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Contemporary
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Editor of the series – Marek Michalik
Institute of Geological Sciences, Jagiellonian University
30-063 Kraków, Oleandry 2a, Poland
marek.michalik@uj.edu.pl

Editors of Volume 36:
Zdzisław M. MIGASZEWSKI and Agnieszka GAŁUSZKA
Geochemistry and the Environment Div., Institute of Chemistry, Jan Kochanowski University in Kielce

Technical Editors:
Agnieszka GAŁUSZKA
Zdzisław M. MIGASZEWSKI
Sabina DOŁĘGOWSKA
Geochemistry and the Environment Div., Institute of Chemistry, Jan Kochanowski University in Kielce

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The significance of environmental geochemistry

Environmental geochemistry is the study on the spatial and temporal distribution and cycling of chemical elements in the outer layers of the Earth, i.e. lithosphere, pedosphere, hydrosphere and atmosphere. The unique position of this discipline is enhanced by its principal objective – an assessment of an element impact on potential health to plants, animals and a man. Environmental geochemistry interweaves with a "sister" discipline environmental biogeochemistry, which is focused on biosphere – a zone of living and decaying matter. The element composition of plants, animals, and humans correlates with the Earth's structure, and life has evolved reflecting mineral and rock occurrences. Originally, geochemical investigations focused only on elements, but at present they also encompass man-made organics. These new chemicals influence both abiotic and biotic systems, and their carcinogenicity and genotoxicity is a concern. Of all the geosystems, the surface and underground waters are the most sensitive to chemical pollution.

Geochemical processes that take place in the environment are far more complex than chemical reactions triggered in laboratories. The chemical composition of final products derived from geochemical processes is often unknown. The main causes which are responsible for hypothetical chemical reactions in the environment include: (i) complex chemical composition of minerals and organic compounds, (ii) presence of colloids in all water and soil systems, (iii) widespread complexation and chelation in water systems, (iv) dynamic activity of microorganisms in all biosphere systems.

Water solutions are complex and unstable multi-phase systems. Hence, it is important to determine physico-chemical and biological parameters that influence mobilization, transport, deposition and remobilization of elements. A small change of pH and redox potential in a geochemical compartment may bring about unpredictable consequence for elements' mobility.

Environmental geochemistry represents the most holistic and interdisciplinary approach in environmental sciences. The significance of environmental geochemistry can be summarized by the sentence: no environmental strategy can exist until we completely understand geochemical and biogeochemical processes occurring at and near the Earth's surface. Moreover, it has found wide application in land use, natural resources and water management, land, post mining and water reclamation, biomining etc. The principal objectives of environmental geochemistry tend to move to biogechemistry, geochemistry of organics, environmental toxicology and medicinal geochemistry.

Zdzisław M. Migaszewski

Invited lectures

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Selected geochemical investigations of the US Geological Survey in Alaska

James G. CROCK[1], Bronwen WANG[2], Larry P. GOUGH[3], Robert EPPINGER[1], Richard WANTY[1]

[1]*US Geological Survey, Lakewood, CO USA; e-mails: jcrock@usgs.gov, eppinger@usgs.gov, rwanty@usgs.gov*
[2]*US Geological Survey, Anchorage, AK USA; e-mail: bwang@usgs.gov*
[3]*US Geological Survey, Reston, VA USA (retired)*

The US Geological Survey has a long history of geochemical investigation in Alaska. The majority of these studies have focused on mineral exploration, but environmental questions and problems have also been studied. The current trend of these studies is a multi-disciplinary approach utilizing a team of investigators which may include botanists, biologists, chemists, geochemists, geologists, and geophysicists. Many different sample media have been collected and analyzed for an ever increasing list of analytes. These media have included soils (individual horizons or depth composites), rocks, stream sediments (Crock et al. 2007), vegetation, (vascular and non-vascular) (Crock et al. 1992a,b; Migaszewski et al. 2009), fauna (tissue separates and whole organisms) (Gough et al. 2004), and water. As analytical geochemistry has advanced, more analytes (both inorganic and organic) are being examined at lower and lower concentrations. New instrumental and dissolution techniques have been applied to study novel elemental isotopic ratios and speciation of inorganic analytes. This presentation will present current examples of these multi-disciplinary studies, with an emphasis on environmental studies. Examples will include baseline/background investigations used for predevelopment assessments of power plants and mining operations, anthropogenic effects on national parks, and geochemical signatures used for fingerprinting wildlife (Gough, Crock 1997; Gough, Day 2010; Wang et al. 2007)..

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Current issues in establishing geochemical background of trace elements

Agnieszka Gałuszka[1], Zdzisław M. Migaszewski[1]

[1]*Geochemistry and the Environment Division, Institute of Chemistry, Jan Kochanowski University, 15G Świętokrzyska St., 25-406 Kielce, Poland; e-mail: agnieszka.galuszka@ujk.kielce.pl, zmig@ujk.kielce.pl*

When considering the history of establishing geochemical element background, a shift from mineral deposit prospecting to solving various environmental issues has been observed. A rapid industrial and civilization development that took place in the second half of the 19th century imposed an introduction of new methods in geochemical prospecting for ore mineral deposits. In exploratory geochemistry a geochemical background has simply been understood as a lack of an anomaly (Hawkes, Webb 1961). The issue of geochemical background emerged again in the latter half of the 20th century with a growing concern of environmental pollution and in searching for the best tool to assess the environment quality. As a result of this different approach, a new meaning was added to the idea of background concentrations of trace element pollutants. In environmental geochemistry the term geochemical background can be defined as "*a theoretical 'natural' concentration of a substance in a specific environmental sample (or medium), considering the spatial and temporal variables*" (Gałuszka 2006). Current issues in establishing geochemical background of trace elements focus mostly on the methodology. The principal issue is how to define and calculate the element background concentrations in relation not only to local pollution sources, but also to more complex processes of long-range transport of pollutants (Reimann, Garret 2005).

There are three methods of establishing geochemical element background: (1) direct (geochemical), (2) indirect (statistical) and (3) integrated (Matschullat et al. 2000; Reimann et al. 2005; Gałuszka 2007). In the geochemical method the background concentrations are measured in samples representing various compartments of natural environment. Two aspects can be considered here: (1) historical (samples are dated or collected as representing pre-industrial period) and (2) contemporary (samples are collected in pristine areas). Statistical approach uses different computational and graphical techniques, which aim at eliminating the outliers from the distribution of statistical population (results obtained). The most common among them are: (i) calculated distribution function, (ii) iterative 2-σ technique, (iii) 4-σ outlier test, (iv) box plots, (v) empirical cumulative distribution function etc. (Matschullat et al. 2000; Reimann et al. 2005). Integrated approach to geochemical background assessment combines both the prerequisite for collecting the samples in relatively pristine areas, and subjecting the results to statistical calculations.

The weak point of both direct and integrated methods lies within subjectivity of selection of pristine environment. The distinction between anthropogenic influence and natural sources of a given substance is a very hard and ambitious task (Reimann, deCaritat 2005). Different additional studies (mineralogical, isotopic, geophysical) may be helpful in making geochemical and integrated methods credible. On the other hand, the statistical approach also has its drawbacks because it requires data processing and an assumption that background concentrations are not represented by the outliers. However, the definition of geochemical background as non-anomalous concentrations of substances is valid only in exploratory geochemistry.

Establishing geochemical background of trace elements is very important for environmental legislation, land-use management, environment- and issue-oriented geochemistry because it helps to decide what level of an element concentration may be regarded as pollution. The critical levels of pollutants may be crucial, for example, in proposing soil quality criteria (Baize, Sterckeman 2001; Crommentuijn et al. 2000). The geochemical background of toxic pollutants is also very important in land reclamation and for forensic purposes for solving cases of environmental crimes (e.g. Costa, Sauer 2005). All these new emerged applications of geochemical background concentrations suggest that this issue needs serious scientific consideration. For the reason that the concept of background concentrations was first put forward by geochemists, they should also be involved in the future studies of this crucial issue.

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Biogeochemistry of trace elements – environmental issues

Alina KABATA-PENDIAS[1]

[1] *Institute of Soil Science and Plant Cultivation – State Research Institute, 8 Czartoryskich St., 24-100 Puławy, Poland; e-mail: akp@iung.pulawy.pl*

Recent and continued development of instrumental methods used for determination of trace elements (TEs) resulted in a rapid increase of data on their concentrations in environmental samples. However, the behavioral properties of TEs in a given environmental compartment and their variability under anthropogenic impact are still not fully understood.

Soil is usually the primary and the most important source of TEs in the food chain. Therefore, having soils with proper TE status is a prerequisite for the production of good (healthy) food. A better understanding of the behavior of TEs in multiphase and dynamic soil systems is presently recognized to be of great significance.

Increased TE contamination due to industrial and urban wastes, agricultural practices and aerial deposition have frequently had harmful impacts on the soil chemical balance, and on TE contents, in particular. Behavioral properties of TEs and variable physical and chemical soil conditions have affected various TE phytoavailability. This is a crucial problem in ecological risk assessment for soils with deficient or excessive TE content, especially for the production of 'healthy crops'.

The behavior of TEs in soils is related to their origin (lithogenic, pedogenic, anthropogenic) and forms. Processes at soil-solution-root interfaces greatly influence the solubility and phytoavailabilty of TEs. These processes and the impact of mezo- and microbiota should be better understood.

There is still not enough knowledge about the behavior of many TEs. A great number of data, both on concentration and behavior, are now available for: As, Cd, Cu, Hg, Mn, Ni, Pb and Zn. Less information is available for: B, Cr, Mo, and Se. We know very little about platinum group metals, lanthanides and actinides. Also the distribution and behavior of some radionuclides should be known better. The balance of TEs in cropped farm soils is still not well known. Some calculations for the EU countries (AROMIS database 2005; Eckel et al. 2005) are as follows (the highest values, in g/ha/yr): Cd, 4.4; Cr, 100; Cu, 347; Ni, 33; Pb, 193; and Zn 838. Almost all these values are reported for France, but the Cu value is for Germany.

Several critical values have been established to estimate and control a proper TE concentration in farm land soils; e.g.: GB – Geochemical Baseline, GD – Geochemical Distribution, IPD – Index of Pedogenic Distribution, PEF – Pedochemical Enrichment Factor, MAC – Maximum Allowable Concentration, TAV – Trigger Action Value. These values, however, should be adjusted to soil types and crop kinds. Recently, various values of TAV for agricultural soils are proposed in the EU countries. These values range as follows (in mg/kg): Cd, 2–10; Cr, 50–450; Cu, 60–500; Ni, 75–150; Pb, 50–300; Zn, 200–

1500. The broad ranges of these values indicate that each agroecosystem should be evaluated in order to produce a risk assessment.

There is still a need for a better understanding the complex reactions existing between the geochemistry of the environment and the health of plants, animals, and humans.

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Recent geochemical investigations at the U.S. Geological Survey

Paul J. LAMOTHE[1], Alan KOENIG[1], Richard WANTY[1], David BORROK[2]

[1]_U.S. Geological Survey, Denver CO 80225, USA; e-mails: plamothe@usgs.gov, akoenig@usgs.gov, rwanty@usgs.gov_
[2]_University of Texas, El Paso, TX 79968, USA; e-mail: borrok@geo.utep.edu_

Exciting new fields of geochemical research have been made possible with the advent, and continued development, of modern instrumentation for the chemical analysis of geological samples. The primary achievements of these advances in geochemical analytical instrumentation have been the ability to determine an ever increasing variety of elements and their isotopes at lower detection limits on increasingly smaller samples. Additionally, some of this instrumentation has been made in handheld portable versions that enable research scientists to obtain real-time measurements of environmentally sensitive elements at remote locations in the field. This presentation will give some examples of recent geochemical investigations that have been untaken with the aid of these novel analytical tools.

One investigation that has been aided by the use of a handheld portable X-ray fluorescence (XRF) analyzer involves the determination of arsenic contamination in river sediments that have resulted from the dumping of mine tailings from a gold mine into a tributary of the Belle Fourche River in South Dakota, USA. The gold ore was associated with the mineral arsenopyrite (FeAsS) and more than 2000 metric tons of As-rich tailings were dumped into the river system daily for 100 years during the peak of mining operations. Recent flood events have widened the main river channel and remobilized some of the legacy mine tailings. The purpose of the project is to characterize and quantify the volume and rate of change of contaminated sediments in this river system. The use of the portable XRF instrument enabled us to delineate arsenic-rich sediment strata which were then sampled for further laboratory analyses.

Another investigation of environmental impacts linked to mining related activities dealt with base metal inputs to an alpine watershed from acid rock drainage sources. The use of a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) in conjunction with field tracer injection experiments enabled the investigators to determine Fe and Zn isotopic signatures and relate them to redox, precipitation, and mixing reactions occurring in the stream. This investigation suggested that Fe and Zn isotopes could be useful for distinguishing between anthropogenic and natural metal loading sources to the watershed, as well as helping to understand in-stream geochemical processes that impact metal transport.

The development of laser-ablation ICP-MS (LA-ICP-MS) instruments coupled with the rapid improvement in UV laser designs has fostered the study of biological systems that are often impacted by geochemical and environmental processes. One such study involves the chemical analysis of tiny bones in the ears of fish using the LA-ICP-MS technique. These bones, called otoliths, grow in concentric rings similar to the growth rings in a tree. The otoliths acquire a growth ring every day for the first 6 months of a fish's life and they contain a fingerprint of the water chemistry wherever the fish swims. This chemical signature can then be used to determine the migration pathways of the fish. These signatures have implications for establishing marine protected areas and for settling international fisheries disputes.

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Contributions

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Dissolution of lead arsenates promoted by organic acids

Tomasz BAJDA[1], Maciej MANECKI[1]

[1]*Department of Mineralogy, Petrography and Geochemistry, Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, 30 Mickiewicz Ave, 30-059 Krakow, Poland; e-mails: bajda@geol.agh.edu.pl, gpmmanec@cyf-kr.edu.pl*

Arsenic and lead are widespread environment contaminants of significant concern for both human and ecosystem health. Secondary arsenate minerals can control the concentration of As and Pb when their amount exceeds the capacity of the available surface ligand-bonding sites and the concentrations of dissolved ions. Minerals containing lead and arsenate are relatively numerous, but rare in nature. Among them, schultenite $PbHAsO_4$ and mimetite $Pb_5(AsO_4)_3Cl$ are probably the most common secondary lead arsenate minerals. It is expected that under typical environment conditions schultenite would convert ultimately to mimetite (Papassiopi et al. 1999). To simulate the reactivity of mimetite in soil-like environments, this research is focused on batch leaching experiments in low-molecular-weight organic acid solutions (LMWOAs: acetate, lactate, citrate) at concentrations relevant to rhizospheric soil solutions. The goal of this study is to determine how LMWOAs influence the dissolution of mimetite and how they affect the release/mobility of lead and arsenate in the soil.

Batch experiments were designed to observe aqueous As and Pb concentration patterns resulting from mimetite dissolution in the presence of acetic, citric, and lactic acids at various concentration (0–20 mM) and pH values (2.5–6.5). The results of an *in situ* atomic force microscopy (AFM), *ex situ* AFM, scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction were combined with previous macroscopic investigations to characterize mimetite reaction with LMWOAs.

The effect of pH on the solubility of mimetite in the presence of LMWOAs was also studied. An organic acids concentration of 0.5 mM/L was selected because this is an imaginary boundary between the typical value of the acid concentrations in soil solutions (up to 0.5 mM) and in the cytosol (0.5–10 mM) (Jones 1998). The apparent solubility of mimetite, calculated on the basis of Pb and As(V) released to solutions, depends on the pH and is higher in strongly acidic (2.5–3.5) and much lower in weakly acidic (4.5–5.5) and neutral solutions (6.5). The abilities of anionic ligands to enhance mimetite dissolution at the same concentration, arranged in decreasing order, are citrate > acetate ≥ lactate.

The results of the experiments performed at the pH range from 2.5 to 6.5 indicated that the effect of organic acids on mimetite dissolution is most pronounced at the pH value between 3.5 and 5.5. To assure maximum sensitivity, the experiment with variable LMWOAs concentrations was run at the pH = 3.5. The dynamics of the concentration of Pb and As(V) in suspension of mimetite and organic acids depended on the type and concentration of organic acids and duration of the experiment. At the initial stage of dissolution of mimetite, less Pb and As(V) was released, whereas the amount of Pb and As(V) in solution increased with time. Mimetite dissolution was dependent on the type of organic acid used. It was found that citric acid enhances mimetite dissolution to the greatest extent. The difference in the amount of released Pb is caused by two factors: system pH and ability of the organic anion to complex with Pb.

The amount of Pb and As(V) released to the solution increases with increasing concentration of organic acid. The total concentrations of both Pb and As(V) were up to 1.5, 2.0, and 5.0 times greater in reaction mixtures containing acetate, lactate and citrate, respectively, than in the control samples containing inorganic nitric acid at a similar pH. The evolution of Pb and As(V) concentrations versus time showed that the process of mimetite dissolution consists of at least three stages, i.e. steadily dissolving stage, approaching equilibrium stage, and standing equilibrium stage. At the concentration between 5 and 20 mM citric acid solutions, the equilibrium was attained after 772 h, whereas in the experiment with 20 mM acetic and lactic acid the standing equilibrium stage appears after 4 h.

It has been suggested that proton- and organic ligand-promoted mechanisms act simultaneously but do not compete with each other and are thus additive. The ligand-promoted dissolution rate R_L can be obtained by subtracting the proton-promoted rate R_H from the total dissolution rate R_{LH}. The anionic ligands chosen in the experiments possess different abilities to complex Pb. The complexing constants with Pb show that citrate is the strongest, followed by acetic acid, and lactic acid is the weakest. Assuming that only anionic ligands controlled mimetite dissolution, the rate order of mimetite dissolution enhanced by the three kinds of chosen organic acids should be as follow: citric acid > acetic acid > lactic acid.

The different erosive character of the acids found for Pb and As(V) dissolution was illustrated by the atomic force microscopy evaluation of acid treated mimetite single crystals. A strong correlation between mineral loss and the type of acid was found for citric acid.

This work was supported by the Ministry of Science and Higher Education grant no. 18.18.140.753.

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Late Cretaceous tuffs from the Hateg basin, South Carpathians, Romania: constraining intrabasinal correlation

Ana-Voica BOJAR[1, 3], Stanislaw HAŁAS[2], Hans-Peter BOJAR[3], Dan GRIGORESCU[4]

[1]*Department of Geology, Salzburg University, Salzburg, Austria; e-mail: ana-voica.bojar@uni-graz.at*
[2]*Mass Spectrometry Laboratory, Institute of Physics, Lublin, Poland; e-mail: stanislaw.halas@umcs.lublin.pl*
[3]*Department of Mineralogy, Universalmuseum Joanneum, Graz, Austria; e-mail: hans-peter.bojar@museum-joanneum.at*
[4]*Department of Paleontology, Bucharest University, Romania; e-mail: dangrig84@yahoo.com*

Geological setting

The South Carpathians extend from the Prahova Valley in Romania to the Timoc Valley in Serbia. To the south, this mountain chain borders with foreland sediments of the Moesian Platform and to the north with the Transylvanian Depression. During the Late Cretaceous time, along the Carpathians, Apuseni and Eastern Alps, sedimentation continued atop the upper plate, in the so called "Gosau type" basins, which had been formed as a result of syncollisional extension. The facies association of the Cretaceous Gosau deposits may vary from terrestrial alluvial to turbiditic sediments spanning stratigraphically the Upper Turonian to the Maastrichtian.

Two different continental formations of Maastrichtian to early Paleogene age are known: the Densuş–Ciula and the Sânpetru Formations. The Densuş–Ciula Formation crops out in the north-western and central part of the basin and is divided into three members with a total thickness of around 2 km. The lower Densuş–Ciula member contains lacustrine marls with volcanoclastics, lying discordantly on the uppermost Campanian flysch deposits (Grigorescu, Melinte 2001; Barzoi, Seclaman 2010). The middle Densuş–Ciula member comprises matrix-supported conglomerates, cross-bedded sandstones and massive red mudstones.

The Sânpetru Formation crops out mainly along Râul Mare and Sibişel valleys, on the central and southern border of the basin. The Maastrichtian age of the middle Densuş–Ciula member and Sânpetru Formation is constrained by freshwater gastropod assemblages, palynology and paleomagnetic data. Paleomagnetic studies were done for the Sibişel Formation, but not for the Densuş–Ciula Formation. As for the last formation, the paleomagnetic signal is disturbed and displays no consistent results (Panaiotu, Panaiotu 2010). Bojar et al. (2010) found in the heavy mineral fraction of the Densuş–Ciula Formation high amounts of magnetic hematite (up to 40%) with tabular crystallographic forms that disturbed the primary magnetic signal.

In order to correlate these two formations, we separated and dated biotites that occur in two tuff layers within the Densuş–Ciula Formation, using the K-Ar method.

Results

The contents of K were determined by thermal isotope mass spectrometry (TIMS) using the isotope dilution technique as described by Hałas (2001). Radiogenic argon concentration (^{40}Ar*) was determined on the instrumental set-up of the Mass Spectrometry Laboratory. The analytical results are presented in table 1.

Table 1. K/Ar dates of the samples examined

Mineral	K (%)	^{40}Ar* [pmol/g]	% ^{40}Ar*	Age ± 1σ [Ma]
AVROM204 biotite	5.70	718.4	52.6	71.3±1.6
RA 12 biotite	3.04	375.3	68.5	69.8±1.3

Discussion

Paleomagnetic studies (Panaiotu, Panaiotu 2010) indicated that the sequence along the Sibişel valley (Sânpetru Formation, southern-central part of the basin) had been deposited between the chron 32n.1 and the end of the chron 31n. Using the correlation between paleomagnetic chrons and absolute ages, the sequence along the Sibişel valley was deposited between approx. 71 to 67.8 Ma. The K-Ar dating of unaltered biotites from two tuff layers, which occur at the base of the Densuş–Ciula Formation, gave ages of 71.3±1.6 and 68.5±1.3 Ma, respectively, thus indicating that these two formations were almost coeval.

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Uptake of arsenates by peat

Zhamilya BOPUROVA[1], Piotr JEZIERSKI[2], Adam JEZIERSKI[3]

[1]*S. Amanzholov East Kazakhstan State University*
[2]*Laboratory of Isotope Geology and Geoecology, Institute of Geological Sciences, Faculty of Earth Sciences, University of Wrocław, 30 Cybulskiego St., 50-205 Wrocław, Poland; e-mail: piotr.jezierski@ing.uni.wroc.pl*
[3]*Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie St., 50-383 Wrocław, Poland; e-mail: adam@wchuwr.pl*

The uptake of various anionic forms of arsenic(III and V) is one of the most important environmental problems. Clays, metal hydroxides and humic substances may exhibit the sorption properties. The principal objective of this study was to present the properties of peat enriched in humic acids that favor sorption of arsenate(V). We use standard analytical techniques as well as EPR (electron paramagnetic resonance spectroscopy). The last method is an important tool for investigating structural properties of humic substances, especially free radicals in their macromolecular matrix. The experimental g parameters and concentration of free radicals are a valuable source of our knowledge about properties of humic acids (contained in peats). This enables us to better understand the uptake of various anionic forms of arsenic. In addition, the peats were characterized by C and N stable isotope composition and C/N ratio.

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Trace element geochemistry in coals from the Southern Cantabrian Zone (NW Spain): preliminary results

Dariusz BOTOR[1]

[1]*Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, 30 Mickiewicz Ave, 30-059 Krakow, Poland*; *e-mail: botor@agh.edu.pl*

Trace elements occurring in coals contribute in a significant way to environmental pollution due to the large amounts of coal combusted (e.g. Querol et al. 1996; Ketris, Yudovich 2009). Most of the Spanish coal basins are located in the Cantabrian Mountains comprising above 70% of the total coal resources (Colmenero et al. 2008). Despite this, only a few studies have been performed on their origin and quality. The Cantabrian Zone represents a foreland belt of the Variscan Iberian Massif. It consists of the Precambrian basement covered by Paleozoic sediments. These were affected by intense thin-skinned tectonics, diagenetic to epizonal thermal events, and several episodes of fluid flow in the Carboniferous–Permian (e.g. Bastida et al. 1999). All the three coal-bearing basins examined are small intramontane structures located along the Sabero-Gordón fault line strike-slip systems of the Southern Cantabrian Zone (SCZ, Fig. 1). The Stephanian coal-bearing clastic sequences (up to 2500 m in thickness) rest uncomfortably over older rocks and were deposited in a pull-apart basins (e.g. Colmenero et al. 2008). The post-Variscan history was characterized by a long period of non-deposition and erosion until the Cretaceous sedimentation (to 800 m) occurred in the area (e.g. Bastida et al. 1999).

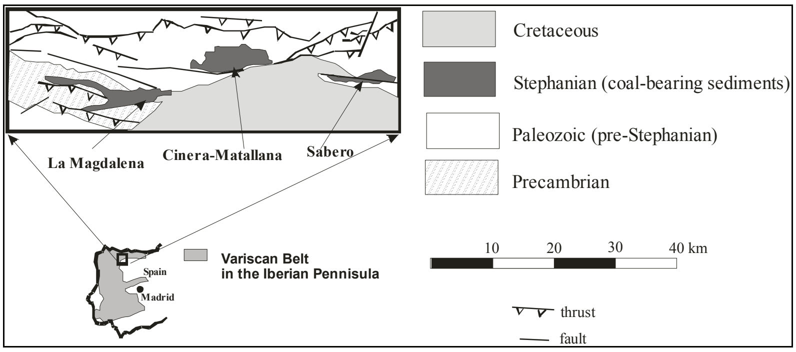

Fig. 1. Simplified geological map showing the location of the analyzed coalfields in the Southern Cantabrain Zone (NW Spain) (based on Bastida et al. 1999; Colmenero et al. 2008)

The Stephanian coal samples examined were collected from the following coalfields: La Magdalena, Cinera-Matallana and Sabero (Fig. 1). Over thirty elements were analyzed by the INAA technique. The sampled coals were crushed and pulverized to obtain homogenous samples suitable for the whole-rock analysis. The INAA analyses were performed in Activation Laboratories, Ltd. (Canada). In addition, some samples were investigated also by an EDS/WDS electron microprobe at Warsaw University. The average vitrinite reflectance values in the analyzed Stephanian coals of the SCZ are in the range of 0.72 to 3.96%. The vitrinite maceral group also predominates in all the coals with contents exceeding 72 vol. %. The coals examined are characterized by extremely variable mineral matter content as evidenced by microscopic examinations and variations in the ash content (A^d 7–42%). The mineral matter contains primarily clay minerals, carbonates and sulphides (Fig. 2).

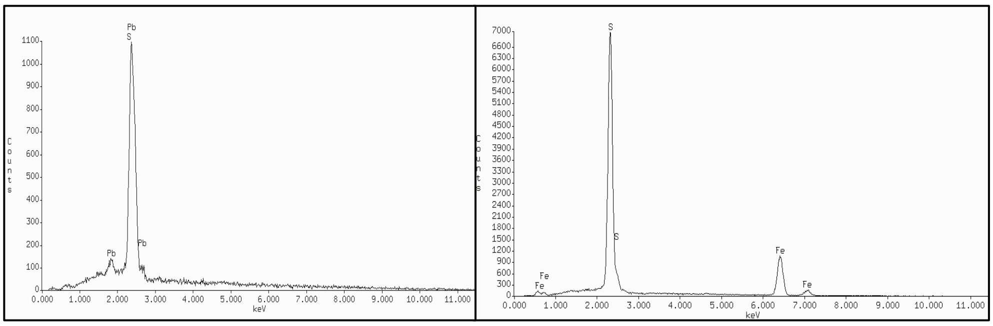

Fig. 2. The most frequent sulphide minerals contained in coals from the SCZ. EDS spectra of galena (left) and pyrite (right)

The coals of the study area exhibit medium to high concentrations of the following elements (Ketris, Yudovich 2009): REE (116 ppm), Ba (538 ppm), As (32 ppm), Zn (107 ppm), Cr (70 ppm), Rb (82 ppm), Co (12 ppm), Sc (9 ppm), Ce (56 ppm), Yb (2.5 ppm), Th (8 ppm) and U (5 ppm), and low concentrations of V, Hg (<1 ppm), Eu (1.2 ppm), Ta (<2 ppm), and a relatively high Th/U ratio (2.2). The LREE/HREE ratios are in the range of 24–44. In contrast, concentrations of Au, Ag, Ir, Se, Sn, Sr, and W are below detection limits of the applied technique. The chemistry of these coals is relatively similar to that of the related tonsteins at least in the Sabero coalfield (Botor 2005).

