to 46% in organic horizons. Bioavailability of Cr reaches a maximum of 7% in organic horizons whereas in endopedons it does not exceed 1%.

Our preliminary results show that distribution and bioavailability of Ni and Cr in serpentine soils are different from one site to another. It may indicate that various types of ultrabasic parent rocks affect the behavior of these elements. However, it should be noted that many other factors such as soil pH, type of vegetation, local climatic conditions etc. may also infuence distribution and mobility of metallic elements in soils.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Historical sandstone epitaphs from Lower Silesia (SW Poland): preliminary results of petrographic investigations

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Sandstone epitaphs, dated mostly from the $16^{th}-18^{th}$ centuries, are found in many localities in the Lower Silesia (SW Poland). They usually cover both outer and inner walls of churches. The sandstones used in most of these epitaphs come evidently from local, Lower Silesian deposits. In many places, especially in external exposition, the stones show evidence of deterioration and need proper conservation treatment. Conservation measures would be facilitated after careful petrographic investigations allowing determination of petrographic features and provenance of the stone material, and its degree of weathering.

Eighteen epitaphs from the external walls of five historical buildings in Legnica and Środa Śląska were selected as representative objects for detailed petrographic studies. The samples were collected with respect to their geographic exposition that controls the influence of weather conditions and, consequently, the intensity of deterioration processes.

A set of representative samples of sandstones was studied using standard petrographic microscopy, cathodoluminescence (CL, "cold" cathode), X-ray diffraction (XRD), scanning electron microscopy and electron microprobe (SEM and EDS), and thermal analysis (DTA, TG).

Microscopic examination allows highlighting the derivation of sandstone materials, and in particular distinguishing between the Upper Cretaceous sandstones coming from the two regions of Bolesławiec and Kłodzko. The most frequent pale yellowish-gray sandstones are fine- to mediun-grained arenites, composed of quartz, with a very small admixture of Kfeldspar and plagioclase, muscovite, and a small but variable amount of siliceous-clayey or siliceous-clayey-ferrigenous matrix.

A typical sandstone, represented by sample 9 from the corner of an epitaph, is a quartz arenite (grain size up to 0.4 mm) with a rather scarce siliceous-clayey matrix. A very small admixture of feldspars and the textural maturity suggest that the stone represents the Upper Cretaceous sandstones of the North-Sudetic Basin. The sample is covered by a weathering crust up to a few mm thick, in which the original matrix phases have been in a larger part removed, and secondary components deposited (including gypsum and soot-like substance).

Some of the epitaphs (e.g. sample 1) are covered by transparent amorphous substance, a kind of resin, up to 1-2 mm thick (Fig. 1). The presence of resin was confirmed by thermal analysis. The resin was used to impregnate the sandstone epitaph in a conservation process, probably during the 19th or 20th century. The use of resins to conserve sandstone historic monuments is a controversial issue (Kopecka et al. 2006; Roselli, Rosati 1992), including determination of the impact of resins on the behavior of mineral components and sandstone structure, and assessment of the preservation state of the stone. Thus, detailed

observations should be helpful in selection of appropriate preventive and conservatory actions. The sandstone epitaphs studied provide an opportunity to investigate the condition of the stone materials that have already been conserved using resins. These problems, in general, have yet been insufficiently recognized and further detailed studies are necessary.



Fig. 1. Results of mineralogical investigation of sample 1. Notice the resin covering the external surface of sample in thin section (macrophotograph and BSE image). Thermal analysis shows the presence of gypsum, clay minerals, Fe hydroxides and organic matter. The clay minerals are also evident from EDS spectrum.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Kaolinite-based sorbent of hexavalent chromium: sorption mechanism, pH effect and desorption behaviour

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Highly water soluble chromates are very toxic and carcinogenic, which makes them undesirable in the environment. Natural or synthetic zeolites and smectites modified with quaternary ammonium salts e.g. hexadecyltrimethylammonium bromide are commonly tested as sorbents of Cr(VI) due to their high surface area (Mozgawa et al. 2011). Minerals of kaolin group which exhibit a 1:1 layer structure possess relatively low specific surface area, however, modification of their interlayer octahedral surface through grafting processes is possible in contrast to e.g. smectites. The covalent bonding of selected organic molecules to inner surface OH⁻ groups leads to formation of new mineral-based nanomaterials with interesting properties. Recently, Letaief et al. (2008) showed that quaternization of grafted kaolinite induced a positive charge in the interlayer which was accessible for CN⁻ ions. In our research Polish kaolinites treated according to this procedure were tested for Cr(VI) immobilization. The study concentrates on the mechanism and pH effect on the Cr(VI) sorption. Additionally, the strength of Cr(VI) binding was tested using desorption procedure.

Kaolin group minerals: M - Maria III kaolinite, J - Jaroszów kaolinite, and H - Dunino halloysite differing in structural and textural features were used as starting materials (Matusik et al. 2011). The main reaction which led to positive charge generation in the mineral interlayer space was a methylation of the mineral previously grafted with triethanolamine (TEA) which gave MM, JM, and HM sorbents. For the methylation iodomethane (CH₃I) was chosen. The samples were characterized using XRD, FTIR, CHNS elemental analysis and ¹³C CP-MAS NMR. The Cr(VI) sorption was carried out in the concentration range 0.02-20.0 mM Cr(VI)/L and pH range 3-11 at a room temperature with sorbent/solution ratio equal to 20 g/L. Desorption experiments were performed according to the procedure described by James et al. (1995). This involved 3 steps: (i) water washing (pH 6, 1 h), (ii) washing with phosphate buffer (pH 7, 2 h), and finally (iii) with carbonate-hydroxide solution (pH 12, 2 h). The Cr(VI) concentration in all experiments was measured spectrophotometrically using the diphenylcarbazide method.

The XRD patterns of MM, JM, and HM indicated the presence of grafted species as the d_{001} value increased from ~7.2 Å to 11.2 Å, 10.9 Å, and 10.8 Å, respectively. Additionally, the C-H stretching bands: 2982, 2896, and 2828 cm⁻¹ as well as C-H bending band: ~1480 cm⁻¹ were noticed in the IR spectra. The bands attributed to the inner surface OH⁻ groups were significantly altered due to interactions in the interlayer. The ¹³C CP-MAS NMR technique confirmed that methylation reaction took place in the interlayer as the signals 62.3 and 59.3 ppm connected to grafted TEA molecules were replaced by signals at 65.2,

57.1, and 51.2 ppm attributed to the formation of an ammonium salt. Thus, the generated charge was located on the central nitrogen and was neutralized with iodide ions. The sorption of the Cr(VI) on the raw kaolinites did not exceed ~12 mM/kg even for the H sample which had the highest specific surface area (50.6 m^2/g). In turn, the sorption observed for the modified minerals increased significantly. For the MM sample it reached ~200 mM/kg (pH_{eq} 5.20-5.40) and ~130 mM/kg (pH_{eq} 6.80-7.90). For the JM sample: ~130 mM/kg (pH_{eq} = ~5.50) and ~63 mM/kg (pH_{eq} = 6.80-8.00), and for the HM sample: ~140 mM/kg (pH_{eq} = 4.50), ~100 mM/kg (pH_{eq} = 4.70), and ~70 mM/kg (pH_{eq} = 6.50-6.90). The sorption increase was observed along with an increasing content of positive nitrogen i.e. MM > JM > HM. It was comparable to that observed for modified smectites and zeolites (Mozgawa et al. 2011). The sorption decrease with a pH increase can be explained by a competition of Cr(VI) with OH⁻ ions. The sorption took place almost exclusively in the interlayer space where the Cr(VI) was ion-exchanged with iodide ions which were found in the solution in molar amount equal to removed Cr(VI) ions. This proved that at a low pH the Cr(VI) was sorbed as HCrO₄ which was the dominant ionic form (\sim 75%). The ratio of released I to removed Cr(VI) at the high pH: 1.4-1.7 indicated sorption of both CrO_4^{2-} and $HCrO_4$. The desorption procedure showed that, regardless of the sorbent, after 3 extraction steps the desorbed Cr(VI) did not exceed 30% of the total sorbed Cr(VI) confirming the presence of strong bonds between Cr(VI) and kaolinites. Moreover, possibly the immobilization of Cr(VI) in the interlayer of the minerals additionally hampered the release of chromium which is desirable from the environmental remediation point of view.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Rare earth elements distribution in spring waters of Świętokrzyski National Park, Poland

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This work presents the results of chemical analyses of rare earth elements (REE), Y and Sc in spring waters collected in Świętokrzyski National Park (ŚNP) during 2011 and 2012. REE form a geochemical association due to their high chemical affinity. They occur in minerals resistant to weathering. Processes occurring at the water-rock system result in a partial immobilization of ionic forms of REE found in the waters. For this reason, they can be used as indicators of geogenic pollution for surface and groundwater (Ryu et al. 2007).

ŚNP is located in the northeastern part of the Kielce county and the northern part of the Świętokrzyski province (south-central Poland). The Łysogóry Range is the backbone of ŚNP. To the north it is separated by the Wilków Valley and the Dębno Valley from the Klonów Range and the Pokrzywiański Range (Fig. 1). A diabase intrusion presumably of Permian age occurs near springs S-2 and S-8 (Czarnocki 1956). In addition, a Holocene travertine crops out near spring S-7 (Gruszczyński et al. 2004). Most of the study area is blanketed by fluvioglacial sands and silts, clays, tills, but especially by loesses that form ravines reaching a few meters deep. The only exception is the Łysogóry Range, which is mostly covered by wooded waste mantle (Pleistocene rockfields with a few paleosoil horizons) reaching a dozen or so meters in thickness. The soil taxonomy reflects the geologic setting of the study area. At higher elevations rankers, cambisols, podsols, arenosols, luvisols and gleysols developed on quartzites and sandstones are prevalent. In contrast, acid gley cambisols, chernozems and gleysols occur in the central valleys.

The study encompassed nine springs in the area of Świętokrzyski National Park (Fig. 1). The springs analyzed are permanent and characterized, by maximum flow yield and low flow variability throughout the hydrological year. All water samples were filtered and stored in cleaned polyethylene sample test-tubes. Unstable parameters, such as temperature (T), pH and electrical conductivity (EC), were measured on site. REE were determined using ICP-MS technique (ELAN DRC II): Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y, Yb at the Environmental Analysis Laboratory of the Institute of Chemistry, Jan Kochanowski University in Kielce.

Of all the elements in the tested waters, Sc (G.M. 2.235 ppb) and Y (G.M. 0.152 ppb) predominated. The highest concentrations were recorded in spring S-1 (Krajno Zagórze), and the lowest in spring S-2 (St. Francis spring). These two springs are located approx. 1 km from one another. The results for two years were normalized using Post-Archean Australian Shales (PAAS) and North American Shale Composite (NASC). The normalized curves are shown in Fig 2. All spring waters exhibited significant positive anomalies of Eu and Sm as well as subordinate positive anomalies of Tm, Lu and Tb. For springs S-1, S-3,

S-6, a slight enrichment of heavy REE was observed. A similar distribution of REE was noted for sandstone aquifers (Biddau et al. 2009; Herong et al. 2011).



Fig. 1. Springs localization in Świętokrzyski National Park



Fig. 2. Normalized REE patterns of SNP spring waters

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



REE concentrations in well and pond waters of the Podwiśniówka area (Holy Cross Mountains, south-central Poland)

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In most geologic reports lanthanoids or lanthanides are assigned to rare earth elements (REE). This element group includes La (Z=57) through Lu (Z=71). However, according to IUPAC (International Union of Pure and Applied Chemistry), Y (Z=39) and Sc (Z=21) are also ascribed to REE. Except for Ce (Ce³⁺, Ce⁴⁺) and Eu (Eu²⁺, Eu³⁺), REE occur in a trivalent state in surface environmental systems and their ionic radii decrease with an increase of atomic number, from 103 pm in La³⁺ to 86 pm in Lu³⁺ ("lanthanide contraction"). This chemical property is a basis for dividing REE into two main groups: (i) light REE (LREE) including La through Eu (or Gd) and heavy REE (HREE) from Gd (or Tb) through Lu, respectively. Some authors also discriminate the third group that partly overlaps LREE and HREE: medium REE (MREE) that comprises Sm through Ho.

The principal objective of this study was to assess a possible influence of acid mine drainage (AMD) pit pond located atop Podwiśniówka Mt. on the chemistry of farmer's well and pond waters in two villages: Masłów II and Marczakowe Doły (about 5 km north of Kielce). The scope of investigation encompassed determinations of physico-chemical parameters (pH, EC, T) and concentrations of REE, Fe^{2+} , Fe^{3+} and SO_4^{2-} in waters of 8 farmer's wells, 2 fish ponds and 1 acid pond. The water samples were collected in three series on the following days: September 13 of 2011, March 13 and June 29 of 2012. The REE determinations were done using the Perkin Elmer ICP-MS/MS ELAN DRC II instrument. The geologic multi-element reference materials applied for measuring element concentrations in the samples were: PPREE1 and SCREE1 (Verplanck et al. 2001).

The waters of Podwiśniówka and Marczakowe Doły acid ponds showed a distinctly lower pH and higher concentrations of REE compared to those in farmer's wells and fish ponds. The best example is the pH values (2.8) and REE concentrations (27.54–84.44 ppb) of the Podwiśniówka and Marczakowe Doły AMD ponds derived from measurements performed on water samples collected on June 29 of 2012. In contrast, the pH values of the waters of farmer's wells and fish ponds varied from 5.4 to 7.5, whereas REE concentrations from 0.26 to 5.62 ppb, respectively.

The results of REE concentrations were normalized to North American Shale Composite (NASC) (Haskin et al. 1968; Gromet et al. 1984). The waters of 8 farmer's wells and 2 fish ponds reveal a strongly positive Eu anomaly similar to that of rocks (Migaszewski, unpubl. data). The only exception is well W4 that additionally exhibits strongly positive anomalies of Ho through Lu (Fig. 1). However, as opposed to rocks, the well and pond waters show a negative Ce anomaly, which may indicate sequestration or

adsorption of this element on clay minerals or Fe-hydroxides during flow of groundwater. In contrast, the two AMD pond waters are highlighted by a distinct Gd anomaly (Fig. 1). Their similar REE profiles suggest that there is a hydraulic connection between these two ponds along an E–W fault zone. The lack of influence of the Podwiśniówka acid pit pond on the chemistry of the farmer's well and fish pond waters is, in turn, evidenced by diverse concentrations of Fe²⁺ (2.0 vs. <0.1 mg/L) and Fe³⁺ (3.6 vs. <0.2 mg/L) ions. The higher pH of the waters mentioned last is closely linked to calcite-bearing till and loess patches that occur at the foot of Podwiśniówka Mt.



