Geology, Geophysics & Environment 2014, vol. 40 (1): 75–161

# XV<sup>th</sup> International Conference of Young Geologists Herl’any 2014

## ABSTRACTS

http://dx.doi.org/10.7494/geol.2014.40.1.75 ISSN 299-8004 | e-ISSN 2353-0790 | Wydawnictwa AGH

# Welcome in Herlandia 2014 XVth International Conference of Young Geologists Herľany 2014 Międzybrodzie Żywieckie, Poland, May, 8th–10th 2014

Maciej Dwornik, Maciej Manecki, Barbara Zahradníková, Marianna Kováčová, Leonard Zahradník, Margaréta Gregáňová, Julián Kondela, Ľubomir Štrba, Ladislav Vizi, Jakub Bazarnik, Jarosław Majka, Monika Kwaśniak-Kominek, Karolina Kośmińska

The 15th International Conference of Young Geologists was held in the Polish Outer Carpathians, in Międzybrodzie Żywieckie, located in the Beskid Mały Mts. All participants were hosted in Niagara resort. The conference was organized by the AGH University of Sciences and Technology (AGH), Krakow (PL), Faculty of Natural Sciences of Comenius University (CU), Bratislava (SK) and the Faculty BERG of Technical University (TUKE), Košice (SK). For several years the members of the scientific committee have been Prof. Dušan Plašienka (CU), Julian Kondela (TUKE) and Prof. Maciej Manecki (AGH). The conference was organized by Ph.D. students from AGH and the members of the Geological Club from Bratislava.

This year 70 young scientists from Poland, Slovakia, Czech Republic and Russia participated in the conference. They presented over 50 talks covering a very wide spectrum of Earth science disciplines such as: tectonics, sedimentology, mineralogy, petrology, paleontology, geophysics, geoengineering and geoinformatics.

The best student presentation in English was awarded with the Rudolf Mock Award. This year, the award went to Karolina Kośmińska, Ph.D. student from AGH, for excellent presentation in petrology on blueschists from Svalbard. The award was presented during closing ceremony by Professor Maciej Manecki.

An important part of the meeting was "evening dinner discussion", where Professor Jan Golonka (AGH) presented his lecture on evolution of the Outer Carpathians. Topic of the lecture was also an introduction to the geological excursion. On Saturday, the participants visited pumped-storage hydroelectric power plant in Porąbka and unique outcrops of cieszynity in Cieszyn area. A guided tour in Brewery Museum in Żywiec ended the excursion. The next conference will return to the original location, Herľany, Slovakia.

***Fig. 1.*** *Karolina Kośmińska (winner of Rudolf Mock Award) and part of commission (from left: Ľ. Štrba, M. Gregáňová & M. Manecki)*

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# Use of bentonite for MSWI fly-ash stabilisation

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Fly-ash produced during combustion processes is usually considered to be hazardous waste. Therefore, its effective treatment is necessary.

Stabilization of hazardous waste by solidification is one of the effective methods of immobilization of pollutants. A solid structure resistant to leaching is created by stabilization. The created stabile structure has to resist the influence of natural factors such as rainfall causing possible leaks of pollutants in the form of leachates.

Having fulfilled the required properties, the stabilized structure can be used as raw material in the construction or reconstruction of pavements as well as in the construction industry. All around the world, the stabilization processes are used for solidification of municipal solid waste incineration (MSWI) including fly ashes.

The MSWI plant in Košice is planning to introduce a technology of solidification as a possible treatment stage before deposition in a landfill.

In the process of stabilization/solidification, several ingredients to achieve the desired result are used. The created solidified structures must be characterized by sufficient compressive strength with a minimum probability of release of pollutants in the event of disruption of its structure. The basic ingredients are water, cement, and other natural materials, such as bentonite. Bentonite is a residual clay, which was created by mechanical and chemical weathering of parent rock in an alkaline medium, mainly volcanic tuffs, rhyolites, basalts, andesites and other predominantly Tertiary rocks. It is plastic rock that has a high sorption capacity. Its chemical and mineral composition depends on the bearing formation. Bentonite contains mainly montmorillonite. Other major components are mainly beidellite, kaolinite, and illite. World reserves of bentonite deposits are estimated as more than 2 millions tons per year mined and discovery of new deposits is assumed (Bentonite 2013).

In the experimental part of the work, the possibility of solidification of MSWI fly-ash was studied using fly-ash from filters (hereinafter referred to as F), and fly-ash from cyclone (hereinafter referred to as C). Several experiments of solidification with different ratios and various combinations of materials were conducted. The results confirm that the method of solidifying of both fly-ashes F and C from the MSWI plant appears to be an effective procedure for their stabilization. The next experiments were concentrated on leaching of heavy metals from the stabilised structures. Atomic absorption spectrometry enabled to detect only small concentrations of heavy metals in the leachates of the stabilized structures. The comparison of measured concentrations of heavy metals in the leachates from solidified fly-ashes with limit values given by valid legislation shows that none of the concentrations of assessed heavy metals achieved or exceeded the limit values.

*This work was supported by the Scientific Grant Agency of the Ministry of Education of Slovak Republic under the grant No. 1/0590/11. This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0068-07.*

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# Blattaria assemblage from J/K sediments of Chernovskie Kopi in Transbaikalian Russia

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The J/K fossil site Chernovskie Kopi in Transbaikalian Siberia (Russia) yielded insect fossils of 15 orders (Vassilenko 2005), descendants of the order Blattaria – the earliest termites (Vršanský & Aristov 2014), and insect trace-fossils (Sukatcheva & Vassilenko, 2011). Recently described cockroach assemblage (Barna 2014) contains five species: *Blattula* sp. (Blattulidae), *Rhipidoblattina* sp. (Caloblattinidae), *Archimesoblatta* sp. (Mesoblattinidae), *Mongolblatta* sp. (Mesoblattinidae), *Rhipidoblatta* sp. (Caloblattinidae) and one undescribed species of the family Liberiblattinidae Vršanský, 2002. Most of 41 specimens were photographed and drawn. The cockroach fossils, preserved as imprints in fine-grained, red-coloured argylites, are represented almost exclusively by imprints of forewings (only one hindwing and one pronotum was found) suggesting a significant transport prior to deposition. The composition of this cockroach assemblage is more simmilar to Early Jurassic assemblages from Australia (Martin 2010), and Germany and England (Vršanský & Ansorge 2007), than to Middle and Late Jurassic assemblages (Vishniakova 1968). Venation deformities recognised on 22.5% of studied cockroach wings, support the claims of mass mutations occurrence near the J/K boundary (Vršanský 2005) and along with low diversity of the assemblage point to a destabilized ecosystem.

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# Paleogeographic characterization of the Early Cretaceous "Urgonian" carbonate platforms

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The objective of the present paper is to show clues which are provided for understanding the development and paleogeographic significance of the Lower Cretaceous carbonate platform sequences in different localities. The results are based mainly on the study of previous works and also on the preliminary results from lithological sections investigated by authors. The Urgonian-type limestone represents a characteristic Barremian and Aptian shallow-water carbonate facies deposited along the northern Tethyan margin. The term *Urgonien* was established by A. d'Orbigny in 1847 for the reef limestones near Orgon (southern France). The facies encloses massive, light-coloured organodetrital limestones with foraminifers (*Orbitolina*) and transitional sediments – detrital or siliceous limestones. Among bioclasts, fragments of bivalves (rudists), corals, hydrozoans, bryozoans, small and large foraminifera (*Palorbitolina lenticularis, Sabaudia minuta*) and algae are the most characteristic constituens. In the Early Cretaceous, the opening of Alpine Tethys was completed and induced the development of carbonate platforms on its northern margin. Urgonian carbonate platforms in the Tethys have been widely studied (e.g. Arnaud & Arnaud-Vanneau 1991, Michalík 1994). Several deposition areas can be distinguished in the Western Carpathians, mainly: the Tatric "Urgonian" Platform (biohermal and lagoonal facies), source of the detritus transported to the Muráň Limestone; and the Manín Urgonian Platform prograding into the Belá Unit during the Aptian. Debris from both platforms was transported into adjacent basins and deposited as allodapic accumulations (Mišík 1990). The oldest hypothesis on the position of the neritic "Urgonian" Lower Cretaceous limestones of the Manín Unit consisting of Podhorie and Manín formations was summarized by Andrusov (1938). He considered the Manín Unit as an independent nappe unit. Later, based on lithostratigraphic and tectonic features, he characterized it as a succession of Central Carpathian affinity. However, its position and the tectonic style are close to Pieniny Klippen Belt structures (Andrusov 1938, Birkenmajer 1977). From the Urgonian-like facies, which occur in the Klippen Belt and the Peri-Klippen Belt we focused mainly on the Manín Unit in the area of the Strážovské vrchy Mts., the Nižná Unit (Nižná Limestone Formation) (Józsa & Aubrecht 2008), Beňatina Klippe (Schlögl et al. 2004) and also in the Haligovce Unit (Haligovce Limestone Formation), which is usually considered as an equivalent of the Manín Unit. In the Outer Carpathians, the Urgonian-type limestones occur exclusively as exotic pebbles in younger deposits. Urgonian facies in the Western Carpathians shows some different features in comparison with other areas in the Tethys realm; e.g. lack of oolitic and oncolitic limestones, small representation of typical lagoonal facies with miliolids and dasycladaceans. The "reef-tufa" cementation, fenestrae, evaporate minerals are also missing, bauxitization is unknown. They use to be affected by silicification (presence of cherts). Dolomitization is almost missing (Mišík 1990).

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Geology, Geophysics & Environment 2014, vol. 40 (1): 82–83

# The complex fault zone within poorly indurated strata in the Orava Basin (Western Carpathians, Poland)

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The purpose of this paper is to identify and characterize a fault zone located within poorly indurated Pliocene clastic strata occurring in the southern part of the Orava Basin on the boundary of Outer and Central Western Carpathians, close to the Pieniny Klippen Belt. The Orava Basin is a part of the Orava – Nowy Targ intramontane basin.

The fault zones within poorly indurated sediments are usually very complex. If the rocks are well indurated, a fault zone is divided into two parts – the fault gouge and the damage zone (Fossen 2010). The fault gouge is characterized by the slip plane and strong deformations such as fractures or clasts' reorientation. Not all the researchers, however, agree with a general fault zone model described by Fossen (2010). This model is indeed appropriate for strongly lithified rocks. In case of poorly lithified sediments, Rawling & Goodwin (2006) and later Gudmundsson (2011) and Loveless et al. (2011) suggested adding the third, additional zone – the mixed zone. It separates the fault gouge and the damage zone and the presence of the deformation bands and clasts' reorientation are its main features. The mixed zone records the initial deformations of the sediment and stays active for some time even after the lithification (Rawling & Goodwin 2006).

Although no displacement of strata can be noticed in the studied exposure, the occurrence of numerous fractured clasts and exposure-scale fissures can be used in the interpretation of a potential fault zone. In order to describe the considered fault's anatomy, the presented research has been concentrated on the identification of three main fault parts occurring within poorly indurated strata: the fault gouge, the mixed zone and the damage zone.

The analyzed exposure, whose length and height exceeds 70 and 15 meters, respectively, is located within a natural scarp in the Cichy Stream Valley. The scarp is mostly NNE-SSW to NE-SW oriented. It is dominated by poorly indurated Pliocene muddy to sand-supported paraconglomerates, mainly comprised of mudstone and sandstone clasts and up to 40% of matrix. The thickness of the rocks observed within the exposure reaches about 15 meters. Besides that, in few places, lense-shaped bodies of sandstone were observed. Their thickness is lower than 1 meter. They appear in the lower part of exposure, close to its easternmost side. From the neotectonic point of view, three groups of structures were recognized: clast-scale fractures, deformation bands and exposure-scale fissures.

The paraconglomerates are dominated by the fractured clasts. The clasts are cut either by one or two sets of fractures. The planes of these fractures mainly strike NE-SW to NNE-SW. In the western part of the exposure, the measurements were the most consistent, while the eastern part shows a greater dispersion of the data. In both western and easternmost parts of the exposure, some clasts are reoriented. Inclination reaches even 90°. Fractured clasts' investigation have yielded information about the intensity of the deformation within the paraconglomerate. The counts have shown that the prevailing amount of the fractured clasts occurs in the western part of the exposure – even 126 counts per square meter. The average amount of fractures observed in the middle of the scarp is 57 per square meter, whereas in the eastern part approximately 30 fractures per square meter were be counted.

The deformation bands have been observed within the lenses of sandstones, located in the center of the eastern part of the exposure. Moreover, the whole exposure is cut by numerous fissures that either cut across or bypass the clasts. Some of them are open and wide, while other are narrow. The fissures differ between themselves in terms of size. Therefore they were subdivided into three groups: (1) cutting the whole exposure, (2) disappearing towards the top of the exposure, (3) inferior (the smallest) ones. Except for one fissure placed on the west, the first group appears mainly in the center of the eastern part of the scarp. Second group is located in the center of the exposure. The third group, in turn, can be observed mainly in the eastern part of the paraconglomerate. Besides the inferior fissures (3), they mostly strike NNE-SSW, similarly to the fractures in clasts.