The concentrations of elements are significantly higher in ashed coal samples. These trace elements can be related to a fluid hydrothermal circulation in SCZ, especially in the areas of the deep-seated faults along the Sabero-Gordon line. The high thermal fluxes can be associated with the magmatic events (Bastida et al. 1999) that seem to have provided the necessary heat to accelerate the thermal evolution of coals in the SCZ up to anthracite coal rank.

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Methanogenic fermentation of lignite: preliminary results

Michał BUCHA[1], Oliwia BIENIEK[1], Katarzyna KUBIAK[2], Mieczysław BŁASZCZYK[2],
Mariusz-Orion JĘDRYSEK[1]

[1]*Laboratory of Isotope Geology and Geoecology, Institute of Geological Sciences, Faculty of Earth Sciences,University of Wrocław, 30 Cybulskiego St., 50-205 Wrocław, Poland; e-mail: morion@ing.uni.wroc.pl*
[2]*Department of Microbial Biology, Faculty of Agriculture and Biology, Warsaw University of Life Sciences, 159 Nowoursynowska St., 02-776 Warszawa, Poland*

The aim of these experiments was to determine the fermentation capacity of lignite under controlled conditions. The lignite samples were collected from the "Kazimierz Północ" Konin Mine deposit. Those with a grain size of <1 mm were placed in 500 ml glass bottles (M9 medium) with various mineral additives, and bacterial inoculum. The experiment was conducted for 30 days at 20°C. Eight variants of the experiment with different mineral additives, and control variant without inoculum were prepared. Gas produced during the fermentation was collected with a syringe whose needle was inserted through the rubber septum. The gas samples were analyzed by gas chromatography. The presence of hydrogen sulphide was confirmed by precipitation of silver sulphide with silver nitrate(V).

As a result of lignite fermentation depending on the experiment variant, a total of gas varying from 10 to 477 mL was obtained. The fermentation gas products contained methane, carbon dioxide, hydrogen sulfide and butyric acid. In seven out of the nine variants production of methane was observed. The maximum content of methane in the gas samples was 55%. Methane appeared about 20 days after the start of the experiment. In the final stage – about 30 days since the start, in 3 out of 9 cases, a decrease of oxygen and an increase of methane levels were noted. In the control sample there was no measurable methane production, which indicates that fermentation of broth was not present (Wise 1990).

The lignite fermentation experiments are being conducted at the Department of Applied Geology and Geochemistry of the Institute of Geological Sciences at the University of Wrocław in cooperation with the Department of Microbial Biology of the Faculty of Agriculture and Biology at the Warsaw University of Life Sciences. The gas samples obtained will be tested by mass spectrometry and the isotopic composition of carbon and hydrogen will be determined (Conrad 2005). The principal aim of this study is to identify pathways of methanogenesis and to develop effective production methods of methane and hydrogen from lignite (Catcheside et al. 1999).

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Quantitative and qualitative differentiation of dissolved inorganic carbon in a groundwater zone at Wygnanowice (Giełczew Upland, SE Poland)

Stanisław CHMIEL[1], Stanisław HAŁAS[2], Sławomir GŁOWACKI[1], Andrzej TREMBACZOWSKI[2]

[1]*Department of Hydrography, Maria Curie-Skłodowska University, 19 Akademicka St., 20-033 Lublin, Poland; e-mails: stanislaw.chmiel@umcs.lublin.pl, slawek.glowacki@umcs.lublin.pl*
[2]*Mass Spectrometry Laboratory, Institute of Physics, Maria Curie-Skłodowska University, 1 M. Curie-Skłodowska Sq, 20-031 Lublin, Poland; e-mails: stanislaw.halas@umcs.lublin.pl, andrzej.trembaczowski@umcs.lublin.pl*

During the water cycle from atmosphere to aquifers, waters are enriched in dissolved inorganic carbon (DIC). The basic source of DIC in groundwater is dissolved carbon dioxide ($CO_{2(aq)}$) generated in soil, whereas HCO_3^- and CO_3^{2-} ions are primarily produced by dissolution of carbonate minerals, predominantly calcite and dolomite. Knowledge of DIC composition ($CO_{2(aq)}$, HCO_3^-, CO_3^{2-}) and carbon isotope ($^{13}C/^{12}C$) ratios may be significant in the study of water flow in the underground medium, estimation of directions of pollutant flow and also in interpretation of anomalous values of some geochemical indices (Szynkiewicz et al. 2006).

The purpose of this study is to determine concentrations of DIC and its $^{13}C/^{12}C$ ratios in shallow groundwater sampled from the spring at Wygnanowice village near Piaski town. The spring belongs to the catchment area of the Giełczew River. At the sampling site a probe (closed polyethylene tube) for soil air sampling at a depth of 0.3– 0.9 m and two probes for soil water sampling (Macro Rhizon type), at depths of 0.3 and 0.9 m were used.

The water samples were collected from the spring discharged from a shallow aquifer located within Quaternary permeable dusty sands. The yield of this spring was relatively low ($Q < 1$ L/s). In addition, the water samples were collected in the spring discharged from the main aquifer that occurs in Cretaceous carbonate rocks. The spring yield (Q) was about 5 L/s after rubble had been removed.

The investigations were preformed in 2010. The water samples for DIC analysis were sampled monthly, whereas the $\delta^{13}C$ in soil CO_2 and in DIC of spring waters were analyzed every 3 months. The CO_2 concentration in soil was analyzed monthly with the MultiRAE portable instrument.

The DIC was calculated as a sum of inorganic carbon species from total alkalinity ($HCO_3^- + CO_3^{2-}$) determined by the titration method and from concentration of dissolved free CO_2, which was determined with Oxyguard CO_2 Analyser. The carbon isotope ratio in soil CO_2 and DIC was determined mass spectrometrically as $\delta^{13}C$. The DIC concentration ranged from 15 to 25 mg/L in the soil water, where the molal fraction of $CO_{2(aq)}$ was about 1/3. The CO_2 concentration in the soil air was in the range of 0.3–1%, whereas the $\delta^{13}C$ averaged about -20‰.

The DIC level of the Quaternary spring water was 25–30 mg/L and almost 2/3 of all carbon species was in the form of $CO_{2(aq)}$, whilst the $\delta^{13}C$ of DIC was below -30‰. In the

Cretaceous spring water the average DIC concentration was about 50 mg/L and molal fraction of $CO_{2(aq)}$ was below 10%. In the soil air and water discharged from the Cretaceous aquifer the $\delta^{13}C$ of DIC was typical for the Lublin Upland area (Staniaszek et al. 1986; Dudziak 1995).

A low $\delta^{13}C$ value of DIC in the Quaternary spring water possibly resulted from the presence of organogenic formations in a drainage zone. They occur in the study area as fossil soils underlying the dusty sands (Harasimiuk et al. 1988).

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Sorption of phosphates and nitrates from aqueous solutions on halloysite clay

Kamil CZECH[1], Magdalena GARNUSZEK[1], Artur MICHALIK[1], Piotr SŁOMKIEWICZ[1]

[1]*Institute of Chemistry, Jan Kochanowski University, 15G Świętokrzyska St., 25-406 Kielce, Poland; e-mail: piotr.slomkiewicz@ujk.kielce.pl*

Halloysite minerals are ubiquitous in soils and mantle rocks, where they form a variety of particle shapes and hydration states. There are only three active mines of this raw material throughout the world, i.e. in the USA, New Zealand and Poland. The Polish halloysite clay is mined in the Dunino quarry near Legnica. The Polish deposit belongs to the largest in the world, supplying about 12 million tons of this raw material. In contrast to other clay minerals, halloysite is characterized by a much larger surface area and larger ion exchange capacity.

The halloysite is a two-layered aluminosilicate showing a hollow tubular structure. The alumina and silica layers curve and form multilayer tubes. This structural property gives the Dunino halloysite the distinct features:

- large surface area (60–500 m^2/g depending on the way of processing),
- large ion exchange capacity,
- chemical high resistance in a wide range of pH.

The sorption property of halloysite and its large porosity make this mineral useful for water and sewage treatment, especially for removing phosphorus and nitrogen, thus constraining biogeochemical circulation of these substances in the environment.

The adsorption process of nitrates and phosphates in water by halloysite was examined using different preparation methods of this natural sorbent:

- dried at temperature of 120˚C for 12 h,
- washed five times in distilled water and next dried at temperature of 120˚C for 12 h,
- activated in 25% sulfuric acid and next dried at temperature of 120˚C for 12 h,
- activated in 50% sulfuric acid and next dried at temperature of 120˚C for 12 h.

The nitrates were determined by the colorimetric method with nitrate salicylate, whereas phosphates by the colorimetric method using phosphate-molybdenic blue. The sorption of nitrates and phosphates by halloysite depended on the preparation methods of this sorbent, concentrations of nitrates and phosphates in water, and time of mixing. The yield of halloysite sorption in relation to concentrations of potassium nitrate and monobasic potassium phosphate for different preparation methods of halloysite is presented in figures 1 and 2.

The results of these experiments showed that the simple preparation methods of halloysite (drying and washing) enabled us to obtain a high sorption yield of nitrates and phosphates from water.

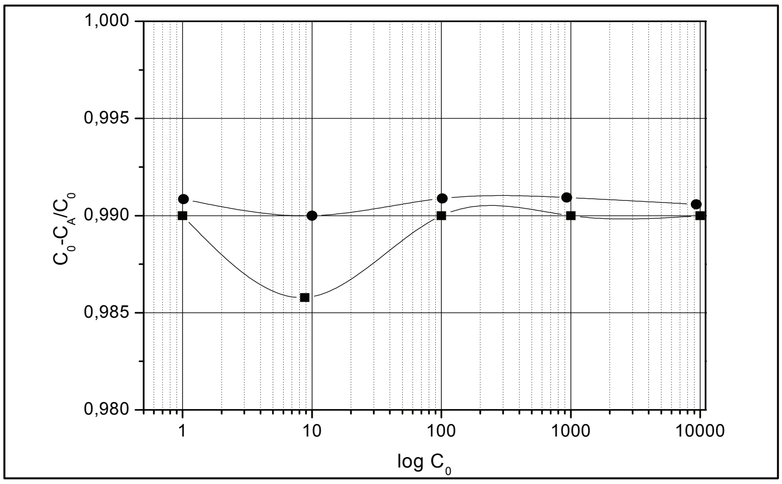

Fig. 1. The yield of halloysite sorption as a function of potassium nitrate concentrations (KNO_3) using different preparation methods of this sorbent

NOTE: C_0 – initial KNO_3 concentration

C_A – KNO_3 concentration in the presence of halloysite

■ – halloysite dried at 120˚C for 12 h

● – washed five times in distilled water and dried at 120˚C for 12 h

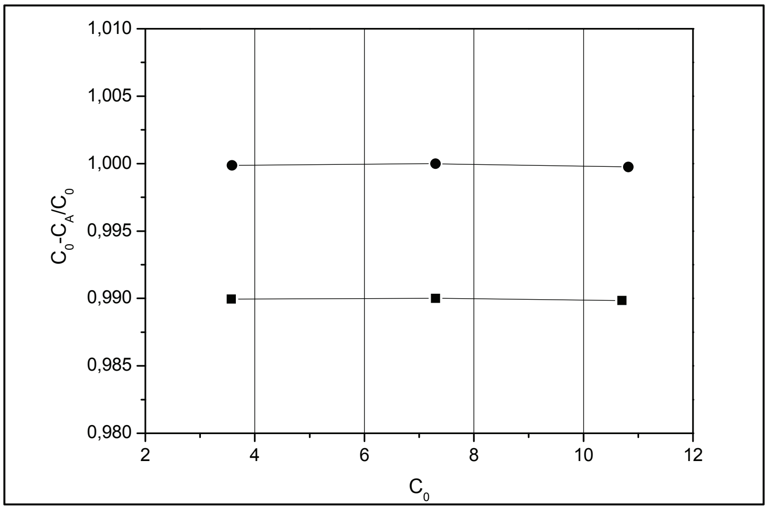

Fig. 2. The yield of halloysite sorption as a function of monobasic potassium phosphate (KH_2PO_4) concentrations using different preparation methods of this sorbent.

NOTE: C_0 – initial KH_2PO_4 concentration

C_A – KNO_3 concentration in the presence of halloysite

■ – KH_2PO_4 dried at 120˚C for 12 h

● – washed five times in distilled water and dried at 120˚C for 12 h

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Chemical properties of Łebsko and Dołgie Wielkie Lakes waters

Jolanta CZERNIAWSKA[1], Waldemar SPYCHALSKI[2]

[1]*Geoecology and Geoinformation Institute, Adam Mickiewicz University, 27 Dzięgielowa St., 61-680 Poznań, Poland; e-mail: jolczer@amu.edu.pl*
[2]*Department of Soil Science and Land Conservation, University of Life Sciences, 5 Szydłowska St., 60-656 Poznań, Poland; e-mail: spychal@up.poznan.pl*

Lakes located along the southern coast of the Baltic Sea belong to the unique features of the land and sea environment. The physical and chemical properties of waters of these lakes are modified primarily by river tributaries and marine waters. Łebsko Lake and Dołgie Wielkie Lake are situated in the central coast of Słowiński National Park. The study conducted in 2008–2009 encompassed analyses of water chemistry in the northern zone of these two lakes. The following ions were determined: chloride, bicarbonate, sulfate and sodium, potassium, calcium, magnesium, iron, manganese. Although the lakes examined are located at a short distance from each other, the results of chemical analyses revealed the presence of two different hydrogeochemical water types. The water of Lake Łebsko belongs to the sodium-chloride type. The chlorides constitute 53% to 64% of the total ion contents. The concentration of chloride ions was in the range of 170 to 1.270 mg/L. The chemical composition of the Łebsko Lake water is strongly influenced by marine waters that infiltrate the mouth of the Łeba River. In contrast, the Dołgie Wielkie Lake water represents a different hydrogeochemical (bicarbonate-chloride) type with significant levels of calcium and sodium. The bicarbonates constitute 42 to 62% of the total ion concentration, whereas chlorides 15 to 24%, respectively. In contrast, calcium ions make up 10% to 17% of the total dissolved ions, whereas sodium ions 7 to 12%. Dołgie Wielkie Lake has no connection with the sea, so the presence of chlorides in the lake water is surprising. It is interesting to note that the concentration of these ions is low and varied from 7.4 mg/L in January 2009 to 19.6 mg/L in November 2008. Based on the 2002–2003 study of several coastal lakes, Cieśliński (2004) indicated the lack of a dominant ion in the Dołgie Wielkie Lake water. Our study performed during 2008–2009 indicated that the specified hydrogeochemical types of waters in Łebsko and Dołgie Wielkie Lakes persisted throughout the observation period. No distinct variation in the ratio of the dominant ions was observed during the monitoring period.

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The use of the soil subhorizon-Ofh for assessing environment quality in the Kielce area, south-central Poland

Sabina DOŁĘGOWSKA[1], Zdzisław M. MIGASZEWSKI[1]

[1]*Geochemistry and the Environment Division, Institute of Chemistry, Jan Kochanowski University, 15G Świętokrzyska St., 25-406 Kielce, Poland; e-mails: sabina.dolegowska@ujk.kielce.pl, zmig@ujk.kielce.pl*

Geoindicators are used for identifying geologic processes and assessing changes in the environment and effects of these changes (Berger 1998). The geoindicators encompass abiotic elements, e.g. sediments, speleothems, groundwaters or erosional features. Of the different geoindicators, soils, but especially topsoils (horizons-O and -A), are commonly used as geoindicators of anthropogenic pollution in the environment (Higgins, Wood 2001). Due to the presence of a large amount of chelating and adsorbing organic matter, topsoils are characterized by exceptionally high adsorbing capacity that enables fixing numerous trace elements and polynuclear aromatic hydrocarbons. These physicochemical properties enable us to establish concentration ranges and an assessment of the mobility of elements and organics within soil profiles and their apparent impact on the chemistry of plants.

The main objective of this study was to examine accumulative properties of the fermentative-humic (Ofh) subhorizon compared to the mixed humic-eluvial (AE) horizon. The previous studies implied that concentrations of polynuclear aromatic hydrocarbons (PAHs) and selected trace elements (Hg, Pb) in the Ofh subhorizon correlated with those in the atmosphere, and therefore, it could be used as a potential geoindicator of environmental quality (Migaszewski et al. 2001, 2002; Gałuszka 2005; Migaszewski, Gałuszka 2008). The Ofh subhorizon consists of organic matter (humic and fulvic acids, humins), clay minerals, and Fe, Mn, Al oxides and hydroxides. It is also a geochemical barrier for volatile and semivolatile organic and metaloorganic compounds which are moved upward from the bottom soil horizons. These properties are responsible for higher concentrations of elements and organic compounds in this subhorizon because most of them are immobilized by sorption and complexation.

The biogeochemical study was conducted in the Kielce region during 2007–2009 (Fig. 1C). For the purpose of this study, 10 soil samples weighing about 0.5 kg each were collected from the Ofh subhorizon and the AE mixed horizon (1A,B). The soil samples were analyzed for 17 PAHs and 33 elements by gas chromatography with mass spectrometer detection (GC-MS) and inductively coupled plasma mass spectrometry (ICP-MS), respectively.

The total PAH content in the Ofh subhorizon varied from 1864 ppb (μg/kg) at site 4 to 3019 ppb at site 3, whereas in the AE horizon from 37 ppb at site 4 to 848 ppb at site 3. In contrast to the AE horizon, the Ofh subhorizon was enriched in all the PAHs determined. Of the 17 individual aromatic hydrocarbons, fluoranthene and pyrene (in 2008), and fluoranthene and fenanthrene (in 2007) prevailed in the Ofh subhorizon and AE horizon. The comparison of hydrocarbons with a different number of benzene rings in a molecule revealed that in all the soil samples examined 4-ring hydrocarbons predominated. The comparison of PAH levels at sites 1 and 4 in 2007 and 2008 showed that the concentrations of hydrocarbons increased, but the ring sequence (4>5>3>6) remained unchanged.

Compared to the AE horizon, the Ofh subhorizon was enriched in Cd, Co, Cr, Cu, Fe, Hg, Mo, Ni, Pb, V and Zn. However, the geogenic elements: Ba, Ce, La and Nd predominated in the AE horizon. The results were similar to those obtained in 2007.

The geochemical studies of soils performed in the Holy Cross Mountains (Wymysłów, Psarska Mt.) during 1998–2003 also showed that the Ofh subhorizon was abundant in Hg, Pb and PAHs compared to the underlying horizons (Migaszewski et al. 2001, 2002). This adsorbing capacity makes the Ofh subhorizon a potential indicator for monitoring the spatial and temporal variability in the atmospheric deposition of organic compounds and trace elements. The Ofh subhorizon is especially suitable geoindicator for light soils depleted in many trace metals.

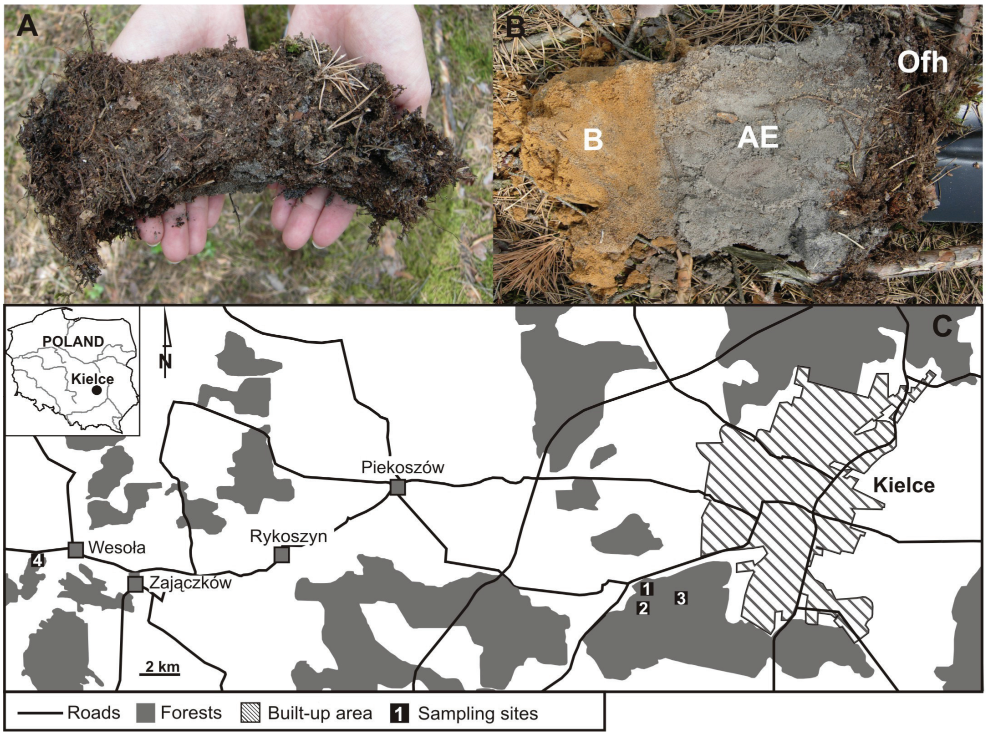

Fig. 1. A – subhorizon-Ofh; B – horizons-B and -AE and subhorizon-Ofh; C – Localization of investigation sites in the Kielce region

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Chemical composition of sediments from two small oxbow lakes near Warsaw (Poland) as an effect of human influence

Luiza GALBARCZYK-GĄSIOROWSKA[1], Michał GĄSIOROWSKI[2]

[1]*Institute of Geochemistry, Mineralogy and Petrology, Faculty of Geology, Warsaw University, 93 Żwirki i Wigury Ave, 02-089 Warszawa, Poland; e-mail: legalbar@uw.edu.pl*
[2]*Institute of Geological Sciences, Polish Academy of Sciences, 51/55 Twarda St., 00-818 Warszawa, Poland; e-mail: mgasior@twarda.pan.pl*

The chemical composition of short sediment cores from two small oxbow lakes located in the Vistula valley near Warsaw (Poland) was studied. The cores were dated using the ^{210}Pb method. These analyses showed that the collected sediments (60 cm and 67 cm long cores) were deposited during the last 150-200 years. The major elements, i.e. Ca, Mg, K, Na, Al, Ti, Cu, Zn, Mn, Fe, S, and P, were determined by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP–AES).

The chemical composition of sediments, i.e. increasing concentrations of elements related to mineral fraction (Al, Fe, K, and Cu) and low concentrations of P and S, allowed us to identify several great flood events in the Vistula basin during the 19th century (1813, 1844, and 1888/89) and the first half of the 20th century (1924, 1934, and 1947). The increase in phosphorus and sulphur concentrations indicates that the construction of dikes against flood has been a major factor inducing eutrophication of the oxbow lakes since 1920s. This study shows that the Warsaw small water bodies are especially sensitive to local disturbances caused by human activity, mainly water management, land-use changes, and agriculture.

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Paleoecology of the Miocene brown coals from the Chłapowo Cliff in Władysławowo, northern Poland

Małgorzata GDAŃSKA[1]

[1] *Geochemistry, Mineralogy and Petrography Department, Faculty of Earth's Sciences, Silesian University, 60 Będzińska St., 41-200 Sosnowiec, Poland; e-mail: mgdanska@gmail.com*

The Chłapowo Cliff, situated on the Swarzewo morainic plateau, is built of glacial and fluvioglacial deposits. Some parts of the cliff comprise exposed Miocene sediments with brown (*US* subbituminous) coal interbeds. The origin of brown coal deposits has not been strictly elucidated. Two alternative theories were proposed. The first one is that all Miocene sediments in the Chłapowo Cliff were formed *in situ* in a stratigraphic continuity of Paleogene sediments (Czochański et al. 2007; Wagner 2007). According to the second theory, the Miocene sediments in the Chłapowo Cliff are a glacial erratic slab. This may elucidate a distinct morphological diversity of the Neogene sediments, assuming original horizontality and stratigraphical sequence of Neogene and Pleistocene sediments (Wagner 2007). The aim of this study was to determine the origin and characteristics of organic matter of the Chłapowo Cliff lignites. Fourteen samples of brown coals were collected from natural cliff outcrops. The brown coal lithotypes were determined according to the Polish lithological classification chart of low carbon content brown coals by Kwiecińska and Wagner (2001). The analyses encompassed: determinations of hydrocarbon group by thin layer chromatography (TLC) method with separation of aliphatic and aromatic hydrocarbons, and polar compounds, as well as determinations of extracted aliphatic and aromatic fractions by gas chromatography-mass spectrometry (GC-MS) method. The GC-MS analysis included the identification of aliphatic hydrocarbons such as *n*-alkanes, tri- and tetracyclic diterpenes, saturated and unsaturated pentacyclic triterpenes (hopanes, oleananes, oleanenes); aromatic hydrocarbons and medium-polarity organic compounds (fatty acids esters, partially aromatic cyclic compounds, some unsaturated organic compounds). These compounds were identified by their mass spectra, retention times compared to previously analyzed standards, fragmentation patterns and literature data (Mc Lafferty 2007; Peters et al. 2005). The analyzed brown coal lithotypes are dominated by detritic and xylithic lithotypes. The ash contents varied from 9.09 to 97.3%. Moisture contents were in the range of 0.50 and 13.45% (on average about 6.0%). In all the extract composition polar compound fraction prevailed and its content varied from 88.18 to 97.44%. The predominance of polar compound fraction in the group composition could have resulted from the low degree of thermal conversion of organic matter. In general, the contents of aliphatic hydrocarbon fraction in the detritic coal extracts is higher than in the other brown coal lithotypes due to the presence of cuticular wax (cutinite) in brown coal organic matter.

The brown coal samples contain *n*-alkanes (n-C_{15} – n-C_{35} range) showing two distribution types: monomodal with a maximum at n-C_{18} – n-C_{20} or bimodal with maxima most commonly at n-C_{15} – n-C_{21} and n-C_{25} – n-C_{35}. The n-alkenes were not found in the samples examined. Two acyclic isoprenoids: pristane (Pr) and phytane (Ph) occurred in variable concentrations. The low values of Pr/Ph ratio (from 0.06 to 0.17) in some samples are probably caused by water-washing or biodegradation (Didyk et al. 1978). Several diterpenes were identified in the extracts with 19 (fichtelite, norpimarane, norisopimarane) and 20 carbon atoms in a molecule (16α(H)-phyllocladane, isopimarane). These compounds come from conifer tissues and occur in elevated concentrations in brown coals of xylithic lithotype. However, they can be considered to be minor components even in xylithes. Oleananes occurred in a few samples only, indicating that angiosperms organic matter participated in the formation of the Chłapowo Cliff brown coals. However, their amount in the profile examined is low.

The low stage of thermal evolution of brown coal organic matter significantly influences its geochemical features, i.e. the chemical composition of extract fractions. This study indicates that there is a correlation between the brown coal lithotype and chemical composition of its extracts, particularly the presence and distribution of biomarkers. High concentrations of pentacyclic triterpanes (mainly ßß-hopanes) in most samples are related to the bacterial input to biogenic matter, particularly in case of detritic brown coals. Primary organic matter of monocotyledons (grasses, canes) seems to be much less resistant to microbial degradation than coniferal organic matter (wood).

The study reveals that the brown coal of the Chłapowo Cliff show relatively low variability of geochemical features, such as group composition of their extracts, thermal maturity and dominating biogenic sources of their primary organic matter as indicated by biomarkers found. This is caused by similarity of biogenic matter type and sedimentary conditions. Brown coal organic matter shows features typical for immature organic matter representing the geochemical stage of diagenesis. This is evidenced by very low values of biomarker parameters corresponding to Rr values of 0.20–0.25%. The predominant biogenic material derived from monocotyledons and bacteria participated mainly in formation of detritic lithotype, whereas in case of xylithic and xylodetritic lithotypes it was derived from conifer wood or in places from angiosperms. These results indicate that the brown coal examined was formed in a bog. The destructive influence of sea waves and high concentration of polar compounds, relatively well soluble in water, causes advanced water-washing in some samples changing values of biomarker parameters.