Fig. 1. NASC-normalized profiles of REE concentrations in the waters of selected farmer's wells and ponds vs. Podwiśniówka (Pw) and Marczakowe Doły (MD) AMD ponds (samples collected on June 29, 2012)

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



LA-ICP-MS study of selected trace element distributions in pyrite from the Podwiśniówka quarry, Holy Cross Mts (south-central Poland)

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Pyrite (FeS₂) is the most common sulfide mineral in the Earth's crust which can be found in igneous, sedimentary, and metamorphic rocks. The wide occurrence of pyrite in different environment compartments and its role in generation of acid mine drainage cause a great interest in the study of this mineral. Its minor and trace element composition has been a subject of many studies since the 1950s, which are summarized in a review paper by Abraitis et al. (2004). The results of trace and minor element determinations in pyrite samples may be useful for the study of ore deposit origin (Zhao et al. 2011).

Pyrite usually contains a number of minor and trace elements (Ag, As, Au, Bi, Cd, Co, Cu, Hg, Mo, Ni, Pb, Pd, Ru, Sb, Se, Sb, Sn, Te, Tl and Zn), primarily as lattice substitutions (Abraitis et al. 2004). The most common stoichiometric substitutions for Fe²⁺ in pyrite are: As, Co, Ni, whereas replacement of S by As may be given as an example of nonstoichiometric substitution. Some authors have stressed that the results of analysis of bulk pyrite samples can be misleading due to the presence of microscopic inclusions of different mineral phases within the pyrite matrix (Craig, Vaughan 1996). This problem may be partially solved with an application of modern instrumental techniques, such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) with the use of matrix-matched standard reference materials for data quantification (Watling et al. 1995). Microanalysis is of special importance in analysis of microcrystalline pyrite samples.

Pyrite samples were collected in the Podwiśniówka abandoned upper Cambrian quartzite quarry where a pyrite zone crops out at the western wall. The microcrystalline pyrite is commonly covered with secondary Fe oxyhydroxysulfate efflorescences (translucent pale green) and goethite/secondary hematite accumulations (brown-red). In places, quartzite-quartz-pyrite breccias crop out. The crypto- to fine-grained As-pyrite is the only sulfide mineral in the study area (Migaszewski et al. 2008). The major objective of this study was determination of Co, Ni, Cu, Zn, As, Mo, Ag and Pb in pyrite samples by LA-ICP-MS and comparison of these results with our previous study conducted on bulk pyrite samples by the XRF method (Migaszewski et al. 2008).

Three samples of pyrite that occur in the form of cement in the quartz-quartzite breccias, were selected for determination of Co, Ni, Cu, Zn, As, Mo, Ag and Pb by LA-ICP-MS. Polished sections of size about 2×2 cm were prepared and subjected to microanalysis by quadrupole ICP-MS ELAN DRC II (Perkin-Elmer) equipped with a 266 nm CETAC laser unit. Argon was used as a carrier gas. A matrix-matched MASS-1 SRM (polymetal sulfide) from USGS and a NIST Glass 610 were used as reference materials for external calibration. The laser beam was fired with energy level 20% at 10 Hz repetition

rate and a spot diameter was 50 μ m. Sample surfaces were ablated with 200 shots at pulse energy of >9 mJ.

The results (Fig. 1) showed depletion of the Podwiśniówka pyrite in most trace and minor elements (except for Cu and As) compared with those in pyrite from different locations (Arbaitis et al. 2004). The samples revealed typical Cu concentrations (7 to 1169 ppm; mean of 100 ppm) and a heavy enrichment in As (1.4 to 8.7%; mean of 2.7%). The results confirmed the high heterogeneity of the trace element spatial distribution pattern in pyrite. Positive statistically significant correlations were found between the element pairs: Co-Ni (R^2 =0.78) and Cu-Ag (R^2 =0.62). The element concentrations obtained from the LA-ICP-MS study shows 2-10 times higher values (except for Mo) than those derived from the bulk pyrite samples with XRF analysis (Migaszewski et al. 2008).



Fig. 1. Geometric mean values and concentration ranges of minor and trace elements in pyrite from Podwiśniówka and typical element concentrations in pyrite from different locations (ppm, in a logarithmic scale; data compiled by Arbaitis et al. 2004).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Heavy metal pollution of Indian sediment

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Heavy metals are one of the major serious pollutants in our natural environment due to their toxicity, persistence and bioaccumulation problems (Tam, Wong 2000). Toxic heavy metals entering the ecosystem may lead to bio-accumulation and bio-magnifications (Zabetoglou et al. 2002).

Aquatic environment in India is highly contaminated with pollutants such as heavy metals and pesticides due to large anthropogenic activities (Sarkar et al. 1997; Saha et al. 2001; Bhattacharya et al. 2003). In the present work, the concentration and sources of the heavy metals (i.e. Ti, V, Cr, Mn, Ni, Cu, Zn, Pb and As) in 18 pond sediments of three industrial cities, i.e. Raipur, Bhilai and Korba (21° 13' 12" N, 82° 40' 48" E) of central India, are described. Their correlation with the black carbon (BC), organic carbon (OC) and carbonate carbon (CC) are discussed.

The sediments were collected in the summer of 2008 by using the established methods. The samples were dried, crushed and particles of <0.1mm in diameter were sieved out. The TXRF and thermal methods were used for the characterization of metals and carbons, respectively.

The sediments are slightly alkaline (pH = 7.8 ± 0.1) in nature. The concentration of the BC and Fe ranged from 4.87 to 9.43 and from 0.97 to 11.75% with mean values of 8.05 ± 0.60 and $5.34\pm1.23\%$, respectively. The concentrations of OC, CC, Ti, V, Cr, Mn, Ni, Cu, Zn, Pb and As were as follows: 70-180, 50-150, 2714-8121, 45-175, 100-392, 127-2595, 31-77, 32-89, 36-626, 7-32 and 7-150 mg/kg with mean values of 134 ± 14 , 103 ± 14 , 4459 ± 577 , 89 ± 15 , 168 ± 36 , 1095 ± 348 , 49 ± 6 , 55 ± 8 , 135 ± 61 , 22 ± 3 and 44 ± 7 mg/kg, respectively. The concentrations of BC, CC, Ti, Mn, Fe and Pb decreased with depth whereas the concentrations of CC, V, Ni, and Cu and As increased with depth.

Variations, correlation, sources, enrichment and toxicity of the determined metals are discussed.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Swiny Castle (Sudetes, SW Poland): a natural laboratory to study lichenological-lithological interrelationships

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The picturesque ruins of the Świny Castle near Bolków (Kaczawa Mountains, SW Poland) are the oldest historical site within the *Piast Castles Route* in Lower Silesia (the castle was mentioned first in 1108, reconstructed in 15th and 17th century). This large fortress, with a regular rectangle base and surrounded by high stony walls, was constructed on the top of a hill that naturally supported its defence power. Our reconnaissance study has shown that the castle is a unique "natural laboratory" to investigate very distinct lichenological-lithological interrelationships. The preliminary investigations comprised detailed field observations (including description of a variety of lichens that grow selectively on different types of stones in the substrate), sampling for petrographic and lichenological laboratory research, and photographic documentation. The optical microscopy and electron microprobe techniques were applied to define petrographic and geochemical characteristics of the rocks – a substrate of lichen species. The lichen species were identified microscopically based on the procedures by Nowak and Tobolewski (1975), Purvis et al. (1992) and Wirth (1995); additionally, thin-layer chromatography (TLC) was applied.

The Świny Castle, including the massive walls, was built of several varieties of rocks. The building complex is founded on sedimentary breccias of Early Permian age that form the castle hill. The breccias are locally exposed, underlying the basement of the main building, and in places occur as scarce additions to the stone material used for constructing the walls. The strongly dominating (nearly exclusive) rock type in the whole construction is Lower Permian rhyolite, with only a small admixture of Paleozoic greenstones, phyllites, Upper Cretaceous sandstones, Miocene basalts and subordinate, but characteristic glacial erratics (granite, quartzite). The stony elements in the walls are bound with lime mortar. The portals, window frames and other decorative elements are made of Upper Cretaceous sandstones. The building stones used in the castle come from nearby sources: the dominant rhyolites and epimetamorphic rocks (Kaczawa greenstones and phyllites) are of local derivation in the closest proximity of the site (Teisseyre 1977), Miocene basalts – most likely from quarries around Jawor or Strzegom (about 12-18 km NE of Świny), and Upper Cretaceous sandstones – either from the Złotoryja-Bolesławiec (20-40 km) or Kłodzko areas (about 60 km of Świny).

The variegated stone material, comprising rocks of various chemical and textural features, together with the mortar, form a substrate on which numerous lichen species intensely grow. It is evident that the lichen species are strongly related to the type of

stone/mortar and may depend also on other factors, such as exposition to climatic factors (sunshine, rain, wind); another general factor is atmospheric pollution. Considering these interrelationships, a few well defined parts of the castle have been selected for more detailed studies. The most spectacular site is the wall of the view terrace on the NW side of the castle.

Preliminary lichenological inspection of the stone walls at the Swiny Castle has proved the presence of more than 20 lichen species, representing 13 genera. The species can be grouped into three categories: obligate calciphiles (basophilous), facultative calciphiles (subneutral-basophilous) and non-calciphilous taxa (neutrophilo-acidophilous), according to Wirth's classification (1995).

Relatively scarce is the group of the obligate calciphilous species, which is bound mainly to the lime mortar, but locally also found on basalts and rhyolites that contain a significant amount of calcium. The presence of these lichens on various types of rocks seems to be facilitated by migration of Ca washed out from the mortar (c.f. Pietrzykowska, Kosowska 2010).

The most widespread is the group of subneutral-basophilous lichens that occur practically on all types of stone materials encompassing over 50% of all taxons.

Considerable differences have been observed between the lichen biota of crystalline rocks (rhyolites, basalts) and stone materials richer in calcium carbonate (including mortar and sedimentary rocks). The biota of the former rocks is much richer and diversified.

The preliminary results of our study performed so far on selected parts of the stony Świny Castle indicated a strong relationship between the spectrum of lichen species and the kind of substrate materials or their chemical features and physical parameters. However, the lichens strongly influence the stone and mortar substrate, accelerating their deterioration. Our interdisciplinary project is in progress and it aims at better understanding of mutual interrelationships between the lichens and the stone substrate as well as deterioration processes that affect various rocks used as building materials.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Petrography, deterioration and lichenology of sandstones from the Pomorski bridge in Wrocław and old Płakowice quarry (a comparative study)

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According to the historical reports (Geissler, Frisch 1926), the sandstone used for the construction of the Pomorski bridge in Wrocław was delivered from the old quarry of Płakowice near Lwówek Śląski. The bridge (Werderbrücke) was erected in 1904 by Zeidler & Wimmel, a company which since 1776 had owned most of the quarries around Lwówek Śląski, from which the famous Upper Cretaceous sandstones were supplied for the construction and decoration of many prominent buildings and monuments in Germany and Poland. Based on this information, comparative studies on petrography and deterioration processes of sandstones of the Pomorski bridge and those in the abandoned Płakowice quarry have been carried out. A specific additional goal was to study lichens growing on the sandstones of the bridge and in their source locality.

The petrographic investigations, including optical microscopy, electron microprobe (EMPA, EDS) and X-ray diffraction (XRD) helped to identify the original stone elements in the bridge, which display petrographic features corresponding to the sandstones from Płakowice. Subsequently, deterioration phenomena were described and compared with sandstones in two environments: on the bridge in the large city centre, and in the old quarry located far from a direct influence of municipal environmental conditions. Weathering products were identified and compared for both localities. Finally, samples with lichens growing on sandstones at both sites were collected and the species defined according to Nowak and Tobolewski (1975), Purvis et al. (1992) and Wirth (1995). For the genus *Lepraria*, additionally, thin layer chromatography (TLC) was applied.

The comparative observations showed considerable petrographic similarities of the samples collected from the bridge and from the quarry. The rocks are yellowish-white quartz sandstones (arenites) of variable grain size. The grain framework is formed mainly of mono- and polycrystalline quartz, with a very subordinate amount of feldspars and lithic components. The grains are moderately rounded and rather well sorted. The interstitial space is filled with a siliceous-clayey matrix.

The external weathering zones on the surface of sandstone specimens showed significant differences between the samples from the bridge and those from the quarry. A frequent phenomenon in the samples from the bridge is relatively thick black crusts containing abundant gypsum, calcium phosphates and organic components. Black crusts in the sandstone samples from the quarry are very scarce and gypsum is also only sporadically discernible. Typical phenomena observed in the quarry sandstones are granular

disintegration and soil-forming processes. These differences obviously reflect the influence of the polluted atmosphere in the large city environment.

The environmental differences of the two sites studied are also evident from lichenological comparative investigations. The lichens on the sandstones of the Pomorski bridge are predominantly represented by widespread crustose species, which are resistant to pollution. In the Płakowice quarry, a large proportion constitutes foliose lichens, often with large thallus. These species are very sensitive to pollution, as the gas exchange in lichens occurs through the entire surface of thallus, which is very large in foliose and fruticose lichens (Fałtynowicz 1995).

Our joint research is in progress and aims at better recognition of the influence of polluted atmosphere in a large city on stone deterioration processes and development of lichen biota.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Detection of multiple organic matter sources in PM10 aerosol particles from Wrocław city using carbon isotope signature and molecular study

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PM10 samples were collected using the hi-flow sampler Stamplex Air Division with Whatmann quartz filter (0.06237 m^2), and a constant air flow of 1.13 m^3 /min. The analyzed samples were collected following a seasonal sampling strategy in 2007, so that they would represent air pollution from all months of the year. The main identified organic compounds were: *n*-alkanes, isoprenoids, polycyclic aromatic hydrocarbons (PAHs), aromatic oxygen compounds, fatty acids and anhydrosugars. Distribution of *n*-alkanes with a predominance of long-chain even-carbon homologues is characteristic for organic matter (OM) of terrestrial origin (including coal). PAH concentrations differ significantly in summer ($13.4-23.3 \text{ ng/m}^3$) and winter ($215.0 - 296.0 \text{ ng/m}^3$) months, but in both cases four-, five- and sixring PAHs of pyrolytic origin predominate. The major organic compound from the investigated extracts is levoglucosan. This commonly described anhydrosugar (e.g. Simoneit et al. 1999; Simoneit 2002) is a thermal degradation product of cellulose and together with other anhydrosugars (like mannosan and galactosan) is regarded as an excellent tracer of biomass burning. Levoglucosan concentrations ranged from 150 ng/m³ in summer months to 3000 ng/m³ in winter.