The fractured clasts' abundance, fissures' presence and clasts' reorientation can be interpreted as the indicators of a potential fault zone. The large amount of fractures in clasts in the westernmost part of the scarp, in combination with first-group fissure presence and clasts's reorientation, leads to the conclusion that it may represent the location of the fault gouge. Whether the gouge is relatively narrow, the observed reorientation might belong to the adjacent mixed zone. The mixed zone seems to occur in few places within the scarp. Its presence can be inferred from deformation bands' location and clasts' reorientation. Quite high background of fractures at the level of approximately 50 per square meter and tension fissures' presence within the whole scarp may indicate of the damage zone location. In this case, the damage zone would cover the largest part of the exposure, leaving the rest of it for a fault gouge and the mixed zone.

The model of the dominant damage zone also matches another theory, associated with a shear zone. In this case, the fissures observed within the scarp could be interpreted as the Riedel fractures related to left-lateral strike-slip fault occurring in the vicinity of the scarp.

*The presented research was founded by Polish National Center of Science – grant UMO-2012/07/B/ST10/04318; title „Neotectonics of NE end of Vienna Basin Fault System".*

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# Weathering of siderite in the polar conditions

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Rapid retreat and thinning of glaciers perturb balance of polar ecosystems. These processes influence global climate (Anderson et al. 2000, Płonka 2009). For better understanding of changes and their consequences for global climate, it is necessary to extend our knowledge about processes occurring contemporary in the forelands of retreating glaciers. Numerous researches were carried out on this subject (Anderson et al. 1997, Bukowska-Jania et al. 2003, Pulina et al. 2003). For example, *uplift-driven climate change hypothesis* assumes that decrease of temperature results from regression of glaciers and is connected with chemical denudation of silicate sediments, which acts as a sink of $CO_2$ from the atmosphere (Płonka 2009). Despite of this, many processes and dependences in polar environment are poorly known.

Retreating glaciers and high chemical denudation observed in Polar Regions play significant role in weathering of regolith. Fast retreat of many glaciers exposures great amounts of fresh and fine sediment. Weathering of rock-forming minerals is a source of ions in waters as well as secondary minerals and nutrients in initial soils. These issues are object of interest recently because intensified weathering in Polar Regions may affect global cycle of many elements, particularly Fe (Anderson et al. 1997, 2000, Brenasconi 2008).

This study is a part of large research, concerning mechanisms, budget and transport of iron from the foreland of fast retreating arctic glacier. The objective of this research is to determine processes and products of siderite weathering in the polar condition. The area of this study is located on the SW part of the Spitsbergen, in the foreland of Werenskioldbreen. It is hypothesized that in Arctic these processes differ significantly from their equivalents in Alpine regions.

Field experiment on Spitsbergen lasted eight years. Samples of the siderite were buried in the surface layer of bottom moraine (in the initial polar soils) 100 m, 250 m and 2000 m from glacier front. This represents a chronosequence of sediment uncovered from underneath the glacier ca. 5-, 10-, and 90-years ago. Samples were recovered after 1 year and after 8 years of burial. Optical microscopy in transmitted and reflected light, scanning electron microscopy SEM/EDS and powder X-ray diffractometry were applied to characterize both, control sample and experimental samples.

Siderite with manganese substitutions sampled from the outcrops of metamorphic carbonate in the vicinity of Werenskiold glacier was used for the experiment. This resembles mineral fragments eroded and transported by the glacier. Characterization of control sample (siderite before the experiment) indicates that it already exhibits advanced stages of transformation into secondary phases. Secondary minerals include oxides and hydroxides of iron, such as: goethite, hematite and lepidocrocite. The same mineral phases were identified in experimental samples recovered after burial. Additionally, 8-year sample shows traces of dissolution.

Weathering of siderite in polar initial soils in the foreland of retreating glacier leads to formation of secondary goethite, hematite and lepidocrocite. These phases appear to be the most stable products of siderite weathering in this environment. There is no difference between the samples buried in very young and in older, more evolved initial soil. Additionally, transformations of siderite are identical in initial polar soils and in the outcrops of siderite rock. Traces of dissolution noticed on the surface of older samples indicate that part of iron is permanently removed from the system by solutions. This process, probably mediated by microorganisms, requires further investigation.

*This work was supported by AGH UST statutory grant no. 11.11.140.319.*

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# A Raman spectroscopic study of hydroxyl analogues of pyromorphite-mimetite solid solutions

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Pyromorphite $Pb_{10}(PO_4)_6Cl_2$ and mimetite $Pb_{10}(AsO_4)_6Cl_2$, minerals belonging to apatite group, receive increased attention recently. Induced precipitation of pyromorphite and mimetite in soil pore solutions or waste solutions belongs to the best remediation and reclamation methods (Ma et al. 1995, Maniecki et al. 2009). These phases are the most stable forms of $Pb^{2+}$ and $As^{5+}$ in the environment. Deficiency of $Cl^-$ in the environment can cause formation of their hydroxyl forms: $Pb_{10}(PO_4)_6(OH)_2$ and $Pb_{10}(AsO_4)_6(OH)_2$ or their solid solutions. Apatite structure allows for extensive and varied ionic substitutions in all positions. The isomorphic substitutions affect unit-cell parameters and chemical properties of these minerals (Botto et al. 1997).

Solid solutions of hydroxyl analogues of pyromorphite and mimetite have not been sufficiently characterized to this day. A detailed description of phases from this series is, however, necessary for optimization of the remediation methods. A Raman spectroscopic study of mimetite-pyromorphite series demonstrated a strong correlation between the positions of the vibrational modes and the As/(As+P) ratio (Bajda et al. 2011). Such a correlation may be used to determine the composition of the examined samples of minerals from the series. The current research is based on the assumption that in the case of solid solutions of their hydroxyl analogues similar correlations occur. Therefore, the aim of this study is structural (X-ray diffraction) and spectroscopic (Raman) investigation of the effect of $PO_4$-$AsO_4$ isomorphic substitution on the structure and vibrational spectra.

Seven phases were synthesized in computer-controlled chemistate at pH = 11 and 80°C by dropwise mixing of solutions containing $Pb^{2+}$, $PO_4^{3-}$ and $AsO_4^{3-}$ in stoichiometric proportions. The composition of the final products was $Pb_{10}[(PO_4)_{6-x}(AsO_4)_x](OH)_2$, where $x = 0, 1, 2, 3, 4, 5, 6$. High-resolution powder X-ray diffraction data was obtained using the diffractometer at beamline 11-BM at the Advanced Photon Source (Argonne National Laboratory, Chicago). A detailed Raman spectroscopy was performed with the use of confocal Raman microscope and OMNIC software (AGH Kraków). The morphology and elemental composition of the samples were characterized by means of Fei Quanta variable pressure SEM/EDS (AGH UST Kraków). Moreover, the chemical composition of synthetic phases was determined by wet chemical analysis.

Unit cell parameters increase with substitution of $AsO_4$ for $PO_4$. Parameter a increases from 9.879 Å to 10.189 Å, while parameter $c$ – from 7.427 Å to 7.516 Å. This is consistent with other solid solution series of lead apatites (Flis et al. 2009). The area under selected Raman effects is also strongly correlated with P and As content. Additionally, systematic shift of the position of Raman effects is observed. The band attributed to the $(AsO_4)^{3-}$ $\nu_1$ symmetric stretching mode shifts from 808 $cm^{-1}$ in $Pb_{10}(AsO_4)_6(OH)_2$ to 814 $cm^{-1}$ in $Pb_{10}[(PO_4)_5(AsO_4)](OH)_2$. The range of the peak positions for the $(PO_4)^{3-}$ $\nu_1$ symmetric stretching mode is even wider: from 918 $cm^{-1}$ in $Pb_{10}[(PO_4)(AsO_4)_5](OH)_2$ to 926 $cm^{-1}$ in $Pb_{10}(PO_4)_6(OH)_2$. The observed correlations may be used for semi-quantitative estimation of As and P content using non-destructive Raman spectroscopy.

*This work was supported by AGH UST statutory grant no. 11.11.140.319.*

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# Optimization of synthesis conditions of pyromorphite-vanadinite and mimetite-vanadinite solid solution series

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Minerals: pyromorphite $Pb_5(PO_4)_3Cl$, mimetite $Pb_5(AsO_4)_3Cl$ and vanadinite $Pb_5(VO_4)_3Cl$ belong to the apatite supergroup. Commonly they form in hypergenic conditions. They are best known from the oxidation zones of lead ore deposits. Natural pyromorphite usually contains admixture of arsenates or vanadates, whereas mimetite or vanadinite contain admixtures of phosphates. Solid solutions of the pyromorphite-mimetite series are well known, while the knowledge about anionic substitutions in vanadinite is incomplete. Therefore, the aim of this study was to find optimal conditions for the synthesis of pyromorphite-vanadinte and mimetite-vanadinite solid solution series. This research will allow to check the range of possible anionic substitutions, formation conditions such as pH, temperature and in, turn, to obtain better knowledge about the properties of these minerals.

Pyromorphite, mimetite, vanadinite and pyromorphite-vanadinite and mimetite-vanadinite solid solutions series were synthesized from aqueous solutions. Solutions containing $Pb^{2+}$, $PO_4^{3-}$, $AsO_4^{3-}$, $VO_{3-}$, $VO_4^{3-}$ and $Cl^-$ ions in stoichiometric molar proportions were dropwise mixing. This method of synthesis allows controlling the stoichiometry of the chemical composition of synthetic precipitates. Synthesis reactions were carried out at various pH and at different temperatures (range from 25°C to 85°C). After the synthesis, suspensions were left for two weeks for aging. Then the suspensions were filtered using a Büchner funnel. The precipitates were washed with double-distilled water and acetone, and then dried. Synthetic precipitates were analyzed using various analytical techniques including X-Ray diffraction (XRD), Scanning electron microscopy coupled with Energy Dispersive Spectroscopy (SEM/EDS), Infrared absorption spectroscopy (FTIR) and Raman spectroscopy.

Results of XRD, SEM/EDS, FTIR and Raman spectroscopy analyzes of studied samples showed that temperature 25°C and pH = 3.5 are optimal conditions to synthesize pyromorphite-vanadinite and mimetite-vanadinite solid solution series. Chervetite $Pb_2V_2O_7$ was formed together with studied phases at lower pH values (1.7, 2.2), or higher temperatures (75°C, 85°C). At pH = 11.5, minerals with hydroxyl groups were formed. It has been observed that the formation of pyromorphite-vanadinite and mimetite-vanadinite solid solution series mainly depends on the pH values. The temperature is less important.

*The project was financed with resources of the National Science Centre, Poland, granted based on decision no. DEC-2013/09/N/ST10/00677.*

Geology, Geophysics & Environment 2014, vol. 40 (1): 89–90

# Dynomenid crabs (Decapoda, Brachyura) from Upper Cenomanian-Lower Turonian nearshore, shallow-water strata in the Bohemian Cretaceous Basin, Czech Republic

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Conditions of preservation of small crabs at nearshore deposits in the Bohemian Cretaceous Basin (BCB) were poor and fossil record is mostly restricted to fragmentary pereiopods, i.e. isolated propodi or dactyli, whereas crab carapaces in the area are rather rare. Excluding three specimens of dynomenid *Graptocarcinus texanus* Roemer, 1887 and one necrocarcinid carapace fragment, no other carapaces are known from the nearshore deposits of the BCB. These partially crushed carapaces lacking chelipeds or other appendages come from the lower Turonian calcareous siltstones at Kamajka. By contrast, crab claws and isolated dactyli are more common in the BCB, but notoriously difficult to identify (Jagt et al. 2010, Veselská 2011). In view of the confused taxonomy of isolated claws, its identity has not been recognised and claws were described as fragments of the necrocarcinid species *Necrocarcinus avicularis* Fritsch (in Fritsch & Kafka 1887). However morphology of crab chelipeds originally described as *N. avicularis* is in fact typical of graptocarcinines (dynomenids); claws are covered with small tubercles and are rectangular in outline with a distinctive bulge on propodus/carpus articulation. The bulge closed the space between propodus and carpus when bent and probably protected the claws when crabs moved between coral colonies or during feeding, similar to extant dynomenids (Jagt et al. 2010, Van Bakel et al. 2012, Kočová Veselská et al., submitted). Jagt et al. (2010) prefer to use parataxonomy for such cases and suggest using “form genus” *Roemerus* Bishop, 1983 for isolated dynomenid chelae.

Between 2001 and 2013, the authors conducted field works in the upper Cenomanian-lower Turonian nearshore, shallow-water bioclastic limestones to marly siltstones at Velim, Chrtníky and Kamajka situated approximately 60–100 km east of Prague along the southern and eastern margins of the BCB, which are interpreted to have been laid down under high-energy conditions (Žítt et al. 1997a, b). During these sessions, 200 kg of rubble were amassed and screened through a 1 mm-sieve with a result of an additional isolated dactyli and cheliped fragments. Whereas strata containing brachyuran crabs at Kamajka are exclusively of early Turonian age, crustaceans from Chrtníky and Velim are from upper Cenomanian and early Turonian nearshore sediments alike.

A recent re-examination of these new finds together with crab chelipeds originally described as *N. avicularis* deposited in the National Museum (Prague) has revealed that all alleged necrocarcinid claws or dactyli from nearshore strata in the BCB indeed correspond to the diagnosis of the dynomenid "form genus" *Roemerus*, in size, ornament, development of the fixed and movable fingers and presence of ovate depressions in dactylus and fixed finger (Veselská 2011, Kočová Veselská et al., submitted). Although still not found connected with carapaces, these claws may be conspecific with the co-occurring, carapace-based species, *G. texanus*, at Kamajka.