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Coupled carbon and nitrogen isotopic analysis with palynological data of PM10 dust in Wrocław city (SW Poland) – assessment of anthropogenic impact

Maciej GÓRKA[1], Elżbieta ZWOLIŃSKA[1], Małgorzata MALKIEWICZ[2], Dominika LEWICKA-SZCZEBAK[1], Mariusz-Orion JĘDRYSEK[1]

[1]*Laboratory of Isotope Geology and Geoecology, Department of Applied Geology and Geochemistry, Institute of Geological Sciences, University of Wrocław, 30 Cybulskiego St., 50-205 Wrocław, Poland; e-mail: maciej.gorka@ing.uni.wroc.pl*
[2]*Department of Paleobotany, Institute of Geological Sciences, University of Wrocław, 32 Cybulskiego St., 50-205 Wrocław, Poland; e-mail: malgorzata.malkiewicz@ing.uni.wroc.pl*

The major goal of this study was to determine origin of carbon and nitrogen in PM10 dust and to assess the anthropogenic impact using isotopic and palynological analysis. According to our best knowledge, any research concerning the coupled investigations of carbon and nitrogen isotopic composition of PM10 with additional palynologial analysis have not yet been done. The coupled carbon and palynological analysis of TSP dust were done by Górka et al. (2009).

The PM10 samples were collected using PM10 Stamplex Air Sampler Division (property of Regional Inspector for Environment Protection (RIEP); equipped with Whatmann quartz filter (0.06237 m^2) with constant flow of air 1.13 $m^3 \cdot min^{-1}$; situated in the Wrocław (SW Poland) centre, at 14/16 Wierzbowa Street. The PM10 samples were collected daily during 2007, but two samples per month were subjected for isotopic analysis and one sample per month for palynological analysis.

Before further analysis the filters were tested for the presence of carbonate species. The quartz filters with PM10 matter for carbon isotopes analysis were combusted with copper oxide (CuO) wire under vacuum at 900ºC using the sealed quartz tubes method (Boutton 1991). The quartz filters with PM10 matter for nitrogen isotopes analysis were combusted with copper oxide (CuO), calcium oxide (CaO) and pure copper wire (Cu) under vacuum at 900/600/20ºC using the sealed-tube combustion technique (Kendall, Grim 1990; Boyd et al. 1994; Yeatman et al. 2001; Widory 2007). Palynological analysis of the PM10 organic material trapped on the quartz filters followed the method used in melissopalynology (Louveaux et al. 1978; Warakomska 2003; Von der Ohe et al. 2004).

The air temperature and some air pollutants (CO, NO_x and PM10) concentrations have been obtained from Regional Inspectorate for Environment Protection (RIEP) in Wrocław. The concentration of PM10 in the 23 samples analyzed varied from 10.5 $\mu g \cdot dm^{-3}$ (June 5th, 2007) to 98 $\mu g \cdot dm^{-3}$ (November 21st, 2007) with an average of 34.9 $\mu g \cdot dm^{-3}$ (standard deviation was approx. 25). The average annual PM10 concentration reported in RIEP (2007) was 34.3 $\mu g \cdot dm^{-3}$ and reached 86% norm of annual PM10 concentration (40 $\mu g \cdot dm^{-3}$). The obtained $\delta^{13}C$ of PM10 varied from -26.9‰ (June 5th, 2007) to -25.1‰ (November 21st, 2007) with an average of -26.1‰ (standard deviation was approx. 0.5). The obtained

$\delta^{15}N$ of PM10 varied from 5.0‰ (September 9th, 2007) to 13.7‰ (June 5th, 2007) with an average of 9.9‰ (standard deviation was approx. 2.0).

Nitrogen in atmospheric particulate matter occurs generally as nitrate and ammonium (Seinfeld, Pandis 1997). Both nitrogen species are predominantly of anthropogenic origin (Seinfeld, Pandis 1997; Widory 2007) and are generated by the oxidation of gaseous NO_x (NO and NO_2) derived from high-temperature combustion processes (vehicles and industrial activity). The chaotic fluctuation of the total nitrogen isotope ratios of PM10 with no seasonal variability has been noted in our investigations. No correlation between the obtained $\delta^{15}N$ values of PM10 and atmospheric NO_x concentrations have been observed, but graphically with the increase of PM10 and NO_x concentration the dominant source of nitrogen can be indicated.

The carbon in air particles is a mixture of the elemental carbon (soot produced during fuel combustion) and organic carbon (incomplete combustion, soils, fugitive dust and compounds of biological origin (López-Veneroni 2009). Inorganic carbonate particles were not detected in the samples analysed. The seasonal (heating/vegetative) variability of $\delta^{13}C$ values has been observed. The depletion in the ^{13}C during vegetative season cannot be explained by an increase of C3 plant parts in dust (palynologically confirmed) and is caused by higher traffic and lower coal combustion input in vegetative season. No correlation between the obtained $\delta^{13}C$ values of PM10 and CO concentrations has been observed. Based on the relation above mentioned, the heating and vegetative season can be distinguished using different carbon isotope signal.

The comparison of $\delta^{13}C$ with $\delta^{15}N$ values indicated seasonally distinguishable sources of PM10 in Wrocław: (i) heating season samples are a mixture of coal and gasoline soot (Górka, Jędrysek 2008) and (ii) vegetative season samples include mainly gasoline soot, but some are also contaminated by coal soot. It can be concluded that the PM10 in Wrocław showed an anthropogenic imprint during the whole-year.

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Oxygen isotopes in authigenic quartz from salt deposits: a possible archive of Earth surface temperature in the Phanerozoic

Stanisław HAŁAS[1], Ana-Voica BOJAR[2], Ludmila KHMELEVSKA[3], Tadeusz M. PERYT[4]

[1]*Mass Spectrometry Laboratory, Maria Curie-Skłodowska University, 1 M. Curie-Skłodowska Sq, 20-031 Lublin, Poland; e-mail: stanislaw.halas@umcs.lublin.pl*
[2]*Institute of Earth Science, Geology and Paleontology, Karl-Franzens University, A-8010 Graz, Austria and Department of Geology, Salzburg University, Salzburg, Austria; e-mail: ana-voica.bojar@uni-graz.at*
[3]*Institute of Geology and Geochemistry of Combustible Minerals, National Academy of Sciences of Ukraine, 3a Naukova St., 79060 Lviv, Ukraine (deceased)*
[4]*Polish Geological Institute, 4 Rakowiecka St., 00-975 Warsaw, Poland; e-mail: tadeusz.peryt@pgi.gov.pl*

We describe a new geochemical tool that can provide temperatures of ancient sedimentary basins in which massive evaporites were deposited. This includes determinations of oxygen isotope composition of finely crystalline quartz (SiO_2) that occurs in large halite (NaCl) bodies combined with measurements of homogenization temperatures of fluid inclusions in halite crystals. These quartz crystals were not affected by post-depositional alterations and they are relatively easy to separate. For the purpose of this study five halite samples were selected from four different evaporite basins spanning the Early Cambrian to Late Jurassic.

The obtained oxygen isotope temperatures refer to locations where evaporites were deposited, i.e. in subtropical zones of the Earth, as it may by estimated from the continents distribution during Phanerozoic times. When the oxygen isotope temperatures are plotted vs. time (Fig. 1), a linear trend is obtained. This evidence suggests the decrease of the Earth's surface temperature from 76°C (Early Cambrian) to 35°C (Late Jurassic). The average drop of the temperature per 100 Ma, which may be estimated by least square fitting of a straight line, was about 9°C.

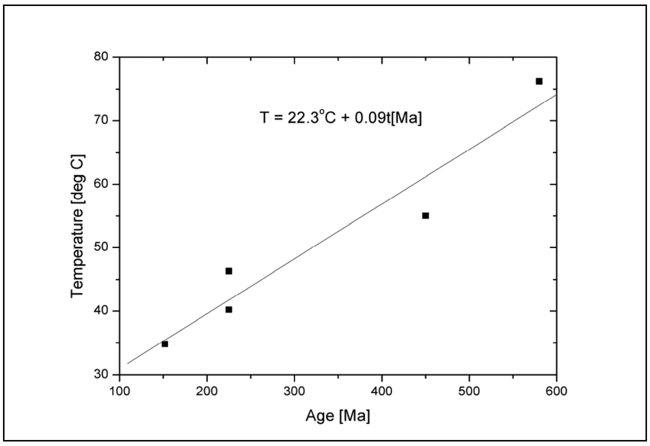

Fig. 1. Oxygen isotope temperatures vs. geologic time

These temperatures are based on an assumption that the $\delta^{18}O$ of brines varied from -1‰ to 0‰ during the halite deposition. The assumption of higher $\delta^{18}O$ values would lead to temperatures higher than those obtained from homogenization of fluid inclusions that already were formed after modest overheating of the halite bodies.

Considering this, the $\delta^{18}O$ values of finely crystalline authigenic quartz record and preserve temperatures of the basins where these salts were deposited.

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Geochemical and isotopic characteristics of rocks from the Kandalkshyan part of the Lapland Granulite Belt in the Kola Peninsula

Stanisław HAŁAS[1], Miłosz HUBER[2], Sergey G. SKUBLOV[3]

[1]*Mass Spectrometry Laboratory, Maria Curie-Skłodowska University, 1 M. Curie-Skłodowska Sq, 20-031 Lublin, Poland; e-mail: stanislaw.halas@umcs.lublin.pl*
[2]*Institute of Earth Sciences, UMCS, 2cd Kraśnicka Ave, 20-718 Lublin, Poland; e-mail: miloh@interia.pl*
[3]*Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, 199034 Saint-Petersburg, Makarova emb 2, Russia; e-mail: scublov@mail333.com*

In all, 18 samples of metamorphic rocks (amphibolites and granulites) and cutting granitoid veins from the most typical formations of the Kola Peninsula were investigated. The rock samples were analyzed for major and trace elements as well as for stable sulfur isotope composition in sulfides. In addition, the selected amphiboles were analyzed for REE.

The results of chemical analysis of the examined rock samples exhibited similarity and convergence due to similar conditions of the metamorphic processes and properties of their protolith. In contrast, veins and metasedimentary rocks displayed different chemical composition. The chemical analysis of mineral pairs from selected metamorphites allowed us to demonstrate their crystallization conditions: temperature in the range of 800–900°C and pressure varying from 11.5 to 12.5 kbar. The distribution patterns of REE concentrations in amphiboles point up to the process of diaftoresis in amphibolite facies.

The zonality of heavy REE concentrations and their content in high-Ca garnets most likely result from the composition of intrusive rocks rather than from metamorphic conditions. The primary magmatic structures were preserved in most of the samples examined. The analysis of selected accessory minerals indicated their origin from deep magmatic zones, whereas the chemical composition of their host rocks gives an evidence for basic magmas. In contrast, granitoid veins represent an acidic environment and cratonic type magmatism.

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Mineral matter and silica concentration in atmospheric dust and human lungs from the Upper Silesia – preliminary results

Mariola JABŁOŃSKA[1], Lucyna LEWIŃSKA-PREIS[1]

[1] *Faculty of Earth Sciences, University of Silesia, 60 Będzińska St., 41-200 Sosnowiec, Poland; e-mail: mariola.jablonska@us.edu.pl*

Quartz and aluminosilicates (e.g. feldspars, glass from combustion processes or clay minerals) were recorded as dominant components of atmospheric dust pollutants in the heavily populated and industrial region of the Upper Silesia.

This study presents the mineral matter and silica concentration in atmospheric dust and the influence of these pollutants on lung deposition. No data have been provided for the levels of human lung exposure to mineral matter and silica in Poland. We analyzed mineral matter and silica concentrations in 15 samples of atmospheric dust from the selected towns in the Upper Silesia. The concentration of mineral matter in collected atmospheric dust varied from 44.47 to 89.47% wt., whereas the concentration of silica was in the range of 2.35% wt. (in winter season) up to 74.69% wt. (in summer season).

The mineral matter and silica concentrations were determined in 40 lung tissues taken from deceased persons (14 females and 26 males) of age from 18 to 98, who lived in the Upper Silesia, Poland. Fourteen lung tissues were taken from smokers. The concentration of mineral matter varied significantly around an average value of 3.28 ± 0.66% wt. (SD 2.06). The lowest level (0.82% wt.) was recorded in female tissues and the highest (10.32% wt.) was revealed in male tissues. The concentrations of mineral matter in lung tissues varied from 0.82 to 7.00% wt. (SD 1.85) for females, and ranged from 1.12 to 10.32% wt. (SD 2.17) for males. The amount of mineral matter increased with the age of lung tissue donors and was significantly higher for people with a smoking habit. The preliminary identification of mineral particles found in lungs revealed the presence of aluminosilicates and quartz as predominant constituents. The silica concentrations (averaged at 3.05 ± 0.84% wt. (SD 1.46)) were determined in 14 lung tissues using wet chemistry. The minimum level (0.37% wt.) was observed in female tissues and the maximum (5.65% wt.) was in smoker male tissues. The highest silica concentrations of non-smokers varied around 3.09% wt. Like in case of mineral matter, the silica concentrations increased with age of donors and were significantly higher in smoker's lungs. In general, male lung tissues contained more mineral matter and silica than female lung tissues. The maximum concentration of mineral matter and silica was recorded in the 50 to 60 age span; for mineral matter the maximum was 3.02% wt. and for silica 4.82% wt. Outside this age category, the concentration of mineral matter and silica decreased, for example: for the 70 to 80 age span the amount of mineral matter decreased to 2.46% wt. and that of silica to 2.14% wt.

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Speciation and mobility of heavy metals (Zn, Pb, As, Cd and Tl) in flotation tailing pond from ZGH "Bolesław" in Bukowno, S Poland

Irena JERZYKOWSKA[1], Marek MICHALIK[1]

[1]*Institute of Geological Sciences, Jagiellonian University, 2A Oleandry St., 30-063 Kraków, Poland; e-mails: irena.jerzykowska@uj.edu.pl, marek.michalik@uj.edu.pl*

Zn-Pd ores mining and processing have been conducted in the Bukowno area (near Olkusz, S Poland) for more than 50 years. It has caused accumulation of about 38 Tg flotation wastes in an area of approximately 110 ha (Pajor 2005). Flotation tailing ponds are significant sources of heavy metals in water, soil and air in this area (Kuzio et al. 2005). The aim of this preliminary study was to recognize forms of heavy metals occurrence and their stability in flotation waste materials.

Four samples (1a, 1b, 2, 3a) of waste materials were collected from the flotation tailing pond in Bukowno. Two macroscopically different (1a – sandy and 1b – silty fraction), gray and homogenous samples, were collected from 6–7 years old material from the pond surface. This part of pond is currently being exploited for recycling purposes. The sample 2 represents newly deposited, homogenous material. It was collected in the vicinity of pipe supplying fresh pulp. Laminated material (sample 3a) was collected from the oldest, reclaimed part of the pond.

Bulk samples were examined using optical microscopy, powder X-ray diffraction and scanning electron microscopy with EDS system in the Institute of Geological Sciences, Jagiellonian University. The chemical analysis of bulk samples was carried out in ACME Laboratories in Canada using ICP-ES (for major elements) and ICP-MS (for trace elements). The seven-step sequential extraction was executed according to the following procedure (Tessier et al. 1979, modified): (1) exchangeable metals extracted using CH_3COONH_4, (2) metals bound to carbonates using acetate buffer, (3) metals bound to manganese oxides with $NH_2OH \cdot HCl$, (4) metals bound to amorphous iron oxides and hydroxides with $(NH_4)_2C_2O_4 \cdot H_2O$ and $C_2H_2O_4 \cdot 2H_2O$, (5) metals bound to crystalline iron oxides with $C_6H_5Na_3O_7 \cdot 2H_2O$ and $NaHCO_3$, (6) metals bound to organic matter and sulfides using H_2O_2, (7) residual metal species extracted with HF, $HClO_4$ and HCl. The chemical composition of extracts was examined using the ICP-MS method in the hydrogeochemical laboratory of the Chair of Hydrogeology and Engineering Geology, AGH-University of Science and Technology.

The sample 1a is dominated (>80%) by coarse silty fraction (0.071–0.02 cm). The samples 1b, 2, 3a are composed of 40–50% of coarse silty fraction and in 30–50% of medium sandy fraction (0.63–0.2 cm). The waste material contains mainly dolomite, calcite, marcasite and in smaller amounts, quartz, galena, gypsum, sphalerite, strontianite, cerussite, Fe-oxy/hydroxides. Marcasite in many cases is partly transformed into Fe-oxy/hydroxides. Cerussite rims around galena are common. The wastes are rich in Fe-oxy/hydroxide concretions containing significant amounts of Pb, Zn, S, and P. In the youngest wastes (sample 2) Zn, Pb, As and Cd are accumulated (70–40%) mainly in residual phases, which are probably primary sulfides. Tl in this sample is in more than 80% bound to organic matter. In the samples 1a and 1b Zn is bound mainly (almost 40%) to organic matter and residual phases. Almost 80% of Pb is accumulated in carbonates in these samples. As dominates (70–90%) in residual sulfides and in a lesser amount (about 10%) in amorphous Fe compounds. In the silty sample 1a Cd is present mainly in exchangeable positions (40%) and in carbonates (30%) but in the sample 1b Cd is accumulated in resistant residual phases (40%) and in organic matter (30%). Tl dominates in organic matter (60-90%). Heavy metal behavior in the sample 3a is similar to the fresh sample 2. Only Zn and Cd were mobilized. Zn is bound to all extracted phases almost in the same amount and Cd is accumulated mainly in exchangeable phases (30%) and in Mn-oxides (20%).

The results show that the 6–7 years old waste material collected from the pond surface is the most evolved. Heavy metals are potentially mobile, accumulated mainly in secondary, soluble phases. In the fresh waste sample, heavy metals are present in the most insoluble residual phases. Heavy metals mobility in the oldest sample 3a is more similar to the fresh than 6–7 years old sample. It can be caused by reclamation and coverage of waste material with sealing soil. The other possibility is that soluble phases containing heavy metals were removed during long time of weathering.

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The UV-irradiation effect on redox potential in freshwater organic sediments – preliminary studies

Piotr JEZIERSKI[1], Adriana TROJANOWSKA[1]

[1]*Laboratory of Isotope Geology and Geoecology, Institute of Geological Sciences, Faculty of Earth Sciences, University of Wrocław, 30 Cybulskiego St., 50-205 Wrocław, Poland;*
e-mails: adriana.trojanowska@ing.uni.wroc.pl, piotr.jezierski@ing.uni.wroc.pl

UV irradiation (ultra violet radiation) is a well-known method of sterilization that brings about deactivation and removal of microorganisms, thus minimizing the risk of infection and preserving easily biodegradable substances. UV is a high-energy electromagnetic radiation that has the capability of destroying macromolecular organic compounds–that show carcinogenic properties. However, the objective of this study was focused on the destructive impact of UV radiation on organic matter of natural organic sediments containing soluble and poorly soluble humic substances. The UV irradiation leads to organic matter mineralization with the release of CO_2 as a final product. Therefore, several experiments were carried out to better understand the electrochemical nature of UV mediated mineralization process in organic sediments.

The organic-rich freshwater sediments from the Siemianowka Reservoir, in which humic acids constitute 53% of organic C, were incubated in a shaker under continues UV irradiation. During these experiments the temperature and redox potential variations were monitored using an automatic registration system.

This preliminary study provided an interesting record of redox potential changes. When the source of UV was turn on, substantial changes of redox potential, reaching 0.5 V, were noted. These changes occurred in cycles in several periods. The rapid changes in redox potential may have corresponded to active forms of chemicals, such as free radicals induced by UV radiation. This phenomenon has never been reported so far, therefore this study will be continued and its scope will be broadened to explain the effects of UV radiation on transformation of organic matter and changes in its biological availability.

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Resistance of carbonate building stones to chemical weathering: experimental assessment in acidic solutions

Ryszard KRYZA[1], Marta PRELL[1], Franciszek CZECHOWSKI[1], Małgorzata DOMARADZKA[1]

[1]*Institute of Geological Sciences, Faculty of Earth Sciences, University of Wrocław, 30 Cybulskiego St., 50-205 Wrocław, Poland; e-mail: ryszard.kryza@ing.uni.wroc.pl*

Petrographic features and petrophysical characteristics determine the resistance of natural building stones to weathering. This is particularly important for relatively “soft” carbonate rocks. Their resistance to frost and salt crystallization damage is crucial, due to the increasing popularity of these stones, also in external architectural usage, in all climatic zones, including cold regions with frequent freezing/melting cycles. In addition, the increasing atmospheric pollution by acidic agents has become a very important factor of building stone deterioration (Charola, Ware 2002).

Three types of carbonate rocks: travertine, limestone and marble, have been studied to determine their water absorption, resistance to salt crystallization damage, and reaction to experimentally modelled acid rain weathering, imitating the polluted urban atmospheric conditions. The acidic agents present in natural acid rains: H_2SO_4, HCl, HNO_3, CH_3COOH and mixture of all the acids (“acid mix”) were tested. The acids selected are common constituents in precipitation and their concentrations are enhanced in a highly polluted urban atmosphere. The two acid concentrations, differing by magnitude, were used in our experiments: 10^{-4} and 10^{-3} mol/L. These concentrations are within the range of the rain acidity in the city of Wrocław (based on the data obtained from the Institute of Meteorology and Water Management in Wrocław; Prell 2008 and refs. therein).

The carbonate samples were cut into regular cubes 2 × 2 × 2 cm. The cubes were immersed into 80 mL of the respective acid solutions and kept for the length of time necessary to achieve pH increase by one unit. The acid treatment of each cube and in each acid solution was repeated three times. The weighted (total) mass loss, and that calculated from quantified concentrations of dissolved Ca^{2+}, Mg^{2+}, Fe^{2+} and CO_3^{2-} ions, were assessed after each acid treatment. Microscopic observations (under binocular) and photographs were made before and after each treatment in the acid solutions.

The time necessary to attain pH value raise by unity in the lower concentrated acids ranged from 3 to 6 minutes and in the acids of ten times higher concentration was considerably longer, between 10 and 30 minutes. Since the molar concentrations of H^+ in sulfuric acid solutions were twice higher than in the respective solutions of the other acids, the carbonate reaction with the sulphuric acid solutions proceeded nearly twice longer. The three experimental repetitions on each cube, in the acid solutions of a defined concentrations, revealed similar total weight loss on treatment in the limestone and marble, whereas much higher loss in the travertine. Compared to the weight loss in acid solutions of 10^{-4} mol/L, the total weight loss (combined dissolution and granular disintegration) in the acids of ten times higher concentration (10^{-3} mol/L) is not ten times higher as one could expect, but only four to five times higher for strong mineral acids used, e.g. H_2SO_4, HCl, HNO_3 and "acid mix" solutions, and twice higher for weak CH_3COOH acid solution. This can be explained by the observed elevated weight loss, far exceeding the chemical equivalence in the lower concentration solutions, due to possible chemically-induced physical detachment of mineral particles (granular disintegration) of the rocks that, apparently, were not entirely dissolved in the acidic solutions. For the clarity, it should be mentioned that disintegrated particles, on average below 10 mg contained in 80 ml of solution, were hardly visible and not quantified separately. The disintegration effect in acid solutions of concentrations 10^{-4} mol/L and 10^{-3} mol/L is, respectively, around twice, and one and a half times higher, in the travertine than in the limestone and marble. As a consequence, in the acidic solutions of higher concentration (higher chemical reaction capacity with carbonates), the granular disintegration becomes less pronounced. It is manifested in lowering of the ratios of total mass loss to mass dissolved in higher concentrated acids.

Each run performed in our laboratory weathering experiment on the carbonate rocks broadly resembled two-month action of the acid rain with acidity fluctuation level reported from the city of Wrocław (data for 2006: total precipitation 562 mm/cm^2 per year, pH between 4.2 and 7.0; Prell 2008 and refs. therein). This conclusion is rationalised on the following reasoning: the total amount of acid solution used for each cubic sample = 3×80 mL = 240 mL; the external surface of cubic sample = $2 \times 2 \times 6 = 24$ cm^2 (here we ignore porosity); consequently, solution volume per square cm is 240 mL/24 cm^2 = 10 mL/cm^2; an approximate annual precipitation in Wrocław = 60 mL/cm^2 per year; 10/60 = 1/6 of a year, i.e. two months precipitation.

The initial stages of acid weathering involve, apart from chemical dissolution, particularly intense physical detachment of rock particles (granular disintegration) significantly contributing to the total mass loss. Travertine was found to be the most prone to salt crystallization damage and to acid weathering, and these features should be taken into account especially in external architectural usage of this stone in cold climate conditions and polluted urban atmosphere.

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Geochemistry of pore waters in the foreland of retreating glacier, Werenskioldbreen SW Spitsbergen

Monika KWAŚNIAK-KOMINEK[1], Maciej MANECKI[1], Grzegorz RZEPA[1]

[1]*Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and* Technology*, 30 Mickiewicz Ave, 30-059 Kraków, Poland; e-mails: monika.kwasniak@gmail.com, gpmmanec@cyf-kr.edu.pl, grzesio@geolog.geol.agh.edu.pl*

This study is a part of the larger project on inorganic and microbial weathering of minerals in the foreland of a glacier retreating due to global warming. Several samples of freshly cleaved rock forming minerals were buried in the sediment in 2005. Chemical characteristics of the pore waters is necessary to fully understand dissolution features, transformations and mineral-bacteria interactions observed on the surface of periodically recovered mineral samples.

Chemical weathering and soil forming processes associated with retreating glaciers contribute to a surprisingly high chemical denudation observed in polar regions. Retreating glaciers uncover fresh regolith, evolution of which may affect the global carbon cycle and as a result have negative feedback on the global climate. In the large scale, atmospheric CO_2 forms carbonic acid providing the protons for silicate mineral dissolution and is transformed to bicarbonate ion ultimately locked into biogenically deposited carbonate on the sea floor:

$$CaSiO_3 + H_2CO_3 \rightarrow CaCO_3 + SiO_2 + H_2O$$

The study area is a foreland of the Werenskiold glacier (SW Spitsbergen). This glacier has been continuously retreating in the last century by several meters a year. It was established elsewhere that carbonate dissolution dominates in the youngest glacial sediments, whereas silicate weathering is the dominant process in the older sediments. The main objective of this study is to correlate the chemistry of pore waters with the distance from the glacier snout. The samples were collected at three locations: 100, 1000 and 1700 m from the glacier snout. The sediment closest to the glacier was uncovered within last 10 years while the farthermost – nearly 100 years ago.

The samples of percolating waters, collected from 30 cm deep trenches, were syringe filtered through 0.2 µm PC membranes and analyzed in the field for temperature, conductivity, pH, Eh, and O_2 content (potentiometry), Ca and Mg (colorimetry), and HCO_3^- (alkalinity titration). The waters significantly differ in composition from surface waters at the same locations. Solutions percolating through the youngest sediments (closest to the glacier) are alkaline (pH > 8) showing low mineralization (conductivity <50 µS/cm), relatively low concentrations of Ca (~20 mg/L) and HCO_3^- (~25 mg/L), with Mg below the detection limit of 1.5 mg/L. The samples collected at two localities farther from the glacier snout indicated nearly neutral waters (pH = 7.7) with higher mineralization (conductivity 630 and 746 µS/cm), higher concentrations of Ca (97 and 126 mg/L), Mg (32 and 46 mg/L), and HCO_3^- (227 and 236 mg/L). Therefore, the correlation between the composition of the waters and the distance from the glacier was observed. The samples differ in the Eh and O_2 content as well. However, there is no correlation between these two parameters and the location of the sampling point. These results are consistent with the maturity of the soils increasing with the distance from the glacier.

This study will shed light on mechanisms of transformations of mineral surfaces in arctic soils using *in-situ* field and analytical techniques. The research site is representative to all Alpine glaciers retreating due to global warming. Alpine glaciers on Spitsbergen offer more representative environment for all polar and semi-polar regions than glaciers on Antarctica.

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Formation of halotrichite [$Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$] in an acid sedimentary environment, Shirkuh Mountain, Taft-Yazd, Iran

Mohammad Ali MACKIZADEH[1]

[1]*University of Isfahan, Department of Geology, Isfahan, Iran; e-mail: ma_mackizadeh@yahoo.com*

This report presents the results of a mineralogical study of a geological-mining environment that led to formation of halotrichite.

The study area is located about 40 km of Taft city in the Yazd province, central Iran. A larger part of the area, which includes the western part of the Shir-kuh Mountain Range, is built of Middle Jurassic batholitic granites. During the Quaternary, formation of a thick waste mantle of leucocratic granite debris has been a dominant process in the western margin of the Shir-kuh batholite. These deposits have locally been mined for quartz and feldspar.

In the study area, these deposits are closely linked to a zone of gas emissions rich in sulfur (H_2S, SO_2?), which led to formation of native sulfur, pyrite and sulfate mineral associations, especially halotrichite. This mineral was examined by the XRD and XRF methods. The weathering of primary sulfides generated halotrichite as a secondary mineral. This mineral may have formed directly from acid sulfate waters during dry periods.