On the other hand, the δ^{13} C value of total carbon varied from -27.6 to -25.3‰, confirming the previous conclusions that the major source of OM from Wrocław city during winter is derived from coal combustion (Górka et al. 2012). However, total extracts of PM10 are relatively depleted in ¹³C with the δ^{13} C values in the range of -41.8 to -30.7‰. Moreover, aliphatic and aromatic organic fractions of extracts are characterized by the δ^{13} C values varying from -36.6 to -19.4‰ and from -35.4 to -26.8‰, respectively. We have not observed any statistically significant relationships between carbon isotopic composition of total carbon of PM10 and extracted fractions from filter (total extracts, *n*-alkanes and PAHs). Hence, we conclude that the isotopic signal reported in the total carbon is mainly undissolved soot originating from coal combustion (heating season) and diesel/gasoline combustion or C3 fragments (vegetative season) whereas compounds present in extracts are a mixture of biomass and coals burning with quantitative preponderance of the first listed source.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



The formation of ZnS and barite pseudomorphs after Ca oxalate crystals in organic rich soil

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Although scarcely described in geological records, Ca oxalates are widespread in biological systems. Calcium oxalate is a common constituent of many different organs and tissues in a wide range of plant taxa. The accumulated amount varies from species to species and may constitute 80% of dry weight of some plants (Horner, Wagner 1995). After the death of a plant, Ca oxalate becomes a component of soil litter taking part in soil processes, i.e. weathering of rocks, solubilization and transport of metals.

The principal objective of this study was to investigate the interactions between biogenic Ca oxalate and heavy metals in organic-rich soil using scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS). The research was carried out in the Bagno Bruch mire (50° 31' N, 19° 2' E) located in a forest complex on the northern limit of the industrial part of the Upper Silesia and 9 km east (downwind) of a zinc-lead smelter (Huta Cynku Miasteczko Śląskie) that has been in operation since 1968. The concentrations of Zn, Pb and Cd in the mire reached 494, 238 and 15.9 mg/kg, respectively (Smieja-Król et al. 2010).

At a depth of 16-18 cm below mire surface, fragments of Scots pine (*Pinus sylvestris* L.) bark were identified among other plant debris. Euhedral crystals of ZnS and BaSO₄ occurred inside the bark cells. Trace amounts of Cd were often associated with a ZnS phase. The crystal form was virtually identical with that of calcium oxalate monohydrate (whewellite CaC_2O_4 ·H₂O), which occurs in large amounts in the bark collected directly from a living Scots pine tree growing on the mire surface.

This finding indicates that decomposition of oxalate facilitate precipitation of slightly soluble Zn, Cd and Ba phases. It also gives an insight into mechanisms of secondary mineral formation in soils.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



New molecular indicator of fossil conifer wood degradation by wood-decay fungi

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Perylene is a five-ring aromatic hydrocarbon ubiquitous in immature to early mature marine and terrestrial sediments and sedimentary rocks as well as peats, lignites and some crude oils. Grice et al. (2009) have recently described perylene occurrence in Holocene sediments rich in fungus spores and their isotopic relationships which indicate that a major source of this compound is associated with wood-degrading fungi. Here, we present the occurrence of perylene in Middle Jurassic fossil wood and Miocene xylites of Poland and its negative correlation with unsubstituted PAHs as well as cellulose content. Both Middle Jurassic and Miocene wood remains are characterized by very low thermal maturity (c.a. 0.2 to 0.3% R_r), excellent preservation of biomarkers and biomolecules and in case of Middle Jurassic fossil wood samples by generally good preservation of anatomical structure caused by early diagenetic mineralization (Marynowski et al. 2007a,b). Based on the macroscopic observations and a lack of oxidation-indicating minerals (Marynowski et al. 2011), only unweathered wood pieces were selected.

The results of analysis of 31 taxonomically defined Middle Jurassic fossil wood fragments indicated a negative correlation between concentrations of perylene and typically identified conifer biomarkers, including: cadalene, dehydroabietane, simonellite and retene. In addition, a good correlation ($R^2 = 0.7$) between the ratio of pervlene to terrestrial biomarkers listed above and (phenanthrene + fluoranthene + pyrene) to these terrestrial biomarkers was shown. This implies that high concentrations of perylene in fossil wood point up to its extensive degradation by fungi during decay (mortification), transportation and early diagenesis. We defined the fossil conifer wood degradation index: WDI = perylene/(perylene+cadalene+retene+simonellite+dehydroabietane) and received a wide range of values, from 0.1 for less degraded wood to up to 0.9 for highly degraded wood. Moreover, the relationship among the relative proportions of perylene and cellulose contents of fossil Miocene wood samples was observed ($R^2 = 0.8$). As known from the literature, fungi preferentially remove cellulose and hemicellulose from the wood, leaving an amorphous residue that is composed mostly of lignin (Enoki et al. 1997). The higher concentration of perylene in cellulose-poor xylites indicates more intensive decay of these wood fragments and confirms the fungal origin of perylene (see also Bechtel et al. 2002, 2007).
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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Investigation of rare earth elements content in ground waters of Poland by using ICP-MS technique

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Investigation of rare earth elements (REE) content in ground water samples carried out in the Central Chemical Laboratory PGI-NRI has aimed at preparation of a method which enables quantitative determination of these elements in natural waters. As ground waters contain low concentrations of REE, it is necessary to apply sensitive measurement techniques.

During this study inductively coupled plasma mass spectrometry ICP-MS (Elan DRC II, Perkin Elmer) was used. This technique is char **determination of element** acterized by low quantification limits, possibility of simultaneous analysis of a wide range of elements (about 70 including REE), short time of measurements and direct analysis of natural water samples in which total dissolved solids (TDS) do not exceed 0.05%.

The analytical method for measurement of selected isotopes of the rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and isotopes causing spectral interferences was developed. The detection limits and quantification limits were assigned and the influence of spectral interferences on the results was evaluated. Moreover, the essential mathematical corrections were established and applied. Because of the lack of the suitable certified reference materials (CRM), the standard addition method was used for checking the correctness of the results obtained.

The present work presents preliminary results of REE determinations in the selected ground water samples. About 250 water samples derived from the wells located in different regions of Poland were analyzed. The selected water samples were used first by the Polish Hydrogeological Survey within the project "Monitoring of ground waters of Poland".

Processing and interpretation of the results give a unique possibility to find relationships between geochemical composition of ground waters and bedrock and allow us to evaluate hydrogeological processes that lead to remobilization, migration and deposition of REE. The analysis of the results obtained from measurements of a significant number of samples, which is planned in the next step of this study, might be used for establishment of background concentrations of REE in the ground waters of Poland.

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Analysis of the garnet samples as the example of application of laser ablation inductively coupled plasma mass spectrometry technique

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The objective of this study was to evaluate the possibility of application of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for direct determinations of the element contents in single mineral grains formed *in situ*. The LA-ICP-MS technique has found a very interesting application in geology, especially in the study of trace element variability (spatial distribution within individual minerals) as well as in determinations of major elements in mineral phases. The main advantages of the LA-ICP-MS technique are:

- direct analysis of solid samples through elimination of wet digestion,
- performing the measurements on a very small sample surface (single point resolution is in a wide range of 10 to 250 µm),
- simultaneous determination of major and trace elements directly within selected part of mineral,
- determination of element isotope ratio,
- low quantification limits of elements (in a range of a few μ g/kg),

- wide linear range of determination (from X μ g/kg to X g/kg).

In this work the LA-ICP-MS technique was applied for analysis of garnet phenocrysts. Garnets are particularly useful for petrogenetic studies because they record the pressure and thermal (p-T) evolution of host rocks. The chemical composition of garnet formation based on chemical equilibrium between other mineral phases (biotite, pyroxene) may reflect dominant temperature conditions of metamorphism in host rocks. Similarly, measuring the chemical composition of individual grains of *in situ* garnet and their chemical gradient of selected trace elements provide information which may be useful for deciphering host rock evaluation. One of the most efficient parameters applied to express the pressure-related variations is rare earth elements (REE) distribution in garnets and the Gd/Dy ratio (P = 3.6 + 5.6 Gd/Dy) of barometric calibration (Bea et al. 1997).

This kind of numerical relationship between the pressure and average Gd/Dy ratio in natural *in situ* garnets derived from metapelitic rocks can be tested only by the LA-ICP-MS technique. The main purpose of this study was to apply the LA-ICP-MS technique for the determination of the concentrations and spatial distribution of selected REE in natural garnets.

The REE measurements were performed at the Central Chemical Laboratory of the Polish Geological Institute using the ablation module (LSX-500, UV Nd:YAG 266 nm, CETAC) connected with the quadruple mass spectrometer (Elan DRC II, Perkin Elmer SCIEX). During analysis different reference materials (SRM NIST 610, SRM NIST 612,

BIR-1, BCR-2, BHVO-2) were used for method calibration and verification of the results obtained. The quantification of the results was possible by using an internal standard and oxide scaling method (as a normalized method). In our investigation the uncorrected concentrations of major elements were converted to the uncorrected oxide concentrations and scaled to 100%, and then used for calculation of normalization factor.

The examined garnets derived from metapelites of the Precambrian basement (borehole Czyże) were predominatly almandine-pyrope-grossular solid solution with a minor admixture of spessartine components (Alm_{69-80} Prp₁₀₋₂₀ Grs₃₋₅ Sps₁₋₅). They revealed rather similar zoning profiles with increasing Fe/Mg ratios at the outermost rim. The core – rim variations showed a gradual increase of enrichment in MREE and HREE and Y during the crystal growth. The Dy and Gd contents in this garnet indicate a significant decompression during crystal growth from the core at the pressure of 9.7 kb (a large grain) and 6.4 kbar (typical core of medium grain) to the pressure of 5.2 and 4.9 kbar for the rims and small crystals. The results provide a significant evidence for the initial burial metamorphism of sedimentary protolith at a great depth and then under a retrograde condition. Therefore, the LA-ICP-MS technique can be used as a new approach for geobarometric studies of the Precambrian basement of NE Poland.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Remediation of soils contaminated with petroleum hydrocarbons: A case study, TBD S.A. Dębica

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Petroleum hydrocarbons make up a significant part of anthropogenic pollution of the environment. Contamination of the soil and water environments is especially dangerous due to toxicity of petroleum products, ease of spreading, long term degradation and a large scale of their occurrence.

The most common causes of soil and groundwater pollution in Poland are: road and rail accidents with cisterns for petroleum products, industrial pipeline accidents and also improper handling and maintenance of oil facilities (Namieśnik, Jaśkowski 1995). Petroleum products cause plugging of the pore spaces between soil particles which are usually occupied by air and water. This results in caking and physicochemical and biological changes in soil. A thin layer of petroleum hydrocarbons covers soil particle surfaces and are bound to the organic components of humus.

The effects of soil pollution by petroleum encompass:

- drastic changes in the chemical composition of soil organic matter,
- reduction of water content and decrease in exchange of air due to plugging of the soil pores leading to increasing demand for oxygen,
- disturbed ratio of organic carbon to nitrogen and phosphorus, which makes it inhabitable for organisms,
- disturbed properties of soil colloids, including ion exchange and pH value (mainly soil acidification).

Petroleum derived products spilt over the soil surface can penetrate to a great depth up to subterranean waters and pose a threat to fauna and flora of polluted areas. The toxicity of petroleum derived products results from their physical and chemical properties. Because of their physical parameters, thick hydrophobic oils block soil pores thus restricting the air supply to deeper soil horizons. The oils also impede, to a great extent, the supply of water to plant roots. Additionally, they glue the surfaces of leaves thus obstructing the passage of light, air and water. Consequently, plants die, which leads to a drop in vegetal productivity. On the other hand, chemical properties of hydrocarbons are responsible for their toxicity to higher organisms, including humans (Surygała, Śliwka 1999; Gawdzik, Gawdzik 2011).

The assessment of a potential environmental pollution can be made after carrying out thorough investigations that combine aspects of geology, microbiology and chemistry. Soil cleaning technologies are generally multi-stage. The most important action is to restrict the spreading of pollution and then to remove the contaminant from the surface of the affected area with mechanical methods.

The problem of soil and water pollution with petroleum products is perfectly illustrated by situation of TBD S.A. in Dębica. This company produces a wide range of paints, varnishes, enamels, primers, cements, plasters, paint thinners, auxiliary materials, and insulation systems for buildings. During many years of production, the environment has totally been polluted, which was confirmed by the Hydrogeotechnika laboratory in Kielce. Due to the complex groundwater conditions and complicated structure of the TBD S.A. in Dębica for on site remediation Selective Remediation Method SRM was selected.

The petroleum substance purification process of the places related to their storage and distribution in the TBD SA in Debica with the SRM method was done with 70 drilled and specially-equipped technological wells evenly spaced around the polluted area and coupled with a specialist underground-water treatment station and ground-air. A total of 21 existing monitoring and maintenance wells were planned for the purification systems designed. In each of the SRM wells the course of purification, including the reduction of pollutants, proceeded differently and was dependent on the settled mode of the change of applied technological processes as well as the initial concentration of pollutants and local migration. In order to intensify the purification process of the soil environment, the drain-depress-vent system multisystem was designed and performed.

The general purification process in the area of TBD SA in Dębica was conducted in three main phases:

- Phase I 24-hour continuous removal of the free products from the wells, in which their occurrence was confirmed. 24-hour continuous pumping of the water from the wells where the original concentration of the sum of hydrocarbons was above 250 mg/dm³ during the period assuring the achievement of the maximum concentration of 50 mg/dm³ in each of the wells.
 - Phase II 24-hour alternate (in a weekly cycle) pumping of the water from all of the wells with the simultaneous alternate air-venting (in a 24-hour cycle) all the wells, by the period assuring the achievement of the maximum hydrocarbon concentration of 10 mg/dm³ in each of the wells.
- Phase III 24-hour alternate (in 24-hour cycle) pumping of the water from the wells in which the concentration of the sum of hydrocarbons was higher than 1 mg/dm³ with the simultaneous alternate air-venting (in 12-hour cycle) of the remaining wells during the period up to 64 month after turning on the purification system or until the achievement of the required level of impurities.