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Geology, Geophysics & Environment 2014, vol. 40 (1): 91–92

# Mineralogical study of the Drazhnje Prospect (Kosovo) – preliminary report

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The mining activities took place in Kosovo since ancient times. The object of interest at these times was gold and silver ores. One of such old mining areas is located in north-east Kosovo, close to the Batlava Lake. Contemporary works include exploration activities and the goal of this research is to determine the features of mineralisation in that deposit. The name Drazhnje is used interchangeably with Çuka e Batllavës. In the close vicinity, there are known also several other base-metal ore bodies that may be of economic interest. During last years, an exploration gallery was built in Drazhnje, which gave an opportunity to collect mineralogical samples of ore from the upper part of the deposit.

The Drazhnje prospect is located in area built of Paleozoic metamorphic complex, Jurassic sediments, ophiolite and Cretaceous flysch sediments. The volcanogenic-sedimentary complex of the Tertiary covers all the older rocks. The mineralisation in Drazhnje prospect is located within marbles, serpentinites and volcanic rocks.

Mineralogical study is focused on the sulphide composition of the ore. Minimum two stages of mineralization can be distinguished. During the first one, pyrite, pyrrhotite, sphalerite and galena were formed. The younger stage comprises marcasite, chalcopyrite, arsenopyrite, stannite and Pb-Sb sulphosalts, mainly boulangerite. The gangue minerals are quartz and carbonates. Carbonates of different compositions belong to the youngest minerals in both stages. In the polished sections we have observed that stannite replaces sphalerite, and bournonite replaces galena. Galena is also being replaced by boulangerite. Evidence for boulangerite presence was confirmed by XRD method. Smithsonite was recognized as a main secondary mineral. It occurs as a greenish-to pinkish collomorphic coating on the surface of other minerals or it fills cavities in the ores.

The Drazhnje deposit exhibits similarities to other Pb-Zn deposits in the area. The mineralization of stockwork character is hosted mainly by carbonates and its genesis is related to the volcanic activity. Preliminary data on ore chemistry indicate that the content of zinc is higher than content of lead, and is estimated at about 4% and 2%, respectively. In the other deposits of Kosovo, these values are reversed. High content of sulphosalts in the studied deposit, like bournonite and boulangerite, indicates that these minerals could be one of important bearers of lead in the Drazhnje deposit. Content of antimony reaches 0.3 wt. %, which could be correlated with relatively low content of lead (around 2 wt. %). During the field studies, we have confirmed that boulangerite is the most common lead mineral in the upper (reachable) part of deposit, whereas galena is not so common. It is worth to add that some amounts of galena have been replaced by bournonite.

In comparison to samples from the other Kosovo deposits, we have noticed unusually high content of stannite, which was found in nearly all of the studied polished sections.

Further exploration and start of extraction of the deeper parts of the deposit will allow collecting more samples that are necessary for future mineralogical and geochemical studies.

*The research was financed by the AGH University of Science and Technology statutory grant no. 11.11.140.320.*

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# The design of field QA/QC programme for geothermal waters sampling on the example of Bańska Niżna PG-P1 and PG-P3 wells

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Samples of long term exploited geothermal waters sometimes show that composition of water has been changed during the exploitation. Those changes can be caused by neglecting appropriate standards application during of sampling or other factors such as: chemical and biological nature of the samples, their temperature, exposure to light, sort of container used, time between sampling and a chemical analysis and overall conditions during transport (ISO 5667-3:2012). The European Union directive (DT 2009) indicates necessity of implementation of the quality assurance and quality control (QA/QC) program related to water monitoring.

According to ISO 5667-1:2006 there is no universal QA/QC program, which could be used for all purposes. Therefore, it is very important to develop an individual field QA/QC program for each research, which will be optimum for a particular purpose of a research.

ISO 5667-14:2004 standard precisely describes techniques used for quality assurance purposes:

- in order to determine precision of sampling, it assumes collecting duplicate samples,
- in order to monitor samples contamination, it assumes analysis of field blank samples,
- in order to determine sample stability during transport and storage, it assumes analysis of spiked samples – samples with the addition of analyte.

Objective of our work was to design the QA/QC program for geothermal waters from PG-P1 and PG-P3 wells in Bańska Niżna exploited by Geotermia Podhalańska Company. It will supplement to the ongoing research. It will involve collection of control samples (duplicate, field blank and spiked), which allows establishing reliability of obtained results of physico-chemical analysis.

Designed program is also a part of extensive monitoring, which will be used to determine the changes of water chemical composition in a given time and to compare them with results from previous monitoring series.

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# Pressure-temperature estimates on blueschists from the Vestgötabreen complex (Western Svalbard)

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In Oscar II Land (Motalafjella area, western Svalbard), an exotic high-pressure (HP) metamorphic unit, namely the Vestgötabreen Complex (Kanat & Morris 1988) occurs. It is thrust over low-grade metasediments (e.g. Labrousse et al. 2008) of inferred Neoproterozoic age. This complex is subdivided into the Lower (LU) and Upper Unit (UU) differing from each other in terms of lithologies and pressure-temperature (*P-T*) conditions. The LU is composed of high pressure-low temperature (*HP-LT*) metasediments with minor intercalations of blueschists, whereas the UU comprises metasediments, more voluminous blueschists and scattered lenses of eclogites. Radiometric dating yield the age of c. 470 Ma for the HP metamorphism in the Motalafjella region (Horsfield 1972, Dallmeyer et al. 1990, Bernard-Griffiths et al. 1993). The *P-T* conditions for carpholite-bearing schists from the LU yield the pressures up to c. 16 kbar and temperatures in the range of 330–450°C (Agard et al. 2005), whereas eclogites from the UU were subjected to 18–24 kbar pressure and temperatures of 580–640°C (Hirajima et al. 1988).

The aim of this study is to decipher metamorphic evolution of blueschists using thermodynamic phase equilibrium modeling. Samples have been collected from the UU, cropping out at the Skipperryggen ridge. They contain mostly garnet, glaucophane, phengite, rutile and chlorite. Additionally lawsonite, ilmenite and epidote can be found in minor amounts. Garnet typically forms euhedral to subhedral porphyroblasts. It contains voluminous inclusions of white mica, epidote, rutile and amphibole. Garnet shows chemical compositional variation from $Alm_{63}Prp_{13}Grs_{22}Sps_2$ in the cores to $Alm_{60}Prp_{19}Grs_{20}Sps_1$ in the rims. The pyrope zoning is bowl-shaped, whereas grossular and spessartine profiles show bell-shaped trends. The almandine content is generally constant through the grain.

The *P-T* conditions were estimated using the phase equilibrium modeling in the NCKFMASHTO system using the Perple_X software (Connolly 2005). Modeling was based on bulk-rock chemistry as well as garnet and phengite compositional isopleths. *P-T* estimates indicate peak conditions of ca. 20 kbar and 520°C. These estimates for studied blueschists from Skipperryggen are in agreement with previous studies on the Vestgötabreen Complex. Also, recent studies in Nordenskiöld Land (south of Oscar II Land) revealed the occurrence of blueschist facies rocks. These blueschists yielded similar *P-T* conditions to blueschists from the Vestgötabreen Complex (18 kbar, 470°C; Kośmińska et al., in press). More regionally, all aforementioned *HP-LT* lithologies may be correlated with the ophiolitic sequence occurring within the Pearya Terrane of northern Ellesmere Island (e.g. Labrousse et al. 2008, Kośmińska et al., in press). Detailed tectonic, petrological and geochronological studies are in progress.

*This project is partially financed by AGH research project no. 11.11.140.319 and by the Swedish Polar Research Secretariat – NOA Svalbard program.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 96–97

# Improved copper sorption on grafted kaolinites of different structural order

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Kaolin group minerals exhibit relatively low sorption capacity as the migration of ions and their sorption in the interlayer space is not possible. The ions attraction is limited to the particles faces and edges through surface complexation and ion-exchange mechanisms. The ongoing research on functionalized kaolinites enabled to synthesize new nanomaterials with possible applications in industry and environmental protection. The modification procedures mainly involve structure alteration by intercalation and/or grafting processes. It is worth to underline that kaolinite 1:1 layer has exposed inner surface hydroxyls which are susceptible for reactions with selected organic molecules and as a results new materials with interesting properties may be obtained. Heavy metals in excessive amount are toxic and may lead to serious health problems. Thus, the purification of heavy metal contaminated aqueous solutions is of environmental importance. The aim of the study was to examine the sorption properties of kaolinites grafted with selected aminoalcohols towards Cu(II).

For the experiments, two types of Polish kaolinites were chosen: well ordered type from Maria III deposit (M) (located about 20 km SW from Bolesławiec) and poorly ordered type from Jaroszów deposit (J) (located about 10 km NE from Strzegom). The modification consisted of (i) a preparation of kaolinite-dimethyl sulfoxide intercalate (MDMSO and JDMSO) and (ii) its further grafting with diethanolamine (DEA) or triethanolamine (TEA) (Letaief & Detellier 2007). The synthesized MDEA, MTEA, JDEA and JTEA samples were examined using XRD, IR and CHNS methods. The Cu(II) sorption equilibrium experiments were performed for the 0.005–10.0 mmol/L concentration range at room temperature (initial pH 5). The suspensions (20 g/L) were shaken for 24 hours. Afterwards, the Cu(II) concentration was measured using AAS method.

The $d_{001}$ reflections for the MDEA, MTEA, JDEA and JTEA increased from 7.2 Å (M and J samples) to 10.2 Å, 10.8 Å, 10.1 Å and 11.0 Å, respectively which confirmed the formation of grafted compounds. The presence of organic molecules resulted in an appearance of C-H stretching bands (2800–3000 $cm^{-1}$) in the IR spectra. Moreover, changes in the O-H stretching region (3600–3700 $cm^{-1}$) were also noticed due to interaction of aminoalcohols with kaolinites hydroxyls. An assumption was made that the sorption of cations will take place by the nitrogen lone electron pair of the grafted DEA or TEA. Thus, the theoretical sorption capacity associated with nitrogen was calculated on the basis of CHNS analysis and was the following: 184 mmol/kg (MDEA), 223 mmol/kg (MTEA), 122 mmol/kg (JDEA) and 323 mmol/kg (JTEA).

The highest Cu(II) sorption was observed for the JTEA sample: 119 mmol/kg, while for the J and JDEA samples it reached 65 mmol/kg and 88 mmol/kg, respectively. The sorption improvement was less pronounced for materials based on the M sample. Both for the pure M sample and the MTEA sample, the sorption capacity was equal to ~62 mmol/kg, while for the MDEA sample it was higher and reached 72 mmol/kg. It can be concluded that the performed modifications have improved the kaolinites sorption capacity. The improvement was due to cations attraction by the nitrogen lone electron pairs after their migration into the interlayer space. Worth emphasizing is that the Cu(II) ions readily form Cu-aminoalcohol complexes in aqueous solutions (Karadag et al. 2001). As a result of such mechanism, the pH value has increased, which is attributed to competitive protons sorption. The adsorption energy, estimated on the basis of Dubinin-Radushkevich equation, for all the reactions was in the 10–14 kJ/mol range. This indicates that the adsorption energy corresponds to energies characteristic for the ion exchange reactions (Debnath & Ghosh 2007). In most cases the sorption isotherms followed the Langmuir model.

*This project was supported by the Polish National Science Centre under research project awarded by decision no. DEC-2011/01/D/ST10/06814.*

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# Tools for 3-dimensional geological layers models generated in spatial database using CGAL library

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Spatial databases are commonly used to generate 2-dimensional (2D) and 3-dimensional (3D) topographic models. Mentioned models sometimes also contain information about geological layers. In that case, analysing data provides extra benefits and facilities that are desirable in presentation of complex and multilayer data (Chrobak 2009, Gotlib 2009).

The possibility of storing and processing the geometry, which is saved in a standardized vector form, is the greatest advantage of spatial databases. The standards (technical documents that detail interfaces or encodings) were presented by Open Geospatial Consortium (OGC) (Open Geospatial Consortium 2014). Geometry of the objects is presented as points, lines, polygons and theirs collections. The standards also include specification about 3D data representation.Those data could be used to describe and create geological models. Another advantage of spatial databases is the possibility of adding own extensions without recompilation of all database source code. The extensions are added as a compiled library with functions, which could be written in a selected programming language (Bac-Bronowicz 2010, Lupa 2012, Lisowski et al. 2013).

This paper focuses on the possibility to extend *PostgreSQL* database using functions that are written on the base of open source Computational Geometry Algorithms Libary (CGAL) project (Aptekorz et al. 2012, CGAL 2014). The extension library contains algorithms that are used in computer graphic and visualization of geometric data. The library was written in C++ language according to the objective-programming paradigm. Presented solution adds function of Delaunay triangulation, which is not implemented in PostGIS (Lisowski et al. 2013). This tool allows to generate Triangulated Irregular Network (TIN) surfaces of geological layers in a simple and functional way. 3D terrain model is created using information from spatial database (2D and 3D objects). In the next step, TIN model is generated, which approximates the modelled geological layers by a network of the triangles (tangent edges). Interoperability and unified data edition was achieved due to using of triangles (represented by triangles which are polygon type, vanished points and lines objects). Nevertheless, generating of 3D models from 2D data with parameter, which would properly represent a surface and terrain layers, is not a trivial task.