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Molecular evidences of widespread wildfires in Laurasia and Gondwana during the Lower and Middle Jurassic

Leszek MARYNOWSKI[1], Michał ZATOŃ[1]

[1]*Faculty of Earth Sciences, University of Silesia, 60 Będzińska St., 41-200 Sosnowiec, Poland; e-mail: leszek.marynowski@us.edu.pl*

Wildfires play a key role in terrestrial ecosystem modeling, but their geological history after higher plants colonization is still not well-recorded (Scott 2010). We used the charcoals and pyrolytic polycyclic aromatic hydrocarbons (PAHs) as proxies of Lower and Middle Jurassic wildfires on both the Laurasia and Gondwana continents. The Laurasian evidence comes from the Hettangian (Marynowski, Simoneit 2009) and Lower Callovian terrigenous deposits of the eastern part of the Central European Basin (Marynowski, Zatoń 2010). We have detected the charcoal fragments co-occurring with unsubstituted polycyclic aromatic hydrocarbons in the Zagaje and Skłoby Fm. from the Hettangian of the Holy Cross Mountains and the Lower Callovian Papilė Fm. of Lithuania. The results derived from this study indicate that forest fires took place at that time. The sum of concentrations of pyrolytic polycyclic aromatic hydrocarbons, including fluoranthene, pyrene, benzofluoranthenes, benzo[*e*]pyrene, benzo[*ghi*]perylene and coronene changed significantly, ranging from 4.66 to 6.57 μg/g TOC for charcoal-bearing clays and sands of the Papilė Fm. and reached even ~1253 μg/g TOC for sandstones and claystones of the Zagaje Fm. Except for pyrogenic PAHs, charcoal-bearing horizons are characterized by the occurrence of oxygene-containing aromatic compounds. The most common are benzo[*b*]naphthofurans, dinaphthofurans, and benzobisbenzofurans, but dibenzofurans and phenyldibenzofurans were also detected. As far as we know, this is the first evidence of wildfires during the Callovian, as evidenced by multi-proxy documentation (Marynowski, Zatoń 2010) and one of the few for the Lower Hettangian. The Gondwanan record of wildfires comes from the Neuquén province in Argentina, where the Upper Aalenian/Lower Bajocian to Bathonian terrigenous sequences are characterized by the occurrence of charcoal and PAHs whose distribution suggests their pyrolytic origin. This is the first multi-proxy evidence of Jurassic wildfires from the Gondwana continent and one of a very few records of wildfires in Gondwana during the whole Mesozoic.

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The geologic signature to the chemistry of spring waters in Świętokrzyski National Park, Poland

Artur MICHALIK[1]

[1] *Geochemistry and the Environment Division, Institute of Chemistry, Jan Kochanowski University, 15G Świętokrzyska St., 25-406 Kielce, Poland; e-mail: artur.michalik@ujk.edu.pl*

The quality of groundwater is controlled by combined interactive natural and anthropogenic factors. Geologic setting and soil cover have a significant and sometimes decisive influence on the chemistry of groundwater, especially in legally protected areas. This study presents the results of chemical analyses of spring waters collected in Świętokrzyski National Park during 2004–2006. Location, geology and geomorphology of Świętokrzyski National Park are described in Field session 2.

The field measurements of pH and electric conductivity (EC) of spring waters enabled identification of two seepage stream areas that differ in water chemistry and quality: (1) the Łysogóry Range and (2) the Klonów and partly Pokrzywiański Ranges. The spring waters of the Łysogóry Range show a relatively low pH with a 3-year geometric mean of 5.7, very low EC (mean of 73 μS/cm). In contrast, the spring waters of Klonów and Pokrzywiański Ranges show somewhat raised values of pH (mean 6.1) and a three times higher EC (mean 224 μS/cm) (Michalik 2007). A relatively small area of Świętokrzyski National Park excludes a considerable diversity in rainwater chemistry. This evidence suggests that the main reason for the higher pH and conductivity values of spring waters is the specific geologic setting of the area examined. The bedrock of the northern ranges of the park consists of sandstones with clayey shale and locally dolomite, limestone and tuffite interbeds as well as subordinate limonite and siderite intercalations (Czarnocki 1956). Some of these rocks show buffering capacity and a potential as a source of various ions.

The results derived from the detailed chemical analyses also displayed the diverse chemistry of spring waters in the Łysogóry Range versus the Klonów and Pokrzywiański Ranges. The spring waters of the Łysogóry Range show very low ion concentrations with the prevalent SO_4-Ca-Cl-Mg and SO_4-Ca-Mg-Cl water types (according to Altowski-Szwiec classification) with sulfates prevailing over hydrocarbonates. In contrast, the spring waters of the northern ranges of the park show some similarities to the neighboring areas of the Świętokrzyski province with predominant hydrocarbonates (HCO_3-Ca-Mg) (Prażak 2002); the SO_4-Ca-Mg water type is scarce.

The spring waters of the Klonów and Pokrzywiański Ranges are characterized by raised levels of most metals. Spring Zr-63 (Pokrzywianka Górna) showed the highest concentrations of Ca, K, Na, B, Cd, Cr, Mg, Sr, U, V, which is probably related to the location adjacent to the calcareous sinter (Dołęgowska et al. 2005). Spring Zr-61 (Psary) exhibited the highest concentration of Fe, SiO_2, Ba, Co, Pb, Sr, Mn, which seems to be linked to the location of the spring near a diabase intrusion.

The geometric mean of $\delta^{34}S_{V\text{-}CDT}$ of soluble sulfates from the spring waters sampled in 2005 and 2006 was +4.3‰. The $\delta^{34}S_{V\text{-}CDT}$ (SO_4^{2-}) of snow samples collected in two consecutive hydrological years were +5.1‰ and +6.8‰. The similar distribution pattern of the $\delta^{34}S_{V\text{-}CDT}$ (SO_4^{2-}) in the snow, soils and partly rocks indicates unequivocally the main sources of soluble sulfates in the waters examined. The seasonal variations of the $\delta^{34}S$ in spring water sulfates are linked to redox processes.

Chemical and isotopic studies indicate that the geological structure of the study area has a decisive influence on the chemistry of spring waters in Świętokrzyski National Park (Michalik 2007).

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An impact of pyrite oxidation on two water bodies in the Podwiśniówka area near Kielce, Poland

Zdzisław M. MIGASZEWSKI[1], Agnieszka GAŁUSZKA[1], Sabina DOŁĘGOWSKA[1]

[1]*Geochemistry and the Environment Division, Institute of Chemistry, Jan Kochanowski University, 15G Świętokrzyska St., 25-406 Kielce, Poland; e-mails: zmig@ujk.kielce.pl, agnieszka.galuszka@ujk.kielce.pl, sabina.dolegowska@ujk.kielce.pl*

The geological setting and various aspects of acid mine drainage (AMD) in the Wiśniówka mining area are briefly discussed in the section: “Influence of pyrite mineralization on the generation of Acid Mine Drainage in the Wiśniówka mining area near Kielce” (Field session 1, this issue; Migaszewski et al. 2008). The principal objective of this preliminary report is to assess the differences in chemistry of two acidic bodies in the Podwiśniówka area: (i) Podwiśniówka pit pond, and (ii) Marczakowe Doły pond about 1 km eastward (Fig. 1 in Field session 1, this issue). The latter one was dug by a farmer and seems to be located within a fault zone extending presumably from the Podwiśniówka quarry. The authors assume that the smaller acidic pond at Marczakowe Doły has partly been draining waters from the bigger Podwiśniówka acidic pit pond. This hypothesis may be supported by the evidence that the water in both ponds has shown similar seasonal variations of pH, conductivity (EC) and concentrations of SO_4^{2-}, Fe^{2+} and Fe^{3+}, regardless of distinct differences in water chemistry. The other working hypothesis is that the Marczakowe Doły acidic pond is additionally recharged by water from another pyrite zone.

Curious enough is the fact that about 150 m north of the Marczakowe Doły acidic pond, there is a dug fish pond recharged from a nearby farm well. The study conducted from October of 2009 through July of 2010 revealed diverse chemistry of these three ponds, but the most surprising is the difference between the acidic ponds. Except for the similar pH, the Marczakowe Doły acidic pond displayed a distinctly higher EC and concentrations of SO_4^{2-}, Fe^{2+} and Fe^{3+} (Kalembasa 2010). This diversity is also highlighted by the results of pH, EC, SO_4^{2-}, Fe^{2+} and Fe^{3+} measurements of pond waters from the Wiśniówka area performed in June and July of 2010 (Table 1).

Table 1. Chemistry of waters in Wiśniówka Mała pit lake (western pond), Podwiśniówka pit pond and Marczakowe Doły ponds in June/July of 2010

Site	pH	EC µS/cm	SO_4^{2-}	Fe^{2+}	Fe^{3+}
			mg/L		
Wiśniówka Mała pit lake (W pond)	4.0/4.3	227/374	145/155	0.1/<0.1	0.1/0.4
Podwiśniówka acidic pit pond	2.7/2.8	610/929	134/196	6.0/2.9	7.5/8.1
Marczakowe Doły acidic pond	2.8/3.3	1402/1524	731/965	40/57.5	28/162.5
Marczakowe Doły fish pond	5.8/6.5	208/327	70/104	<0.1/<0.1	<0.1/0.3

The fieldwork also indicated that the sediment of the two acidic pit ponds differed in color. It was gray in places gray-blue and orange in Podwiśniówka, as opposed to orange in Marczakowe Doły (Fig. 1). The X-ray diffraction analysis showed that the Podwiśniówka sediment patterns the mineralogical composition of the exposed rock series and comprises: quartz, illite (-$2M_1$), kaolinite (-$1M_d$), and subordinate hydroxy-green rusts (apparently described by the formula $Fe^{2+}{}_2Fe^{3+}(OH)_7$), goethite (α-FeOOH), hematite (γ-Fe_2O_3) and jarosite. In contrast, quartz, smectite and poorly crystalline goethite (presumably with an admixture of ferrihydrite ($\sim Fe(OH)_3 \cdot 1.8H_2O$) predominate in the Marczakowe Doły acidic pond. This study is ongoing and encompasses trace element and S and O isotope determinations. Both element and isotope signatures will enable us to pinpoint the source of the Marczakowe Doły acidic pond water.

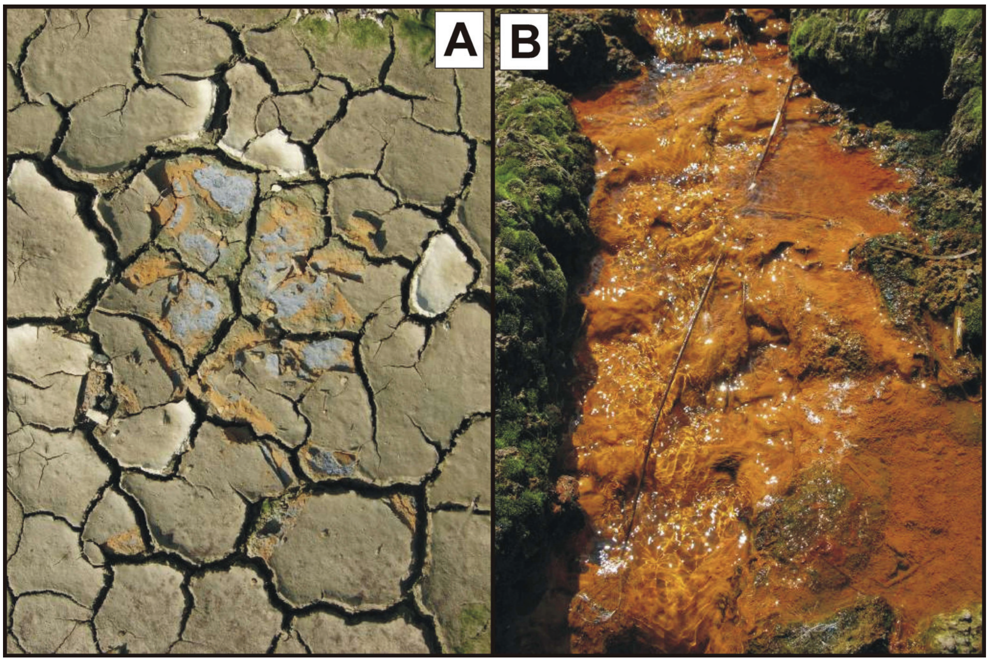

Fig. 1. Sediments in two acidic pit ponds: (A) Clay minerals (gray), hydroxy-green rusts (gray-blue) and goethite (orange) in Podwiśniówka; (B) "Yellow boy" (goethite) in Marczakowe Doły

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Oxygen isotope analysis of shark teeth phosphates from Eocene deposits in Mangyshlak Peninsula, Kazakhstan

Andrzej PELC[1], Stanisław HAŁAS[1], Robert NIEDŹWIECKI[2]

[1]*Mass Spectrometry Laboratory, Maria Curie-Skłodowska University, 1 Maria Curie-Skłodowska Sq, 20-031 Lublin, Poland, e-mails: andrzej.pelc@umcs.lublin.pl, stanislaw.halas@umcs.lublin.pl*
[2]*Institute of Geological Sciences, Wrocław University, 9 Maks Born Sq, 50-204 Wrocław, e-mail: rnied@ing.uni.wroc.pl*

Since two decades silver orthophosphate (Ag_3PO_4) has successfully been used in oxygen isotope analysis of natural phosphates. The Ag_3PO_4 technique was first developed by Wright and Hoering in 1989 and published in detail by Crowson et al. (1991). Natural phosphates, both biogenic and abiogenic, can be relatively simply converted to Ag_3PO_4 by digestion in HF and subsequent precipitation with $AgNO_3$ solution.

There are three methods of converting Ag_3PO_4 into a permanent gas amenable for ^{18}O isotope analysis by IRMS:

1. The fluorination method, initially developed by Clayton and Mayeda (1963) for silicates in 1963. Although oxygen extraction is quantitative in reaction with BrF_5, ClF_3, or F_2, it requires at least 15 hours for completion.
2. A rapid oxygen extraction method by graphite reduction was developed by O'Neil et al. (1994) in which Ag_3PO_4-graphite mixtures sealed in silica tubes were heated in a resistance oven to 1200°C.
3. High temperature conversion of Ag_3PO_4 to CO in a glassy carbon reactor held at 1450°C (Vennemann et al. 2002).

This study inspired us to carry out detailed observations of the graphite reduction of Ag_3PO_4 in vacuum conditions (Pelc, Hałas 2010). We applied resistance heating of Pt-Ir boat in vacuum, which is routinely used in Mass Spectrometry Laboratory for oxygen extraction from sulfates. The following measurements at final reaction temperatures varying from 430 to 915ºC were made: (i) CO_2 extraction yield, (ii) oxygen isotopic composition of CO_2, (iii) mass loss of the reactants. Our study leads us to further improvements of the oxygen isotope analysis of phosphates.

The CO_2 yield and oxygen isotopic composition were determined using a calibrated dual inlet and triple collector isotope ratio mass spectrometer. We noticed the following three stages of the reduction process:

1. At temperatures below 590°C only CO_2 is formed, whilst silver orthophosphate decays to pyrophosphate.
2. At higher temperatures 590–830°C predominantly CO is formed from silver pyrophosphate which decays to metaphosphate.
3. At temperatures above 830°C appears a noticeable sublimation of silver orthophosphate.

These observations were accompanied by the oxygen isotope analysis of the obtained CO_2. The measured $\delta^{18}O$ value of the laboratory standard varied from -11.93‰ (at the lowest temperature) to -20.32‰ (at the highest temperature). The optimum reduction temperature varied from 780 to 830ºC. At this temperature range the oxygen isotopic composition of CO_2 is nearly constant, whereas reaction efficiency is nearly complete. The determined difference between $\delta^{18}O$ value of oxygen in silver phosphate and that in CO_2 extracted from this phosphate is +0.70‰.

The teeth of three species of Eocene sharks *Isurolamna bajarunasi, Macrorhizodus americanus* (both species represent family Isuridae) and *Usakias wardi* (family Alopiidae) were investigated. All teeth were collected by N.I. Udovichenko. These species were found in the Kujlus outcrop (Middle Bartonian, Shorym Fm., foraminiferal zone *Globigerina turcmenica*; nannoplankton zone NP17) and Usak outcrop (uppermost Bartonian/lowermost Priabonian, Shorym Fm./Aday Fm.; the uppermost part of the foraminiferal zone *Globigerina turcmenica* – the lowermost part of the foraminiferal zone *Globigeraspis tropicalis*; nannoplankton zone NP18) in Mangyshlak Peninsula (stratigraphical data according to Zhelezko, Kozlov 1999). Marls of the Kujlus outcrop were deposited during transgression and marls of the Usak outcrop were deposited during regression (Zhelezko, Kozlov 1999). Isuridae and Alopiidae represent pelagic, active swimming sharks, but some species of Alopiidae are bathypelagic (Zhelezko Kozlov 1999; Cappetta 1987).

The results of isotopic analyses of the shark teeth are reported in Table 1. There is a good correlation between $\delta^{18}O$ in a phosphate and $\delta^{18}O$ in a structural carbonate of apatite ($R^2 = 0.92$). Data of $\delta^{18}O$ suggest relatively warm (subtropical) waters in both Middle Bartonian and Late Bartonian, however sharks from Usak locality lived in much warmer waters than sharks from Kujlus. The high water temperature during the latest Bartonian may be related to the regression and shallowing of the basin. The $\delta^{18}O$ from the *Usakias wardi* teeth both in Kujlus and Usak outcrops suggest that this species lived in colder (deeper) waters than *I. bajarunasi* and *M. americanus*. The relatively distinct differences in the $\delta^{13}C$ values between different teeth of the same species suggest that the $\delta^{13}C$ may reflect isotopic exchange with carbon from dissolved inorganic carbon.

Table 1. Isotopic composition of oxygen and carbon in Bartonian shark teeth from Mangyshlak Peninsula.

Outcrop	Age	Shark species	$\delta^{18}O_{VSMOW}$[‰]		$\delta^{13}C_{VPDB}$[‰]
			Phosphate	Carbonate	
Usak	U. Bartonian	*I. bajarunasi*	16.63	24.64	-0.77
		M. americanus	18.3	25.45	-1.05
		U. wardi	20.17	25.91	-0.06
Kujlus	M. Bartonian	*M. americanus*	19.85	26.08	-1,05
		I. bajarunasi	20.22	26.21	-1.56
		U. wardi	21.1	27.06	-2.91

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Geochemistry of waters and bottom sediments in landslide lakes of the Babiogórski National Park

Dariusz SALA[1], Grzegorz RZEPA[1]

[1]*Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, 30 Mickiewicza Ave, 30-059 Kraków, Poland; e-mail: saladariusz@wp.pl*

The Babiogórski National Park (BNP) with an area of 3391.55 ha is situated in the eastern part of the Beskid Żywiecki (Polish part of the Western Outer Carpathians). It was founded in 1954 to protect local ecosystems: the Carpathian spruce forests, a dwarf mountain pine belt and alpine meadows. In 1977 BNP was assigned to the Biosphere Reserve network, and was encompassed with the UNESCO program "Man and Biosphere" as one of the first protected areas in Poland (Omylak 2004).

The Polish part of BNP comprises about 19 natural water bodies that were formed mostly by landslides. They are located primarily on the forested northern slope of the Babia Góra Mt. (lower and upper forest belts). Only three ponds, that are located in the highest part of the mountain, belong to the dwarf mountain pine belt. These small lakes (up to about 450 m^2 in area) are fed up by streams. This is the main reason why most of the small lakes are ephemera, usually disappearing during the summer. Only the largest may persist all year round (Sala, Rzepa 2008). In spite of nearly two hundred years of scientific research in the area of the Babia Góra Mt., these natural reservoirs are still relatively poorly recognized.

The goal of this study is to assess the contamination of the landslide lakes located within BNP and to evaluate possible pollution sources. The water and bottom sediment samples were collected from 12 lakes during the summer field works in 2007 and 2008. The electrolytic conductivity (EC), pH and temperature of the water were measured *in situ*. The chemical analyses of the water included: determinations of main cations and anions by the titration, colorimetry and AAS methods (spectrometer Philips PU-9100x), and of trace metals by the ICP-MS method (spectrometer Perkin Elmer, Elan 6100). In addition, selected physicochemical parameters, such as color, turbidity, odor, BOD (biological oxygen demand) and COD (chemical oxygen demand) were measured. The bottom sediment samples were analyzed for trace metals (Cd, Cr, Cu, Pb, Zn) by AAS using the procedure developed by the U.S. EPA for heavy metals in soils, sediments and sludges (Soon, Abboud 1993). Micromorphological observations and chemical analyses were carried out using FEI Quanta 200F scanning electron microscope equipped with energy dispersive spectrometer (EDS).

The water samples are acidic to nearly neutral (pH 4.1–7.4) with low mineralization (EC values range from 22 to 225 μS/cm). Most of these samples represent a calcium–bicarbonate type. The high COD and BOD values of 5.3 to 238.2 mg O_2/L and 0.02 to 4.82 mg O_2/L, respectively, indicate high amounts of organic matter (Sala, Rzepa 2008). The lowest pH values are recorded in the small ponds located within small peat areas. It is interesting to note that these lakes are also characterized by the lowest values of EC (20–80 μS/cm). The dominant role of organic matter in the chemical composition of these waters is highlighted by intense color (up to 240 mg Pt/dm^3), organic odor and high COD (about 240 mg O_2/L). The chemical composition of the water samples from the larger ponds is different. These are less acidic showing relatively high EC values, exceeding 100 μS/cm.

The water samples represent a calcium–bicarbonate type or calcium–magnesium–bicarbonate type. The Ca^{2+} and HCO_3^- concentrations reach 40% mval. The minor and trace element concentrations were usually low. Among them, only Fe shows elevated levels in most cases (up to 1.6 mg/L). Several samples contained elevated Mn and Al concentrations reaching 0.3 mg/L and 0.9 mg/L, respectively. The highest concentrations of these elements were found in the ponds with the lowest pH, but the richest in organic matter. The results suggest that the landslide ponds are not polluted and the elevated values of some parameters are probably related to the natural geochemical processes.

The trace metal concentrations in the bottom sediments are also usually low. However, they vary depending on the sediment type and location of the lakes. The selected trace metal concentrations are as follows: 9.27–65.06 mg/kg (Zn), 6.08–22.05 mg/kg (Pb), 1.65–6.71 mg/kg (Cu) and 0.19–4.63 mg/kg (Cr). The Cd content is elevated, ranging from 1.12 to 25.94 mg/kg, with an average of 10.57 mg/kg (Sala, Rzepa 2009). A distinct relationship between the Cd content in the sediment and its concentration in the water is noticed. This may suggest that the raised levels of Cd in the waters resulted from the geochemical interactions with sediments rather than from the atmospheric deposition.

The scanning electron microscope observations and the EDS analyses indicate that the bottom sediments are composed mostly of the organic matter and detritic minerals (quartz and feldspars). Except for these natural constituents, small (up to several mm across) spherical particles probably of industrial origin are also found. Those showing smooth surface and aluminosilicate composition are presumably a result of the combustion of fuels. The particles with more rough surfaces, composed nearly entirely of iron oxides, may be related to emission from the metallurgic plants.

The field observations and laboratory results indicate that the water samples from ponds are not contaminated by trace elements. The elevated concentrations of Fe, Mn and Al are the result of natural geochemical processes. The bottom sediments, however, contain dust particles of anthropogenic origin and show raised Cd concentrations. The previous studies (e.g. Grodzińska 1978) also reported high Cd and Pb contamination levels in soils and mosses, suggesting that the pollution was probably caused by emissions from the Upper Silesian and Ostrava industrial districts. However, it should be noted that the snowpack from the Babiogórski National Park, is not polluted by Cd (Łajczak 2004), indicating only a small supply of this airborne element in recent years. The BNP is currently less vulnerable to anthropopression than in previous years.

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3D depiction of geochemical data - a tool for estimation diffusion delay in non-linear system

Ewa SŁABY[1], Michał ŚMIGIELSKI[2], Andrzej DOMONIK[3]

[1] *Polish Academy of Sciences, Institute of Geological Sciences, Research Centre in Warsaw, 51/55 Twarda St., 00-818 Warsaw, Poland; e-mail: e.slaby@twarda.pan.pl*
[2] *Institute of Geology, Faculty of Geology, Warsaw University, 93 Żwirki i Wigury Ave, 02-089 Warszawa, Poland*
[3] *Institute of Hydrogeology and Engineering Geology, Faculty of Geology, Warsaw University, 93 Żwirki i Wigury Ave, 02-089 Warszawa, Poland*

Magma mixing presents an open system with non-linear dynamics (Perugini et al. 2008). However, it is commonly believed that if mixing is the only process occurring in a system, linear correlations must be observed between concentrations of any two chosen elements. Consequently the mixing equation is a linear equation combining the composition of the hybrid, the two end-member magmas and the degree of the process progress (Langmuir et al. 1978). Such a rule is well applicable for whole rock composition data. Mixing is also well registered in mineral domains grown from regions in which magmas mix intimately. In contrast it seems that the Langmuir et al. (1978) rule is not usable for micro-scale modeling. On the base of 3D depiction of geochemical data collected on crystal domains some models have been constructed. The domains chemical heterogeneity was determined with use of LA-ICP-MS. For the depiction as well as further proceeding with the data new multi-method approach have been developed. The models show that in the crystal domains the relationships between concentrations of two elements of different mobility do not follow the schema, which could be expected for mixing of two end-member magmas, e.g. linear correlation. Due to the intensive stirring, the magma domains chaotically advected to the crystal result in slightly different composition of crystallizing phase. The diffusion of elements progresses with different speed among these domains. Some of them are able to spread across magma domains faster, other move with some delay. Due to the different diffusivity speed, linear correlations cannot be observed between concentrations of randomly chosen two elements within the active magma domains and respectively crystal domains. The developed mathematical models are complementary and give possibility to assess the degree of the elements exchange between both magmas, e.g. the degree of magma blending. The models also allow us to estimate easily the deviation from the linearity of the behavior of elements at different stages of mixing.

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Minerals in Bory mire (Sosnowiec, southern Poland): formation, stability and trace element uptake

Beata SMIEJA-KRÓL[1], Arkadiusz BAUEREK[2], Barbara FIAŁKIEWICZ-KOZIEŁ[3]

[1] *Faculty of Earth Science, University of Silesia, 60 Będzińska St., 41-200 Sosnowiec; e-mail: beata.smieja-krol@us.edu.pl*
[2] *Department of Environmental Monitoring, Central Mining Institute, 1 Gwarków Sq, 40-166 Katowice; e-mail: abauerek@gig.katowice.pl*
[3] *Faculty of Biology and Environmental Protection, University of Silesia, 9 Bankowa St., 40-007 Sosnowiec; e-mail: basiaf1234@poczta.fm*

Constructed wetlands and peat containing remediation systems are used for low-cost, effective treatment of diluted wastewater, like acid mine drainage. Natural peatlands are known as effective geochemical barriers for trace elements. Peat-accumulating ecosystems efficiently remove chemical elements from surface and underground waters (Syrovetnik et al. 2007) and retain airborne particulate pollutants (e.g. De Vleeschouwer et al. 2007). In this study, we investigated a heavily polluted mire in its initial stages of peat accumulation to depict processes responsible for heavy metal retention.

The Bory mire is located in southern Poland, in the middle part of the Upper Silesia Industrial Region. The mire covers an area of 6.68 ha, whereas the average thickness of the peat deposit is 20–30 cm. The mire developed in an abandoned sand-pit, in which exploitation was probably ceased prior to the Second World War (Chmura, Molenda 2007). The mire is supplied both with underground waters and precipitation.

The peat samples were collected from the depth of 5 and 15 cm at three sites covering a change in the pH from 4.1 to 6.2 and gradient of nutrient availability from relatively nutrient poor to nutrient rich. The latter distinction was made basing on the differences in vegetation type growing on the mire (from communities dominated by *Sphagnum sp* to those dominated by *Phragmites australis*) and electrolytic conductivity (from 191 to 276 μS/cm, respectively).

The chemical analyses of both peat and water samples were conducted using the atomic absorption spectrometry (AAS) method for major elements and the inductively coupled plasma mass spectrometry (ICP-MS) method for trace elements. The solid samples (inorganic particles and peat) were investigated using field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS). The crystalline phases were identified using an XRD technique.

The contents of Zn, Pb and Cd in the peat samples were high, up to 1347, 1260 and 43 ppm, respectively. The same trace metals analyzed in water reached a concentration below 0.5 ppm.