The contaminated soil was successively removed from the excavation by implementing sequences of drainage strings and protective barriers. In order to keep the selection of soils, contamination was determined by measuring the total concentration of petroleum substances using photoionization detector PID *Mini Rae* 2000. The contaminated soil was transported and temporarily stored in a specified area with the bottom and sides lined with foil to avoid release of leachate to the groundwater. The stored soil was also covered with foil to protect against the precipitation. The excavation formed by the removal of contaminated soil was filled in the lower part with pure mineral material (e.g. sand) and rest with clean cohesive soil from a dump.

Environmental contamination with petroleum and petroleum products as gasoline, diesel, home heating oil, lubricants, waxes, diluent, resins and asphalts is one of the main current environmental problems. Most of these products are toxic to living organisms, some of which are carcinogenic even in small amounts (especially aromatic hydrocarbons) playing an important role in the etiology of cancer. Therefore awareness and prevention of environmental contamination with petroleum is of prime importance.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Carbon isotope analyses of PM10 dust in the vicinity of Bogatynia (SW Poland) as an indicator of anthropogenic impact

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This study aimed at determining the origin of atmospheric aerosols in the vicinity of the Turów lignite mine. An attempt was made to identify the source of pollution, i.e. from the increase in industrial pressure or from natural processes. Samples of the PM10 dust were collected at 10 sites located in the immediate vicinity of the Turów lignite mine within about 1km of the pit. Sampling was done twice at 24-hour intervals in each of the selected locations from 7th to 26th April of 2008 by means of a stationary automatic aspirator TRC Tecora Skypost PM. The instrumentation was adapted to the use of quartz filters QM-A Whatman with a diameter of 47 mm. The PM10 concentrations varied from 15.40 µg/dm³ (7th April, 2008) to 99.28 µg/dm³ (17th April, 2008) with an average of 48.92 µg/dm³. The δ^{13} C (OC) of PM10 values varied from -19.89‰ (11th/12nd April, 2008) to -28.56‰ (21st/22nd April, 2008), with an average of -23.65‰. The δ^{13} C (EC) of PM10 values was in the range of -24.13‰ (21st/22nd April, 2008) to -25.58‰ (16th April, 2008), with an average of -24.99‰. As it was expected, the δ^{13} C values measured in lignite from the pit, with a mean value of -25.76‰, may also be a potential source of PM10.

The carbon isotopic composition of organic and elemental carbon was analyzed to identify potential sources of PM10 dust in the vicinity of Bogatynia. The total carbon (TC) in aerosols can be considered as a mixture of two fractions: organic carbon (OC) and elemental carbon (EC), also known as soot or black carbon (BC). Both monitoring of the ambient PM10 dust and the carbon isotopic analyses were conducted during spring at ten points around the overcast mine. The spatial variation of carbon isotopic composition (distinguishing OC and EC), concentration of PM10 dust, and the air mass backward trajectories were analyzed. The results indicated the high concentration of PM10 in the study area. Carbon isotopic studies showed that the main sources of OC in PM10 are fragments of plants, as well as coal and wood combustion in the home furnaces, and largely the mine pit. Moreover, they indicated that volatile organic compounds are precursors for potential sources of organic carbon (OC). In contrast, the precursors for elemental carbon (EC) are road traffic and home furnaces. Maps of backward trajectories of air masses indicated that the dust was partly derived from the outside of the Polish borders.

Invited lectures

Dating of Minerals and Rocks XI

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Possible errors of Ar ages on young basalts: methods for their recognition and correction

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The first K-Ar age determinations on Plio/Pleistocene alkali basalts in the Carpathian basin gave mostly the correct geological age, but older and sometimes younger ages were measured too. Younger ones were due to secondary effects. Older ages were the result of Ar(ex), but this could be mostly corrected by using the isochron methods. In the Nógrád-Novohrad area ages measured for the neighbouring Slovak territory were similar (2.60-1.9 Ma). However, ages of 7.24-4.65 Ma have been obtained for whole rock samples and fractions of the Somoška (Somoskő) hill, and isochron ages have been also older (6.02-4.40 Ma). It has been demonstrated by a mathematical approach that even perfect isochron ages can be erroneous, if there is a linear relationship between the concentrations of K and Ar(ex) (Balogh et al. 1994). The question is: how to recognize this error and how to correct it? The answer is based upon the geochemical identity of Ar(atm) and Ar(ex). A correlation is likely between the Ar(ex) and K concentration, if this exist between the Ar(atm) and K concentrations, while this correlation is highly unlikely for samples with similar Ar(atm) contents. Fortunately, it has been possible to find 4 samples of this rock in which K concentration is different (Fig. 1) and the Ar(atm) is similar [(1.06-1.11)x10⁻⁶ ccSTP/g]. Very accurate and reliable isochron ages were measured on these samples (Fig. 1). It has been shown (Balogh et al. 2005) that this error is the same when the Ar-Ar method is applied.



Fig. 1. Samples from Somoška (Somoskő) in the isochron diagrams

18 Ar-Ar age determinations have been performed (Wijbrans et al. 2007) on alkali basalts from the Bakony-Balaton Highland Volcanic Field (BBHVF), central part of Transdanubia, Pannonian Basin. Ages obtained for the onset, termination and culmination of volcanism were in line with earlier K-Ar ages (Balogh et al. 1986), but serious age-difference has been obtained for the basanite plug of Hegyestű, where 5.97±0.41 Ma isochron age has been accepted for the real age of volcanism. In contrast, Ar-Ar ages were 7.78±0.07 Ma (isochron) and 7.94±0.03 Ma (plateau). Tracing the cause of this bias, a possible error has been recognized when leucite-bearing basalts are dated. New K-Ar dating in Debrecen confirmed the young ages, but results in Okayama agreed with the Ar-Ar data. However, only the laboratory in Debrecen was working with whole rock samples. The treatment with acids (Amsterdam: HF; Okayama: HCl) dissolved minerals with high K content, thus leucite appeared responsible for the biased ages. When in Debrecen baking temperature of the extraction line was reduced to 150°C prior to degassing, K-Ar ages became similar to the results of the other two laboratories. It remained to answer what have caused it: very low closure temperature of fine effective grain-size of leucite or a structural change of it fastened the low temperature release of Ar(rad)? A set of samples have been loaded in the extraction line and measured after stepwise rising of the baking temperature. In the Arrhenius diagram diffusion parameters did not fit a straight line, i.e. activation energy was



changing above 150°C (Fig. 2): the age decrease was caused by structural change (Balogh et al. 2010). Ages measured at <150°C baking temperature agreed with values obtained on samples treated with acids; at higher baking temperatures ages were gradually decreasing.

Fig. 2. ⁴⁰Ar(rad) release from a sample of Hegyestű after stepwise baking the extraction line

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Stable isotopes, mineralogy and absolute age dating of Miocene volcanics and alteration products in the Alpine-Carpathian-Pannonian area

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The Neogene evolution of the Alpine-Carpathian-Pannonian area was accompanied by frequent volcanic activity (Szabo et al. 1992; Balogh et al. 1994; Dobosi et al. 1995; Downes, Vaselli 1995; Downes et al. 1995; Ebner, Sachsenhofer 1995; Embey-Isztin, Dobosi 1995; Harangi et al. 1995a,b; Kaliciak, Zec 1995; Konecny et al. 1995; Lyashkevich 1995; Pécskay et al. 1995a,b; Seghedi et al. 1995; Vaselli et al. 1995; Moriya et al. 1996; Sachsenhofer 1996; Slapansky et al. 1999; Nemeth et al. 2001; Ebner et al. 2002; Seghedi et al. 2004; Handler et al. 2006; Pécskay et al. 2006; Bojar et al. 2008; Kralj 2011; Seghedi et al. 2011). Volcanism started during the Eggenburgian (~19.5 Ma) in the Pannonian Basin and in the West Carpathians. The youngest ages are 35 to 150 ka (Moriya et al. 1996) in the East Carpathians (Perşani and Harghita Mountains). According to the data, the Neogene to Quaternary time span of volcanic activity in the region covers over 19 Ma and can be classified as a calc-alkaline and an alkaline type.

Miocene to recent medium to high-K calc-alkaline volcanism. Parallel to the inner margins of the Alpine-Carpathian Mountains as well as in the Apuseni Mountains high-K calc-alkaline volcanic rocks and subordinate shoshonites have been found. Calc-alkaline volcanism in northern Hungary is intermediate between medium- to high-K calc-alkaline (Downes et al. 1995). The volcanism in the Styrian Basin is high-K to shoshonitic (Slapanski et al. 1999). This volcanism produced basaltic to rhyolitic lava flows, with a general W to E age trend. The volcanism started in the Styrian Basin (16.8 to 15.5 Ma) (Handler et al. 2006; Pécskay et al. 1995a,b; 2006) and the Danube Basin (16.5 to 15 Ma) (Kantor et al. 1987). The age of calc-alkaline volcanism is lowering to the east and southeast with the youngest ages found in the East Carpathians, i.e. Calimani-Harghita Mountains (10.6 to 0.15 Ma) (Peltz et al. 1986; Szakács et al. 1993; Moriya et al. 1995; Pécskay et al. 1995a,b; 2006).

Sarmatian to recent alkaline volcanism, dominated by alkali basalts. The age ranges from 11.5 to 0.1 Ma (Pécskay et al. 1995a,b; 2006). The oldest ages are again found in the western part of the Pannonian and the western marginal basins (11.5 to 10.5 Ma Styrian Basin and 12 to 10.5 Ma Danube Basin). The age of the alkaline volcanism in the Alpine-Carpathian-Pannonian region is generally younger than the calc-alkaline one and, in regions with calc-alkaline and alkaline volcanism, it post-dates the former after an interruption. Two age peaks can be roughly put in evidence for the alkaline volcanism, at 12 to 8 Ma and 4 to 0 Ma. There is not such an obvious trend in age development as for the calc-alkaline volcanism. Alkaline volcanism is scattered in isolated clusters over the western part of the

Carpathian-Pannonian region. Regionally, the alkaline volcanism is more frequently represented in the northern and western parts of the Pannonian Basin. The exceptions are small occurrences in the Banat, Muntii Apuseni and Calimani-Harghita Mountains, showing ages less than 2 Ma (Pécskay et al. 1995a,b; 2006). The alkaline volcanism in the region is represented by nepheline basanites, nephelinites, trachyandesite, trachybasalts, nepheline tephrites and hawaaite (Embey-Isztin, Dobosi 1995; Dobosi et al. 1995; Harangi et al. 1995a; Pécskay et al. 1995a,b; 2006; Harangi, Lenkey 2007) and they occur as lavaflows, scattered necks, cinder and tuff cones. Mantle-derived ultramafic xenoliths and megacrysts of amphiboles and pyroxenes are frequent in these tuffs and less common in lava flows of the alkaline volcanism (Kurat et al. 1991; Zanetti et al. 1995; Dobosi et al. 1998; Dobosi, Jenner 1999; Dobosi et al. 2003; Demeny et al. 2005). The most prominent occurrences are in the Styrian Basin and adjacent Burgenland and Slovenia (Scharbert et al. 1981; Kurat et al. 1991; Balogh et al. 1994; Coltori et al. 2007; Kralj 2011), the Banat and South Harghita Mountains (Downes et al. 1995), the Little Hungarian Plain (Falus et al. 2007), Nograd (Konecny et al. 1995; Dobosi, Jenner 1999; Demeny et al. 2005) and the Balaton-Bakony area (Embey-Isztin et al. 2001; Dobosi et al. 2003).

During the last years we have undertaken different isotopic analyses (hydrogen, oxygen, sulfur, strontium, K-Ar) combined with mineralogical studies of volcanics and alteration products from the Alpine-Carpathian-Panonnian region in order to elucidate aspects related to their genesis, alteration and age of formation. These studies covered an area of the Apuseni Mountains, Abramut and Styrian basins (one basin situated to the east whereas the other to the west of the Pannonian basin).

Neogene volcanic rocks from the Apuseni Mountains, have δ^{18} O values of 5.5 to 5.9‰ for clinopyroxenes, biotites and amphiboles, slightly higher than those of phenocrysts in alkali basalts from elsewhere in the Carpathian–Pannonian region (5.0 to 5.34‰) (Dobosi et al. 1998). The ⁸⁷Sr/⁸⁶Sr ratios for clinopyroxenes (0.7041) and amphiboles (0.7042–0.7042) are lower than bulk rock ⁸⁷Sr/⁸⁶Sr, but values for the plagioclase and groundmass are generally higher. The higher δ^{18} O, δ D and ⁸⁷Sr/⁸⁶Sr for the oldest rocks (15–13.5 Ma) suggest a differently enriched (possibly lower crustal) source. The rocks younger than 13.5 Ma have the uniformly lower δ^{18} O, δ D and ⁸⁷Sr/⁸⁶Sr in their mafic phenocrysts, which correlate with the narrow range and low values of bulk rock ⁸⁷Sr/⁸⁶Sr ratios. These are different from most of the other calc-alkaline volcanic rocks in the Carpathian–Pannonian region. The study demonstrates the importance of fractional crystallization, with a small assimilation for some of the rocks that show an increase in the δ^{18} O and ⁸⁷Sr/⁸⁶Sr ratios in their later phases. It is plausible that three melting mechanisms may have operated individually or coupled (leading to local magma mixing) to generate the complex calcalkaline non-subductional magmatic association in the Apuseni Mountains.