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Geology, Geophysics & Environment 2014, vol. 40 (1): 100–101

# Implementation of digital maps and documentation of the site based on geographic information system for the selected regions of oil trail

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GIS is a well-organized database, which allows storing information about objects and phenomena that includes both Earth and its surface. Nowadays, rapid technological development can be observed. Databases (geodatabase) are designed to enable presentation of the world, as well as to allow multi-dimensional analysis of the collected information regarding a space (Chrobak 2009, Gotlib 2009). This solution creates a kind of object-oriented map, which includes spatial and numerical data collected from various sources and combined together, such that these form a coherent representation of geospatial (Bac-Bronowicz 2010, Dorożyński 2010, Gotlib et al. 2005). This provides a rich source of comprehensive information with possible multiple access, both in the form of simultaneous read and work (Dorożyński 2010, Lupa & Piórkowski 2012).

Members of the "KIWON" Scientific Society at the Faculty of Geology, Geophysics and Environmental Protection AGH proposed the idea of creating a full documentation of selected areas of the Podkarpacki Region, which was studied thoroughly by them in the last several years. The first stage of the project includes creating a three-dimensional model of the terrain surface based on data from the scanning of air (LiDAR). The modeled area will cover selected areas of the Oil Trail, especially around the Bóbrka and Ustrzyki Dolne. Szlak Naftowy is a cross-border route connecting the places related to the birth and history of the oil industry. The main axis of the route goes through Jasło – Krosno – Sanok – Lesko – Ustrzyki Dolne, and the further part is located in the Ukrainian side. The latter area is not a matter of our study.

The main aim of the project is developing digital maps of selected regions of Szlak Naftowy based on Geographic Information System. Maps will provide integrated information on topographical, geological and environmental occurrence of the selected areas of oil and gas from the Krosno area to the Polish-Ukrainian border. The purpose of this study is to create a detailed three-dimensional map of two areas, (1) the Bóbrka area and (2) Ustrzyki Dolne (Polana deposit). The map will present ground surface and ground three-dimensional model, developed on the basis of borehole data. These models will be developed in two independent systems, enabling the creation of three-dimensional models of the substrate (ArcScene and Petrel). Additionally, a comparative analysis will be carried out on both output models. Point clouds acquired by laser scanning LIDAR method will be used in creating a digital model of the terrain surface. A complementary NMT based on satellite data (InSAR method) will be created as well. The planned result of this work is a digital, interactive map that will provide opportunity of analyzing individual layers to oil and gas in the studied area and the creation of visualization ground, consideration natural and anthropogenic objects.

To summarize, a database containing the coordinates of the waypoints and the localized geological and environmental information will be formed through reconnaissance vehicle that includes updating and verifing the locations of the pits and natural leakage of oil and natural gas along the trail of Szlak Naftowy, as well as photographic documentation.

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# Petrographic composition and origin of the Dębowiecki conglomerate, Carpathian Foredeep (Poland) – preliminary results

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The Dębowiecki conglomerate is a coarse-grained Miocene sediment, which occurs in the western part of the Carpathian Foredeep between Cieszyn, Jastrzębie and Bielsko (Poland). This unit includes varigrained conglomerates and coarse-grained sandstones. The thickness of the unit may reach up to 260 m. The Dębowiecki conglomerate was mentioned for the first time by Petrascheck (see Konior 1965). However, Tołwiński (1950) described this conglomerate in detail and placed it into the so-called "dębowiecki layers".

This research aims to determine the composition and origin of the Dębowiecki conglomerate's clastic material. At current stage, 22 samples from the Dębowiecki IG 1 borehole were selected. The fraction larger than 2 mm was used for the petrographic analysis. Four petrographic groups were distinguished among the clastic material. Mudstones, sandstones, fragments of carbonates and crystalline rocks have been identified.

Mudstone pebbles form the largest group, amounting to 23–57%. They are represented by gray, gray-brown to black rocks. Pebbles characterized by high cohesiveness dominate. Sharp-edged and subrounded clasts are predominant, which may indicate a short transport of the material from the source area. Gray, very concise mudstone pebbles with poorly encased grains are very similar to the Carboniferous mudstones which can be found south-west from Dębowiec. It can therefore be assumed that a large part of the material comes from direct substratum of the Dębowiecki conglomerate made of productive Carboniferous, namely the Poręba beds, which are included to the paralic series. The Poręba Beds (Namurian A) occur within the Upper Silesian Coal Basin (Kotas & Malczyk 1972).

The sandstones are represented by numerous petrographic varieties (3–24%). The light-grey, with a tinge of brown sandstones, with silica or silty-silicate cement may be of productive Carboniferous origin. The light-green, fine-grained sandstones with glauconite resemble flysch deposits. The dark-grey sandstones may be of Culm origin.

The white-yellow, white or beige limestone clasts (0–11%) indicate the similarity to the Devonian carbonates known from the Śląsk Cieszyński basement. Some of them have also strong affinity with the carbonate exotics from the Carpathians. Among magmatic rocks (0–6%), the granitoids are prevailing. They may come from the flysch deposits, or from the Cieszyn Ridge.

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# Paczółtowice – unique carboniferous "marble"

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The Paczółtowice "marble" is a unique Carboniferous limestone modified in the later Carboniferous- Permian times as a result of plutonic and tectonic activity that resulted in the rocks inhomogeneity. Three varieties of the Paczółtowice "marble" can be distinguished.

The first and prettiest variety of the Paczółtowice "marble", called "polish onyx", is a multicolour, middling and thickly-crystalline calcite vein with thickness up to 20 m. It is probably Permian lateral secretion in the Carboniferous limestone, which was formed by the hydrothermal processes. Second variety is a multicolour Carboniferous limestone modified by warm, Fe-rich dilutions related to the volcanic activity known from the Dębnik anticline. It is represented by white, grey and reddish "marble" exhibiting unusual diffusion rings. The third variety is a calcareous breccia of this Carboniferous limestone joined together with multicoloured calcite.

These limestones are called "marbles" because they show similar technical properties like marble *sensu stricto*. The Paczółtowice "marble" has favorable technical properties and significant parts of the deposit have a high decorative value. Hence, it was a valuable material used for many monuments. Most often, this colorful limestone was combined together with the Dębnik marble, which exhibits a deep black colour after polishing. Both marbles together give a fantastic contrast and wonderful decorative effect in the monuments.

The Paczółtowice "marble" was discovered in the Paczółtowice village which is situated 6 km from Krzeszowice and occurs within the "Kraków Valleys" Landscape Park (southern Poland). This area is protected because of its valuable geology, fauna and flora. In such situation, there is a conflict between any desire to deposit development and the requirements of the protection of nature and landscape. The peculiarity of this "marble" tends to maintain deposits in the balance sheet as a reserve of raw material for a small retrieval, mainly for reconstruction of existing monuments.

Exploitation of the "marble" could be possible in parts of the deposit, but appropriate environmental and landscape rigors must be respected. The quarry face could expose the details of the geological structure of the site. After finishing exploitation, a quarry would improve its landscape value and become a fantastic geotouristic attraction.

*Research is supported by the AGH University of Science and Technology, Faculty of Geology, Geophysics and Environment Protection in Krakow as the grant no. 11.11.14 0.17.*

Geology, Geophysics & Environment 2014, vol. 40 (1): 104–105

# AGH University of Science and Technology in three-dimensional web world

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In recent years, the number of geoportals was constantly increasing all over the world. In Poland, the main reason of growth is implementation of the INSPIRE Directive. The most important goal of creating geoportals is to provide Spatial Data for the Polish Spatial Infrastructure (Głowacki et al. 2005). Theirs architecture is oriented to services and interaction with any user (Akinci & Cömert 2008). All technological solutions should give the user the possibility of using data from many sources in one platform (Nowacki & Opach 2009). Most of Geographic Information Systems represents only the view of the "bird's eye" without giving the possibility of three dimensional viewing of the actual situation on the ground. What you can see is the land surface as an object map or ortophotomap. However, currently a demand of GIS applications designed for fully three-dimensional data is growing. This approach is commonly used for presentation and spatial analysis (Scianna 2013). Thanks to the modern capabilities, ensuring high quality of three-dimensional models is easy (Shioda 2000).

Geoportal AGH – Spatial Information System of the AGH University of Science and Technology – was established in order to provide updated data, allowing moving around the campus. This functionality has been ensured by the construction of site (geoportal). The combination of a vector map along with a number of tools allowing searching by attribute makes it possible to search for any building or room available for students' classes. Geoportal AGH will also include data on the news and current events related to the life of the university, for example: repairs of roads, conferences and recruitment. All this is available in a modern, interactive application that was created based on the latest technologies for maximum usability and support for each user.

Now in progress is the creation of three-dimensional model of the AGH campus and its implementation on the mentioned above server www.gis.agh.edu.pl becoming its integral part. The work involves the use of data obtained from surveying and external facade images of objects in order to create a model resembling the real and its rendering.

Contractors of the grant will be students of the Faculty of Mining Surveying and Environmental Engineering. Substantive support to the project was provided by our partner – ESRI Poland. Through the financial support of the Scientific Society named after Stanisław Staszic we can present our achievements in the international area.

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# Fault zone imaging based on refraction seismic surveys

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Refraction surveys were carried out along the border lines between Outer Carpathians, Inner Carpathians and Pieniny Klippen Belt. Measurements were focused on imaging transition zone structured by para-conglomerates, sandstone and clays lenses, crossing in near neighbourhood of Stare Bystre, village in the southern part of Poland. The geological and geophysical investigation was conducted to prove that occurring on site, main fault (NW-SE) has a system of smaller discontinuities.

Para-conglomerate exposure, which was localized close to survey area, was cut by observable system of cracks. That geological evidence could be an effect of previous fault activity and suggests its continuation up to core of fault zone – covered by Neogene river sediments. In this case non-direct, refraction method was applied to confirm existence of a local bedrock faulting.

Seismic acquisition was extremely focused on determining any changes of elevation and estimated P-wave velocity of buried para-conglomerates. Surveys were carried out in azimuthal schema, fitted to field conditions. 24-channels seismograph and 10 Hz geophones were used. Hypothetical discontinuities were estimated after analyzing high resolution seismic records. The obtained geophysical data had a volumetric character which allowed easier interpratation and was better related to initial assumptions about geological form of fault zone.

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# Surveying support in geophysical methods

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Traditional methods to identify the geological structure of the rock mass are based mainly on the analysis of cores from boreholes. Today, more and more often geophysical methods are introduced to support classical methods or completely replace them. One of the major advantages of this type of measurement is non-invasive analysis of the rock mass. Due to the nature of this type of geophysical measurements and calculations, they must be supplemented by surveying information. Gravimetry and microgravimetry are commonly used technologies to detect voids, located shallowly under the ground. They are based on the determination of changes in the vertical components of the force of gravity at a point. Determination of the value of gravity gives only apparent image of change. To be able to fully describe studied phenomenon we should also take into account the topographic correction of rock masses located close to the measured point. Modern geodetic measurement methods used to determine the digital terrain model with high precision allow increasing the quality of the results of the study. To register terrain over the caves, which were the subject of research, total station technology and terrestrial laser scanning were applied. This allowed to create a fully metric terrain model in form of a cloud of points. The accuracy of both methods can be determined at the level of several millimeters. To calculate the correction for the excavation created three-dimensional models of voids located under the surface. They were also used to control the data obtained from gravimetry. The conclusion of our study was that geodetic measurements are important elements of geophysical researches.

ISSN 299-8004 | e-ISSN 2353-0790 | Wydawnictwa AGH

Geology, Geophysics & Environment 2014, vol. 40 (1): 108–109

# The kinetics of heavy metals immobilization by modified halloysite

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Halloysite is a clay mineral, belonging to the kaolinite group. Its structure is composed of stacked 1:1 layers built from octahedral (alumina) and tetrahedral (silica) sheets, linked through hydrogen bonds formed between oxygen atoms of tetrahedral sheet and inner surface OH groups of octahedral sheet. Due to the fact that Poland has several kaolin deposits, it is important to undertake research concerning possible application after appropriate modification (Matusik & Bajda 2013, Matusik & Kłapyta 2013, Matusik et al. 2013). Beyond harmful properties, the decisive factor in the selection of heavy metals was their high prevalence in the environment. The purpose of the research was to analyze the kinetics of heavy metals immobilization by natural and modified halloysite.

The mineral (H) used in the study came from Polish deposit located in Dunino near Legnica, which is owned by the Intermark company. The sample, apart from halloysite, which exhibits a tubular morphology, contains kaolinite forming plates. The modification procedure involved two following steps. Firstly, material was intercalated with dimethyl sulfoxide (DMSO) by mixing 12.5 g of mineral with 90 mL DMSO and 10 mL $H_2O$ (HDMSO). The second step involved grafting process, in which the HDMSO was refluxed with 150 ml of diethanolamine (DEA) for 24 h at 180°C under argon flow. Afterwards, the final sample (HD) was washed with isopropanol and subsequently with water to remove DMSO remnants and the excess of DEA. The materials were characterized using XRD and IR methods. The materials sorption affinity towards Pb(II), Zn(II), Cd(II) and Cu(II) was investigated. The experiment was carried out for a mixture of all four metals (multi-element system) at equal 1 mmol/L concentration at initial pH 5.2. The material either H or HDEA (1 g) was mixed with 50 mL of solution (20 g/L – solid/solution ratio). The suspension aliqouts were collected after 0.5, 1, 1.5, 2, 3, 4, 5, 6, 8, 10, 15, 20, 30 min, filtered immediately, and further analyzed using AAS method.