The inorganic fraction is dominated by aluminosilicate spheroidal fly ash particulates originating from coal combustion, proving that an important addition of pollutants comes from dust deposition. The aluminosilicate spherical particulates are stable in the peat environment. Limited dissolution of some of them is likely related to higher iron content.

Hematite and barite (the latter originating from coal combustion) are dissolving in the peat layer. Among the new-forming minerals, cubo-octahedral pyrite microcrystals are abundant. They commonly form framboids. Zn, Pb and Cd are immobilized in the form of sulphides, which are nucleated inside peat organic debris. Galena (PbS) form nanoparticle aggregates showing a cubic outline, whereas ZnS and less common CdS are typically spheroidal. The size of individual aggregates varies from 200 nm to 1 μm. A progressing aggregation process of spheroids toward structures of about 10 μm was also observed. Microorganisms and bacterially-induced extracellular polymeric substances (EPS) were commonly observed to be associated with the sulphides.

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Authigenic minerals in the Bagno Bruch mire (Southern Poland) contaminated by trace metals through atmospheric deposition

Beata SMIEJA-KRÓL[1], Jerzy WIEDERMANN[2]

[1]*Faculty of Earth Sciences, University of Silesia, 60 Będzińska St., 41-200 Sosnowiec, Poland; e-mail: beata.smieja-krol@us.edu.pl*
[2]*Materials Properties and Structure Laboratory, Institute for Ferrous Metallurgy, 12 Miarki St., 44-100 Gliwice, Poland; e-mail: J.Wiedermann@imz.pl*

Human impacts have caused dramatic changes in the geochemical cycle of many elements, and the possible effects of these changes have given rise to increasing concern on a regional and global scale. Peatlands are ecosystems that play an important role in the cycling of trace and toxic elements in natural environment. They serve as natural geochemical barriers, effectively accumulating elements dispersed in the environment due to anthropogenic activities. In this study, we investigated formation of authigenic minerals containing heavy metals in the acid mire heavily polluted through atmospheric deposition.

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 mire occurs in a shallow depression on fine-grained clayey and sandy fluvioglacial sediments. The Bagno Bruch covers a total area of about 39 ha. The thickness of the peat averages 90 cm, in places reaching 205 cm. The mire is supplied mainly by rainwater with a probable influx of groundwater.

The mire was drained by an orthogonal series of ditches and channels about 60 years ago. The drainage system lowered the water table level in the mire, which seems to have been one of the causes of peat degradation. The degree of humification (von Post scale) changes from H2 near the surface to H8 below 32 cm.

An 80 cm-long core was taken from the Bagno Bruch mire using a 10×10 cm stainless steel Wardenaar corer, and cut into 1-cm slices using a stainless steel knife. The field emission scanning electron microscopy (FESEM) and energy dispersive spectrometry (EDS) were used to investigate the mineral matter associated with the organic constituents in the peat.

High metal concentration, reducing conditions and probably microbiological activity led to formation of several authigenic minerals, among which aggregates of ZnS and barite are the most common.

The authigenic ZnS forms spheroids 0.5–3 μm in diameter (Fig. 1a). These spheroids are grouped in loose aggregates, occurring typically inside organic tissues. Some of the authigenic ZnS grains are hemispheroidal, indicating growth after attachment to an organic surface. One aggregate usually contains tens to hundreds of spheroids. High magnification images show that the individual spheroids have an irregular surface and are composed of randomly oriented tabular particles reaching tens of nanometers in size. The authigenic ZnS is commonly enriched (up to ~4% by weight) in Cd, whereas As and Cu are scarce.

The ZnS mineralization zone is restricted to a relatively narrow peat layer within a depth range of 14–22 cm. In places, ZnS mineralization also occurs around 30 cm down.

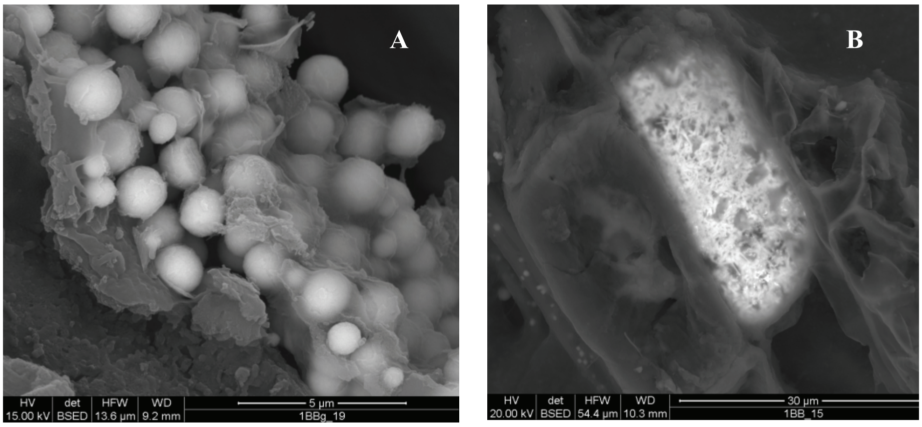

Fig. 1. (a) Loose aggregate of ZnS spheroids, depth 19 cm, (b) tabular barite inside plant cell, depth 15 cm (BSE images)

Authigenic barite form tabular crystals inside plant cells (Fig. 1b), which are often enriched in Pb and/or contain inclusions of galena. The authigenic barite was observed within the depth range of 11–24 cm. Most of the barite present in the samples constitutes an artifact formed after removing the peat profile from the mire and the peat drying; these form a very wide "mineralization zone" at a depth between 3 and 36 cm.

The minerals are redox sensitive: sphalerite (ZnS) is stable in a reducing environment (low pE values), whereas barite needs oxidizing conditions to persist (higher pE values). Calculations done using the PHREEQC program for Windows shows that only a narrow redox range (0.18–0.93 pE and 1.42–1.93 pE) is optimal for their coexistence at pH 4 and 3, respectively. As the conditions prevailing in a mire upper peat layer are changeable with respect to pH, metal concentrations and water table level (inducing changes in pE values), this would explain the preferred mineral precipitation inside plant debris, which probably maintains more stable redox conditions than the environment outside organic tissues.

The results highlight the importance of mineralogical information to predict the metal speciation and long-term fate in natural and constructed wetland systems.

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Radioactivity of coal mine waste formed in the Sobieski Mining and Power Plant in Jaworzno

Danuta SMOŁKA-DANIELOWSKA[1]

[1]*Faculty of Earth Sciences, University of Silesia, 60 Będzińska St., 41-200 Sosnowiec, Poland; e-mail: danuta.smolka-danielowska@us.edu.pl*

This report presents the results of geochemical and mineralogical analyses of coal mine waste obtained from seed washer, sludge washings and waste during the process of sludge enrichment. The mining waste form in the process of mechanic coal treatment at the Sobieski Mining and Power Plants. The following radioactive and rare earth elements (REE) were detected: U, Th, La, Ce, Nd, Sm, Y, Gd, and Dy. In addition, the specific activity of natural radionuclides (K-40, Ra-226, Ra-228, Th-232, and U-238) was measured and REE-rich mineral phases were identified. The waste samples were analyzed for lanthanides and actinides using the instrumental neutron activation analysis (INAA). The specific activity of the waste examined was measured with the gamma spectrometry technique. The mineral phases were identified using the electron scanning microscopy (SEM) method. The concentration of REE in the samples examined displayed the similar sequence: Ce > Nd > La > Y. The samples of seed washer waste are characterized by the highest specific activity of K-40 (max. 710 ± 42 Bq/kg). The specific activity of Ra-226 isotope is the highest in the samples of seed washer waste and sludge enrichment showing the maximum values: 77 ± 5.3 Bq/kg and 73 ± 2.1 Bq/kg, respectively. The activity of Th-232 isotope is the highest in the waste samples derived from sludge enrichment (max. 47 ± 1.3 Bq/kg). The REE-rich mineral phases are represented mostly by phosphates, i.e. monazite and xenotime.

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Geochemistry of the 2004 tsunami deposits – diagnostic features and environmental impacts

Witold SZCZUCIŃSKI[1]

[1]*Institute of Geology, Adam Mickiewicz University in Poznań, 16 Maków Polnych St., 61-606 Poznań, Poland; e-mail: witek@amu.edu.pl*

The December 2004 tsunami left deposits with a thickness varying from a few millimeters to tens of centimeters over a roughly one-kilometer-wide tsunami inundation zone around the Indian Ocean. These deposits were studied from the geochemical point of view in a coastal zone of the Andaman Sea in Thailand by a team from Adam Mickiewicz University in Poznań. The present contribution presents two aspects of these studies: 1) diagnostic features (e.g. salinity indexes) of tsunami deposits and their preservation in time, and 2) potential environmental impacts of tsunami deposits. Sampling of tsunami deposits and reference soils was done two months after the tsunami had occurred and then after 1, 2, 3 and 4 years to record the postdepositional changes. A wide range of sample treatment procedures and analytical techniques were applied. They included analyses of "salts" in water soluble fraction and heavy metals in acid-leachable fraction (Szczuciński et al. 2005, 2007), Al in liable fraction (Zioła-Frankowska et al. 2009), fractionation of Hg (Boszke et al. 2006), fractionation and speciation of As (Kozak et al. 2008b) and bulk sediment analyses. The tsunami deposits were enriched in "salts" in water soluble fraction. However, most of them were removed during the first rainy season (Szczuciński et al. 2005, 2007). They were also enriched in heavy metals (particularly in Pb), which were highly correlated with Cl^-, probably forming common compounds (Szczuciński et al. 2005). The tsunami deposits were also enriched in As. Its content was similar to that after the following rainy seasons, but its form changed from a mixture of As(III) and As(V) into As(V) only (Kozak et al. 2008b). The other elements, i.e. Ba, Mn, Sr and U, regarded as typical salinity indexes, occurred in the tsunami deposits in much higher concentrations than in the local reference soils. The environmental impact of tsunami deposits revealed at least two features. Firstly, they covered old soils and served as a new initial soil depleted in organic matter (Szczuciński et al. 2006), secondly, the deposits served as a potential source of toxic amounts of heavy metals, arsenic and salts. The documented changes of chemical evolution of the tsunami deposits, as well as the preliminary studies on bioaccumulation of heavy metals in new growing plants, proved the potentially dangerous elements to be of relatively modest bioavailability (Kozak et al. 2008a,b).

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Geochemical effects of mining on geological environments, North-west Isfahan, Central Iran

Batoul TAGHIPOUR[1], Mohammad Ali MACKIZADEH[2]

[1]*Department of Earth Sciences, Faculty of Science, University of Shiraz, Iran; e-mail: taghipour@shirazu.ac.ir*
[2]*Department of Geology, University of Isfahan, Isfahan, Iran; e-mail: ma_mackizadeh@yahoo.com*

This is a preliminary report on the effect of mining process on the environment in the area situated north-west of Isfahan. The study area is located in the marginal part of the Cenozoic magmatic belt of Central Iran, (Ghorogh Chi Pass, Meymeh city). Triassic pyrite-bearing black shales are the main lithologic constituents of rock formations in the area examined. This sequence was affected by alteration processes forming a clay mineral deposit.

The mine ceased operation two decades ago. There is a periodic acidic pond in abandoned open pit that formed during mining activities. Oxidation of pyrite has produced acidic waters and secondary rare minerals. As a result of this process ferricopiapite $Fe^{3+}_{2/3}Fe^{3+}_4[(OH) \mid (SO_4)_3]_2 \cdot 20H_2O$ and other sulfates have been formed (Wenk, Bulakh 2004).

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The use of isotopic composition of fish scales for identification of fish origin

Andrzej TREMBACZOWSKI[1]

[1]*Mass Spectrometry Laboratory, Institute of Physics, Maria Curie-Skłodowska University, 1 Maria Curie-Skłodowska Sq, 20-031 Lublin, Poland; e-mail: andrzej.trembaczowski@poczta.umcs.lublin.pl*

The tissues of animals are built of proteins. Hobson (1999) suggests that the isotope ratios are useful markers for understanding the ecology of migratory animals and for explaining relations between food and animal tissues.

The isotopic composition of the animal tissue reflects its diet. Of the different tissues, especially the fish scales contain the isotopic record of the whole life of a fish, whereas the muscles may provide information about last months. The isotopic composition of fish scales reflects that of most common diet, which is derived partly from river water (autochthonic diet) and partly from outside the river (allochthonic diet). In big rivers an autochtonic diet dominates, whereas in small streams an allochthonic diet is more significant. Reared fish fed on commercial pellets extremely differs in isotopic composition compared to wild populations.

This paper presents the differences of S and C isotopic composition in fish scales extracted from: (1) wild fish (trouts and graylings) from the Polish rivers (SE Poland), (2) reared fish (rainbow trouts) from commercial pond farms, and also (3) sea trouts, living in the Baltic Sea and caught in the Pomeranian rivers.

The isotope signature of the scales extracted from the fish living in different rivers differs significantly accordingly to distinct habitat conditions (kind of available diet), whereas the δ-values of reared rainbow trout scales is closely linked to the isotopic composition of pellets used for feeding. This information may be used to recognize the origin of fish; wild-reared or anadromous-resident form.

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Isotopic signatures of enzymatic mineralization of organic sulphur in freshwater sediments

Adriana TROJANOWSKA[1], Wojciech DRZEWICKI[1]

[1] *Laboratory of Isotope Geology and Geoecology, Institute of Geological Sciences, Faculty of Earth Sciences, University of Wrocław, 30 Cybulskiego St., 50-205 Wrocław, Poland;*
e-mails: adriana.trojanowska@ing.uni.wroc.pl, wojciech.drzewicki@ing.uni.wroc.pl

A great amount of sulphur in soil and sediments is incorporated in organic matter. Nriagu and Soon (1984) estimated that sulphate esters and carbon bounded sulphur, from which SO_4^{-2} is easily mobilised due to microbial activity, constitute 50 to 90% of the total sedimentary sulphur.

The arylsulphatase (EC 3.1.6.1.) – hydrolytic enzyme secreted by microbial communities catalyses irreversible hydrolysis reaction of sulphate esters coupled with a release of sulphates (Tabatabai 1982). Therefore arylsulphatase from the biochemical point of view is responsible for organic sulphur mineralization and sulphur turnover in sediments and soil (Speir, Ross 1978).

Investigations have been carried out in the shallow, eutrophic, freshwater dam reservoir Sulejow (Central Poland) in its riverine, transition and lacustrine parts. The sediment samples were collected monthly from May to October 2006.

Arylsulfatase activity was analysed in fresh sediments immediately after sampling, using the spectrophotometric procedure described by Tabatabai and Bremner (1970) with pNPS as substrate. Bacteria were enumerated using fluorescence microscopy (Nikon Eclipse 400) in samples DAPI stained (Porter, Feig 1980).

Organic matter content was analysed as a loss of ignition at 550°C (Håkanson, Jansson 1983). The total sulfur content (TS) was determined in the homogenized dry sediment using Vega5135 MM Tescan scanning electron microscope with EDX Link 300 ISIS Oxford Instruments spectrometer.

The sulphate content in sediments was determined gravimetrically as precipitated $BaSO_4$ derived from washing out the sediments. The obtained pure $BaSO_4$ precipitate was then prepared for isotopic analysis (combustion with catalysts at 950ºC and cryogenic purification) (Mizutani, Oana 1973; Yanagishawa, Sakai 1983). The isotopic analysis ($\delta^{34}S$) was carried out using a MI-1305 mass spectrometer in the Department of Mass Spectrometry at Maria Curie-Skłodowska University in Lublin.

The average $\delta^{34}S$ (SO_4^{-2}) values in a riverine zone reached -5.93 ± 2.20‰, whereas in transition and lacustrine zones -9.20 ± 1.14‰ and -6.75 ± 1.89‰, respectively.

The highest average arylsulphatase activity was recorded in a transition zone 312.94 ± 317.43 μg·g d.w$^{\cdot -1}$ h^{-1}, where the highest organic matter content (average of 12.29 %) and the total sulphur concentration (average of 4.08 mg·g) were noted. The analysis of variance (ANOVA) did not confirm a statistically significant difference between studied parameters recorded in the riverine, transitional and lacustrine parts of the reservoir.

The statistically significant positive correlation between the arylsulphatase activity and sulphates content ($r = 0.73$, $p = 0.00$) as well as total sulphate ($r = 0.49$, $p = 0.04$) in sediments was recorded, which confirms an important role of this enzyme in sulphur turnover in sediments. This conclusion is supported by the negative correlation between the arylsulphatase activity and $\delta^{34}S$ (SO_4^{-2}) ($r = -0.46$, $p = 0.05$), as isotopically light sulphates are released from organic matter due to enzymatic microbial activity. The $\delta^{34}S$ (SO_4^{2-}) showed also a strong negative linkage to total sulphur ($r = -0.54$, $p = 0.02$) and lack of relationship with sulphate concentration.

Sulfur isotope ratio in sulfates from sediments (-7.29‰ in average) was lower than in sulfates from water (4.45‰ in average) as reported by Lewicka-Szczebak and co-authors (2009) in the same reservoir and period. This evidence suggests that the water column is supplied in sulphates by sediments.

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Application of modified clinoptilolite-heulandite adsorbents in removing volatile organic compounds from the air

Dariusz WIDEŁ[1], Jerzy OSZCZUDŁOWSKI[1]

[1]*Institute of Chemistry, Jan Kochanowski University, 25-406 Kielce, 15G Świętokrzyska St., Poland; e-mail: jerzy.oszczudlowski@ujk.kielce.pl*

Natural zeolites belong to the most popular microporous hydrated aluminosilicate minerals with Na, K, Ca and Mg as exchangeable cations. The zeolites formed through deposition and weathering of volcanic ash in lake or shallow marine environments. They occur in many places throughout the world, including: China, Japan, North America, Cuba, India, New Zeland, Italy, Greece, Hungary, Ukraine, and Georgia (Ciciszwili et al. 1990). The group of natural zeolites comprises about 40 minerals, but clinoptilolite, heulandite, philipsite and mordenite are of greatest importance. Clinoptilolite and mordenite tuffs are commonly mined and widely used in industry (Bish, Ming 2001).

These minerals possess a clinoptilolite-heulandite structure that gives them unique physical and chemical properties, such as: high adsorptive capacity and ion-exchange selectivity, large surface area, relatively high heat and mechanical resistance (Armbruster 2001). Owing to their physical and chemical properties, zeolites are widely used as: natural adsorbents, ion exchangers, desiccants, molecular sieves, catalyst carriers in chemical industry, building engineering, agriculture and environmental protection (Guisnet, Gilson 2002). Natural zeolites are applied for removal of heavy metals from municipal, metallurgical and mining waste water as well as they permanently neutralize low-level radioactive wastes. Metal ion-exchanged natural zeolites are used for removal of ammonia, volatile organic compounds, sulfur dioxide, hydrogen sulfide, chlorinated hydrocarbons from sewer gas (Askley et al. 2003) and waste water (Mier et al. 2001). Clinoptilolite is the main component of zeolite deposits in the State of San Luis Potosi, Central Mexico (Oszczudłowski, Krasoń 2003).

The adsorption properties of clinoptilolite-rich zeolites from Central Mexico have been studied using an inverse gas chromatography method. The chemical and phase composition of these aluminosilicate species is relatively homogeneous. The thermally- and chemically-modified zeolite samples were applied for adsorption of volatile organic compounds, especially chlorinated hydrocarbons (tetrachloroethylene and trichloroethylene) from the contaminated air (Oszczudłowski et al. 2008). The zeolite samples were crushed with a hydraulic press and then sieved to separate individual fractions. The 30–60 mesh fractions was calcinated at 673 K for 2 hours. The acid-modified clinoptilolite was obtained after treatment with a 3M aqueous solution of HCl for 2 hours at temperature of 363 K in the Soxhlet apparatus. The H-form of zeolite was washed in distilled water, dried at room temperature and calcinated at 673 K for 2 hours. The scope of physical and chemical study of the clinoptilolite samples encompassed: (1) thermal analysis in the temperature range of 293–1273 K, (2) chemical analysis using the XRF and ICP-MS methods, (3) X-ray diffraction ($2\theta = 5\div60°$), (4) determination of textural properties (specific surface, volume of pores, porosity), (5) determination of low-temperature adsorption isotherms of nitrogen at 77 K, (6) measurement of adsorption of selected volatile organic compounds from the gas phase using the inverse gas chromatography method. A chromatographic glass column of 0.61 m long (2 ft × OD ¼ in. × ID 2 mm) was filled with adsorbents at a height of 60 mm. Prior to the analysis, the adsorbents were conditioned in the carrier gas (helium) stream for about 12 hours at 473 K. To better interpret the results, the peak profile method together with the Microcal Origin computer program was applied. The determinations were made with the gas chromatograph HP6890.

The following conclusions may be drawn from this study:

1. The natural zeolites are thermally stable up to 873 K; at 673 K over 90% of water is removed from the zeolite.
2. The chemical composition of natural zeolites is very complex, but the concentration of heavy metals is very low.
3. The phase composition of natural zeolites is crystallographically clear, no loam phases in zeolites were detected.
4. According to the IUPAC classification, the low-temperature adsorption isotherms of nitrogen belong to the type IV and to the type of the hysteresis loop H1.
5. The specific surface area of natural zeolites does not exceed 20 m^2/g. The activation and dealumination with a 3 M HCl solution result in increasing the specific surface area up to 100 m^2/g.
6. The adsorption isotherms of tetrachloroethylene from the gas phase on the natural zeolites correspond to anti-Langmuir character in the temperature range of 345–365 K and Langmuir character above 493 K.
7. The thermally- and chemically-modified natural zeolites can replace carbon adsorbents in removing traces of volatile organic compounds from the air.

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Single particle analysis of aerosols in Kraków (Poland)

Wanda WILCZYŃSKA-MICHALIK[1], Mateusz DAMRAT[2], Łukasz TYRAŁA[2], Witold BOROWIEC[3], Marek MICHALIK[2]

[1]*Institute of Geography, Pedagogical University, Kraków, 2 Podchorążych St., 30-084 Kraków; e-mail: wmichali@up.krakow.pl*
[2]*Institute of Geological Sciences, Jagiellonian University, 2A Oleandry St., 30-063 Kraków; e-mails: l.tyrala@gmail.com; damrat@op.pl; marek.michalik@uj.edu.pl*
[3]*Institute of Geography and Spatial Management, Jagiellonian University, 7 Gronostajowa St., 30-387 Kraków; e-mail: borus911@interia.pl*

A high concentration of particulate matter (PM) in atmosphere of Kraków has always been a great concern for local and state authorities. The concentration of PM10 and PM2.5 in the air often exceeds permissible values.

The aim of this study, based on single particles analysis, is to characterize aerosols in Kraków and their seasonal variations and to determine of pollution sources. Morphology, chemical composition and particle size were determined using the SEM-EDS method. The aerosol samples were collected on the Petrianov filters and transferred onto polycarbonate filters for SEM observations.

Seasonal variation of the aerosol composition is similar to the results of previous studies by Kozak and co-authors (1998). Quartz, feldspars and mica-like particles are abundant, but irregular aluminosilicate particles of non-stoichiometric composition dominate. Particles with Si+Al content above 69 wt.% (considered to be aluminosilicate) represent roughly 40% of the analysed aerosol samples. The Al/Si ratio varies widely depending also on the content of minor components. Spherical aluminosilicate particles are present in all the samples examined. A moderate positive correlation between the Si and Al content in aluminosilicate particles is noted. A significant amount of aluminosilicate particles contains also S and Cl, which indicates their mixed composition (aluminosilicate with sulphate and chloride compounds).

Carbonate particles (calcite, dolomite or non-stoichiometric Ca, Mg, Fe carbonates) and sulphates are also common in the analysed samples. The Ca and Na (or Na+K) sulphates dominate in this group, but stoichiometric composition of gypsum or other phases is rarely noted. Only in several particles the Ca+S content is above 90 wt.% (value typical of gypsum). Barite particles and Fe sulphates are subordinate, whereas pure chloride particles are scarce. The correlation between the Cl and Na or K content is very weak. The results indicate that particles of mixed composition (Ca, Na, Mg, Fe sulphates and chlorides) dominate in the samples examined. The particles with Na+Cl content above 90 wt.% are absent (except for one example).

Carbonaceous particles are relatively common in the aerosol samples collected in winter season. Soot particles usually contain S^-, Cl^-, Na^+, K^+ and other ions.

Fe oxides, metallic iron, other metal-rich particles are present in numerous samples. Fe-rich particles are spherical or irregular. Because of the large steel works emission in Kraków, Fe-containing particles were analyzed thoroughly. The particles with more than 90 wt.% of Fe contain less than 2 wt.% of Si and less than 1 wt.% of Al. The particles with the Fe content between 90 and 40 wt.% contain up to 30wt.% of Si and up to 24 wt.% of Al. A group of particles from this Fe content range, contains Cr (4,8–27 wt.%) and Ni (5,7–14,7 wt.%). The particles with Fe content below 28 wt.% are characterized by a strongly variable content of other elements (e.g. Si from 9 to 55 wt.%; Al from 7 to 35 wt.%; S from 0.4 to 50 wt.%).

The single particle analysis of aerosols gives possibility for detail classification based on chemical composition, size and morphology, but a precise determination of their source (natural/anthropogenic and local/distant) is difficult.

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Geochemical features of fossil fuel contaminants found in urban wastes

Anna WOJTOŃ[1], Monika FABIAŃSKA[1]

[1]Faculty of Earth Sciences, University of Silesia, 60 Będzińska St., PL-41-200 Sosnowiec, Poland; e-mail:monika.fabianska@us.edu.pl

Thirteen samples of sludge collected in accordance with Polish standards at the sewage "Centrum" in Siemianowice Śląskie were used for hydrocarbon determinations. They were subjected to extraction with dichloromethane for 8 hours in a Soxhlet apparatus. Preparative thin layer chromatography (TLC) has been used for assessing the extract group composition. Aliphatic, aromatic hydrocarbons and polar compound fractions were separated. Samples solutions in DCM were applied as bands onto the activated 20x20 cm semi-preparative glass plates pre-coated with silica gel 60 F_{254} (Merck). Plates were developed in a TLC tank (50 min in saturated vapor condition) with *n*-heptane as an eluent. The fractions were differentiated by fluorescence of aliphatic (lack of fluorescence) and aromatic bands (blue-violet) in UV light and by comparing with reference compounds (*n*-eicosane, phenanthrene and isoquinoline) developed on the same plate. The received fractions have been eluted from silica gel in short glass columns with dichloromethane (aliphatic and aromatic compounds) or with a mixture of dichloromethane: methanol = 4 : 1 (vol : vol) (polar compounds). GC-MS analyses were performed using the gas chromatograph Agilent Technologies 5890 II equipped with a capillary column HP-5 (length = 60 m, internal diameter = 0.20 mm, thickness of stationary phase film = 0.25 mm, carrier gas – He). The gas chromatograph was directly coupled with the mass detector HP 5971 working under EI (Electron Impact) = 70eV. The mass spectra, total ion chromatograms (TIC) and ion chromatograms were recorded in the full scan mode and developed using the MS Data Analysis computer program (Hewlett-Packard). The obtained results were compared with literature data, previous analyses of standard compounds, and typical distributions of compounds groups published in literature (Wiley 2000, Peters et al. 2005).

The following compound groups of the geochemical origin were found in the sludge extracts: *n*-alkanes in the range of *n*-C_{14} to *n*-C_{39}, acyclic isoprenoids (mainly pristane and phytane), steranes, tri- and pentacyclic triterpanes. Of these compounds, *n*-alkanes predominate in all the samples examined. Triterpenes and steranes are present in lower amounts. Triterpenes group comprised of tricyclic triterpenes from C_{19} to C_{28} and pentacyclic triterpenes (hopanes, moretanes) showing much higher concentrations. Steranes encompassed the compounds with 27 (cholestanes) to 29 (stigmastanes) carbon atoms in a molecule. Stigmastane and cholestane diastereomers revealed the highest concentrations, whereas the ergostane group (C_{28}) displayed the lowest concentration in all the samples. In addition, saturated fatty acids, saturated fatty acids with one double binding and their esters were also identified. Polycyclic aromatic hydrocarbons (phenanthrene, fluorene, pyrene, chrysene, biphenyl, perylene, benzopyrene) and alkylbenzenes occurred in smaller amounts.