The previous mineralogical studies from the northwestern Transylvania Basin (Seghedi et al. 2000) or the Costui–Maramures Basin (Damian et al. 2007) have shown that the zeolites found in tuffs of Badenian age consist mainly of clinoptilolite (40–90%) with minor amounts of mordenite or phillipsite. These tuffs have a similar stratigraphic position to other volcanic tuffs from the Transylvanian Basin (Dej Tuff, Ciupagea et al. 1970), the Maramures Basin (Cochemé et al. 2003), the Gutâi Mts. (Kovács et al. 1997; Kovács, Fülop, 2003), the Apuseni Mountains (Seghedi et al. 2004), the Beregovo and northern Trans-Tisza regions (Pécskay et al. 2006), the Slãnic Tuff in the foreland of the Eastern Carpathians (Marunteanu 1999), and the Styrian Basin (Bojar et al. 2004; Handler et al. 2006). The Abramut Basin is situated in north-western Romania and corresponds with the Derecske Basin from the Hungarian sector of the Pannonian Basin. In boreholes, several tuff interbeds were recorded. In order to compare them with the previously known

occurrences, micro-faunal and mineralogical (qualitative and quantitative) investigations were performed for the borehole interval analyzed. Detailed lithostratigraphic data from borehole in the Abramut Basin, located in the north-western part of Romania, revealed the presence of turbiditic deposits containing several layers with tuff/tuffaceous materials in the Lower Badenian. Detailed quantitative and qualitative X-ray diffraction data (XRD) derived from different tuff layers show a mineralogical association comprising analcime, quartz, volcanic glass, smectite, mica, calcite, K-feldspar, glass and minor quantity of chlorite and albite (Bojar et al. 2012). The presence of analcime suggests that the albite isograd for the interval studied has never been reached and the maximum temperatures for the studied borehole interval have been lower than c. 125°C since the Early Badenian.

The third study area is situated in the Styrian basin, which was part of the Paratethys realm, a land-locked remnant sea. The basin formed during Miocene eastward tectonic extrusion and orogen-parallel extension (Neubauer, Genser 1990). There are several published studies concerning stratigraphy, geochronology, geomagnetism and paleogeography of basin deposits (Steininger, Bagdasarjan 1977; Ebner, Sachsenhofer, 1995; Rögl 1998). The sedimentation started in the Ottnangian (early Miocene); the preserved thickness of the deposits reaches c. 4 km. The Gleichenberv volcanic body, high K calc-alkaline, is the only one in the Styrian basin that shows extensive hydrothermal alteration. K-Ar dating of primary volcanic biotite and alteration products (alunite) suggests that the emplacement of the volcanic body and hydrothermal alteration took place synchronously, 15 Ma ago (Bojar et al. 2008). The stable isotope compositions of the alteration products, such as opal, barite, pyrite and alunite combined with crystallographic investigations indicate temperatures between 150 and 200°C for the formation of the alteration zones. The calculated stable isotopic compositions of the parent fluid, responsible for the alteration, show an exogene marine component, which interacted with the host rock. Sulfur isotopic compositions of sulfur, sulfides and sulfates indicate disequilibrium, and progressive oxidation. This fact, combined with the mineral zonation of the alteration zone, reflects not only change in the pH, but also change in the fO₂ of the ascending fluids.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Construction of age-depth models using calibrated radiocarbon dates

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A problem of age-depth models based on radiocarbon dates is one of the most important issues of construction of chronological scale for archaeological or geological profiles (cores, trenches). As it was presented by Blaauw (2010), in many publications procedures for constructing of age-depth models are not explained sufficiently and some of them use inadequate simplifications in interpretation of radiocarbon dates. The main reason of this problem is a specific form of results of radiocarbon date calibration, which are presented as a probability distribution of possible values of the calendar sample age. These results often should be interpreted as a few alternative values of the calendar age of sample and hence it is impossible to present the calendar age of sample calculated using a calibration procedure as a single number (point estimate), in the form of "age \pm uncertainty". However, this form of results ("age \pm uncertainty") is necessary for all "classical" methods of construction of age-depth models.

In recent years there have been created a few programs that enable construction of agedepth models using probability distribution of possible values of the calendar age of sample. Probably the most popular of them is OxCal calibration program, which offers different procedures for construction of deposition models - Sequence, D Sequence, V Sequence, U Sequence, P Sequence (Ramsey 2008). This presentation shows a couple of examples of absolute chronologies constructed with the use of age-depth modeling procedures of OxCal program. Two examples concern analysis of peat sediments, which originate from a specific type of peat bogs, called "landslide peat bogs" (Margielewski 2006). These peat bogs are situated in the depressions developed within the landslide landforms located in the Polish Outer Carpathian (Pcim Sucha in the Beskid Makowski Mountains and Jesionowa in the Beskid Sądecki Mountains). The models use OxCal function *P* Sequence to construct absolute chronological scales for each of the peat bogs. The age-depth relationship obtained in this way allows us to estimate calendar ages of some important events for investigated sites (Michczyński 2011; Margielewski et al. 2010, Margielewski et al. 2011). The third example concerns another type of sediment, namely lake sediment. It presents new complex statistical model of the Lake Soppensee (Switzerland) chronology, which joins two types of accessible chronological information together (Michczyński 2011, Hajdas et al. 1993). The first type of information is represented by the varve chronology constructed for laminated part of Soppensee sediment (depth 540 - 360 cm) and fitted to the IntCal09 radiocarbon calibration curve. The second type of information is represented by radiocarbon dates obtained for non-laminated or partially laminated parts of the sediment. The model of the Lake Soppensee chronology has been constructed using OxCal 4.1 program and consists of three parts included in Sequence function. The main part is the varve chronology, which is fitted to the IntCal09 using

OxCal wiggle-matching function $D_Sequence$ on a base of 54 radiocarbon dates. The two remaining parts concern time periods before and after accumulation of laminated sediment. They are constructed using OxCal age-depth model function P Sequence.

The presented chronologies enable the author to discuss some methodological problems of a construction of age-depth models using the OxCal program and to formulate conclusions and recommendations, which concern methodology of chronologies construction.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Preliminary clay mineral data on burial history of the Holy Cross Mts, Poland

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Burial and thermal history of the Paleozoic core of the Holy Cross Mts has been a subject of ongoing debate for the last forty years (Narkiewicz et al. 2010), based on interpolations of stratigraphy and lithofacies, organic indices of diagenesis, and 1-D and 2-D modeling. In this contribution, clay mineral tools have been applied: XRD of clay fraction of shales to evaluate the maximum paleotemperatures and K-Ar dating of illitesmectite from bentonites to date these maximum paleotemperatures (Środoń 2007). The Ostrówka and Kowala quarries (Devonian-Carboniferous) and Janczyce-1 borehole (Upper Devonian) were studied in the Kielce zone, and the Bukowa Góra quarry (Devonian) plus Jeleniów-1 borehole (Ordovician) in the Lysogóry zone.

In Ostrówka the maximum paleotemperatures are estimated as 135°C, based on 20%S in illite-smectite, in Kowala: 116-134°C (28-21%S), in Janczyce-1: 128-135°C (23-20%C), in Bukowa Góra: >177°C (<11%S), and in Jeleniów-1: >200°C (<5%). The difference in the degree of diagenesis between the Kielce and the Lysogóry zone is apparent.

In Kowala the K-Ar ages range from 192 to 228 Ma (Early Jurassic-Late Triassic), in Ostrówka: 329 Ma (Early Carboniferous), in Bukowa Góra: 336 Ma (Early Carboniferous), and in Jeleniów-1: 368-373 Ma (Late Devonian).

More data are required to interpret with some confidence the burial history of the region. At this stage it seems clear that in the Lysogóry zone the Late Paleozoic diagenesis was more advanced than in the Mesozoic burial diagenetic episode, as the K-Ar ages did not record the Mesozoic contribution. Analogous K-Ar dates had been recorded earlier from different areas of the Peri-Tornquist margin of the East European Craton (Środoń et al. 2009; submitted). The one sample date for Ostrówka has to be verified. The Kowala dates can be interpreted as an overprint of the more advanced Mesozoic diagenetic episode over the less advanced Paleozoic episode.

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ORAL AND POSTER Contributions

Dating of Minerals and Rocks XI

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Effect of fertilization and vegetation on the formal K-Ar age of <2 µm-sized minerals of soil

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It is known that (i) treatment with fertilizers changes the structure of $<2 \mu$ m-sized clay minerals in soil (Meunier, Velde 2004), and (ii) in the Hungarian Plain the formal K-Ar age of Plio/Pleistocene sediments is mostly Mesozoic (Balogh, Árva-Sós 1974). This implies that change of formal K-Ar age (from now on: K-Ar age) of TOT clay minerals might be used for studying the important process of mineral changes (Nemecz 2006) in soils.

As a first step, sample pairs were measured from the same soil, one from the surface of a never fertilized old forest as reference, the second from the nearby fertilized plough-land. Age data (Table 1) show that the assumed effect exists. Similarity of age decrease shown by samples from the plough-land may be explained tentatively by some saturation effect.

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No	Locality	Size of K ⁴⁰ Ar(rad)		d)	Age	<u>t(p)</u>	
K-Ar		fraction	%	$10^{-5} \text{ cm}^{3}/\text{g}$	%	My±σ	t(f)
7148	Hencida (p)	<2 µm	2.827	1.644	62.2	143.7 ± 5.8	0.883
7150	Hencida (f)	<2 µm	3.300	2.005	70.1	162.7 ± 6.3	
7147	Nagyerdő (p)	<2 µm	2.538	1.185	61.2	116.3 ± 4.7	0.881
7149	Nagyerdő (f)	<2 µm	2.430	1.299	76.6	132.0 ± 5.1	
7607	Pocsaj (p)	<1 µm	3.047	1.447	72.0	118.2 ± 4.6	0.882
		<0.5 µm	2.964	1.084	69.4	91.7 ± 3.6	0.880
7606	Pocsaj (f)	<1 μm	3.115	1.685	81.8	134.0 ± 5.1	
		<0.5 µm	3.016	1.258	75.2	104.2 ± 4.0	

Table 1. K-Ar "ages" of minerals from soil near Debrecen: p - plough-land, f - forest

The results for soils treated with known amounts of NPK fertilizers are shown in Table 2. Some decrease of age can be assumed for samples 2, 4 and 7, and this effect is clear for samples 10 and 11, which received the greatest amount of K. Samples 8 – 11 received NP fertilizers too, the ratio of (age:10,11)/(age:8,9) is 0.836, i.e. it is greater than observed for samples in Table 1. However, if the age of the unfertilized sample No. 1 is used as reference, the (age:1)/(age:10,11) ratio is 0.880, similar to the one for samples in Table 1. The cause of this is not clear. However, (age:8,9)>(age:1), as if NP treatment would have increased ,,age". This is possible, if NP treatment have decreased the K/⁴⁰Ar(rad) ratio of the TOT clays. This may happen, since K is sited in interlayer position, while the recoiled ⁴⁰Ar(rad) may stop at any position in the mineral. The measurements above have shown that fertilizers change the the K-Ar age of clay minerals. Detection of this change needs

reference soil, which was treated with known dose of fertilizers, or was not treated at all. However, such a well known soil is usually not available. This limits the applicability of K-Ar method for studying mineral changes in soils. In addition, plants transport K from the deeper to the surface layers of the soil (Stefanovits 1992), i.e. vegetation acts as K fertilizer.

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Code	Ν	Р	K	(1)	(2)	K	⁴⁰ Ar(rad)	K-Ar age±σ
						%	10^{-5} ccSTP/g	(M year)
1	0.0	0.0	0.00	1.88	-1.88	2.340	1.164	123.6 ± 4.8
2	0.0	0.0	2.07	2.48	-0.41	2.542	1.147	115.1 ± 3.6
3	0.0	0.0	4.15	2.67	+1.48	2.503	1.223	121.0 ± 3.9
4	0.0	0.0	6.22	2.78	+3.44	2.679	1.254	115.7 ± 3.7
5	3.5	0.0	2.08	3.47	-1.39	2.482	1.325	132.4 ± 5.2
6	3.5	0.0	4.15	3.80	+0.35	2.443	1.290	130.9 ± 5.1
7	3.5	0.0	6.22	4.22	+2.00	2.622	1.259	119.5 ± 4.6
8	7.0	1.75	0.00	2.44	-2.44	2.193	1.125	127.4 ± 5.1
9	7.0	3.5	0.00	2.00	-2.00	2.305	1.237	133.0 ± 5.1
10	7.0	3.5	7.06	2.15	+4.91	2.975	1.281	107.5 ± 4.2
11	7.0	3.5	7.06	2.35	+4.71	2.806	1.240	110.2 ± 4.4

Table 2. K-Ar ages of <2 μ m-sized minerals in soils treated with NPK, N, P, K, (1) and (2): N, P₂O₅, K, K uptake by plants and K balance in t/ha/35 years

K is captured very fast by clay minerals. This suggests that deeper layers might be used as reference. 3 K-Ar ages from different depth (Table 3) show that this age difference exists. It is caused by (i) fertilizers, or (ii) K transported by the plants. This effect is smaller, if the plants were removed from the site. Deeper layers might be also older due to the K loss.

No	Code	Depth	K	⁴⁰ Ar(rad)	Age±σ
K-Ar		cm	%	10^{-5} ccSTP/g	(M year)
7884	101	0-30 cm	3.220	1.784	137.2 ± 5.3
7885	102	30-60 cm	3.034	1.990	161.3 ± 6.2
7886	103	60-90 cm	2.782	1.901	167.7 ± 6.4

Table 3. Influence of the depth on K-Ar age

As it has been shown, vegetation and fertilization cause a structural change in clay minerals in soil, and this change, which depends on a number of processes is reftlected in the K-Ar ages too. Understanding of this complex process needs selective study of changes caused by vegetation and fertilization. This might be done by proper selection of a site for study, performing experiments with variable doses of fertilizers and applying additional methods for preparation and study of clay minerals. Due to the old formal K-Ar ages of soils and versatility of deposition, the Hungarian Plain appears to be very suitable for the elaboration of this new, promising method for soil diagnostics.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Luminescence age of Vistula River overbank deposits in western part of Warsaw Basin

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The Lower Vistula River valley is formed by the anabranching multichannel river system (Kalicki, Szmańda 2009). The age of the Lower Vistula River overbank deposits were researched with the use of the radiocarbon method (Wiśniewski 1985; Niewiarowski 1987; Tomczak 1987), luminescence method (Szmańda et al. 2004) and archaeological methods (Biernacki 1968). Our research shows that the oldest madas have been accumulated since the Subboreal age. However, the previous (in 2002) luminescence dating of overbank alluvia in Torun documents the Subatlantic age of madas.