The XRD patterns showed that the modification did not alter all halloysite layers. The 10.4 Å peak of the new complex, and the 7.3 Å peak of raw mineral were observed. The IR spectra of H sample in 3700–3600 $cm^{-1}$ region revealed four distinct bands attributed to different vibration modes of inner surface and inner hydroxyls. After DMSO intercalation new bands at 3540 $cm^{-1}$ and 3503 $cm^{-1}$ were noticed connected to interlayer hydrogen bonding S=O...HO between DMSO molecules and OH hydroxyls of the octahedral sheet. The bands at 3022 $cm^{-1}$, 2936 $cm^{-1}$, and 2918 $cm^{-1}$, were due to C-H stretching vibrations of DMSO methyl groups. The IR spectra after DEA grafting, showed the disappearance of bands related to DMSO molecules indicating their removal.

The adsorption behavior of tested heavy metals onto raw and modified halloysite differs. In the experiment with H sample the equilibrium was achieved almost immediately. On the other hand, in the case of HD sample the sorption increased gradually and the equilibrium was reached after about 30 min. The relatively slowest uptake was particularly noticeable for Cu(II) and Pb(II). The sorption on raw halloysite may take place through surface complexation and/or ion-exchange. The sorption on natural halloysite was found to follow the sequence Pb(II) > Zn(II) > Cu(II) ≈ Cd(II), which reflects the cations hydrolysis behavior. After 30 minutes the sorption capacity for H sample reached 15 mmol Pb/kg, 6 mmol Zn/kg, 1.5 mmol Cu/kg, 1 mmol Cd/kg. The final pH decreased to 4.2 confirming the protons release characteristic for surface complexation mechanism. The sorption on modified halloysite was found to be the following: Cu(II) > Pb(II) > Zn(II) ≈ Cd(II). The sorption reached an equilibrium equal to: 25 mmol Cu/kg, 20 mmol Pb/kg, 10 mmol Zn/kg and 8 mmol Cd/kg. It is worth to mention that 16-fold increase for Cu(II) and 8-fold increase for Cd(II) were noticed. In particular the Cu(II) sorption increase is due to formation of Cu(II)-DEA complexes. The final pH of solution increased to 5.3 due to competitive sorption of protons to amine nitrogen of the DEA.

*This project was supported by the Polish National Science Centre under research project awarded by decision no. DEC-2011/01/D/ST10/06814.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 110–111

# Structural and Raman spectroscopy studies of schultenite – phosphoschultenite isomorphic series

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In many countries, there is a problem of lead and arsenic soils contamination. Lead can be immobilized using phosphate amendments (Cao et al. 2003). This technique, however, results sometimes in arsenic migration. Mineral phases, which can precipitate in this conditions include schultenite $PbHAsO_4$ and phosphoschultenite $PbHPO_4$. Only recently it has been experimentally shown that these minerals can form a continuous solid solution series in Earth surface environments (Zembal 2012). Therefore, it is important to extend our knowledge on the properties of schultenite-phosphoschultenite solid solution series in order to solve certain environmental problems.

For the first time, Raman spectroscopy was used to characterize schultenite, phosphoschultenite and their solid solutions. The main objective of this research is the identification and interpretation of systematic changes in the results of X-ray diffractometry and Raman spectroscopy applied to synthetic schultenites with various P to As ratio. Six samples were synthesized from aqueous solutions at ambient conditions. The ratio of P/(P + As) varied from 0 to 1 by 0.2 (Zembal 2012).

Schultenite $PbHAsO_4$ and phosphoschultenite $PbHPO_4$ belong to monoclinic crystallographic system. The standard model of the *P*2/*c* symmetric group was used in the calculation of unit cell parameters. The results show systematic increase in unit cell parameters with substitution of P for As in the series: parameter *a* from 4,6737 to 4,8588, parameter *b* from 6,6381 to 6,7528 and parameter *c* from 5,7617 to 5,8495.

The Raman spectra have also shown systematic variation in stretching and bending vibrations in the series. The $\nu_1$ stretching As-O band shifts from 463 $cm^{-1}$ in schultenite $PbHAsO_4$ to 469 $cm^{-1}$ in P-substituted schultenite while $\nu_4$ bending As-O band shifts form 824 $cm^{-1}$ to 841 $cm^{-1}$. Similar is observed in phosphoschultenite: the $\nu_1$ stretching P-O band shifts from 555 $cm^{-1}$ to 569 $cm^{-1}$ and $\nu_4$ bending P-O band shifts form 905 $cm^{-1}$ to 940 $cm^{-1}$ with increasing P content. Observed shifts in position of Raman effects correlate linearly with As-P substitution: the bands originating from vibration modes shift to higher wave numbers with the substitution of P for As from schultenite $PbHAsO_4$ towards phosphoschultenite $PbHPO_4$. This can be explained by the fact that atomic mass of As is higher than that of P and that As-O bonds are longer than P-O bonds.

The results extend our knowledge about schultenite-phosphoschultenite isomorphic series. Systematic shifts of Raman effects correlate strongly with chemical composition of analyzed phases. This is associated with systematic linear variation in the height (between 4,403 and 411 units for As-O $\nu_4$ bending band and between 825 and 70 units for P-O $\nu_4$ bending band) and area under certain peaks on Raman spectra (between 71,423 and 30,805 units for As-O $\nu_4$ bending band and between 28,982 and 2,095 units for P-O $\nu_4$ bending band). Current findings suggest that it is possible to estimate the overall P/(P+As) ratio in mineral samples by precise determination of the position and area under the respective Raman spectra and comparison with standard measurements.

*This work was supported by AGH UST statutory grant no. 11.11.140.319.*

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# Preliminary results of mineralogical investigations of Cambrian rocks from the Pieprzowe Mts. (Sandomierz Upland, Poland)

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The mid-Cambrian rocks exposed in a topographic scarp adjacent to the Vistula River within the Pieprzowe Mts. (Sandomierz Upland, South East Poland) were the subject of preliminary petrological and mineralogical studies. The Pieprzowe Mts. are a unique geological feature because of their unusual pepper-like coloured weathering cover.

The Pieprzowe Mts. are a stratotype area for the Pieprzowe Mts. Shale Formation (mid-Cambrian) defined by Orłowski (1975). This formation consists of the following sedimentary and meta-sedimentary rocks: clay shale, quartz-mica schist, quartzite and conglomerate. Despite over 150 years of research on this formation some geological and mineralogical problems are still awaiting explanation (for example the origin of phosphate nodules in conglomerate layers). The scarcity of fossils and complicated tectonic structure of the formation are the reasons why its sequence stratigraphy is especially difficult to detect. Trilobites characteristic for the mid-Cambrian were found only at one locality within the conglomerate layers, and this age was extrapolated to other units of the Pieprzowe Mts. Shale Formation. Michniak (1969) claims that the same age cannot be ascribed to the whole rock succession because of petrographic diversity of the constituting rock types. Kowalczewski (1995) suggests that the age of the formation should be extended from the Early Cambrian to Early Ordovician (Early Tremadocian). Majority of research devoted to the Pieprzowe Mts. strata focused on stratigraphy, sedimentology and tectonic analysis. Petrographic descriptions of those rocks were given by Samsonowicz (1916, *vide* Orłowski 1964) but mineralogical analyses were done rather sporadically (Kuhl 1931a, b, Michniak 1969).

This paper is devoted to the preliminary mineralogical description of quartz-mica schists and quartzites. The analysis involved observations under transmitted light polarizing microscope. In addition, scanning electron microscopy (SEM) equipped with Energy Dispersive Spectroscopy detector (EDS) was used.

During preliminary studies of quartz-mica schists, it was found that quartz, which is a dominant component of this rock occur as both, terrigenous grains and authigenic filling of veins. Quartz is also present within the lithic grains of quartzites that are common in the quartz-mica schists. Kaolinite appears in two genetic forms: (1) as a product of mica transformations, and (2) as an authigenic mineral. Accessory mineral assemblage consists of zircon, framboidal pyrite and Ti-oxides. The Fe-oxides result from chemical weathering.

In the mineral composition of quartzites angular, xenomorphic, nonundulatory quartz prevails, which is locally impregnated with phosphates. A single grain of apatite was encountered. Very fine veins composed of secondary carbonates occur within the rock. Accessory minerals are represented dominantly by piryte, which does not have the framboidal character typical for sedimentary rocks.

In the light of the aforementioned preliminary results, it is inferred that these rocks were subjected to strong diagenesis and bear traces of hydrothermal processes. Presence of apatite in quartzites sheds a new light on the problem of the origin of phosphate nodules within the conglomerates. According to the present study, the authors suggests that the quartzites may be older than the quartz-mica schists, based on the presence of quartzite lithic grains within them.

This paper informs about the research project aiming to characterize the weathering products occurring within the Pieprzowe Mts. It can be observed that a lot of secondary minerals is present here such as: kaolinite, alunite (Kuhl 1931a, b), Fe and Mn-oxides. It seems that weathering processes and theirs products are still not sufficiently explained. There is a hypothesis that jarosite could also form here. Further research will be carried out using various analytical techniques to improve our understanding of these processes.

*The work is supported by the AGH University of Science and Technology (Krakow, Poland) statutory research project no. 11.11.140.319.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 114–115

# Basin-centered gas accumulations in Rotliegend Sandstones

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Permian Rotliegend Sandstones are the most important gas reservoirs in north-west Europe (Gast et al. 2010). Those sandstones were deposited in playa, fluvial and aeolian depositional systems (Kiersnowski et al. 2010) and may host both conventional and unconventional deposits. The reservoirs are supplied in hydrocarbons by the Carboniferous sediments, lying directly beneath. Some of the unconventional accumulations may occur in conditions of Basin-Centered Gas System (BCGS). Basin-Centred Gas Accumulations (BCGAs), associated with BCGS, are gas-saturated, abnormally pressured, have a low-permeability reservoir and commonly lack of down-dip water contact (Law 2002). Two types BCGAs can be distinguished – direct and indirect, and they differ in the attributes of the system – the type of organic matter, thermal maturity, sealing and the distance of hydrocarbons migration. Direct Basin-Centered Gas Systems may occur in the area of the Polish part of the Permian Basin. The purpose of the present work was to indicate the Aeolian Permian Rotliegend sandstones as a reservoir rocks for direct Basin-Centered Gas Accumulations, according to the petrophysical properties and reflectance of vitrinite measurements.

Analysis was performed on fifteen core samples located within the aeolian sediments of Eastern Erg (center of Polish part of Permian Basin) from the depth interval 3,559.3–4,275.9 m. Random reflectance of vitrinite was measured under oil immersion using Carl Zeiss Axioplan microscope in reflected monochromatic non-polarised light. Mean reflectance values were calculated for all measurement.

Permeability measurements were done on plug-type samples (cylindrical with diameter 25.4 mm and length of between 20–40 mm. Plugs were drilled perpendicularto the cylinder axis. Values of average capillary diameter were obtained from porosimetric analysis on bulk samples with AutoPore 9220 mercury porosimeter.

In each sample, the organic matter was dominated by vitrinite-like matter what could indicate humic organic matter typical for gas prone source rocks. The measured vitrinite reflectance values indicate that organic matter reached the maturation stages of hydrocarbon generation characteristic for the gas window phase (Ro > 2%). Values of average capillary diameter provedweak filtration. Permeability results shown typical values for tight sandstones from BCGS, lower then 0.1 mD.

Analysis performed on aeolian Rotliegend sandstones from the area of Eastern Erg confirmed their potential as a reservoir rock for Basin-Centered Gas Accumulations. Humic type of organic matter and values vitrinite reflectance corresponding to gas window are specific for BSGAs. The analyzed samples of the aeolian Rotliegend sandstones are characterized by very low permeabillity, not exceeding 0.1 mD and slow flow rates, what determines capillary sealing of the accumulation. Short distance of hydrocarbons migration was confirmed by the location of Carboniferous source rocks. All those factors allow to classify the aeolian Rotliegend sandstones as a potential reservoir rock for Basin-Centered Gas Accumulations.

*The research was financed by the AGH University of Science and Technology statutory grant no. 15.11.140.350.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 116–117

# Preliminary results of sedimentary architecture of Rudzkie layers in area of Silesia Coal Mine (Upper Silesian Coal Basin, Poland)

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The Upper Carboniferous coal-bearing succession of the Upper Silesian Coal Basin is divided into four great, lithostratigraphic units. One of them is the Mudstone Series.

The aim of the study was to identify the depositional architecture of the Rudzkie Layers (which belong to Mudstone Series) in the area of Silesia coal mine in the Upper Silesian Coal Basin. The depositional architecture is equivalent to the fluvial architecture defined by Miall (2006).