The distribution patterns of biomarkers and their parameters suggest that the dominant component of organic matter in the sludges was a petroleum material of unspecified origin. However, its geochemical features indicate that its most likely source was crude oil (or its derivatives) showing a relatively high degree of thermal maturity, as evidenced by the Carbon Preference Index (CPI) values close to 1.0. This evidence suggests a catagenic stage of thermal evolution corresponding to Rr 0.7–0.8% (Bray, Evans 1961; Eglinton, Hamilton 1967; Barthlott et al. 1998).

Pentacyclic triterpenes also show mature distribution type, with moretanes (hopanes β α) occurring only in low concentrations in the extracts. The presence of hopanes with a longer side-chain (C_{35} and C_{34}) indicate the source of petroleum rather than the coal-related organic matter since hopanes distribution in coal extracts is much shorter and usually ends at C_{33} hopane (Peters et al. 2005). This conclusion may also be supported by the absence of diterpenoids in the samples. Diterpenoids are the main component of matter derived from terrestrial plants (conifers) and can be found in the extracts of lignites, bituminous coals and other organic matter of terrestrial origin (Noble et al. 1986; Otto, Wilde 2001). On the basis of the ratio Pr/Ph we can assume that the kerogen which is the source of this oil was deposited in anaerobic environment since the values of a Pr/Ph ratio are less than 1.0 (Didyk et al. 1978). However, it is also possible that crude oil as a contamination in sludges was subjected to biological degradation in the wastewater treatment process. The last suggestion can be confirmed by the values of pristane to n-C_{17} and n-C_{18} phytane ratios which are only slightly over 1.0. There is "cutting out" in the lighter *n*-alkanes distribution in the range of n-C_{13} to n-C_{20}, which is a typical feature of slightly biodegraded or water-washed crude oils (Palmer 1993). The aromatic compounds present in the samples examined probably also come from petroleum, though some of them can be attributed to the products of combustion or other sources, such as, bituminous coals, ashes from coal/biofuel combustion or coal wastes stored nearby. It is difficult to identify the individual sources of these compounds, but the nearby sewage treatment plant could be a source of petroleum.

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Leachability of sulfate ions from the sulfur ore pile (Jeziórko sulfur mine, southeastern Poland)

Krzysztof WOŁOWIEC[1], Krzysztof JĘDRZEJCZYK[1]

[1] *Geological Enterprise, 3A Hauke Bosaka St., 25-214 Kielce, Poland; e-mails: krzysztof.wolowiec@pgkielce.pl krzysztof.jedrzejczyk@pgkielce.pl*

Sulfur is an element that takes part in many geochemical processes in natural environment. These processes are multi-faceted and strongly dependant on physical and chemical conditions, often leading to enrichment in sulfate ions and acidification of soils and waters. Both well and opencast exploitation of sulfur deposits has an impact on environment quality and human health. Except for this direct influence of sulfur mining, the other activities related to sulfur extraction play an important role in increasing an overall environmental impact. The sulfur mining sites and neighboring lands are potentially jeopardized areas.

The aim of this study was to determine the amount of sulfate ions which are leached with rainwater from the sulfur (over 90% S) ore pile more than 5 m high. In all, 33 sulfur ore samples were collected from different depths of 11 boreholes and several soil samples. Water extracts were prepared according to the validated procedure. The gravimetric method was applied to determine sulfate ions in water extracts.

Table 1 presents the concentrations of SO_4^{2-} in water extracts from sulfur ore samples collected from two boreholes O-1 and O-9. A strong correlation between the sulfate ions concentration and sampling depths was noted. The lowest sulfate concentration was recorded in samples collected near the top of sulfur ore tip. This evidence suggests that sulfate ions are washed out from the pile top as a result of weathering.

The results of the laboratory analysis enabled us to establish the amount of leachable sulfate ions, as well as the degree of influence of sulfur ore pile on the environment.

Table 1. Concentration of sulfate ions in water extracts from samples collected from boreholes O-1 and O-9

Borehole	Sampling depth (meters below sulfur pile top)	SO_4^{2-} (g/kg of dry weight)
O-1	0.5	6.4
	2.0	10.3
	3.5	11.6
	5.4	13.7
O-9	0.5	4.6
	2.0	7.0
	4.0	23.0

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Spatial and seasonal changes in salinity of coastal lakes – new insights from Lake Sarbsko, northern Poland

Michał WOSZCZYK[1], Henry BOKUNIEWICZ[2]

[1]*Department of Quaternary Geology and Paleogeography, Adam Mickiewicz University, 27 Dzięgielowa St., 61-680 Poznań, Poland; e-mail: woszczyk@amu.edu.pl*
[2]*Marine Sciences Research Center, Stony Brook University, Stony Brook, New York, USA; e-mail: hbokuniewicz@notes.cc.sunysb.edu*

Between December 2007 and September 2008 we obtained a high-resolution dataset on water chlorinity in the coastal Lake Sarbsko (17º 37’ E, 54º 46’ N). The Cl^- concentrations were measured on December 13th 2007, and April 10th, July 10th and September 17th 2008 in surface, bottom and pore waters from the upper 5-cm layer of bottom deposits from 50 stations located throughout the lake.

It was established that chlorinity of the lake waters displayed appreciable spatial and temporal variations. In December 2007 Cl^- concentrations in pore waters varied between 38.8 mg/L and 351.7 mg/L with the highest values recorded in the western part of the lake and in the close proximity to the Sarbsko Barrier. It is interesting to note that during winter the concentrations of chlorides in pore solutions were much higher than in overlying waters (38.6–97.9 mg/L) and displayed a different pattern of spatial distribution. In April 2008 the concentrations of Cl^- in the lake waters were distinctly lower than in December 2007 (34.3–74.8 mg/L). However, their spatial distribution in surface and interstitial solutions were similar. In July 2008 the lake waters were highly depleted in Cl^- (8.0–68.0 mg/L) and displayed no clear trends in spatial variation of chlorides. In September 2008 the Cl^- concentrations in Lake Sarbsko water slightly increased compared to summer months (27.7–50.0 mg/L) and gradients between the western/northern and central part of the basin started to build up.

The distribution of chlorides in Lake Sarbsko waters in winter and spring corresponds to the spatial changes in lithology of surface deposits. The increased concentrations of Cl^- were observed in the area occupied by organic matter-enriched sediments (Fig. 1).

To explain spatial and temporal changes in chlorinity of the lake water~~s~~ we consider three physical processes:

1. Seepage under the barrier from the Baltic Sea. The saline water from the Baltic Sea could seep under the barrier beach into the lake when wind-driven storm surges are high in the Baltic against the Sarbsko Barrier (cf. Bokuniewicz, Pavlik 1990; Rapaglia et al. 2009). Likewise, the water could leave the lake by this route when the Baltic is set down. The amount of this flow, if any, could change with the seasonal pattern of storms.
2. Groundwater seepage across the sea floor from the land south of the lake could contribute to the pattern. This, too, could cause seasonal changes depending on the recharge (rainfall).

3. Gravitational, density-driven convection from the open lake water into the surface layers of the sediments. If the saltier (higher density) water comes into the lake, the overlying water will be denser than perhaps, lower-salinity or higher temperature pore water and the denser water will seep into the sediments displacing the original, less-dense pore water. The rate of any such exchange depends not only on the density difference but also on the permeability of the sediments.

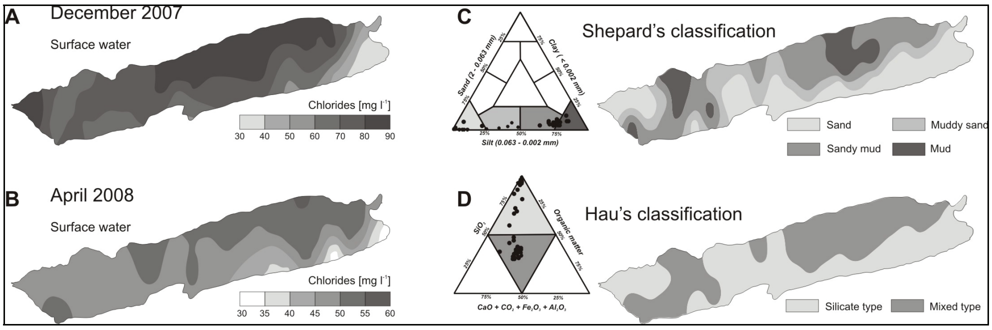

Fig. 1 Spatial changes in chlorinity of surface waters of Lake Sarbsko in December 2007 (A) and April 2008 (B) and distribution of lithofacies in the lake (C and D).

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Composition and origin of organic matter in surface sediments of Lake Sarbsko, a highly eutrophic and shallow coastal lake (northern Poland)

Michał WOSZCZYK[1], Achim BECHTEL[2], Jens FIEBIG[3], Mikołaj KOKOCIŃSKI[4]

[1] *Department of Quaternary Geology & Paleogeography, Adam Mickiewicz University, 27 Dzięgielowa St., 61-680 Poznań, Poland; e-mail: woszczyk@amu.edu.pl*
[2] *Applied Geosciences & Geophysics, University of Leoben, 5 Peter-Tunner-St., A-8700 Leoben, Germany; e-mail: achim.bechtel@mu-leoben.at*
[3] *Department of Geosciences – Palaeontology, J.W.Goethe-University, 1 Altenhöfer Allee, 60438 Frankfurt a. M., Germany; e-mail: Jens.Fiebig@em.uni-frankfurt.de*
[4] *Department of Hydrobiology, Adam Mickiewicz University, 89 Umultowska St., 61-614 Poznań, Poland; e-mail: kok@amu.edu.pl*

Sediments of coastal basins are composed of mineral and organic matter originating from river input, marine ingressions and autochthonous biological sources. As a result of this, sediments formed therein are heterogeneous and reveal considerable spatial lithological and geochemical variability. Moreover, due to the very small depth of coastal basins, a large portion of surface deposits is exposed to gravitational currents or wind-driven turbulence, and hence is often resuspended, which influences the composition and preservation of organic compounds.

In our study we demonstrate that in a very shallow, productive and well oxygenated polymictic coastal lake, fresh sedimentary organic matter is only poorly decomposed, however, its chemical composition display appreciable spatial variability. The surface sediments of Lake Sarbsko are characterized by the TOC content in the range of 0.34–17.35%. The extractable organic matter (EOM) content varies from 49.6 to 165.7 mg/g TOC and is negatively correlated with the TOC/N ratio. EOM is dominated by asphaltenes (40–69%), whereas the concentration of NSO compounds ranges from 28 to 58%. The saturated and aromatic hydrocarbon contents are 1–8 and 1–3% of EOM, respectively. The relatively low molar TOC/N ratio (5.67–9.99) as well as the $\delta^{13}C_{TOC}$ (-29.3 to -27.4‰) and $\delta^{15}N$ (0.6–2.3‰) indicate the predominance of well preserved autochthonous organic matter with minor contribution of terrestrial organic compounds.

The autochthonous organic matter of Lake Sarbsko is mainly produced by cyanobacteria, diatoms and bacteria. The relatively high contents of low-molecular *n*-alkanes, C_{27}-sterenes and C_{18} fatty acids (FAs) are indicative for phytoplankton-derived organic compounds. The $C_{18:3}$ and $C_{18:2}$ FAs, long-chain *n*-alkenes and diplopterol are attributed to cyanobacteria. C_{16} FAs and epibrassicasterol are assigned to diatoms and ßß-hopanes are known as markers of bacterial activity. Interestingly, the distribution of methyl-hopanes, indicative for methanotrophic bacteria, roughly corresponds with the occurrence of CH_4 within the surface deposits. The presence of terrestrial organic matter is evidenced by the odd-numbered C_{25}-C_{31} *n*-alkanes, long-chain saturated FAs and *n*-alkanols ($> C_{20}$), as well as sitosterol.

The abundance of cyanobacteria and diatoms in the lake, inferred from biomarkers, was compared with the composition of phytoplankton in the lake. Both cyanobacteria and diatoms were present in the lake waters the whole year round. Thirty-six taxa of cyanobacteria were found in Lake Sarbsko during the study period. The highest number of species (23) was noted during summer, 19 species during spring and autumn and 12 species during winter. The greatest number of taxa was found within Chroococcales order, belonging to genera *Apahanocapsa*, *Chroococcus*, *Mersimopedia* and *Microcystis*. Of all the detected cyanobacteria, four species were present during all seasons: *Chroococcus limneticus*, *Microcystis wesenbergii*, *Planktolyngbya contorta* and *Planktolyngbya limnetica*. Seventy-eight diatom taxa were identified within phytoplankton in the lake waters. The highest number of species (61) was observed in autumn and the lowest (39) in summer. Most of the taxa present throughout the year were rather infrequent. By far the most abundant were *Fragilaria ulna ver. acus* in autumn, *Fragilaria virescens* during winter and spring as well as *Nitzschia palea* in summer.

Excursion

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Geodiversity and geologic heritage protection in Kielce; route: (1) Upper Devonian fossil reef and other geologic features at the Kadzielnia Geologic Reserve, (2) traces of Old Polish mining at the Karczówka Landscape Reserve, (3) recumbent fold at the Ślichowice Geologic Reserve

Zdzisław M. MIGASZEWSKI[1], Agnieszka GAŁUSZKA[1]

[1]*Geochemistry and the Environment Div., Institute of Chemistry, Jan Kochanowski University, 25-406 Kielce, 15G Świętokrzyska St., e-mails: zmig@ujk.kielce.pl, agnieszka.galuszka@ujk.kielce.pl*

The city of Kielce holds up a unique geologic position among the regional capital cities of Poland and Europe. It is located in a forested hilly area that reflects the geologic setting of the western part of the Holy Cross Mountains, which are the only Paleozoic inlier in Central Europe located south-westward of the Teisseyre-Tornquist Line close to the East-European Platform (Żylińska et al. 2006). Nearly all the Paleozoic units occur in or near the city limits. Most of the built-up area lies on Upper Devonian carbonate rocks of the Kielce-Łagów Synclinorium that abuts on two Lower Paleozoic tectono-structural units: the Łysogóry Block (Fold, Thrust, Slice?) in the north and the Kielce-Klimontów Anticlinorium in the south (Znosko 1996). The Kielce-Łagów Synclinorium consists of numerous synclines and anticlines composed of Devonian – Lower Carboniferous rocks.

There are five nature reserves in the city area: four geologic reserves (Wietrznia, Kadzielnia, Ślichowice, Biesak-Białogon) situated in abandoned quarries, and towering Karczówka Mt. with a monastery complex assigned to landscape reserves (Fig. 1).

(1) Kadzielnia Geologic Reserve

The Kadzielnia Mt. is located in the south-central part of downtown Kielce. Established in 1962, the reserve occupies an area of about 0.6 hectares (Wróblewski 2000). The characteristic feature of this site is the Geologists' Rock (295 m a.s.l.) that predominates over the landscape (Fig. 2A). This steep cliff and neighboring sheer rock faces are all that remained of an abandoned quarry, in which high-grade limestone was extracted for lime production from 18th century through 1962. There are paved paths for pedestrians, self-guided trails, a small pond named "*Emerald lake*", an amphitheater for 5 000 seats at the bottom of the quarry (Fig. 2AB).

The Kadzielnia Mt. consists of Upper Devonian limestones (Fig. 3). The Geologists' Rock is composed of lower and lowermost middle Frasnian flat-lying, massive limestones with stromatoporoids, corals and subordinate brachiopods, cephalopods as well as rare trilobites and placoderms (Szulczewski 1979; Stupnicka, Stempień-Sałek 2001). This is the best exposed fossil reef in Poland, and deeply cut pit faces give an exceptional insight into this structure. The stromatoporoid-coral limestones are capped by a sequence of thick-bedded detrital limestones (calcarenites, calcirudites) passing upward into micritic Manticoceras limestones and then into Cheiloceras limestones (Szulczewski, 1979). There are many pink to greenish micrite-filled neptunian dikes cutting both diagonally and parallel the Frasnian limestone beds (Szulczewski 1979).

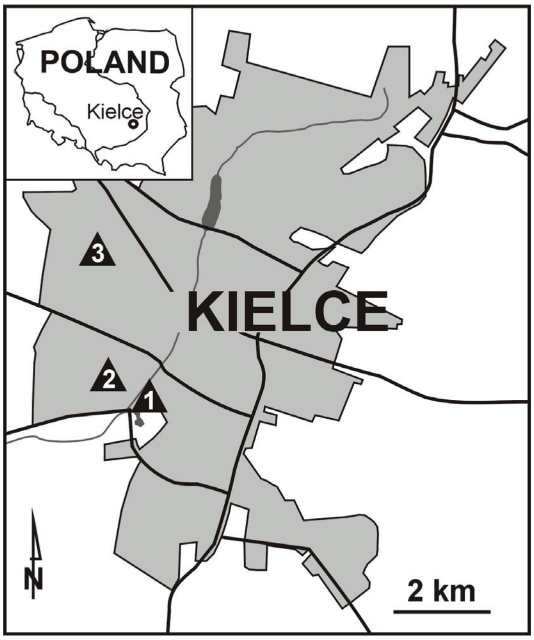

Fig. 1. Location of Kadzielnia (1), Karczówka (2), Ślichowice (3) reserves (Góry Świętokrzyskie, 2006)

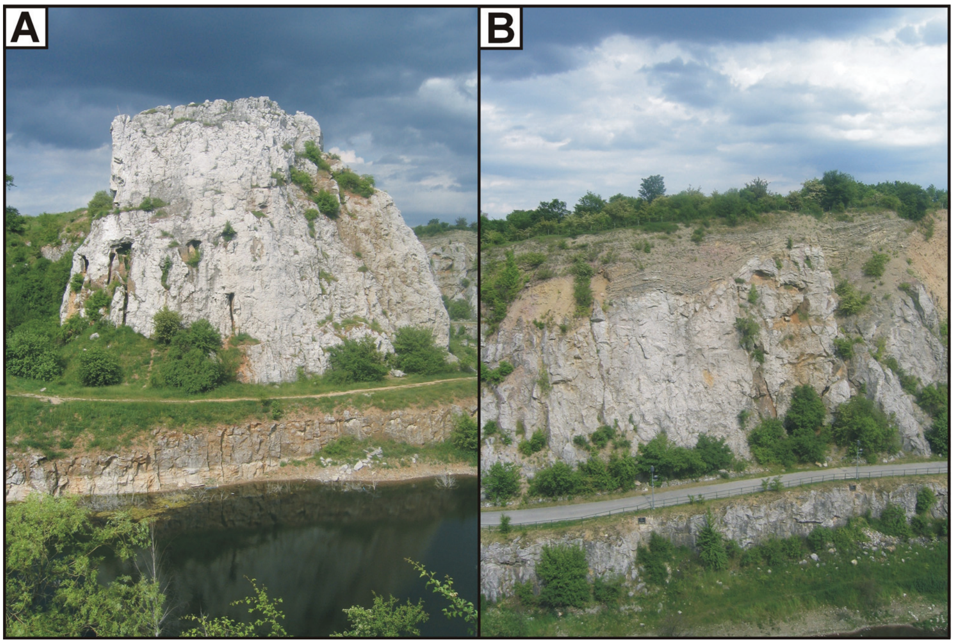

Fig. 2. (A) "*Emerald lake*" at the pit floor and Geologists' Rock pierced with caverns and caves; (B) Frasnian-Famennian contact on the eastern rock face

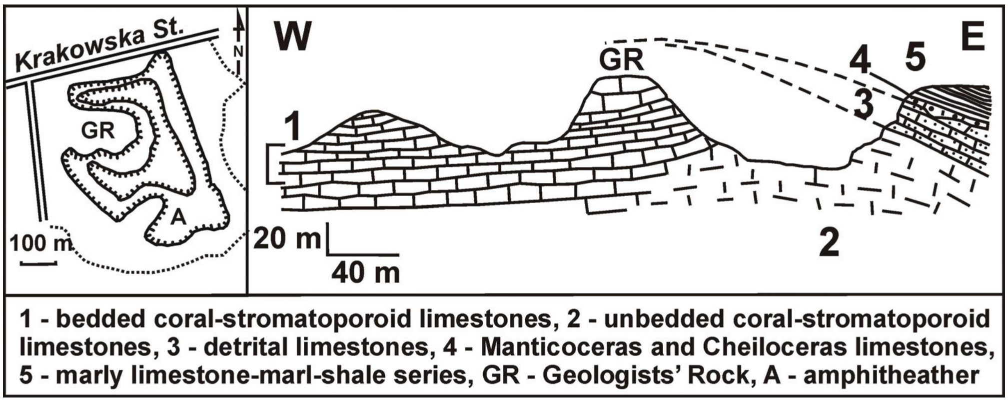

Fig. 3. Simplified geologic cross-section through the Kadzielnia quarry (after Szulczewski 1976, modified)

The other feature of this place is karstification that has been developed since the Permian period. There are 26 caves and numerous caverns on 2-3 levels, most of them formed mainly in Neogene and Pleistocene, after uplifting of the area (Urban et al. 1997). The most famous is a 10 m long "*Devil's Hole*" in the Geologists' Rock and a 180 m long "*Kadzielnia Crevice*" in the eastern rock face reaching 180 m in length. An interesting fact here is that a large number of fossil bones of Pleistocene rhinos, cave bears, steppe rodents and Lower Triassic stegocephals were found in cave earths (karst fills). In some places, veins of calcite ($CaCO_3$) with galena (PbS) and barite ($BaSO_4$) cut limestone series.

The top of the Geologist's Rock is a good observation point from which the whole pit and the surrounding Kielce area is visible. The Frasnian series is overlain by somewhat arched Famennian thin-bedded, alternating marly limestones, marls and marly shales with goniatites, nautiluses and placoderms characteristic of distal facies. The contact between these two rock series crops out on the eastern face of the quarry along the asphalt alley that also traces a fault zone (Fig. 2B).

Kadzielnia Geologic Reserve is formally assigned as a representative geosite selected for the European Network and has national site accession number T 08 (http://www.iop.krakow.pl/geosites).

(2) Karczówka Landscape Reserve

The Karczówka Landscape Reserve was established in 1953. It takes up an area of about 27 hectares. The pine and beech wooded mount (335 m a.s.l.) is topped with a 17–18th century baroque monastery complex. The mount consists of Frasnian reef limestones similar to those exposed in the Kadzielnia Geologic Reserve.

This place was a significant lead ore mining center in the 15th through 18th century. At that time galena was also mined in other localities of the Holy Cross Mountains, including the Kielce, Łagów and Chęciny–Miedzianka areas. There are numerous remains of mostly filled-in pits, adits and shafts dating back to that mining activity (Fig. 4A). They extend along galena-calcite-barite mineralization zones rooted in faults running close to the north-south direction (Rubinowski, 1971). According to Kotański (1968), there were at least 3 220 shafts in this and surrounding area. The lasting memory of these events is an about 1.5-meter high statuette of Saint Barbara, the patron saint of miners and geologists, which is placed in a small chapel of the monastery (Fig. 4B). This is a unique piece of art made of one out of three galena lumps that were extracted from the Saint Barbara shaft (more than 100 m deep) at the nearby Grabina Mt. by a miner named Hilary Mala in 1646. Out of the remaining two smaller pieces of galena, two statuettes were made: Our Lady with the baby Jesus stored in an aisle side of the Kielce cathedral and Saint Anthony in a village church near Radom. There is a superb view of Kielce and surroundings from the church tower and northern terrace.

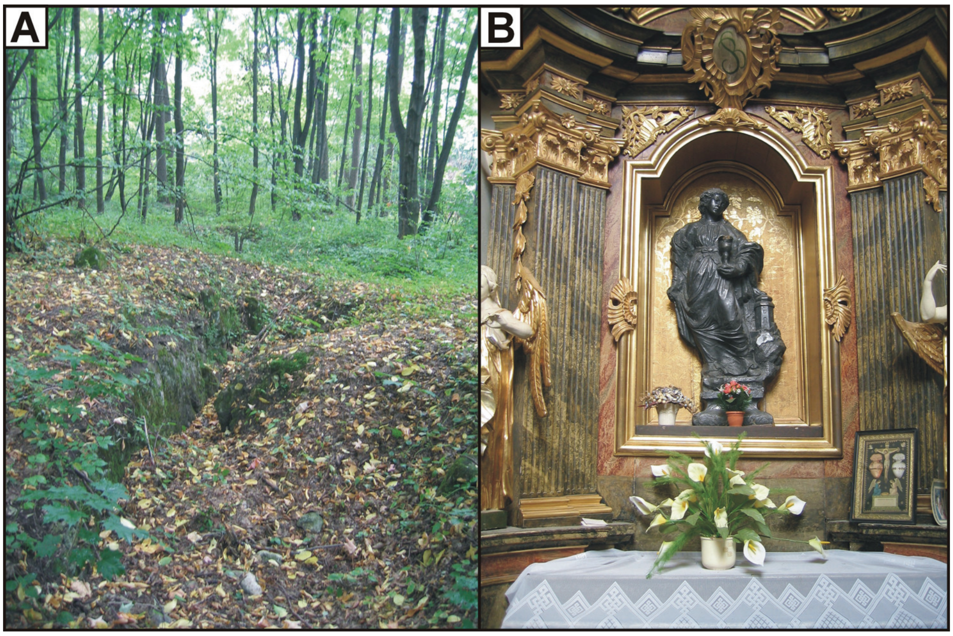

Fig. 4. (A) Pit near the top of Karczówka Mt.; (B) Saint Barbara statuette of the Karczówka chapel

(3) Ślichowice Geologic Reserve

The *Jan Czarnocki* Geologic Reserve at Ślichowice Mt. (303 m a.s.l.) was established in 1952. It occupies an abandoned quarry with an area of about 0.55 hectares. The first geologist who described this site was Jan Czarnocki (1889–1951), a famous researcher of the Holy Cross Mountains, hence the name of this reserve (Wróblewski 2000).

Both Frasnian and Famennian rocks are exposed here. However, compared to the Kadzielnia limestones, the Frasnian series at Ślichowice is represented by marly, in places bituminous limestones with marly shales interbeds belonging to a deeper facies near a coral reef. The most spectacular is the eastern face of the quarry, where a recumbent fold composed of Frasnian limestones is exposed (Fig. 5). This is an educational example how rock masses could be deformed under tectonic stress during Variscan orogeny.

In places, both Frasnian and Fammenian limestones are pierced by calcite veins with traces of polymetallic ore mineralization (Ni, Co, Fe, Cu, Zn, Pb, As). An interesting side note here is that, except for chalcopyrite, galena, sphalerite, pyrite, marcasite, tennantite, bravoite and gersdorffite, some grains of native gold grains reaching a few millimeters in diameter were also found (Karwowski et al. 1997).

Fig. 5. Frasnian recumbent fold at the Ślichowice Geologic Reserve

Ślichowice Geologic Reserve is listed in the Polish Database of Representative Geosites selected for the European Network under national site accession number T 09 (http://www.iop.krakow.pl/geosites).

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Field session 1

Influence of pyrite mineralization on the generation of Acid Mine Drainage in the Wiśniówka mining area near Kielce

Zdzisław M. MIGASZEWSKI[1], Sabina DOŁĘGOWSKA[1], Agnieszka GAŁUSZKA[1]

[1]*Geochemistry and the Environment Div., Institute of Chemistry, Jan Kochanowski University, 25-406 Kielce, 15G Świętokrzyska St.; e-mails: zmig@ujk.kielce.pl, sabina.dolegowska@ujk.kielce.pl, agnieszka.galuszka@ujk.kielce.pl*

Study area

The geochemical study of acid mine drainage (AMD) in the Wiśniówka mining area has been performed since 2002. The scope of this investigation has encompassed three acidic water bodies: (1) Wiśniówka Mała pit lake, (2) Podwiśniówka pit pond, and (3) Marczakowe Doły pond located about 1 km east of Podwiśniówka (Figs. 1-3). Each of these water bodies differs in size and chemistry. The geologic setting and tectonic style of this area is highly complex and arouses many controversial views (Żylinska et al. 2006 and references cited). In general, the Wiśniówka massif is built primarily of the Upper Cambrian (Furongian) Wiśniówka Sandstone Formation (Orłowski 1975). This formation comprises quartzites and quartzitic sandstones and siltstones with clayey shale, tuff and bentonite interbeds. Locally, pyrite mineralization zones occur. The largest one crops out in the Podwiśniówka abandoned quarry (Migaszewski et al. 2007a, 2009). This study is ongoing and its principal objective is to elucidate complex geochemical interactions in/between water columns and sediments in these three water reservoirs.