The presented results of the OSL dating relate to the age of madas that were taken from the Holocene flood plain (Florek et al. 1987) located in the western part of the Warsaw Basin (Fig. 1). Three profiles of the overbank alluvia were performed (Fig. 1): (1) Wyk – in the natural levee on the river island near Wykowo, (2) Tro – in the flat surface of the flood plain near Troszyn Polski, (3) Jan – in the flood basin near Januszew. Seven samples of madas were collected from these profiles for the luminescence analysis (Fig. 1).



Fig. 1. Location of the Vistula River overbank alluvia profiles in the western part of the Warsaw Basin. Table presents ages received for each sample expressed in years

In order to estimate equivalent dose (ED) quartz grains have been separated from sediment samples in the way common for optically stimulated luminescence (OSL) dating (Oczkowski, Przegiętka 1998). Mineral grains about 100–200 μ m in diameter were obtained with sieves and then the quartz fraction was extracted using heavy liquids. Finally, the samples were etched in 40% hydrofluoric acid (Weckwerth et al. 2011). Aliquots for OSL measurements were prepared in the following way: small aluminum discs were covered by silkospray and subsequently quartz grains were deposited on them.

All OSL measurements were carried out using the RISØ TL/OSL System TL-DA-20 equipped with conventional Hoya U-340 filters and EMI 9235QB PMT photomultiplier. Blue LED stimulation module (450-550 nm, 80 mW/cm²) was applied as an optical stimulation source. For the OSL excitation, a 90 Sr/ 90 Y β source giving a dose rate of about 134 mGy/s was utilized.

To determinate the ED, the single aliquot regeneration dose protocol (SAR) was applied. Forty-eight aliquots for every sample were measured. A preheat test was performed prior to the study for each sample. Six different values of temperature were chosen in this test in order to determine the proper temperature of preheat for the SAR protocol (Aitken 1985; Murray, Wintle 2006). Almost for all samples the right temperature was 240°C and for two of them, 260°C. For more reliable results a recycling ratio test (one regeneration dose was repeated) and recuperation test for the regeneration dose equal 0 was implemented (Murray, Wintle 2006). Only aliquots for which the test results were correct (the recycling ratios fall within a range of acceptability 90-110%) were included in the final calculation of equivalent dose.

The annual dose that consists of dose due to beta and gamma radiation (during etching an alpha dose contribution was eliminated) was estimated by means of the gamma spectrometer Canberra System 100 equipped with an HPGe detector that allows determining the radioactivity of isotopes present in sediment sample. Using the data obtained from gamma spectrometry, the value of the annual dose could be computed (Oczkowski, Przegiętka 1998).

The results of OSL dating are presented in the table inserted in figure 1. Considerable errors of the obtained values are due to the young age of the samples. The young samples show a weak luminescence, which is measured with lower precision. Another cause of errors in this case is the finite size of the smallest laboratory dose that can be delivered to the aliquots by the beta radiation source in the luminescence reader.

There are two models of genesis in anabranching fluvial systems (Teisseyre 1992): (1) transformation from the braided river system through accumulation of overbank alluvia on the river bars, (2) transformation from the meandering river system through the channel avulsion. The young age of the madas studied shows that contemporary Vistula River anabranching fluvial system was transformed from the braided river system.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Challenging K-Ar dating of the Quaternary tephra from Roxolany, Ukraine

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The first study on the Roxolany loess profile, located on the left bank of the Dniester liman near Odessa, Ukraine was presented at the international loess symposium (Putievoditel 1976). The study included the paleomagnetic characteristics, granulometric analysis and mineralogical composition of sediments as well as several radiocarbon dates. In 1998 Tsatskin et al. (1998) presented description of the Roxolany profile, stratigraphic interpretation of loess-soil horizons, and interpretation of paleomagnetic data and their correlation with the oxygen isotope stages (MOIS). The authors also identified the Bruhnes/Matyama boundary in the profile and correlated it with those of Central Europe and China. According to their stratigraphic interpretation, the tephra horizon found in the loess section of the profile corresponds with the MOIS 12, i.e. the period from 400 through 450 thousand years ago (Sartori 2000). Subsequently Gendler et al. (2006) reported the following paleopedological and magnetostratigraphic findings, and correlations of the loess units and fossil soils in the profiles of Roxolany and the nearby Novaya Etuliya.

Many years of comprehensive research conducted by Gozhik's team (Putivnyk 2000; Gozhik et al. 2007) brought a number of new data in the diagnosis of the Roxolany profile (palynological, malacological and paleontological analysis as well as TL and C-14 dating). They enabled the authors to develop the profile's chronostratigraphy. The results confirmed the continuous sedimentation from about 800 thousand years ago until the Holocene. Moreover, they gave a number of clues to different stratigraphic interpretation of the profile, in particular with regard to its upper part.

In 2011, in order to dispel the arising stratigraphic doubts concerning dating of the Roxolany profile, dozens of samples for luminescence and radiocarbon dating were collected under the grant N N306 474 138 "Correlation of key loess profiles of Ukraine". The whole profile was based on the facts found in four outcrops, which together comprise the loess-soil sequence from the contemporary soil (S0) to the Dnieper L3 loess (dn) which developed in MOIS 8. In profile 2, at a depth of 9.65 m, in a homogeneous loess layer of about 11 m in thickness positioned between the fossil soils horizons (second and third one from the top) a thin tephra layer was found. No doubt, this is the same layer of volcanic ash that was described before by Tsatskin et al. (1998). The sample collected from the tephra

layer was subjected to Ar-Ar dating. It was assumed that this geological marker might be a reference to the TL, OSL and radiocarbon dates, and that the date obtained from the tephra analysis can answer what its age and origin is.

The radiocarbon analyses were carried out with the accelerator mass spectrometry (AMS) technique. The dates obtained for the samples from the two soil horizons overlying the tephra layer (profile 1), indicated the age of about 30 ka BP, while for the paleosol lying 10 m deeper – 23.2, 20.0 and 25.4 ka BP. These dates correspond with the results of TL dates for loess samples 11-14 obtained in the Gdańsk laboratory (collected from the tephra and its immediate surroundings), whose age falls between 25.4 and 27.7 ka. The C-14 and TL dates, therefore, confirm the stratigraphic scheme developed by Gozhik et al. (2007). The tephra layer occurs in the Bug loess (bg) from the Upper Pleniglacial of the Weichselian Glaciation (MOIS 2), and the two soil horizons located above it are the stratigraphic units of the interphase rank: the Prychernomorsk (pc) unit and the Dofinivka (df) unit. The paleosol underlying the bg loess is the Vytachiv (vt) unit of the Middle Weichselian (MOIS 3). The luminescent (OSL) dates of the same 11-14 samples showed an inversion and reached 143.8, 112.8, 110.6 and 97.0 ka, which would indicate their Eemian and Early Weichselian age (MOIS 5) and which is inconsistent with the geological facts. The origin of the tephra is unclear at this stage of research, but the Carpathian volcanoes are taken into account. The traces of this volcanic ash were observed in the Carpathians, the Caucasus and in the Eifel region in Germany. According to Ukrainian scientists (Gozhik, Bogucki), who attended fieldwork in Roxolany, the tephra deposition took place in the Upper Pleniglacial of the Weichselian Glaciation.

The Roxolany profile is within the range of the tephra scattering field connected with the extreme event of the Campanian Ignimbrit /Y5' eruption. It is estimated that as a result of this catastrophic explosion, about 200 cubic kilometres of volcanic rock were expelled into the atmosphere. The profiles containing the Y/5' tephra are known from many countries of southern and south-eastern Europe as well as from numerous cores collected from the bottom deposits of the Mediterranean Sea (Fedele et al. 2002 a,b; Pyle et al. 2006) and extend east to the archaeological sites in the villages of Kostenki and Tambov-on-Don in Russia (Hoffecker et al. 2008). It is noteworthy that the petrographic characteristics of this tephra, described in more proximal to the site of the eruption (in the Campi Flegrei region in Italy) and better preserved sites, including those in the caves of Italy (Cremaschi, Ferraro 2007), Greece (Doukal et al. 2011), Croatia and also in Romania, is very similar to the composition of pyroclastic interbeds in the Roxolany profile. The distal pyroclastic material from the Ukraine examined by the authors, was contaminated with terrigenous material, and similarly to the Campanian Ignimbrite, is dominated by amphibole, clinopyroxene and biotite crystals (commonly covered with volcanic glass) or individual volcanic glass shards, usually weathered into clay aggregates. The age of the Y/5' tephra of 39.3 ka (Middle Pleniglacial of the Weichselian Glaciation), often quoted in specialist literature, is not in a substantial conflict with the existing geochronological research findings regarding the Roxolany profile. Tsatskin et al. (1998) and Sartori (2000) report the Ar-Ar date of 50 Ma (± 3) for the Roxolany tephra.

The new determinations of K-Ar dates for the Roxolany tephra were performed in the Mass Spectrometry Laboratory, UMCS, Lublin, using a low blank Ar extractionpurification line (Hałas 2007). Initially, a heavy fraction from the loess sample was separated, from which unexpectedly large amounts of radiogenic argon (Ar*) was extracted, therefore we decided to reanalyze carefully separated two dominant K-bearing mineral fractions, amphibole and biotite. The results of this dating are shown in Table 1. It should be noted that analytical errors are rather small due to precision determination of potassium by the isotope dilution method and a high fraction of the radiogenic argon obtained (about 42% for amphibole and 21% for biotite). Surprisingly, the potassium content in biotite was very low (1.74%). The obtained dates are rather consistent and they point not to a Quaternary volcanism, but perhaps to a weathering product of Neogene Carpathian rocks, like magmatic andesites.

No.	Sample	Locality	% K	Ar*	% Ar*	Age
	_	-		[pmol/g]		[Ma]
1	amphibole	Roxolany	1.40	30.08	41.9	12.3 ± 0.15
	_		1.40	$28.81^{\#}$	$42.9^{\#}$	$11.9 \pm 0.15^{\#}$
2	biotite	Roxolany	1.745	44.16	21.25	14.5 ± 0.15

Table 1. K-Ar dates for 2 different mineral separates from Roxolany tephra

^trepeated independent determination

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Improvements of %K determination for K-Ar dating by isotope dilution method

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Among a few analytical methods of potassium determination, like flame photometry, AAS, ICP spectrometry, X-ray fluorescence analysis, neutron activation analysis etc., the isotope dilution method appears to be most precise and accurate. Recently, we have improved this approach by using spike ⁴¹KCl solution, which is acidified with commercial 85% H₃PO₄. The reason of this acidification is twofold: (1) evaporation of spike solution is highly limited, hence it can be more accurately weighed on an analytical balance, and (2) this phosphoric acid is directly used for dissolving of powdered mineral samples.

The following equation is used for %K calculation from experimental data (Hałas 2001; Hałas 2012):

$$\mathcal{V}_{0}K = A \frac{M-S}{N-M} \frac{m_{S}[g]}{m_{N}[mg]}$$

where N, S, M are measured ${}^{39}\text{K}/{}^{41}\text{K}$ isotope ratios for the natural sample, spike and mixture, respectively; $m_S[g]$ is a mass of spike in grams, $m_N[mg]$ is a mass of natural sample in milligrams; A is the calibration constant.

In routine measurements we use about 20 mg of powdered hornblende and 4 g of spike to receive M value close to unity. In case of analysis of micas, which are abundant in potassium, it is necessary to increase the amount of spike.

The next improvement, which we have achieved recently, is the replacement of single filament with triple filament in a thermal ionization ion source. This approach enables us to measure two spiked samples in one loading procedure to the ion source. This leads to a significant saving of time of analysis. Moreover, this approach reduces isotope fractionation of measured sample because potassium is evaporated as a heavy molecule of K_3PO_4 .

The last, but not least improvement, is the use of a convenient software for *on-line* recording of mass spectra and data processing elaborated by Dr. Tomasz Pieńkos.

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Sm-Nd dating and stable isotope geochemistry of sulfides and U-Pb ages of layered intrusions from the northern part of the Baltic Shield

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We present new Sm-Nd data for the main ore-bearing rocks of the layered Fedorovo-Pansky intrusion, the Monchetundra massif and the Pilguyarvi (Pechenga) deposit. The results coincide with up-to-date geochronometry and new U-Pb ages of zircon and badeleyite. They were also compared with the stable sulfur isotope composition of sulfides and with the contents of main elements in these minerals. The possibility of using sulfide minerals for the Sm-Nd isotope-geochronological dating method of mafic-ultramafic intrusions has been considered by Serov and Mitrofanov (2005), Serov et al. (2007) and Serov and Ekhimova (2009).

The selected sulfide samples were analyzed with optical and electron microscopy (Hitachi SU6600 with EDS attachment) in the Electron and Optical Microscopy Laboratory, Maria Curie-Skłodowska University, whereas the δ^{34} S values of sulfides were determined in the Mass Spectrometry Laboratory, Maria Curie-Skłodowska University. These samples were dated by the Sm-Nd method, which was described by Kong et al. (2000). The Sm-Nd dates were compared with the relevent dates of zircon and baddeleyite obtained by the U-Pb method with the mass spectrometer in the Kola Science Center, Russian Academy of Science in Apatity (Russia).

In all the collected samples, the folowing minerals were present: pyrite, chalcopyrite and pentlandite (Huber et al. 2009; Bayanova et al. 2010). These sulfide samples were subjected previously to the REE analysis (Nerovich et al. 2009; Ekhimova et al. 2011; Elizarova, Bayanova 2012).

The results of geochronometric analysis of the chalcopyrite-pentlandite ore from gabbroides of the lower horizon of the Fiodoro-Pansky Tundra massif show 2467±39 Ma (Sm-Nd, from sulfide) and 2470±9 Ma (U-Pb from zircon). The anortosite with Pd-Pt elements from the upper horizon reveals the age of 2447±12 Ma (Sm-Nd) and 2442±74 Ma (U-Pb). The oldest rocks, with ε Nd(T) = 1.0±0.5 parameter, were formed by the mantle plutonism, which corresponds well with the δ^{34} S data (Huber et al. 2009). The latest age of crystallization is most likely associated with postmagmatic processes, whereas the measured δ^{34} S values pointed to non-primitive magmas (Huber, Hałas 2008).

The gabbronorites from the Pentlanditovaya Ushchelie ravine deposits in the lowermost part of Monchegorsk pluton exhibited 2489±49 Ma (Sm-Nd) and 2501±5.6 Ma (U-Pb), respectively. The difference between these two ages may be explained by contamination of

supracrustal material or a secondary injection of magma showing a diverse isotope signature.