Thickness of the Rudzkie Layers was analysed in the area of 21 km$^2$ between Czechowice-Dziedzice, Rudułtowice, Ćwiklice, Goczałkowice-Zdrój, Grzawa and Kaniów. The author constructed geological cross-sections and maps of the quantitative parameters which show sandstone, mudstone/siltstone and coal amounts and their relationship.

Geological cross-sections and thickness maps have been drawn to illustrate the sedimentary architecture of the Rudzkie Layers (the Mudstone series). The cross-sections show the structure and relationships between the lithesomes (sandstone, mudstone, siltstone and coal) in vertical plane. The term lithesome present the geometry and distribution of sandstone bodies, not only their lithofacies, and is used also by other authors e.g. Kędzior (2008). The cross-sections show also wedging out of some lithosomes and lateral transitions to lithesomes of different lithology, which occur on very short distance. It indicates rapid changes in the conditions of sedimentation. In addition, thickness maps complete this picture and allow tracing lateral variations in a lithesome geometry. The thickness of sandstone and a percentage of sandstone in the selected intervals suggest the presence of channel tracts. The coal bodies are the characteristic elements of the architecture because of their lithology. The analysis of geological cross-sections constructed through the upper part of the Rudzkie Layers (from 401 to 406 coal seams) within the mining field – KWK Silesia allowed to determine the presence of sandstone bodies with a thickness from 1.5 m to 40 m. The claystone and siltstone lithosomes dominate in the profile of the Rudzkie Layers reaching several tens of meters in thickness and they are much thicker than the sandstone bodies.

The analysis of the cross-section and the thickness maps of the sediments revealed that the Rudzkie Layers were deposited on an extensive alluvial plain probably constructed by meandering river systems as suggested by authors studying the sediments of the Mudstone series Doktor & Gradziński (1985, 2002). The fluvial sediments were accumulated both within a channel and the overbank areas. The thick sandstone bodies (whose thickness exceeds 5 m) are considered as the channel fills. Other, thinner sandstone bodies represent the deposits of a proximal or a distal floodplain (in crevasse splays). Fine grained sediments (mudstones and siltstones) and the phytogenic materials were deposited in the overbank areas.

*Research was funded by a grant no. 15.11.140.337.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 118–119

# Competitive sorption of selected anions on modified halloysite

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Halloysite is a polytype of kaolinite exhibiting a 1:1 layered structure with the chemical composition of $Al_4Si_4O_{10}(OH)_8$. Synthesis of new materials based on kaolinites has received wide attention recently (e.g. Dedzo et al. 2012). Soluble forms of chromium, arsenic and phosphorus found in excessive amounts in waters are toxic and/or carcinogenic and may cause health problems. Thus, the aim of this work was to investigate the sorption of aqueous Cr(VI), As(V), and P(V) on natural halloysite and halloysite grafted with diethanolamine.

Halloysite (H) sample was obtained from the Intermark Company which exploits the Dunino deposits formed as a result of basalt weathering, located in NW Poland near Legnica. The modification consisted of two steps. Firstly, the intercalate of the mineral with dimethyl sulfoxide (DMSO) was prepared. For this purpose 12.5 g of the mineral was dispersed in a mixture of 90 mL DMSO and 10 mL $H_2O$ for 5 days at room temperature (HDMSO sample). Secondly, the HDMSO was refluxed with diethanolamine (DEA) (100 g/L ratio) for 24 h at 180°C under argon flow. The centrifuged product (HD) was washed with isopropanol and subsequently with water to remove unreacted DEA and DMSO remnants and dried at 65°C. The material was characterized using XRD, IR and SEM methods. Adsorption experiments were conducted at 5 mmol/L Cr(VI), As(V), and P(V) concentration in the single-element system for initial pH 3, 6, 9 and in mixed double-element system (1:1 anion molar ratio) for the initial pH 3. For the equilibrium studies, the H and HD samples were shaken in adequate solution (solid/solution ratio 20 g/L) for 24 h at room temperature. Afterwards, the supernatant solution was analyzed for anions. The Cr(VI) concentration was determined by 1.5-diphenylcarbazide method, while the P(V) and As(V) concentrations were determined by molybdenum blue method.

The XRD confirmed the formation of an intercalate with DMSO as the characteristic $d_{001}$ peak at 11.2 Å appeared. After DMSO treatment, the intensity of four distinct bands in the OH stretching region (3,700–3,600 $cm^{-1}$), which are characteristic for the natural halloysite, changed as a result of interaction between the mineral and DMSO. Also the bands attributed to the C-H stretching vibrations of DMSO methyl groups were found at 3,021, 2,937 and 2,920 $cm^{-1}$. The interlayer grafting of DEA led to fixing of basal spacing at 10.34 Å. After water washing the IR spectra showed only bands related to the grafted DEA molecules, which confirms the derivative stability (Matusik & Bajda 2013). As the cation exchange capacity (CEC) of the H sample is low, the adsorption process takes place mainly at the crystal edges. It was assumed that the protonated amine group of DEA will attract the anionic species. The results show that such modification does not improve the anion sorption properties of halloysite. The sorption increased only in case of Cr(VI) from 4 to 9 mmol/kg at initial pH 9 (single-element system). The highest sorption was observed in acidic system due to lack of competitive OH ions. In this case, sorption of Cr(VI) was 27 mmol/kg for H and 28 mmol/kg for HD. In contrast, the H adsorbed 108 mmol P(V)/kg in single-element system, while HD adsorbed only 50 mmol P(V)/kg. Adsorption of the As(V) was higher for the H sample and equal to 67 mmol/kg. A comparison of the obtained results for P(V) and As(V) to the sorption efficiency of HDTMA-modified zeolites (respectively: 80 mmol/kg and 35 mmol/kg) and HDTMA-modified smectites (respectively: 75 mmol/kg and 45 mmol/kg) indicates, that the natural halloysite is a promising sorbent with regard to the studied anions (Mozgawa et al. 2011). In the single-element system the sorption increased as follows: P > As >> Cr. In turn, in the double-element system the competitive sorption was observed. Thus, the sorption of P(V) was lowered in the presence of Cr(VI), while in competitive P(V)-As(V) system the sorption of As(V) dominated. The mechanisms which contribute to the sorption were mainly surface complexation. Further investigation requires thermodynamic studies and the use of i.e. XPS (X-ray photoelectron spectroscopy).

*This project was supported by the Polish National Science Centre under research project awarded by decision no. DEC-2011/01/D/ST10/06814.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 120–121

# Assesment of contamination of water and sediments in the Wilga River, Poland

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The Wilga River, one of the dextral tributaries of the Wisła, is one of the most polluted rivers in Kraków region. In the middle section it drains the Swoszowice region which is known for the natural mineral spring waters that are rich in sulphides, bicarbonates, calcium and magnesium. In the lower section of the Wilga valley an extensive, old dumps of soda factory are located. The waste consists in 70% of $CaCO_3$ and remaining 30% are $CaCl_2$, $SiO_2$, Ca-phosphates, Ca, Mg and Ba-sulphates and NaCl (Wójcik & Morawski 2009).

The aim of this study is the geochemical contribution to the assessment of the state of the environment of the Wilga River based on characteristics of water and bottom sediments. In contrast to the previous studies which concentrated on the polluted parts of the Wilga, this project aims at a systematic analysis of natural background in the upper parts as well as anthropogenic effects in the lower parts of the river.

Sediments and water samples were collected from six locations from springs to the mouth of the river. Temperature, pH and specific conductivity were measured on site. Chemical composition of water (major and selected trace elements) was determined by atomic absorption spectroscopy AAS (Na, K, Cu, Zn, Pb, Cd, Mn, Fe), by titration ($Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, $Cl^-$) and by spectrophotometry UV-VIS ($SO_4^{2-}$, $PO_4^{3-}$). X-ray fluorescence spectrometry (XRF) was applied for determination of major and trace elements in the sediments. This was accompanied with qualitative mineralogical characteristics using powder X-ray diffraction (XRD).

The results were compared with the previous studies (Wójcik & Morawski 2009). From springs to just below Swoszowice the chemical composition of water and sediments as well as concentrations of trace elements are at the level of regional geochemical background. No influence of natural (sulphide) mineral springs was detected in Swoszowice. This is probably a result of small volumes of spring water compared to the volume of the Wilga River there. Elevated ion concentrations are apparent, however, in the river waters near the Kraków Soda waste dumps. This was also determined before by Wójcik & Morawski (2009). With respect to geochemical background in the upper parts of the river, chloride concentration increases from 80 mg/L to 466 mg/L, sodium increases from 40 mg/L to 230 mg/L, and calcium from 84 mg/L to 146 mg/L. This is associated with increase in Zn content in sediments. The water type changes from $HCO_3$-Ca-Cl-Na above to Cl-$HCO_3$-Na-Ca type below the dumps area.

Discharges and leakage of industrial waste dumps and agricultural waste (possibly resulting from extensive reclamation of post-industrial area) appear as major reasons of water quality deterioration in this area. All the parameters indicating pollution, however, are lower than measured 5 years ago indicating improvement and positive effects of remediation procedures applied in contaminated area.

*This work was supported by AGH UST statutory grant no. 11.11.140.319.*

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# Organic matter sources in aerosol $PM_{10}$ from Wrocław, Poland

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The natural and anthropogenic contributions of hydrocarbon groups (aliphatic and aromatic), as well as total organic carbon, in atmospheric $PM_{10}$ dust (particulate matter < 10 μm) collected from Wrocław (SW Poland) were assessed using combined molecular (gas chromatography-mass spectrometry GC-MS) and stable carbon isotopic (isotope-ratio mass spectrometry IR-MS) analyses. The $PM_{10}$ samples were taken using the hi-flow sampler Stamplex Air Division with Whatmann quartz filter (0.06237 $m^2$), and a constant air flow of 1.13 $m^3$/min in the seasonal sampling program in 2007, and represent air pollution in all months of the year.

The $\delta^{13}C$ values of the total carbon varied seasonally from –27.6 to –25.3‰. The isotopic mass balance calculations showed greater coal burning input, reaching 70.5%, in the heating season and dominant transported sources 47.0% in the vegetative season. The $\delta^{13}C$ values of the aliphatic fractions (from –36.6‰ to –29.4‰), indicated a dominant anthropogenic origin (gasoline/diesel/coal combustion). The *n*-alkane distribution with relatively low CPI (carbon preference index) values confirmed that coal combustion and petroleum product use in vehicles were important sources of the $PM_{10}$ in Wrocław. On the other hand, high values of % WNA (wax *n*-alkane content), especially in vegetative season, and $C_{max}$ (carbon number maximum) ≥ 27 in 81% of the samples suggested that the influence of biogenic sources was also significant. Petroleum and coal combustion emissions were confirmed by the presence of hopanes and moretanes. The molecular analysis of the concentrations and diagnostic ratios of the polycyclic aromatic hydrocarbons (PAHs) and the $\delta^{13}C$ values of the aromatic fractions (from –35.4‰ to –26.8‰) indicated that the main PAH sources were also represented collectively by combustion of liquid fuels and coal. Based on PAH discrimination diagrams it is also clear that the main organic carbon source is derived from coal, biomass and petroleum combustion in both seasons. However, taking into account the PAH concentrations during the vegetative and heating seasons, coal and biomass burning seem to be their major source. The high concentration of polar organic compounds such as levoglucosan, mannosan and galactosan confirmed a significant contribution of biomass burning to the total anthropogenic input, especially in the heating season.

The general conclusions derived from coupling of organic tracer analysis and carbon isotopic data of $PM_{10}$ was that the total carbon (including insoluble soot) is likely derived from fossil fuel combustion, while the extractable organic matter is a mixture from different sources with significant inputs of biomass burning. We have also shown that dominant organic tracers do not always represent the major input source in aerosol PM and the unresolved part of the organic matter (soot) is important in the carbon budget.

*This research was supported by grants from the University of Wrocław no. 1205/M/ING/11 and 1017/S/ING/11-IX/mg (for MG) and University of Silesia grant for young scientists (for MR).*

Geology, Geophysics & Environment 2014, vol. 40 (1): 123–124

# Sub-sea tailings deposition leach modeling

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Submarine deep-sea tailings deposition is an alternative method of the land-based mine-waste disposal, whereby mineral ore is converted into slurry and transported via a pipeline to processing plants located at the coast. The tailings are then discharged into very deep water offshore where they usually cover large parts of the sea bottom. This type of deposition is applied only in few countries: Norway, Papua New Guinea, Philippines, Chile and Turkey. It is, however, a controversial method of mine tailings disposal primarily due to the hazardous chemicals used during processing and deposited metal sulfides which may dissolve and affects the sea environment.

The overall objective of this project is to evaluate the copper leaching potential from tailings on the example of the proposed submarine tailings disposal in Repparfjorden discharged from two hydrothermal copper vein type deposits – Nussir and Ulveryggen, exploited by Nussir ASA. The two deposits are 5 km apart and will be processed by the same processing plant. This experiment gives better understanding of the reactivity of sulfide minerals in a saline system during submarine deposition.

Planned by Nussir ASA, processing the ore by a flotation system will produce two types of flotation tailings material. These two tailings streams will be mixed with the flotation water, possibly aided by a flocculent, which will be extracted in a thickener afterwards. Seawater will then be added to the material prior to being discharged via a pipeline into the fjord that is at least 90 meters deep.