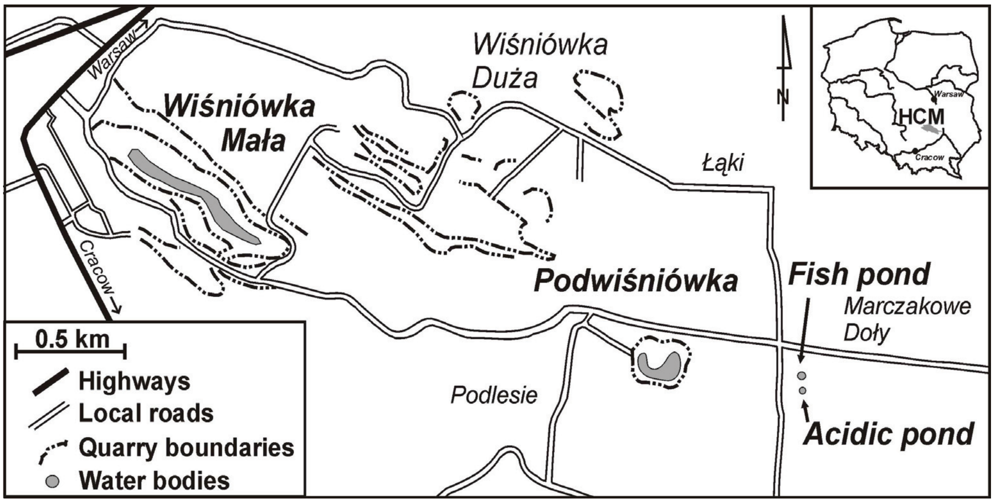

Fig. 1. Location of acidic water bodies in the Wiśniówka mining area

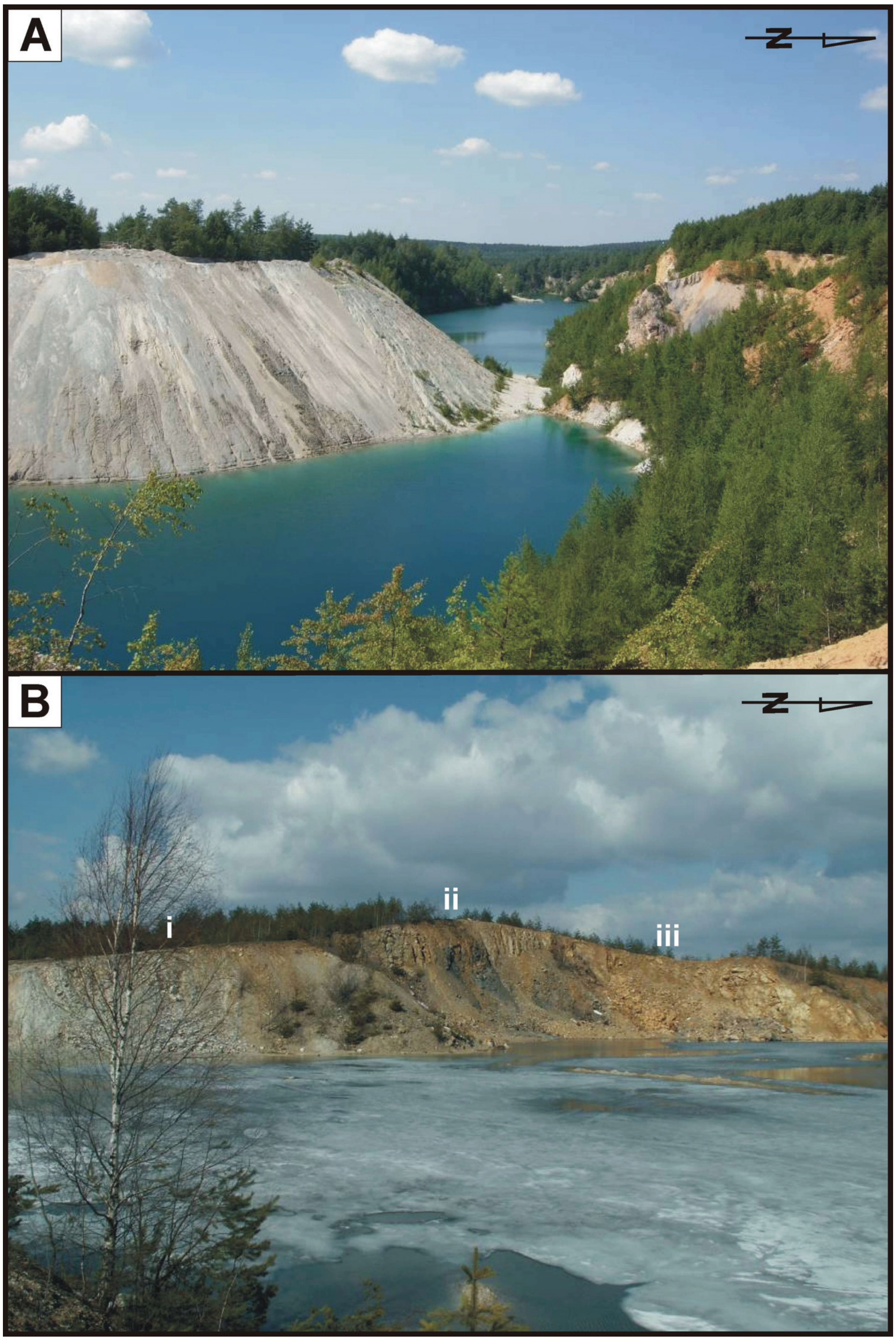

Fig. 2. (A) Wiśnówka Mała pit lake divided by tailings pile into two ponds; (B) Podwiśniówka pit pond with exposed western face composed of 3 series (tectonic slices): (i) tuff-bearing quartzites; (ii) pyritaceous quartzites with clayey shale interbeds; (iii) iron-bearing quartzites

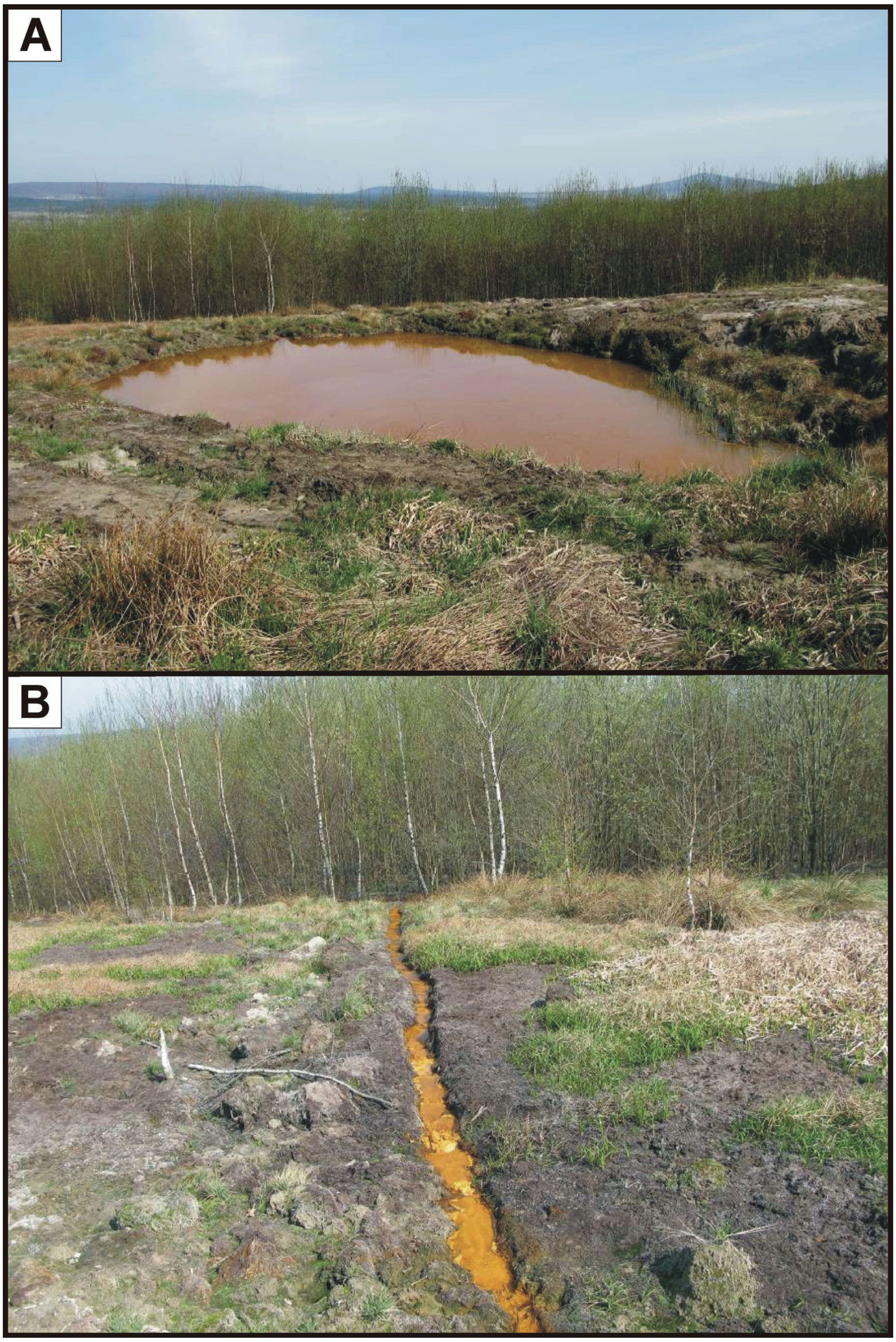

Fig. 3. (A) Marczakowe Doły acidic pond; (B) Outflow from the pond – channel veneered with yellow-light brown goethite and presumably ferrihydrite ("yellow boy")

Generation of acid mine waters

The AMD is a natural process that occurs in areas of pyrite and iron-bearing sulfide mineralization. The pyrite is a mineral which undergoes rapid bacterially-induced oxidation, according to simplified reactions:

$$FeS_2 \text{ (pyrite)} + 3{,}5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \text{ (1)}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \text{ (2)}$$

These two reactions bring about strong acidification of waters. Fe^{3+} is replenished through oxidation of ferrous iron to ferric iron (3):

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \text{ (3)}$$

Subsequently, the dissolved ferric ion undergoes hydrolysis, and ferric hydroxide precipitates (4):

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3H^+ \text{ (4)}$$

The AMD studies have revealed that the reaction (4) is very complex and at least three minerals (schwertmannite, ferrihydrite and goethite) precipitate. These complex ochreous minerals seem to control acidity of pit pond and lake waters (e.g. Bigham et al. 1990; Schwertmann et al. 1995). Schwertmannite is a Fe(III)-oxyhydroxysulfate assigned to metastable akaganéite-like phase (β-FeOOH) with tunnels occupied by sulfates (Bigham et al. 1990). Its chemical formula is differently reported by various authors, for example, $Fe_8O_8(OH)_6SO_4$ by Bigham et al. (1996). Schwertmannite with trace to minor amounts of goethite (α-FeOOH) forms in the pH range of 2.5 (or 2.8) to 4.5, whereas jarosite [$XFe_3(SO_4)_2(OH)_6$, where X is usually Na^+, K+, NH_4^+, or H_3O^+] dominates at the pH <2.5 (or <2.8) (Bigham et al. 1996). In turn, the gradual transformation of schwertmannite through more crystalline ferrihydrite ($\sim Fe(OH)_3 \cdot 1.8H_2O$) and goethite ($\alpha$-$Fe^{3+}O(OH)$) occurs at the pH range of 3 to 7 releasing protons (Bigham et al. 1996).

STOP 1: Wiśniówka Mała pit lake

The results of detailed geochemical study conducted during 2005–2006 in the Wiśniówka Mała acidic pit lake were summarized in a separate report (Migaszewski et al. 2008). They indicated that there was a spatial and temporal variability in concentrations of most elements and sulfur isotope ratios between two ponds separated by tailings pile (Fig, 2A). The water of western pond displayed a lower pH in the range of 3.0 to 4.4 (geometric mean of 3.7), a higher EC (390 µS/cm), and higher concentrations of sulfates (156 mg/L) and most ions. The concentrations of Fe^{2+} and Fe^{3+} were very low and averaged 0.8 and 0.4 mg/L. In contrast, the eastern pond water revealed a higher pH (mean of 4.4), lower EC (293 µS/cm), and lower sulfate (90 mg/L) and trace metal levels. It is interesting to note that the same difference in chemistry was recorded between the western and eastern part of this lake before it was divided into two ponds. Alkalinity of the entire lake water was below 0.1 mg/L $CaCO_3$. The presence of more acidic water in the western pond may be explained by an occurrence of inundated pyrite zone. This is also evidenced by the negative $\delta^{34}S$ in soluble sulfates that distinctly differ from those in soil and rainwater sulfates.

The similar variations were recorded in the stable sulfur isotope ratios. The $\delta^{34}S_{V\text{-}CDT}(SO_4^{2-})$ values in the water of the western pit pond varied from –6.8 to –4.6‰ (mean of –5.6‰), whereas the water of the eastern pit pond from –2.2 to –0.9‰ (mean of –1.6‰). No distinct difference in the $\delta^{18}O_{V\text{-}SMOW}(SO_4^{2-})$ was noted between the western and eastern pit ponds. The comparison of oxygen isotope ratios in soluble sulfates and water indicated the anaerobic pathway of pyrite oxidation. Based on the equation recommended by Taylor and Wheeler (1994), the calculation was made that about 88% (eastern pond) to 91% (western pond) of oxygen in the sulfate molecule was derived from water during formation of soluble sulfates.

Of these two separated ponds, the western one exhibited slight chemical and isotopic stratification. The water at a depth of 15.6 m revealed a somewhat lower pH, the highest EC and SO_4^{2-}, Fe^{2+} and Fe^{3+} concentrations as well as the most negative $\delta^{34}S$ and the $\delta^{18}O$ in soluble sulfates.

STOP 2: Podwiśniówka pit pond

The basic geochemical study of the Podwiśniówka acid pit waters was performed during 2004–2007. The bottom of the abandoned quarry is partly filled by an acidic pond whose surface varies depending on precipitation. During the spring snowmelt or heavy rains it enlarges to at least 150×80 m in area and 1.5 m in depth. At the top of the eastern rock face there is a small pond of 15×5 m in area located outside the pyritaceous zone within the tuff-bearing series, and its chemistry is influenced primarily by precipitation.

The acidic pond water revealed a seasonal variability in pH, EC, and concentrations of sulfates and ferric and ferrous ions (Migaszewski et al. 2007a, 2008). The pH varied from 2.4 to 3.5 and EC from 341 to 1656 μS/cm. These two parameters reached even 1.5 and 14.3 mS/cm in strongly acidic puddles that appeared occasionally at the foot of pyrite-bearing wall. The concentrations of sulfates in the pit pond water were in the range of 55–314 mg/L, whereas Fe^{2+} and Fe^{3+} in the range of 1.4–14.8 mg/L and <0.2–23.6 mg/L. The puddles mentioned above showed the highest contents of sulfates (7750 mg/L).

The more recent chemical analyses performed during 2009–2010 exhibited nearly the same values. The highest EC values (1013 μS/cm) and Fe^{3+} and SO_4^{2-} concentrations were recorded in mid January of 2010, when the pond was covered with ice (Kalembasa 2010). Like in the previous study, no statistically significant correlations were found between pH and EC or sulfate and iron concentrations. This evidence suggests that various environmental factors (influxes of meltwater and stormwater, droughts, insolation) combined with interactions between iron oxyhydroxides and oxyhydroxysulfates may play an important role in the water chemistry.

The comparison of stable sulfur isotope ratios in pyrite (mean of –25.4‰), sulfate efflorescences on pyrite surfaces (–25.6‰), and soluble sulfates of strongly acidic puddles (–22.3‰), acidic pit pond water (–15.6‰) and control small pond water (+9.2‰) indicates that oxidation of pyrite and leaching of oxyhydroxysulfates are a starting point for generating acidic waters of the pond and intermittent puddles and leads to formation of various iron precipitates. Moreover, the comparison of stable oxygen isotope ratios in soluble sulfates and waters suggests that oxidation of pyrite is induced primarily by bacterially catalyzed iron oxidation path (Fe^{3+}) with a periodical influence of dissolved atmospheric oxygen (see reactions 1 and 2).

The pit pond sediment near the pyrite zone reveals an increased amount of As (1111–1879 mg/kg). This element is derived primarily from veined pyrite and pyrite-bearing clayey shales.

It should be mentioned here that the scope of investigations conducted in the Podwiśniówka quarry has also encompassed rare minerals, such as gorceixite and xenotime (Migaszewski et al. 2007b; Migaszewski, Gałuszka in press). The main objective of the mineralogical studies is to elucidate the age of pyrite mineralization in the Wisniówka mining area.

Influence of acid mine waters on Scots pine

The biogeochemical study of Scots pine (*Pinus sylvestris* L.) conducted in the Podwiśniówka quarry displayed numerous negative changes in needles that encompassed yellowing, chlorosis, dark spots, necrosis, twisting around axis, as well as dwarfism of individual trees (Fig. 4AB). The most distinct changes in pine trees were noted on the pit floor within the pyrite zone that is periodically inundated by meltwater and stormwater. The preliminary chemical analysis revealed raised concentrations (maximum values in parentheses) of Al (0.08%), As (3 mg/kg) and Sr (13 mg/kg), as well as lowered concentrations of K, S, P, Fe, Mn and Zn in the examined pine needles compared to those from natural ecosystems of the Holy Cross Mts (Gałuszka, Migaszewski 2008). The visible negative symptoms seem to be linked to the depletion of biogenic elements, particularly K (0.30–0.48%), P (0.049–0.073%) and S (<0.010–0.018%) or decreased bioavailability, and to an excessive amount of phytotoxic and bioavailable Al (5.99%) and As (171 mg/kg) in pit soils.

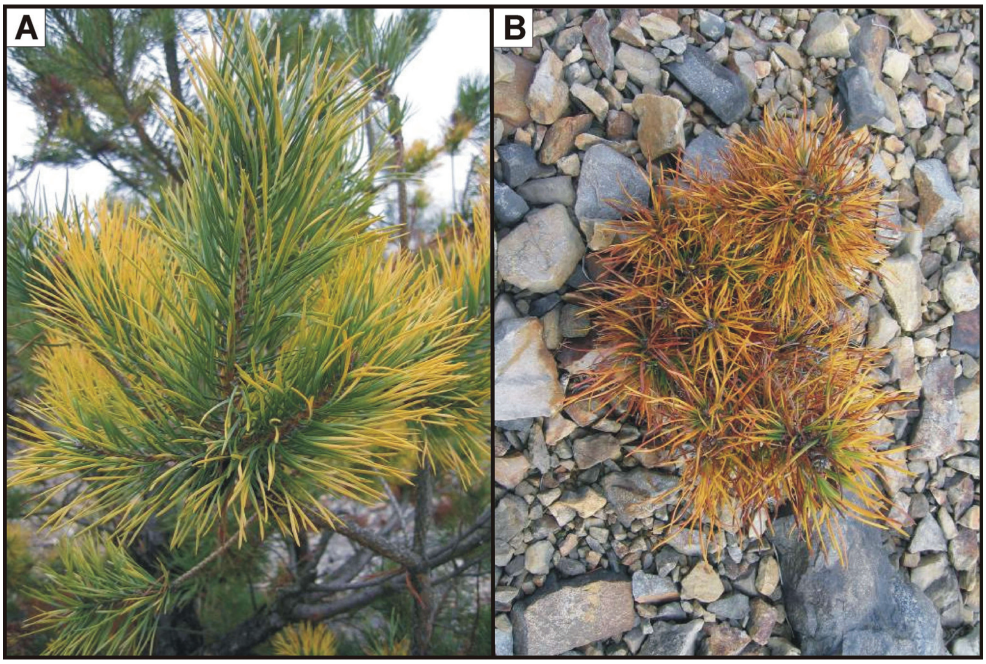

Fig. 4. (A) Scots pone needles showing chlorosis (pit verge near pyritaceous zone; (B) Scots pine exhibiting dwarfism and necrosis of needles

STOP 3: Marczakowe Doły acidic pond

Of the numerous wells and ponds in the Wiśniówka mining area, the most interesting is the acidic small pond at the Marczakowe Doły village, located about 1 km east of the Podwiśniówka abandoned quarry. It was dug a couple of years ago by a farmer and since that time the surface of the Podwiśniówka pit pond has steadily decreased, which is especially evidenced during drought periods. The pH of this small pond water was similar to that of the Podwiśniówka pit pond water, especially during autumn of 2009 and spring of

2010 (Kalembasa 2010). However, the conductivity and SO_4^{2-}, Fe^{2+} and Fe^{3+} concentrations are distinctly higher (Table 1). Moreover, the water of the Marczakowe Doły acidic pond is brownish and the bottom of the outflow is yellow to light brown (Fig. 3AB). It is noteworthy that the chemistry of water in a well and another artificial pond placed about 150 m north of the small acidic pond examined is completely different (Table 2). The water drawn from the well is used for drinking, whereas the neighboring pond is stocked with fish. Considering this, the acidic pond seems to be located on a fault that extends in the west-east direction from the Podwiśniówka quarry. The preliminary results of this study are discussed in the Contribution section by Migaszewski and coauthors.

Table 1. Chemistry of waters in Podwiśniówka pit pond and Marczakowe Doły ponds in October of 2009/January of 2010 (Kalembasa 2010)

Site	pH	EC µS/cm	SO_4^{2-}	Fe^{2+}	Fe^{3+}
			mg/L		
Podwiśniówka acidic pit pond	2.8/2.9	588/1013	126/261	9/2.5	9.2/16.9
Marczakowe Doły acidic pond	3.1/3.8	1370/1242	685/739	55/160	30/6
Marczakowe Doły fish pond	5.8/5.8	420/421	155/157	<0.1/<0.1	<0.2/<0.2

Summary

Compared to the Purple Pond in the Sudetes (southwestern Poland) and similar sites throughout the world, the examined pit water bodies in Wiśniówka Mała and Podwiśniówka are characterized by low concentrations of sulfates, iron and other trace metals. Based on this and other isotope studies performed in the Holy Cross Mountains, including the Wiśniówka area, the conclusion can be drawn that the SO_4^{2-} in the Podwiśniówka pit pond water originated primarily from pyrite oxidation, whereas the Wiśniówka Mała pit lake water comprises a mixture of SO_4^{2-} derived from the following sources (each of them marked by specific isotopic signature): (i) pyrite oxidation by two natural oxidants, i.e. oxygen and ferric (Fe^{3+}) iron, (ii) leaching of soluble sulfates from soils and waste material, as well as (iii) subordinate deposition of airborne sulfates. In contrast, the Marczakowe Doły pond water is genetically linked to the Podwiśniówka pit pond water, however, it is possible that mixing of waters from different sources may trigger generation of ferrihydrite and goethite and acidic waters with high concentrations of sulfate and iron ions.

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Field session 2

Geochemical studies in Świętokrzyski National Park

Agnieszka GAŁUSZKA[1], Zdzisław M. MIGASZEWSKI[1], Artur MICHALIK[1],

[1]*Geochemistry and the Environment Div., Institute of Chemistry, Jan Kochanowski University, 25-406 Kielce, 15G Świętokrzyska St., e-mails: agnieszka.galuszka@ujk.kielce.pl, zmig@ujk.kielce.pl, artur.michalik@ujk.kielce.pl*

Świętokrzyski National Park – location, geology and geomorphology

Established in 1950, Świętokrzyski National Park (ŚNP) (Fig. 1) is the second oldest national park in Poland. It occupies the central part of the Holy Cross Mountains (HCM) covering an area of about 7.626 hectares. The HCM belong to low- and medium-height mountains with relative elevations exceeding 300 m in some places. ŚNP comprises two wooded mountain ranges, i.e. the Łysogóry in the south and the Klonów in the north, separated with the partly marshy and wooded Wilków – Dębno Valley. There are also three enclaves (Serwis Forest, Chełmowa Mt. and Zapusty Scarp) within the park boundaries.

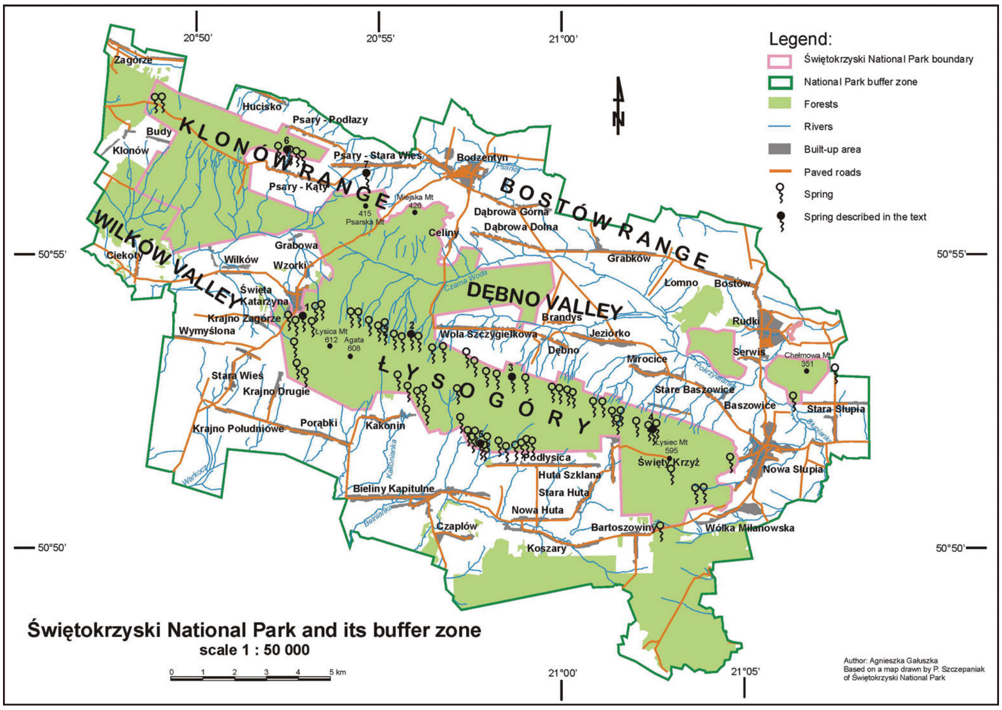

Fig. 1. Location of springs in Świętokrzyski National Park and its buffer zone

These three geomorphologic and geologic units extends nearly parallel (WNW–ESE). The Łysogóry Mts are the highest ridge of HCM reaching 15 km in length. It forms a swell with the highest mounts at its two ends: Łysica Mt. (612 m a.s.l.) in the west and Łysiec Mt. (595 m a.s.l.) and Holy Cross Mt. (580 m a.s.l.) in the east.

Geomorphology reflects geologic setting of this area. The Łysogóry Range (middle part of the Main Range) is composed of Middle and Upper Cambrian quartzites with silstone and clayey shale interbeds, the Wilków – Dębno Valley comprises Ordovician and Silurian clayey shales, siltstones and graywackes, and the Klonów Range is built of Lower Devonian quartzitic sandstones with siltstone and clayey shale interbeds (Fig. 2). The only exception is the Zapusty Scarp consisting of Middle Devonian dolomites. The southern boundary of the Łysogóry Mts delineates the Holy Cross Fault (HCF) that separates two tectono-structural units: the Łysogóry Block in the north and the Małopolska Block in the south.