The samples from Pilguyarvi of Pechenga massif are dated at 1950±58 Ma (Sm-Nd), which is compatible with the U-Pb age of this massif (Hanski et al. 1990; Bayanova 2004).

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New equipment in the Lublin thermoluminescence laboratory

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Since its establishment in 1980, the Lublin thermoluminescence laboratory has specialized in the age determination of Pleistocene deposits. TL dating of pottery and other materials, such as clay daub, bricks and cherts, has been conducted since 2005. Till 2011 the laboratory had been equipped with instruments produced in Poland: two thermoluminescence readers (model RA'94 made by Mikrolab Kraków) and two gamma spectrometers with scintillation detectors (made by Polon-Izot Milanówek). The second spectrometer was bought in 2010. It enables obtaining very high reproducibility of the results. The measurement results obtained for the same samples with the use of these two spectrometers are similar or differ maximally by 3%.

A new reader of thermoluminescence and optically stimulated luminescence, produced by Technical University of Denmark, was purchased in 2012. The Risø TL/OSL Luminescence Reader (Model TL/OSL-DA-20) is equipped with a heating system, which is able to heat samples up to 700°C, while 400°C is the upper temperature limit for the Polish readers. The instrument contains also four systems for measuring optically stimulated luminescence. These are two sets of LED's for determination of optically stimulated luminescence in typical mineral samples (i.e. weighted portions of several milligrams), and two laser sets – in single grains about 300 µm in diameter.

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The Baga-Gazriin Chuluu A-type granite - the problem of selection of appropriate dating technique

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The Baga-Gazriin Chuluu (BGCh) granitic pluton is located in central Mongolia, about 250 km SW of Ulan Bator. This granitic body covers an area of about 120 km² and lies in the Altaid orogen. The BGCh granitic pluton is situated close to the Mid-Mongolian Tectonic Line (Tomurtogoo et al. 2005), which was formed as a result of the closure of the Mongol-Okhotsk Ocean in the Mezosoic (ended in the Late Jurassic-Early Cretaceous) (Cogne at al. 2005). Petrographically, the Baga-Gazriin Chuluu granites are divided into three textural varieties (Machowiak, Stawikowski submitted^a):

- coarse-grained equigranular, locally coarse-grained porphyritic granite occurring mainly in the inner part of the pluton studied;
- medium-grained porphyritic granite found in the entire area of the pluton;
- fine-grained equigranular granite (s.c. haplogranite) and fine-grained porphyritic granite (occurring predominantly in the marginal zone).

The geochemical composition of BGCh granites is homogeneous and typical for A-type granites. The studied pluton is accompanied by numerous greisen veins, tungsten-tin mineralization and displays conspicuous REE enrichment.

Fresh granitic samples of three main textural varieties were selected for ⁴⁰Ar/³⁹Ar dating in Activation Laboratories Ltd., Canada. The mineral fractions containing biotite were separated using heavy liquids. Subsequently, the biotite flakes were segregated under the microscope. The obtained mica concentrates were sent to Activation Laboratories Ltd. The Ar isotope composition was measured with a Micromass 5400 static mass spectrometer.

The most precise and still becoming more common method in geochronology of acidic magmatic rocks is the U-Pb zircon dating using sensitive high resultion ion microprobe (SHRIMP). This technique was also planned to be applied for the granites from the BGCh pluton. It appeared that zircon would be a common accessory mineral of the studied granites. Such supposition was based on relatively high, extremely homogenous concentrations of zirconium in the rocks (except for a few samples): Zr 61-142 ppm; av. 105 ppm. These values do not differ from the average Zr amounts in granitic melts. Unfortunately, contrary to all expectations arisen from geochemistry, separation of a number of zircon grains sufficient for SHRIMP technique application (minimum 50 crystalls with >50 microns in diameter) turned out to be impossible. The earlier experiences of the authors with zircon separation for SHRIMP dating were positive and never connected with any difficulties concerning grain frequency, both for the Żeleźniak intrusion and the Karkonosze granite (Machowiak, Niemczyk 2006; Machowiak, Armstrong 2007).

In case of the BGCh granites, the microsopic observations indicated that zircon crystals occur almost exclusively as very small inclusions in dark, or less frequently white micas, which is perhaps the main source of the problems for obtaining the required grain concentrates. Thus, the authors were forced to apply an alternative radiogeochronological method – dating of biotitic concentrate using 40 Ar- 39 Ar technique.

The material for this study was prepared assuming that greisenization processes, widely observed in the BGCh pluton, could disturb ⁴⁰Ar-³⁹Ar isotope ratios in micas (e.g. Smith et al. 2005). In order to avoid their negative influence on dating results, the detailed microscopic observations were conducted. They aimed at selecting the granite samples containing fresh, homogenous biotite devoid of any evidence of greisenization. The sample selection was additionally verified by analysis of the field data. The geological mapping revealed that the greisenization zones are most strongly concentrated in the outer part of the BGCh pluton, at its contact with country rocks. The frequency of the greisen veins increases also in the areas of intensive fracturing of the granitic body. The samples for dating were chosen from the locations situated in the remote distance from the greisenization zones (Machowiak, Stawikowski submitted^b).

The biotite concentrates for the radiometric studies were prepared from the samples representative of three main granite varieties occurring in the BGCh pluton. Using the ⁴⁰Ar-³⁹Ar technique, the following results were obtained:

- 201.0 ± 1.8 Ma for coarse-grained granite,
- 211.9 ± 2.0 Ma for medium-grained granite,
- 209.4 ± 1.6 Ma for fine-grained granite.

As evidenced by the microscopic studies of the BGCh granite, zircon and other minerals with elevated REE contents (e.g. monazite) form very small, numerous inclusions in micas, almost never occur as bigger crystals in the rock. It is confirmed by the above-mentioned problems with zircon grain separation for SHRIMP dating. The zircon crystals of the BGCh granites are homogenous, without zoning or inherited cores. Moreover, the micas that host numerous zircons, occupy interstitial positions between main mineral components of the granite studied (Qtz, Or and Ab). The BGCh pluton is supposed to have originated from relatively "dry" magnatic melt, where water and other fluids, which were transmitters of complex ions responsible, e.g. for the REE content increase, appeared at the late stage of crystallization (Machowiak et al. submitted). Thus, the micas and accessory minerals, including zircon, could have appeared as mineral phases in the late stage of granite crystallization. Despite the common opinion that zircons from granitic rocks can be easily dated by SHRIMP technique, the presented case study verifies this opinion. The position, size and frequency of zircon grains, which are big enough for dating, are dependent on details of petrogenesis of granites studied.

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Noble gas constraints on genesis of therapeutic waters from SE Poland

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The territory of southeastern Poland, but especially its southern part, is rich in various mineral and therapeutic waters of high quality. The balneological resources of the region and in particular its mineral and therapeutic waters of Iwonicz Spa, Lubatówka and Horyniec Spa are exceptional. The previous studies (Baran, Hałas 2010, 2011) have shown that these waters are mixtures of recently recharging water, ascending salty dehydration water and brine from oil fields. Five groundwater samples have so far been analyzed for noble gas concentration and isotope ratios. The results obtained are summarized in Table 1.

Locality	He-10 ⁸	Ne-10 ⁷	$Ar \cdot 10^4$	Kr · 10 ⁸	Xe-10 ⁹	R/R _a	^{14}C (nMC)	NGT (°C)	Remarks
Horyniec RIII	37.2	2.79	4.55	10.34	14.6	0.210	25.55	7.6	CE
Lubatówka-12	604.6	< 0.01	< 0.02	< 0.01	< 0.01	0.012	n.a.	-	Lot of gas (CH ₄)
Lubatówka-14	104.9	< 0.01	< 0.02	< 0.01	< 0.01	0.014	n.a.	-	Lot of gas (CH ₄)
Iwonicz-II	4.6	0.14	2.42	6.63	10.3	0.978	n.a.	13.0	SD, contains CH ₄
Klimkówka-27	5.7	1.29	2.84	6.68	9.2	0.470	n.a.	18.4	DD, contains CH ₄
AEW (995 hPa, 0°C)	4.6	2.03	4.01	9.59	14.10	0.983			

Table 1. Noble gas concentrations, helium isotope ratios and calculated noble gas temperatures of the therapeutic waters in southeastern Poland

ccSTP: cubic centimetre at standard pressure and temperature (1013.25 hPa, 0°C)

AEW: air equilibrated water

 R/R_a : ³He/⁴He isotope ratios in the water (R) and atmosphere (R_a)

pMC: percent modern carbon

NGT: noble gas temperature

CE: closed-system equilibration model

SD: solubility driven equilibration model DD: diffusive degassing model

n.a.: not analyzed

Based on the chemical and isotopic analyses of noble gases, three genetic groups of therapeutic waters can be distinguished:

1. Lubatówka waters are enriched in helium. They are mainly of crustal origin, which is evidenced by the isotope ratios (R/R_a represents the ${}^{3}\text{He}/{}^{4}\text{He}$ isotope ratio (R) compared to the atmospheric isotope ratio (R_a)). These low R/R_a ratios (0.012 and 0.014) show that radiogenic ${}^{4}\text{He}$ prevails in these waters. It is in good agreement with

the previous findings. The Lubatówka water can be assigned to typical brines from oil fields. This water contains methane which has light carbon isotopic composition, whilst carbon isotope ratio of bicarbonate attained extremely heavy $\delta^{13}C_{PDB}$ values (+19.9 to +24.0‰) as a result of isotope fractionation. Moreover, the other noble gases, namely neon, argon, krypton and xenon were not detected in the Lubatówka samples. The explanation of this pattern is that the water is in a contact with a huge gas phase composed mainly of methane, and the atmospheric noble gases could escape from the water to the gas phase. Additionally, methane gas bubbling through the brine aquifer was able to carry away the originally dissolved gases from the water. On the other hand, if these waters were of dehydration origin, as can be seen from the stable isotopic composition of water ($\delta^{18}O_{SMOW}$: +1.25‰, $\delta^{2}H_{SMOW}$: -31‰), the concentrations of noble gases (except for helium) would have to be substantially low.

- 2. Iwonicz-II and Klimkówka-27 waters contain relatively low concentrations of He, close to the solubility equilibrium. Klimkówka-27 waters contain a small amount of radiogenic He, which is evidenced by the R/R_a value (0.47). The R/R_a (0.978) of Iwonicz-II waters is close to the atmospheric ratio. However, these samples have suffered subsurface degassing. It can be seen from Ne-Ar-Kr-Xe concentrations that some noble gases are missing. We are aware from the previous studies that these waters are mixtures of freshly recharging waters similar to those of Lubatówka. The lack of heavier noble gases can be explained by dilution of noble gas concentrations in the methane-rich waters. Using two degassing models (Aeschbach-Hertig et al. 2008), we could calculate recharge temperatures (13.0°C and 18.4°C, respectively), but these temperatures have to be handled with care.
- 3. Róża-III seems to be groundwater that infiltrated the surface in the middle Holocene (¹⁴C content: 25.55 pMC). Noble gas concentrations do not show subsurface degassing, therefore a reliable noble gas recharge temperature could be calculated using the closed-system equilibration model. The recharge temperature obtained is 7.6 °C, which is in good agreement of the mean air temperature of the Horyniec region during the Holocene.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Age-depth model for Eemian stalagmite from Orlova Tchuka cave (Bulgaria)

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In the last ten years many Holocene stalagmites were used as a high resolution palaeoclimatic data source. However, there are only a few examples of such records from Eemian speleothems. A stalagmite from the Orlova Tchuka cave is a 165 cm long columnar type stalagmite. It is a potentially very good source for paleoclimatic data. An important stage of paleoclimatic record construction is chronology derived from the profile studied (= stalagmite). The principal advantages of speleothems are the possibility of reliable dating using a U-series method and a known relationship between calcite isotope (C and O) composition and climatic factors. Several samples from an axial part of the Orlova Tchuka stalagmite were collected for isotope dating. The comparison of three techniques of age-depth modeling software published by Sholz and Hoffman (2010), (2) MOD-AGE – age-depth modeling software using Monte-Carlo simulation (Hercman, Pawlak 2012) and (3) age-depth modeling system which uses genetic algorithm for searching the best age-depth relationship.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Testing of two new possible methods of determination of diagenetic and detrital ages from K-Ar dates of clay fractions contaminated with detrital illite

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Illite in shales is a mixture having both diagenetic and detrital origin. Ages of both components of this mixture can provide valuable information on various aspects of sedimentary basins history. Diagenetic age helps to constrain the thermal evolution of basins, while the age of detrital component offers a substantial support for constraining the sedimentary material provenience. The information of the end member ages is, however, very difficult to extract because it is impossible to separate these two fractions physically.

One of the most popular approaches of extraction of diagenetic and detrital ages is named "illite age analysis" (IAA) and is based on the XRD quantification of the ratio of diagenetic to detrital illitic component in three (or more) different grain size fractions (Pevear 1992). Illite polytype $2M_1$ is considered to be detrital, while polytype 1M and illite 1Md to be diagenetic. There are possible, however, also different assumptions of these end member fractions.

The first of new approaches uses illite crystal thickness distributions measured from Xray diffractograms as proxies for diagenetic and detrital components. Three different approaches to the problem have been proposed: (i) Uhlik et al. (2000), (ii) Dudek and Środoń (2003) and (iii) Aldega and Eberl (2005). Each divides illite crystal thickness distributions into diagenetic and detrital contribution in a different way.

The results of testing of all these approaches show that, although none of the methods has given satisfactory results, the modified approach of Dudek and Środoń (2003) works the best on the studied set of samples. This methodology, combined with the MODELAGE approach (Szczerba, Środoń 2009) can find an application in more favorable cases than these investigated in this study (bimodal distributions of fundamental particle thickness, e.g. bentonites contaminated with detrital material).

The second approach is based on chemical analyses of a few grain size fractions with different proportions of diagenetic to detrital illite. The idea behind is to analyze contents of elements, which concentrate in illitic minerals. This is e.g. potassium, argon, boron or lithium. On the basis of these analyses a set of equations is constructed for each fraction.

Solving this set of equations should lead to the determination of potassium and argon in end member fractions and in this way the diagenetic and detrital ages.