Four kinetic test set-ups containing 0.5 kg of material and 2 L of seawater were prepared for an experiment that runs for 100 days, by recirculation of the leachate (batch experiments). Seawater was routed through pipes at a constant flow rate of 1–2 m/h via a peristaltic pump which arose from about 4 L/h water exchange rate in the column. The columns were run at a temperature of approximately 10°C. The seawater leachate was saturated by oxygen up to 80–100% in order to maintain condition providing sulfide oxidation leaching. Nine leachate samples were collected from each column for analysis of dissolved constituents and physical parameters.

Results show that there was a distinct increase in copper concentration while other hazardous elements did not show significant changes. Copper concentrations reached 0.025 mg/L after 100 days. Towards the end of experiments (from 70–100 days), the leaching rate leveled off with time. Subsequent Cu concentrations indicated that there no more copper was released. Reaction was halted likely because sulfide particles have been consumed or encapsulated by iron hydroxides.

The leaching reaction rate observed in this test resulted in a much lower copper contamination than previous estimates (Akvaplan-NIVA, 2011). Following the experiment results the estimated reaction rate is approximately 12.7 mg/m$^2$/year, what involves approximately 5.75 kg/year of Cu release for proposed 2.4 km$^2$ of tailings deposition area or approx. 9.75 kg/year in 4.0 km$^2$ after a year from disposal closure. This is significantly less than the annual copper discharge from a river naturally leaching deposits (500–600 kg/year). It was assumed that the copper is being leached only from the surface of the tailings deposit. This is primarily due the saturated condition of the sediments which prohibits oxygen supply through the deposit. Therefore available oxygen is quickly used up, thereby halting sulfide oxidation (Walder & Rzepka 2013). This research revealed that copper leaching is a two-stage process: (1) initial rapid dissolution of secondary Cu minerals formed from previous sulfide oxidation, related to the tailings material disposing period, and (2) long term slow surface-based leaching of sulfide from tailings material settled on the bottom.

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Geology, Geophysics & Environment 2014, vol. 40 (1): 125–126

# Influence of aeration on zeolite suspension microfiltration

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The effects of air injection under various conditions on the experimental results were investigated on microfiltration apparatus. In the experiments zeolite from the area of Nizny Hrabovec was used. Different patterns of flow in the microfiltration system under changing conditions were monitored. The particular flows were photographed and evaluated.

If the particles in suspension are of larger dimensions than the membrane pores, the particles settle slowly and accumulate on the membrane surface and form a highly concentrated layer. Due to the formation of this layer the accumulation of solute at the membrane wall and thus sometimes irreversible clogging of the membrane occurs (Vera et al. 2000). The sedimentation of particles on the surface and in the pores of the membrane results in a reduction in the flow and growth of energy consumption. However, there is great potential to reduce this concentration polarization and fouling. At present, two-phase flow studies are of experimental nature and focus mainly on improving the conditions in filtration (Mikulášek et al. 2002). The injection of gas helps to reduce concentration polarization layer so that it improves the hydrodynamic conditions near the surface of the membrane. The results of the study suggest that the improvement of the flow should be achieved by providing appropriate conditions, using the multi-phase microfiltration, low liquid velocity, by mean speed of the gas injected (Qian et al. 2012).

The use of a two-phase flow is considered to be the preferred method to overcome the concentration polarization. During the process gas is directly injected at a given pressure and speed into the feed (Bakalár 2013). Cui & Wright (1996) observed improvement in flow of up to 320% if used two-phase flow with gas injected into the suspension in their experiments.

Under normal circumstances gas-liquid two-phase vertical flow exhibits different flow patterns including dispersed bubble flow, slug–flow, churn flow, and annular flow as the gas to liquid ratio increases. Bubble flow occurs when the bubbles are significantly less than (e.g. < 60%) the tube or channel size. The bubble behaviour is similar to the bubbles in a stationary liquid. Slug-flow (also called plug-flow) occurs when the gas flows as large bullet-shaped bubbles approaching the diameter of the tube or channel size (Cui & Wright 1996, Vera et al. 2000).

*This work was supported by the Scientific Grant Agency of the Ministry of Education of Slovak Republic under the grant no. 1/0590/11. This work was supported by the Slovak Research and Development Agency under the contract no. APVV-0068-07.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 127–128

# Reconnaissance observations on heterogeneous succession within the Menilite beds (Oligocene) at Skrzydlna, Outer Carpathians

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The quarry outcrop at Skrzydlna near the southern margin of the Silesian Nappe central sector (Polak 2000) exposes a heterogeneous succession that occurs within the Menilite beds (Oligocene). The aim of this work is to present preliminary observations on details of lithological, sedimentological and structural development of this sequence.

The discussed succession belongs to a structure identified as the Skrzydlna scale, and is underlain by the classic lithological association of the Menilite beds present in the region that shows the predominant palaeoucrrent directions towards the SW: dark brown siliceous menilite shales, thin-bedded and fine-grained turbidite sandstones associated with black siliceous shales and ferroan concretions (Polak 2000). This is overlain by siliceous sandstones with shales and intercalations of marl.

The observations presented here document several previously unpublished details of ca. 50 metres thick succession that comprises the following complexes (in stratigraphically ascending order): (i) sandstone, medium grained, totally devoid of mudstone layers and composed of massive amalgamated beds; (ii) dark shales with very thin sandstone interbeds characteristic for the Menilite beds; (iii) thin- to medium-bedded light grey weathering marls passing upwards into laminated marls; (iv) chaotic polymictic conglomerate/sedimentary breccia (ca 17 m thick), matrix- to clast-supported, which rests upon the underlying marl unit with a pronounced erosional contact; (v) massive, channel-fill sandstone with thickness changing laterally from 2 to 1 meter; (vi) three turbidite sequences: fining upwards (F-U) to medium and thin-bedded sandstones with subordinate mudstones that pass to a coarsening upwards (C-U) succession of massive, amalgamated sandstone beds (the most "proximal" facies type), which grades into a F-U sequence.

The characteristic sedimentary features of this succession include:

- features of some turbidite beds that are characteristic for supply from hyperpycnal flows;
- occurrences of linked debrites (turbidite beds succeeded by co-genetic debrite);
- slump beds and creep-deformed sandstone dykes;
- slide sheets of intrabasinal rocks;
- large-scale debris flow beds (olistostrome beds) containing blocks as large as ca. 2 metres across.

Structurally, these strata are deformed by networks of joints, which show density and orientation differing between individual lithological complexes. This probably reflects variations in competence of compositionally and texturally different units, eg. the marl complex labelled (iii) above the overlying debris flow deposit (iv).

ISSN 299-8004 | e-ISSN 2353-0790 | Wydawnictwa AGH

The above features suggest that the discussed succession originated as a result of interplay of mass-transport deposition (MTD) and sedimentation out of a variety of turbidite flows. This conclusion expands the earlier interpretation of this association as an olistostrome intercalated within the Menilite beds of the Skrzydlna area advanced by Cieszkowski et al. (2012) and Cieszkowski (2006). The features outlined above imply the position in the basin proximal to a tectonically active, elevated source area and supply by combination of debris flows, slumping, slab-sliding, and periodic contribution of terrigenous detritus directly from a fluvial system on the adjacent land.

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# Perylene and other terrestrial biomarkers identified in the Middle Jurassic conifer wood and their palaeoenvironmental significance

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The occurrence of perylene in the Middle Jurassic fossil wood from Poland is described, along with its correlation with unsubstituted polycyclic aromatic hydrocarbons (PAHs) as well as cellulose content. Perylene is especially common in immature/low maturity organic matter (OM), largely of terrestrial origin (e.g. Louda & Baker 1984, Jiang et al. 2000, Grice et al. 2009). It has been found in diverse recent environments, such as marine and terrestrial sediments, including peats, as well as ancient deposits, including brown coal and hard coal, crude oil and sedimentary rocks (review in Marynowski et al. 2013). Here we link perylene, a product of wood-degrading fungi, to conifer biomarkers in fossil wood material of different ages. Middle Jurassic wood remnants were of relatively low maturity (ca. 0.2–0.4% vitrinite reflectance Rr), had excellent preservation of biomarkers and biomolecules and generally good preservation of anatomical structures due to early diagenetic mineralisation. The results from described (most taxonomically defined) fossil wood fragments demonstrated a negative correlation between the concentration of perylene and those of generally typical conifer biomarkers (e.g. cadalene, dehydroabietane, simonellite and retene). We defined a conifer wood degradation index as: CWDI = perylene / (perylene + cadalene + retene + simonellite + dehydroabietane); and observed a wide range of values (0.001 for less degraded wood to 0.95 for highly degraded samples). We determined similar $\delta^{13}C$ values for perylene from the fossil wood samples (from –26.4% to –27.8%), whereas the values for the conifer biomarkers were slightly higher and varied from –25.6% to –26.6%. In contrast, pyrene was depleted in $^{13}C$ (from –27.5% to –28.2%). The carbon isotope values of perylene are consistent with an origin from wood-degrading fungi.

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ISSN 299-8004 | e-ISSN 2353-0790 | Wydawnictwa AGH

Geology, Geophysics & Environment 2014, vol. 40 (1): 130

# Seismic modelling as a support tool for interpretation of seismic data from Strachocina gas field

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Seismic reflection is the most significant method in hydrocarbon prospecting which uses the principles of seismology to estimate the properties of the Earth's subsurface from reflected seismic waves (Ashcroft 2011). Accurate interpretation of reflection seismic data is one of the most important elements of a successful oil and gas exploration program.

Proper interpretation of seismic data requires an understanding of the subsurface formations and how they may affect wave reception. To do this seismic modeling is done.

Seismic modeling is a topic for which approximations pay a critical role. Seismic modeling is done to investigate the expected seismic response from a given subsurface model (Kasina 1998).

In this paper author presents the application of seismic 1D and 2D modelling for interpretation of the 107-2-96K profile, recorded in Strachocina gas field. Seismogeological models were made using borehole data and the geological sections. Theoretical seismic sections were computed with the Tesseral software (Hinds & Kuzminski 2002).

A geological identification of seismic horizons was made on the basis of synthetic seismograms calculated for the borehole Strachocina-45. 1D synthetic seismograms are formed by simply convolving an embedded waveform with a reflectivity function (Yilmaz 2001).

For clear identification of faults and correlation of seismic horizons with geological ones 2D seismic modeling was prepared. Seismogeological model and calculation of theoretical seismic sections were made in Tesseral software (Hinds & Kuzminski 2002).

The results of seismic modeling used in geological interpretations enabled the reconstruction of gas horizons and allowed for more reliable identification of faults.

*The author is thankful to Ph.D. hab. M. Stefaniuk for care and advice. The research materials are delivered by Ph.D. Tomasz Maćkowski.*

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ISSN 299-8004 | e-ISSN 2353-0790 | Wydawnictwa AGH

Geology, Geophysics & Environment 2014, vol. 40 (1): 131–132

# Quantitative determination of ammonium salts in organo-zeolites by infrared spectroscopy

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In recent years, the feasibility of using fly ash from the combustion of coal for the synthesis of zeolites has been studied (Belviso et al. 2010, Derkowski et al. 2010). One of the many uses of zeolites is to leverage their properties to act as organic sorbents (Bowman 2003). Unfortunately, the sorption process of organic substances on zeolites is hampered by the negatively-charged surface of the crystallites (Jashua & Bowman 2009). In order to increase the chemical affinity of the zeolite's surface to the organic molecules, its modification by organic surfactants is necessary. This leads to the formation of an organo-mineral complex with improved sorption properties. It has been found that organo-zeolites may be used to remove volatile compounds in a pure form, and those which occur in nature as impurities of air, water and soil (Damjanović et al. 2010, Vidal et al. 2012). Therefore, it seems reasonable to search for an organo-zeolite sorbent which is cheap, efficient and environmentally-friendly (Apreutesei et al. 2008).

The zeolites modification takes place only on the outer surface of the crystallites as the ammonium salts' molecules are too large to enter the zeolite's channels. Therefore, external cation exchange capacity (ECEC) is an important property in the synthesis of organo-zeolites. The type of surfactant introduced and its amount, often given by ECEC values, is crucial-subsequently leading to the formation of materials differing in sorption properties. Thus, it is essential to determine the effectiveness of modification by examining the amount of surfactant adsorbed on zeolites' surface. In the experiments, a Na-P1 zeolite synthesized from fly ash remaining after coal combustion and a natural Ukrainian zeolite were transformed into organo-zeolites. This involved the replacement of original exchangeable cations ($K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$) by organic cations from the following salts: hexadecyltrimethylammonium bromide (HDTMA) and octadecyltrimethylammonium bromide (ODTMA) in amounts equal to 0.25, 0.50, 0.75 and 1.00 of ECEC. ECEC for synthetic zeolite Na-P1 was determined, and it was 24.4 meq/100 g, which corresponds to a single layer (1.0). The aim of this study was to use the infrared spectroscopy (FTIR) to determine the quantity of the surfactant adsorbed on the crystallites surface. The FTIR spectra were collected by a Thermo Scientific Nicolet 7600 spectrometer using the DRIFT technique. The CHN analysis was used to investigate the modification efficiency through quantification of the attached surfactant. The normalized intensity of selected bands attributed to C-H stretching vibrations in the 3,000–2,800 $cm^{-1}$ region was compared with CHN results. The results revealed a high correlation ($R^2 > 0.99$) between spectroscopic and chemical analyses. The band intensities compared with the efficiency of modification enabled to obtain appropriate calibration curves. This proved that FTIR could be used for a fast determination of the surfactants amount in the obtained organo-zeolites.