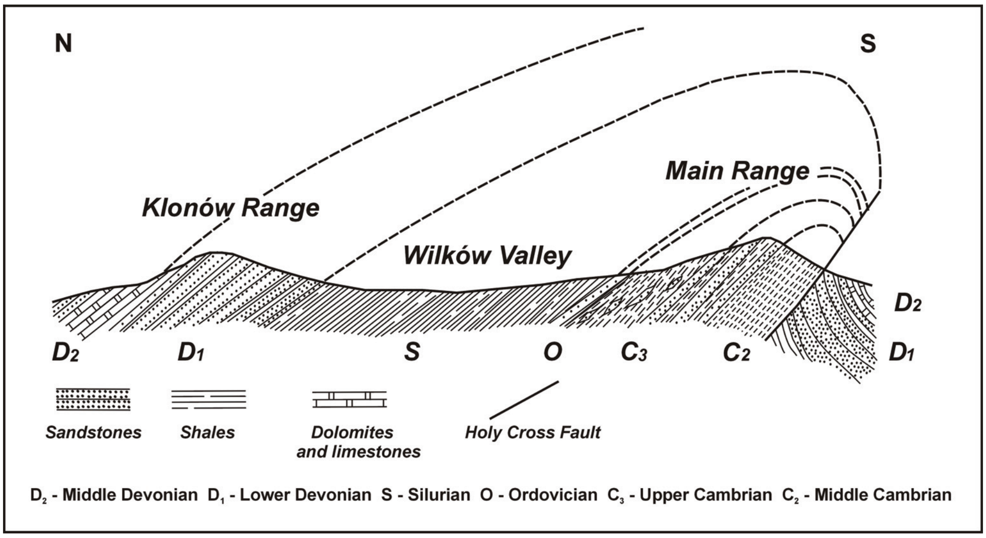

Fig. 2. Simplified geologic cross-section through the northern part of the Holy Cross Mountains (Kotański 1959)

The characteristic feature of the Łysogóry Range and the principal geologic attraction of the park is the rockfields (see Stop 1). Called "gołoborza" in Polish, they occur primarily on the northern slopes of Łysica Mt. and Łysiec Mt. (Fig. 4A). In general, these rock block and debris covers formed in Pleistocene periglacial climate in conditions of low temperatures and scarce vegetation. The recent studies have shown that these covers are genetically linked to cryoplanation terraces and periglacial tongue solifluction of landslide type. As a result of weathering of quartzite cliffs during the Middle Polish glaciations, rock mounds accumulated on sandstone-shale terraces at cliff foots. The accumulated material slid down the slope forming a zone of solifluction lobes (Jaśkowski et al. 2002). These covers are composed of quartzite-clayey debris and 4 fossil soil horizons, reaching at least 17 m on the northern slopes (Cieśliński, Kowalkowski 2000). The northward dip of rock beds facilitated gravity movements of weathering waste in this direction.

The Łysogóry slopes are almost completely forested with a prevailing stand of beech and fir. The presence of dense forest floor combined with thick complex block and debris covers favors water retention. These two combined factors elucidate the presence of numerous springs in this park (see Field Session section – stop 3).

Geochemical investigations

The geochemical investigations in ŚNP were conducted during 1994–2006 (Migaszewski, Pasławski 1996; Migaszewski 1998; Migaszewski et al. 2002, 2004, 2009; Gałuszka 2005; Michalik 2008). Some of them were parts of larger environmental studies. The scope of investigations encompassed: rocks and soils, bioindicators (Scots pine needles and bark, lichens and mosses), and about 60 springs (Fig. 1) and additionally the Dębno stream.

The geochemical investigations of rocks, soils and plant bioindicators were conducted during 1994–2000. They included determinations of major and trace elements, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides and phenols, as well as stable sulfur isotope ratios. These studies indicated a steady decrease of environment pollution in ŚNP, for example, a considerable drop of sulfur (from 0.096 to 0.042 mg/kg) was observed in lichens *H. physodes* in a period of three years. The same trend was also recorded in the pH of pine bark that decreased from 3.3–4.5 in 1995 to 3.0–3.4 in 1996. It reached a lower pH similar to that (2.8–3.4) in the Białowieża Forest (Grodzińska 1980). Except for Zn, the concentrations of trace metals and sulfur remained nearly the same during 1994–2000 (Table 1). It should be mentioned here that higher concentrations of different elements in topsoil were associated not only with the degree of air pollution, but also with the soil types featured by the different content of natural sorbents, i.e. clay minerals, organic matter and Fe- and Mn-oxides and hydroxides. The tallest mountains of the region partly making up Świętokrzyski National Park also showed an elevated concentration of most elements. Thus, the topsoil of Łysica Mt., the highest mountain of HCM was greatly abundant in many chemical elements and organic compounds. The highest content of Pb (398 mg/kg), S (0.152%) and PAHs (1905.83 µg/kg), and simultaneously the lowest pH value (3.3) was recorded in soils at this mount. Elevated levels of many elements were also observed at Wierzejska Mt. near Kielce and at Święty Krzyż Mt. The δ^{34}S values (averaging +5.0‰ in different media) indicated that pollution emissions came from the industrialized western and southwestern sector of Poland (Upper Silesia, power plant in Konin), as well as from local sources, primarily from combustion of coals in domestic furnaces.

Table 1. The content of sulfur and selected trace metals in one-year pine needles (*Pinus sylvestris* L.) and topsoil collected during 1994–1996 and in 2001 at Psarska Mt.

Sampling year	Ba	Cd	Cu	Hg	Mn	Ni	Zn	S
	mg/kg (ppm)							%
1-year needles (1994)*	5	1.0	9	0.020	577	17	59	0.072
1-year needles (1995)*	3	0.6	6	0.015	468	7	50	0.068
1-year needles (1996)*	<1	0.5	5	0.014	271	4	32	0.041
topsoil (1995)*	56	<0.5	12	0.189	588	5	51	0.053
topsoil (1996)*	46	<0.5	27	0.236	388	7	46	0.051
topsoil (2000)**	109	0.8	9	0.170	993	7	425	0.068

*Migaszewski (1998); Gałuszka (2005)

The studies of springs (Michalik 2008; Migaszewski et al. 2009) and the Dębno spring and stream (Szostak 2004) in ŚNP revealed a relatively low pH, electroconductivity (EC) and low concentrations of trace elements. Based on the chemical parameters, two main types of spring waters have been distinguished in ŚNP (Michalik 2008). The first type occurs in the Łysogóry Range and is characterized by a low pH (<6.0) and a very low conductivity (<80 µS/cm). The second type occurs in the Klonów and partly Pokrzywiański Ranges revealing a higher pH (>6.0) and a much higher conductivity (>200 µS/cm) (Table 2). The spring waters of the Łysogóry Range show very low ion concentrations with the prevalent SO_4-Ca-Cl-Mg and SO_4-Ca-Mg-Cl water types. In contrast, the spring water chemistry from the remaining part of ŚNP is similar to that from the neighboring areas of the Świętokrzyskie province with hydrocarbonates prevailing over sulfates (HCO_3-Ca-Mg) (Prażak 2002). Michalik (2006) indicated that only some of the trace metals (Ba, Cu, Mn and Zn) occurred in slightly higher concentrations (Table 2). The spring waters of the Klonów and Pokrzywiański Ranges are characterized by raised levels of most metals.

There are numerous geologic and anthropogenic factors that influence physicochemical and chemical parameters of groundwaters. The specific geologic setting of Świętokrzyski National Park influences both the geomorphology and the distribution pattern and discharge of springs, as well as chemistry and quality of spring waters. Of various geologic factors, the bedrock lithology and chemistry plays the most important role. The influence of bedrock is more highlighted when comparing the pH, EC and element composition of spring waters from the Łysogóry Range and scattered mountains that occur in the northern section of the park (table 2). The Łysogóry Range is characterized by lack of acid-buffering rocks with prevailing quartzites and quartzitic sandstones across the landscape. In addition, the largest number of springs and a distinctly lower pH in this area is affected by the presence of a dozen-meter thick waste mantle containing quartzite fragments and blocks with a substantial admixture of clay and organic material. This protective cover also enables the subsurface retention and adsorption of airborne pollutants. In contrast, the northern mountains within the park boundaries contain occasional carbonate interbeds.

Table 2. Comparison of water chemistry in selected springs in 2004 and 2006

Spring no./year	pH	EC µS/cm	$CaCO_3^-$ mg/L	SO_4^{2-}	NH_4^+	NO_3^-	Cl^-	Ca	Fe	K	Mg	Na	SiO_2	Ba	Cu	Mn	Zn
				mg/L										µg/L			
1/2004	6.2	69	<0.1	5.2	<0.05	14.0	3.7	6.4	0.01	0.7	1.8	2.1	8.6	12.0	7.0	3.0	29
1/2006	5.2	33	3.5	5.6	<0.10	13.8	3.2	6.3	0.01	0.7	1.8	2.0	8.6	13.8	15.8	5.0	82
2/2004	6.0	93	<0.1	13.2	0.05	7.7	4.2	8.2	<0.01	1.2	3.6	2.8	10.3	13.0	7.0	<1.0	84
2/2006	5.4	50	13.9	11.4	<0.10	8.3	<2.0	7.6	<0.01	0.8	3.4	2.5	10.2	14.3	1.2	0.9	86
3/2004	5.8	65	<0.1	6.1	<0.05	8.2	3.0	5.8	<0.01	0.9	2.3	2.1	9.3	15.0	<2.0	6.0	136
3/2006	5.2	50	6.9	5.5	0.10	9.4	<2.0	5.2	<0.01	0.7	2.0	1.7	8.8	15.2	1.5	2.2	140
4/2004	5.2	83	<0.1	16.2	<0.05	10.1	3.6	7.7	<0.01	0.6	1.8	2.0	8.3	54.0	<2.0	49.0	140
4/2006	5.1	52	<0.1	7.3	0.10	9.2	8.1	5.2	0.02	0.9	1.3	2.1	7.9	22.8	1.3	6.8	30
5/2004	5.7	65	3.5	4.1	<0.05	5.3	1.9	6.4	<0.01	0.5	2.4	1.9	8.6	6.0	<2.0	1.0	16
5/2006	5.4	47	6.9	4.1	<0.10	6.4	<2.0	6.2	0.01	0.6	2.3	1.8	8.5	6.9	0.8	1.0	19
6/2004	5.2	192	<0.1	56.3	<0.05	11.5	6.3	19.0	<0.01	1.8	5.7	3.0	15.2	42.0	2.0	761.0	132
6/2006	5.6	126	24.0	45.0	<0.10	12.2	7.3	19.4	0.02	1.7	6.9	5.0	12.8	27.0	2.0	19.1	26
7/2004	6.8	497	255.0	13.2	0.09	0.03	7.3	78.4	0.75	1.5	22.6	6.9	16.0	83.0	<2.0	421.0	<3
7/2006	6.7	413	288.0	11.4	0.30	<0.5	5.5	73.0	0.85	1.3	20.1	6.0	14.5	84.4	0.8	358.3	11

NOTE: For location of springs see Fig. 1

The anthropogenic stress is a factor whose influence on natural environment has greatly increased lately. However, a number of case studies conducted in ŚNP indicated that the influx of contaminated meltwater or stormwater affected primarily the chemistry of stream waters recharged by springs, and spring waters linked to shallow groundwater circulation system. The best example is the Dębno stream, where the lowest pH and highest EC was recorded after thawing of thick snowpack in the spring of 2004. The pH of stream water dropped from 5.7–6.2 in October of 2003 to 4.9–5.1 in March of 2004, whereas the EC increased from 49–60 μS/cm to 85–92 μS/cm, respectively. In contrast, these two parameters remained unchanged (4.8–5.1, 61–81 μS/cm) in the Dębno spring water that recharges the stream (no. 2 in Fig. 1). This spring is characterized by the highest yield (about 4 m^3/h) compared to the remaining springs of ŚNP. However, in many springs the side inflows of meltwater or stormwater to shallow sections of underground water outflows may periodically disturb spring yield and spring water chemistry as evidenced by monitoring of the Saint Francis spring (no. 1 in Fig. 1). Its yield varied from 1.8 m^3/h (May of 2004) to 3.8 m^3/h (April of 2005), whereas the pH was in the range of 5.1 (January of 2005) to 6.6 (November of 2006) (Fig. 3).

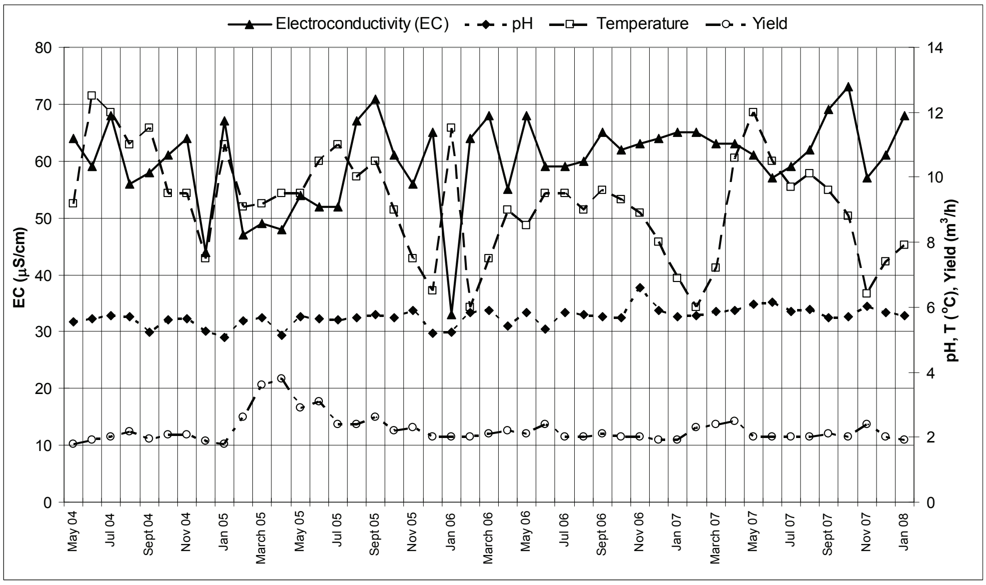

Fig. 3. Temporal changes of pH, EC, temperature and yield in the Saint Francis spring during 2004–2008

In most springs the change in water chemistry and yield was not substantial and the results may lie within measurement uncertainty, but in the Saint Francis spring (no. 1) the difference reached 1.5 pH units. In 2006 conductivity was higher in all the springs examined, especially in the Saint Francis spring, where the EC value was more than doubled. Of the major components found in the spring waters examined, only sulfate and chloride ion concentrations of the spring no. 4 showed a substantial variability. The most distinct changes were recorded in trace element concentrations, especially Al, Mn and Zn in the springs no. 4 and 6. These two springs have partly been affected by human activity, e.g. cloister buildings and tourist infrastructure located atop Holy Cross Mount (no. 4) and nearby outbuildings (no. 6), and long-range and local emissions. The other springs have not distinctly been impacted by anthropogenic sources. However, this issue requires further investigations in terms of spring yield and chemistry.

A 3-year monitoring is too short to record any trends due to periodical changes of many environmental and anthropogenic factors. Nonetheless, airborne pollution does not seem to greatly influence the chemistry and quality of spring waters in ŚNP.

Systematic long-term measurements of pH, EC and selected ion concentrations in the springs examined could be a cheap and effective method of recording changes in the ŚNP environment. The archival data published in environmental and monitoring reports would also be useful in geoindication studies. The example of such approach is the comparison of the number of springs (expressed as spring density index) recorded in the Łysogóry Range in the sixties of the 20th century by Rogalińska and Rogaliński (1972) with the results derived from the present study. The spring density index increased from 1.9 in 1960 to 3.1 in 2000.

STOP 1: Łysiec Mt. and Holy Cross cloister

Observation platform

The Holy Cross massif consists of two mounts: Łysiec (Bald) Mt. and Święty Krzyż (Holy Cross) Mt. The former mount is famous for the largest Pleistocene rockfield ("gołoborze") that occurs on its northern slope. There is a spectacular view from the observation platform both on the rockfield and the Wilków–Dębno Valley rimmed by the Klonów and Pokrzywianka Ranges (Fig. 4A). The characteristic wooded Chełmowa (Helmet) Mt. is the oldest nature reserve in the Holy Cross Mountains, established in 1920. This represents a stand of Polish larch (*Larix decidua subsp. Polonica* Domin.). The origin of the rockfield was described in the Świętokrzyski National Park section. Another tourist attraction is the rock embankment that extends in an eastward and westward direction from the entrance to the observation platform. It surrounds a place of pagan worship in the 8th and 9th centuries. People who lived in the Holy Cross Mountains at that time believed in three deities, named: Świst, Poświst and Pogoda.

Holy Cross cloister

Holy Cross Mt. and the former Benedictine cloister are frequently visited by tourists due to their central location and a scenic view of the wooded Jeleniów Range (eastern part of the Maine Range). The transversal Łysogóry fault shifted this range southward during the late Variscan movements. Near the northern stone gate leading to the cloister, a quartzite cliff crops out (Fig. 4B).

The Holy Cross cloister was founded by Benedictines presumably in the place of the pagan shrine. The monks arrived in Poland from Monte Casino (Italy) in the 12th century. According to the legend, the Hungarian King Emeryk donated the Holy Cross reliquaries to the cloister as a token of gratitude for miraculous escape. When he and the Polish King Bolesław Chrobry got lost in the pristine forest, the red deer with a cross in its antlers appeared showing them the way out. This motif and the Benedictine double cross often appear in local architecture and paintings. The name of this mount and the whole mountains comes from the Cross reliquaries. In the medieval times, the cloister was the largest religious center of the Polish Kingdom. Many Polish kings made pilgrimages to this holy place. Burned and plundered many times, the cloister was rebuilt and extended through the centuries. During the January Uprising in 1863 and 1864, this place was the headquarters of commander-in-chief Langiewicz and the assembly point of the Polish insurgents who fought a battle with Russian Tsar troops. During the Second World War, the cloister was converted into a prisoners-of-war camp for Russian soldiers. More than 5000 of them died of hunger and disease. Inside the cloister, visitors can notice a variety of architectural pieces representing the Romanesque, Gothic, Renaissance, Baroque and Classical periods, for example, 15th century gothic cross vaults in the gallery or a beautiful 17th century Baroque Oleśnickis' chapel with marble gravestones. The cloister museum stores a copy of the 13th century Świętokrzyskie sermons which are the earliest examples of Polish writing.

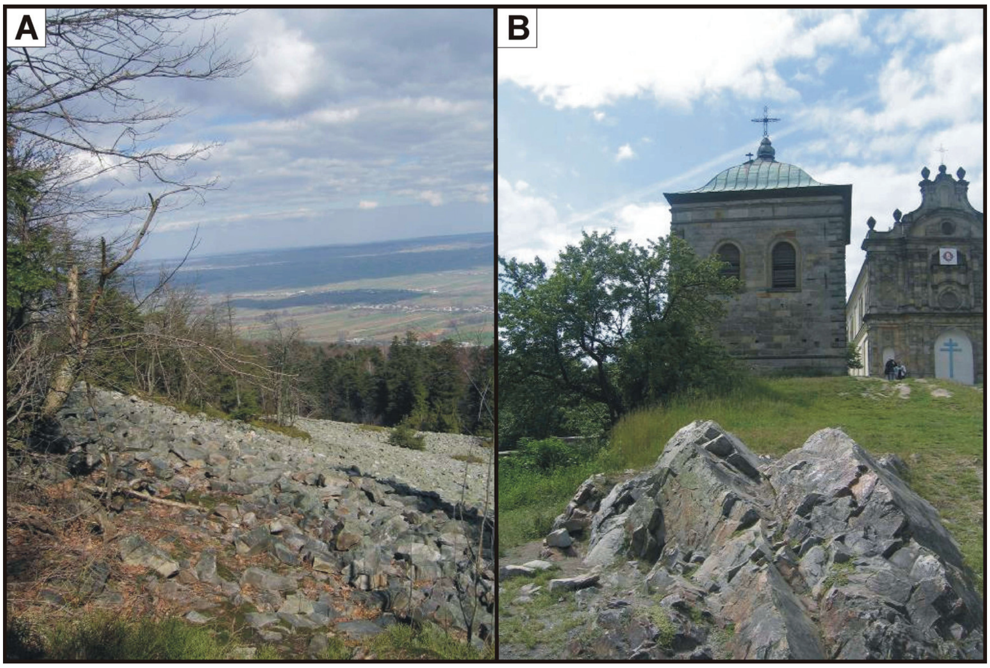

Fig. 4. (A) Rockfield on the northern slope of Łysiec Mt.; (B) Quartzite outcrop near the Holy Cross cloister

The red tourist trail descends from the Holy Cross cloister to the small town of Nowa Słupia along the King's Road. Its name derives from pilgrimages of Polish kings who walked on foot the length of this road in the Middle Ages. The road cuts the rock embankments and outcrops of quartzites. Near the entrance to the park, there is a statue of a pilgrim made of sandstone. The legend says that if he reaches the cloister, there will be the end of the world.

STOP 2: Museum of ancient metallurgy at Nowa Słupia

About 200 m from the entrance to ŚNP there is a museum of ancient metallurgy. This small museum stores artifacts, including slugs (Fig. 5A), Roman coins, ceramics, weaponry, as well as a faithful reconstruction of primitive smelting furnace. Each furnace consisted of alternating layers of iron ore, charcoal and flux forming a heap covered with clay. The air was forced into the furnace by leather blowers. The clay primitive smelting furnace was used only once. Smelting of iron was a low-yield process, manufacturing about 1–2 kg of pig iron. When the smelting was finished, the furnace was broken, and a piece of pig iron removed for processing in blacksmith shops. This process is reconstructed each year during August festivities at Nowa Słupia. The slugs, which are the only remnants of that smelting, were found in numerous places in the northeastern part of the Holy Cross Mountains. Archeologists discovered that the furnaces were grouped in triple or fourfold rows to retain heat.

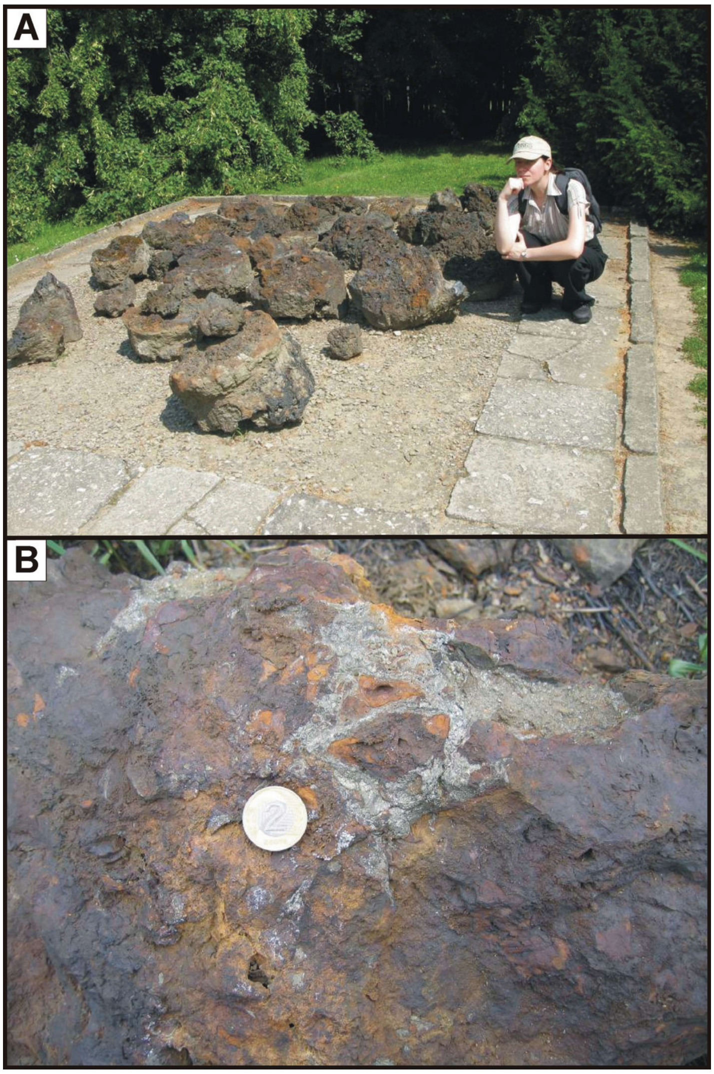

Fig. 5. (A) Slag blocks at the museum of ancient metallurgy at Nowa Słupia; (B) Hematite-pyrite ore from Rudki

The northeastern part of the Holy Cross Mountains seems to have been the most important center of iron metallurgy in ancient "barbarian" Europe. Its boom fell on 1st through 4th century. This suggestion is evidenced by hundreds of thousands of slug heaps found by peasants in their farmlands. Silver coins with effigies of Roman emperors, which were excavated in many places, give an evidence for the presence of Roman merchants who came to this area to buy iron and weaponry. According to some historians, this area was presumably an armory of German tribes, some sort of military base located far from the Roman Empire borders.

The slugs contain up to 50% of iron being a high-grade ore for ironworks. In the interwar period, between the First and Second World War, peasants sold slugs to steelworks in nearby Ostrowiec Świętokrzyski and in the Upper Silesia. The "Pokój" Steelworks in Nowy Bytom (Upper Silesia) alone smelted about 100 000 tons of slugs.

The iron ore (hematite, goethite and limonite) was extracted in a nearby abandoned mine at Rudki (Fig. 5B). The peak of its exploitation dates back to the 1st through 4th century, which is evidenced by radiocarbon dating of wooden mining tools and linings. This place was rediscovered by the geologist Jan Samsonowicz in 1922. He found that the Rudki ore deposit consisted primarily of pyrite (actually marcasite) and siderite capped with hematite. The ore mineralization occurs within Middle Devonian dolomites and is rooted to the transversal Łysogóry fault. The mining operation started in 1922. Originally, siderite and hematite were mined. However, the main mineral raw materials were pyrite and uraninite. The former was extracted during 1933–1969 for manufacturing sulfuric acid and the latter during 1956–1968. The uranium ore consists of marcasite fragments cemented by colloidal uraninite. This breccia forms lenses and veins reaching 20 m long and 0.4 m thick.

STOP 3: Springs in ŚNP near Huciska

One of the highest yield spring and stream (no. 4 in Fig. 1) is located on the northern slopes of the Łysogóry Range (Fig. 6AB). In the upper part this stream divides into two separate branches – the western disappears and flows out again to the surface (Fig. 7).

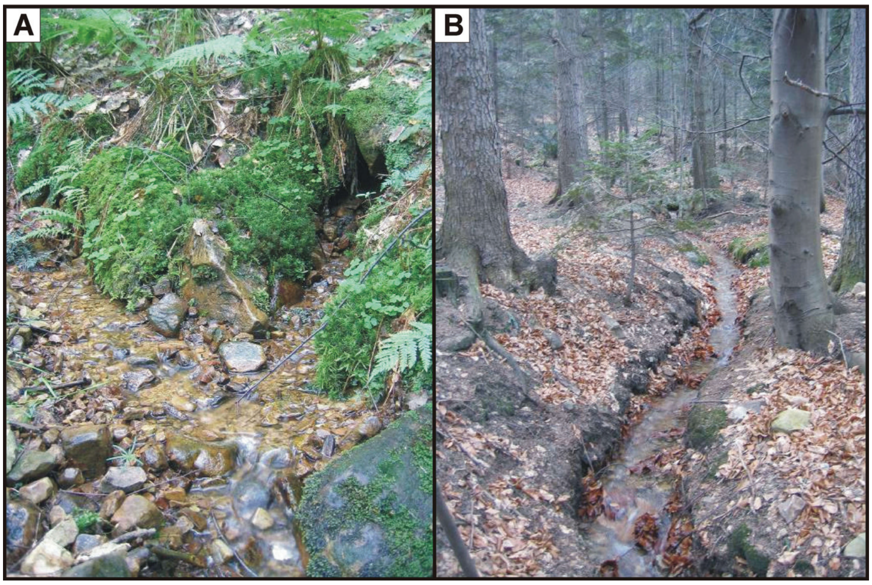

Fig. 6. (A) Double spring on the northern slopes of Łysiec Mt.; (B) Stream flowing out of the spring

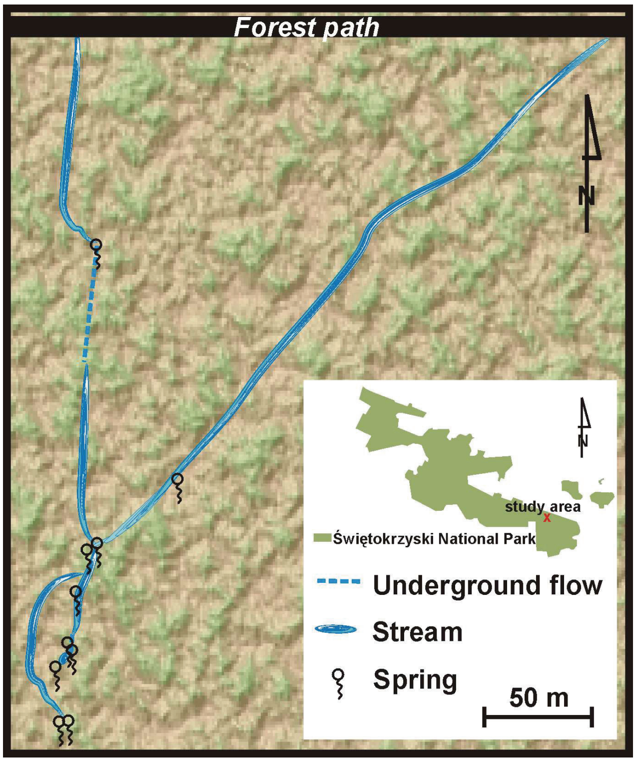

Fig. 7. Location of springs and streams near Huciska

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