It was found that this approach, if supported by additional data (e.g. quantitative XRD), has a potential to constrain results of other methods or serve as an independent method of extraction of diagenetic and detrital ages of mineral mixtures. This approach is based on the assumption that the selected elements are located only in the illitic fraction and that their

contents in the diagenetic and the detrital illite differ significantly. Therefore, the application of this approach is restricted to the cases fulfilling these criteria.

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Excursion



MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Tour of Kielce: "Devonian story"

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(1) Center of Geoeducation in Kielce

The Center of Geoeducation in Kielce is located in the southeastern part of the Wietrznia Abiotic Nature Reserve. In this area it encompasses a building and a self-guided trail. The building architecture is well integrated into the landscape of the abandoned quarry (Fig. 1). The Center was opened on March 24th of 2012 and since then it has been the main site of geotourist attraction on the Holy Cross Mountains Archeologic-Geologic Trail. The whole investment was financed by the European Regional Fund within the framework of Operational Programme: Innovative Economy.



Fig. 1. A general view of the Center of Geoeducation in the abandoned Wietrznia quarry

The Center of Geoeducation is a place, where visitors can easily acquire geologic and geographic knowledge using the latest methods and techniques of education. The scope of its activity includes: theoretical and practical geoeducation classes, field tours of different geotourist sites in Kielce, sightseeing of Earth's Gallery and traveling on 5D capsule to the Earth's interior. The pivotal part of Earth's Gallery is a permanent exhibition that includes the Devonian history of the Holy Cross Mountains and presentation of various geologic processes that have formed the earth's surface in this area. During Devonian time (416 – 359 Ma) the contemporary Holy Cross Mountains area was covered by a shallow sea surrounding the Laurussia continent located in the subtropical climate of the southern hemisphere. The exhibition describes a fascinating story of encroachment of aquatic verterbrates on land, thriving and disappearance of tropical reef that ended with a mass extinction of many animal species, tectonic movements, formation of caves and valuable mineral deposits and land-forming processes. Specimen models, natural samples and colorful display-boards enable better understanding of different processes and phenomena that took place in the Holy Cross Mountains (Figs. 2, 3).

Another highlight worth seeing is a polishing shop led by Mr. and Mrs. Jędrychowski. It is well equipped with specialist rock saws, grinding and polishing machines. Young people are taught how to identify and collect minerals, rocks and fossils as well as how to saw, grind or polish these specimens. Participants of these courses get also information on mineral and rock formation and location, and various aspects of mineralogy, petrology and geology. This educational activity contributes to broaden geologic knowledge among the general public.



Fig. 2. Model of Devonian placoderm (extinct class of prehistoric armored fish); some specimens reached even 9 m long



Fig. 3. Dr. Agnieszka Gałuszka and Dr. Paul Lamothe of U.S. Geological Survey stand in front of a wall chart showing the Late Devonian Mass Extinction (about 374 million years ago) recorded in the Kowala quarry near Kielce

(2) Geology of Wietrznia quarry

Wietrznia Mt. (312 m asl) is located in the southern part of downtown Kielce at the junction of two strees: Wojska Polskiego and Tarnowska (Fig. 4). This mount makes up the southeasternmost part of the Devonian Kadzielnia-Białogon Range. Established in 1999, the Zbigniew Rubinowski Abiotic Nature Reserve takes up an area of 17.95 hectares. Its central part is occupied by an abandoned quarry composed of a row of 3 bench workings about 1 km long, 100-300 m wide and 20-50 m deep. They form three pits: (i) western (Wietrznia), (ii) central (Międzygórz) and (iii) eastern (Międzygórz Wschodni). During 1893-1974 limestones were extracted for manufacturing burned lime in nearby limekilns and aggregates for building and road construction (Wróblewski 1999; Złonkiewicz 2009).

The nearly 100-m thick profile consists of uppermost Middle (Givetian) and Upper Devonian (Frasnian and Fammenian) carbonate rocks assigned to the so-called Wietrznia beds. The profile consists of three series: A (thick-bedded limestones), B (thin- and middle-bedded marly limestones and marls), C (mostly medium-bedded limestones with marly limestone interbeds) (Fig. 5). Unlike Kadzielnia Mt., Frasnian reef limestones are strongly reduced and replaced by marly limestones and marls. In general, they represent a deeper marine facies, but the presence of detrict limestones indicates the close proximity of reef barrier. However, distinct facies variations are also recorded within a small area of the

quarry, from the shallowest facies in the central pit (Międzygórz) to the deepest in the western pit (Wietrznia) (Kotański 1959; Szulczewski 1979, 1995; Wrzołek 2005; Narkiewicz et al. 2006; Złonkiewicz 2009). These limestones contain numerous fossils of corals, brachiopods, bivalves, gastropods, trilobites, bryozoans, and in places remains of placodermi (Kotański 1959; Bijak 2005; Wrzołek 2005). The Frasnian limestones are overlain by the Fammenian thin-bedded marlaceous limestones and clayey shales representing deeper facies of distal shelf or even continental slope (Fig. 6). The Fammenian series locally contains hematite (Fe₂O₃), pyrite (FeS₂) and pyrite-hematite concretions.



Fig. 4. Localization of the Wietrznia quarry



Fig. 5. Carbonate series A, B, C exposed on the northern wall of the western pit; lateral fault (solid line)



Fig. 6. Contact of Frasnian limestones and Fammenian marly clayey shales and marls; Frasnian limestones are strongly faulted and karstified (central part of the quarry)

Frasnian limestones are cut by a network of tectonic faults. There are numerous longitudinal and lateral faults mostly of Late Carboniferous - Early Permian age (Figs. 5-7); some of them were reactivated in the Paleogene and Neogene during the Alpine orogeny. The largest fault, which is located north of the quarry, shifted southward the eastern part of the Kadzielnia-Białogon Range. Folds occurring in the Fammenian marly clayey shales and marls resulted from detachment of this "soft" series from the "rigid" Wietrznia limestone series. A zone of oblique-slip faults can be traced on the northern wall of the Międzygórz and Międzygórz Wschodni pits. The strike shift formed a deep fissure about 100 m wide, which was filled with a tectonic breccia (Złonkiewicz 2009). This breccia can be observed on the northern walls as well as in pillars left after quarrying for limestones (Fig. 7). Some of these fault fissures are also filled with calcite CaCO₃, galena PbS, barite BaSO₄ with subordinate copper sulfides, malachite Cu₂[(OH)₂|CO₃] and azurite Cu₃[OH|CO₃]₂ (Rubinowski 1971a,b). Calcite veins, lenses and druses are of different origin (hydrothermal, karstic or vadose) and age. Some of them can be assigned to the socalled "rose-like" calcite which formed in the Late Permian and Early Triassic (Migaszewski et al. 1996).

The Upper Pemian conglomerates, composed of local rock fragments cemented by calcite, occur in the southern part of the Wietrznia quarry as waste mantle averaging several meters thick. These terrestrial rocks formed due to erosion of the uplifted Holy Cross Mountains during Variscan orogeny in the Late Carboniferous.

Another interesting formation that arouses much controversy among geologists is a dolomite outcrop that occurs in the southeastern part of the deepest western pit. The southward-dipped dolomite chimney reaches about 30 m in diameter, piercing the

uppermost Givetian and lowermost Frasnian limestones (Fig. 7). The dolomites locally contain pyrite aggregates a few centimeters across. Most geologists recognize this dolomite outcrop as an apical part of the Devonian dolomite formations. However, according to the petrologic and isotopic study performed by Migaszewski (1990, 1991), these rocks are a product of hydrothermal dolomitization induced by submarine hot spring activity during Devonian time. This is evidenced especially by the specific microtextures of some petrographic dolomite varieties and the results of stable carbon and oxygen isotope determinations. The $\delta^{13}C_{PDB}$ varied from 0.4 to 1.1‰ whereas the $\delta^{18}O_{PDB}$ from -10.7 to -2.6‰. A distinct variation of temperatures (44 to 107°C) derived from "oxygen thermometer" and confirmed by measurements of homogenization temperatures of gaseousliquid inclusions, is indicative of hydrothermal activity. The other disputable question is the temporal relationship between these dolomites and surrounding limestones, i.e. whether dolomitization occurred at the synsedimentary-early diagenetic stage within the Devonian-Carboniferous basin (Migaszewski 1990, 1991) or later at the epigenetic stage during the Variscan orogeny (Narkiewicz, 1991).



Fig. 7. A triangle-shaped outcrop of the dolomite chimney (dashed line) on the southern wall of the western deepest pit; lateral fault (solid line) outlines the western contact of dolomites with surrounding limestones (western fault side is downthrown about 10 m)

The Wietrznia reserve is also the right place for studying karstification of limestones and marls. This process has been facilitated by strongly faulted and fissured rocks. These enable migration of rainwater into the bedrock. There are numerous ancient and recent karstic forms in the central and eastern parts of the quarry (Urban 1996; Stupnicka, Stempień-Sałek 2006; Złonkiewicz 2009), including karrens, cracks, fissures, voids, pipes, sinks, avens and caves (Figs. 6, 8). The biggest cave reaching about 60 m long is located in the Międzygórz pit (Fig. 8). In the Międzygórz Wschodni pit a fragment of karst ravine or karst funnel has been preserved. Most of these karstic forms and tectonic fissures are filled with internal sediments (claystones, siltstones, terra rosa, flowstones) and rock debris, including karstic breccias. The red color derived from iron oxides and hydroxides is indicative of weathering in a tropical climate. They are dated primarily at the Late Permian – Early Triassic and partly at the Paleogene or Pleistocene and Holocene (Urban 1996; Złonkiewicz 2009).



Fig. 8. Various forms of karstification in the central (Międzygórz) pit; entrance to the cave is located in the thickets to the right

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Field session



MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Tour of Romanesque Cistercian abbey in Wąchock and Neolithic Flint Mine at Krzemionki

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(1) Romanesque Cistercian abbey in Wąchock

The Cistercian abbey in Wąchock is the best preserved Romanesque cloister in Poland (Fig. 1). This building complex lies in the northern part of the Świętokrzyskie province.



Fig. 1. Cistercian Abbey in Wachock

The abbey was founded in about 1179 by the Cracow bishop Gideon who brought a master builder Simon from Italy. He started building a three-nave basilica with a transept and a presbitary with side chapels. The outer walls were faced with a two-color yellow and redbrown) sandstone. In the 15th century the church was rebuilt in the Gothic style and in the 16th century an abbot palace was added to the building complex. In the forties of the 17th century the cloister was converted into the baroque style by adding two corner towers in the western wing and a high tower in the central part. The cloister was inhabited by Cistercian monks who came from the Burgundian abbey in Morimond (France). The order was suppressed in 1819, and the church was taken over by the local parish whereas the cloister became the seat of the Mining Office. Cistercians returned to the cloister in 1951.

There are numerous architectural elements preserved from the former cloister, including armarium (strongroom), chapterhouse, fraternia (room of common work), solitary confinement cells, garth in the eastern wing, dormitorium on the second floor, and refectory with rich Romanesque stonework (Fig. 2).



Fig. 2. Refectory with rich Romanesque stonework

(2) Neolithic Flint Mine at Krzemionki

Krzemionki, also known as Krzemionki Opatowskie, is an archeological reserve that encompasses Neolithic complex of striped flint mines (Krukowski 1939; Rajewski 1971; Węgrzynowicz, Miśkiewicz 1972; Bąbel 1975, 2003; Michniak 1992). This site was discovered by the famous Polish geologist Jan Samsonowicz in 1922 (Samsonowicz 1923). The Krzemionki Reserve is located about 5 km north-east of Ostrowiec Świętokrzyski.

The striped flint (also named chert by geologists) was extracted during 3900–1600 BC (Fig. 3). At that time the Krzemionki area was one of the biggest flint mining centers in

Europe There are over 2700 shafts connected with a network of radial extraction drifts (Fig. 4). The average depth of drafts varied from 4 to 9 m, whereas extraction drifts were up to 0.7 m wide and 0.6 to 1.2 m high (Fig. 4). In some drifts safety pillars and remnants of propping were found. The walls of underground workings are in places covered with charcoal drawings.



Fig. 3. Complex chert nodule from the Krzemionki - Ożarów zone



Fig. 4. Underground workings at Krzemionki

The raw material was used for manufacturing various tools, but especially axes and chisels. Some remnants of flint tool workshops were discovered on the surface of mining field. There is a reconstruction of late Neolithic – early Bronze settlement located near the mining field. The tourist trail connects two mines and is about 465 m long.

The striped cherts occur in uppermost Oxfordian platy limestones. They form concretions and nodules varying from a few centimeters to 2 m across. In the Krzemionki mines, Michniak (1992) distinguished two chert subhorizons (Figs. 4, 5). Most chert concretions and nodules consist of concentrically arranged stripes showing white through grey and dark brown colors (Fig. 3). They are hard and massive, and built of nearly 100% authigenic crypto- and microquartz (Migaszewski et al. 2006; Migaszewski, Migaszewski 2008; Król, Migaszewski 2009).



Fig. 5. Simplified geologic profile of Krzemionki flint mine (Michniak, 1992)

Cherts, including those of the Holy Cross Mountains, belong to the most mysterious rocks, the origin of which still arouses much controversy among geologists in spite of many

studies that have been conducted throughout the world for decades. The cherts make up a large group of siliceous rocks that form in various geochemical environments – from sedimentary through igneous and metamorphic (Michniak, 1992; Pieńkowski, Gutowski 2004; Migaszewski et al. 2006 and references therein). According to the best documented lithologic, petrologic and isotopic studies carried out by Migaszewski and co-authors (e.g. Sharp et al. 2002; Migaszewski et al 2006), the Krzemionki cherts are of synsedimentary – early diagenetic origin, and were formed as a result of an episodic influx of SiO₂-rich fluids from submarine hot springs, and subsequent multistage processes of crystallization, dissolution (etching) and reprecipitation (cementation) of silica accumulations.

Compared to their equivalents in Poland and abroad, the Krzemionki cherts are highlighted by the most beautiful and unique pattern, which combined with possibility of obtaining lustrous polish make them invaluable raw material that has been sought after on the jewelry market (Fig. 6). The Holy Cross Mountain cherts are attractive not only for geologists and jewelers, but also for archeologists, due to the fact that they played a great role in the material culture of man in Poland and neighboring countries during the Paleolithic and Neolithic periods.



Fig. 6. Striped cherts are a precious raw material for manufacturing jewelry and decorative stone accessories (from authors' collection)

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