*We gratefully acknowledge the support of NCBiR having provided grant PBS1/A2/7/2012.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 133–134

# Changes in physical structure during calcination of carbonate rocks

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Limestone and other carbonate rocks are commonly used as sorbents for removing sulfur oxides from coal combustion flue gases. The process is based on chemical reaction between calcium oxide CaO and sulfur dioxide $SO_2$, which results in formation of anhydrite $CaSO_4$. CaO required for the reaction is produced by thermal dissociation of calcite $CaCO_3$ which is the major constituent of each limestone. Calcite during calcination is decarbonized according to the reaction $CaCO_3 \rightarrow CaO + CO_2$. The quality of such sorbent is usually being related to its total uptake of sulfur dioxide, which is frequently considered to depend mainly on chemical composition of the sorbent, especially $CaCO_3$ content. However, there are premises that the rate of desulphurization of contaminated gases depends more on the structure of the products of limestone calcination than on $CaCO_3$ content. Exceptionally significant is the surface area of CaO which results from its high porosity. The formation of such structure can be affected by several factors among which the structure of the raw material, its porosity and pore distribution along with crystallinity and the size of crystals are considered to be the most important issues. The current study demonstrates that the size of calcite crystals plays a key role in developing high porosity during limestone calcination in spite of calcium carbonate content in raw material.

Four samples of different carbonate rocks were investigated:

1) crystalline limestone with well-developed calcite crystals of size 1–2 mm; 98.75 wt. % $CaCO_3$;
2) micrite limestone with calcite crystals of size not exceeding 2 μm and 94.08 wt. % $CaCO_3$;
3) limestone with calcite crystals of size up to 50 μm dispersed in a micrite background; 94.75 wt. % $CaCO_3$;
4) marble with crystals up to 1 mm; 96.08 wt. % $CaCO_3$.

The samples were ground to 0.125–0.250 mm particle size and calcined in the fixed bed at 850°C for 1 hour. The observation for differences in morphology of raw and calcined samples were conducted using Scanning Electron Microscopy (SEM). The particles and pore size distribution were characterized by BET analysis using low-temperature nitrogen adsorption technique. The content of $CaCO_3$ in raw samples was calculated using total Ca content which was determined by titration with EDTA after digestion of samples with hot hydrochloric acid.

SEM images revealed a regular system of cracks in the sample 1. The whole surface of calcite grains fractured and became very rough and porous. Sample 2, which was cryptocrystalline, did not show such behavior. Cracks and fractures did not occur, but under large magnification a slight porosity could be observed. Large crystals of the third sample cracked in a similar way to sample 1. Noteworthy is also the fact of creating little voids on the grain contact. Calcite crystals in sample 4 fractured along wide cracks into large fragments. Smaller clefts also occurred but they created irregular pattern, in contrast to sample 1.

BET analysis confirmed foregoing SEM data. The calcination process increased the porosity and surface area of the investigated samples which was more evident with respect to more crystalline samples. Moreover, the pore distribution changed significantly. Calcination was followed by formation of the new porosity of samples, especially in mesoporous and macroporous range.

Cracks in coarse calcite crystals enhance calcination by creating fast diffusion ways for $CO_2$ escape. They could play similar role in sorption of $SO_2$, hence the structure of raw sorbent becomes more significant issue with respect to flue gases desulphurization problem.

*The research was financed by the AGH University of Science and Technology statutory grant no. 11.11.140.319.*

# Amber cockroaches, wood decomposers, dinosaur dung, clean Mesozoic ground and eusociality

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Among unresolved enigmas of ancient terrestrial ecosystems functioning, the origin of social life, wood decomposition, provisioning of dinosaur dung and cleanness of Mesozoic ground belong to most important ones (Zherikhin 2002).

Sample from dinosaur-aged (125-million-year old) amber of Lebanon provided partial answer for all these questions (Vršanský et al. 2013).

An immature individual of the cockroach family Blattulidae was preserved with coprolites partially extruded from the body and containing particles of wood indicating external pre-digestion. Based on distribution curves (obtained using ST) a hypothesised was advanced that source of the wood particles were dinosaur feces. Additionally, identical particles of wood were discovered in dung of Mesozoic dinosaurs and lystrosaurs (Fiorelli et al. 2013, unpublished), supporting the present claims in unrequiring chewing of wood by cockroaches.

The presence of processed wood with smooth edges is important in providing evidence for the occurrence of lignolytic endosymbionts in ancient cockroaches, which are transferred only in multigenerational organisation of population structure (e.g. in termites).

In contrast to intuition, masses of dinosaur dung did not decay automatically as they contain too much nitrogen (as in birds) and normally would be deposited analogically to guano (high proportion of phosphorus). Nevertheless, after the extraction of nitrogen, dung is further exploited by plants, microorganisms and animal decomposers. This is in sharp contrast to exploitation of mammal dung and its fixed rapid exploiters. Nevertheless, also mammal dung can prevent growth of plants including grasses (see example from present-day Australia, where introduction of dung beetles was necessary – Bornemissza 1960).

Huge amounts of dinosaur dung would cover surface and prevent growth of the lowest levels of plants, which would allow the significant erosion. Thus, thanks to an amber cockroach we now know that Mesozoic forests were rather clean due to clean-up services provided by cockroaches (no other dung-provisioning insects are known from the beginning of the Mesozoic).

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Geology, Geophysics & Environment 2014, vol. 40 (1): 136

# Simulation of energy production from renewable energy sources in the Małopolska region

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Dynamic development of the renewable energy sector is related to an increase of environmental pollution, as well as an increase of awareness of the risks associated with the consequences arising from the excessive use of conventional energy sources.

Taking into account the requirements of the European Union, Poland is facing a difficult task related to the growth of the share of renewable energy sources (RES) to 15.5% by 2020 year.

The aim of our work was to create a simulation of the Małopolska region, performed in two different directions. The first direction, assumed the specific value of increment of development in the electricity sector based on alternative energy sources. The second one indicated opportunities for growth of heat production from renewable energy sources on the basis of the geological conditions and the possibility of the development of unconventional sources of energy in the Małopolska region.

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# Correlation between organic and inorganic indicators of thermal maturity in Dukla Nappe (Polish Outer Carpathians)

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Correlation between organic (vitrinite reflectance (Ro) and Rock-Eval $T_{max}$ temperature) and inorganic (mixed layer illite/smectite (I/S)) indicators of thermal maturity depend mainly on the maximum temperature achieved by the rock and the time exposure of this temperature. During sedimentary or tectonic burial of rocks, clay minerals may react diversely to organic matter due to heat flow features and the duration of heating (Aldega et al. 2005).

The aim of this study was to correlate maximum paleotemperatures of the Oligocene Menilite Shales from the Polish Outer Carpathians determined based on vitrinite reflectance and Rock-Eval pyrolysis data to those calculated using I/S ratio. The analysis was performed on eight claystone samples collected from natural exposures of the Dukla Nappe. Four of them were taken in tectonic windows within the Magura Nappe: Świątkowa and Grybów tectonic windows. All samples were analyzed by vitrinite reflectance, Rock-Eval and smectite to illite conversion.

Reflectance of vitrinite and huminite macerals was measured under oil immersion using Carl Zeiss Axioplan microscope in reflected white and blue (fluorescence) light. Standard deviation was calculated for all measurements. The values of Ro were converted into paleotemperatures according to Barker & Pawlewicz (1986).

The degree of smectite to illite conversion is shown as the percentage of smectite (%S) in I/S. To define this percentage X-ray powder diffraction was used (Dudek & Środoń 1996 and references therein). Maximum paleotemperatures were estimated according to Šucha et al. (1993).

Rock-Eval pyrolysis was conducted on Delsi Instruments apparatus equipped in TOC module to determine: a) total organic carbon content (TOC), b) the amount of residual hydrocarbons generated during pyrolysis of organic matter ($S_2$) and the temperature of maximum of $S_2$ peak ($T_{max}$).

The Rock-Eval data indicate that the analysed samples are rich in organic matter, predominantly of oil-prone Type II kerogen. Values of $T_{max}$ vary from 421°C to 453°C, and were re-calculated into vitrinite reflectance values using equation proposed by Jarvie et al. (2005) and then into paleotemperatures indicating range between 42–153°C. The Ro values vary between 0.45–1.0% indicating paleotemperatures between 51–154°C. The analyzed rocks contain 12–40% S in I/S suggesting paleotemperatures between 104–176°C. Usually, paleotemperatures determined from I/S are higher than those achieved using organic indicators.

In both, present and previous (Waliczek & Więcław 2013) studies, a strong positive correlation between organic maturity indicators was observed. The good correlation between the organic and inorganic paleotemperature indicators was noticed for all samples collected from tectonic windows of the Dukla Nappe, where organic matter is mature (above 0.7% in Ro scale). For samples containing immature or early-mature organic matter maximum paleotemperatures calculated from I/S data are 40–70°C higher than those calculated based on results of organic matter investigations.

The higher maturation of samples from tectonic windows than those from the Dukla Nappe are probably related to the overburden of these rocks by the Magura Nappe.

Illitization process is probably time-independent (Pollastro 1993, Środoń 1995) whereas vitrinite reflectance stabilizes in normal burial coalification after about $10^6$–$10^7$ years (Barker 1989). The good positive correlation between the organic and inorganic paleotemperature indicators occurs only for samples from tectonic windows which might lead to the conclusion that these sediments were temperature-affected by at least $10^6$ years.

*The research was financed by the AGH University of Science and Technology statutory grants no. 11.11.140.322 and 15.11.140.348.*

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# New data on burial and exhumation within Orava-Nowy Targ Intramontane Basin (Western Carpathians): results of vitrinite reflectance studies

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The aim of the study was to determine the maturity of organic matter in the Neogene sediments of the Orava-Nowy Targ Intramontane Basin and to estimate, according to vitrinite reflectance (Ro), maximum paleotemperatures affecting studied sediments. The area of research is located in southern Poland and northern Slovakia, on the boundary between the Inner and Outer Carpathians. The Neogene and Quaternary deposits, which are filling the basin, discordantly overlie folded strata of the Magura Nappe (Outer Carpathians), Podhale flysch (Inner Carpathians) and Pieniny Klippen Belt (Birkenmajer 1979).

The analysis was performed on eleven miocene claystone and coal clay samples collected from four outcrops in Polish part of the basin and one outcrop in Slovak part of the basin. Microscope analysis of organic matter in reflected white light was carried out for each sample. Random reflectance of huminite was measured under oil immersion on randomly oriented grains using Zeiss Axioplan microscope in reflected monochromatic non-polarised light. The values of Ro were converted into paleotemperatures according to Barker & Pawlewicz (1986) equation.

It was not possible to calculate paleotemepratures in ten samples due to low maturity of organic matter and to low carbonization degree of coal. Only for one claystone sample from Chochołów reflectance of vitrinite measurement was positive. The value of Ro for analyzed sample was 0.366%, which indicate paleotemeprature of about 25°C (early stadium of diagenesis). Previous analysis of the organic matter in the studied area was carried out by Nagy (1996). Comparison of the results of the measurements of the vitrinite reflectance in the mentioned article match the values described in this study. However the temperatures associated with the burial history proposed by Nagy (1996), do not correlate with the temperatures calculated from the equation of Barker & Pawlewicz (1986). Due to the temperature differences it is problematic to correspond with the burial history of studied area proposed by Nagy (1996).

*The research was financed by the NCN grant no. UMO-2012/07/B/ST10/04318.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 140

# Different methods for shale volume determination

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One of the most important steps in well log analysis is proper evaluation of shaly formations. Clay minerals may cause a lot of problems with calculating porosity or water saturation (Jarzyna 1997). There are several different methods that allow us to determine the volume of shale in the geological formation. It is a fact that choosing correct technique is often a problem which many well log analysts must struggle with (Bassiouni 1994). This paper shows the results that interpreter might obtain using different types of methods for quantitative determination of shale content.

Well logs used for the calculation of the shale volume come from Borehole A-1, which is located in west central Poland in Greater Poland Voivodeship. The first method for the determination of the shale volume was the Gamma Ray technique. This method allowed to calculate the amount of shale using only one log as an input (Ellis & Singer 2008). Both nonlinear and linear equations were applied to calculate the volume of shale. The second technique used is the Neutron-Density Method (Techlog Manual 2011), where two logs were used as an input data source, Neutron Porosity log (NPHI) and Bulk Density (RHOB). The third and the last method for calculating the volume of shale in Borehole A-1 was Resistivity technique, with deep resistivity log (Schlumberger 1998). The results obtained with each technique were compared to each other and then combined together. The last step allowed to calculate the final volume of shale (Schlumberger 1998).

Since each technique gave different results, and it was impossible to choose the correct one, the combination of methods had to be applied for the calculation of shale volume. The errors for every method have a tendency to increase, not to reduce, the apparent shale volume (Schlumberger 1998), therefore a "minimum combination" was applied, meaning that the minimum values of all the variables (calculated shale volumes) were used as an input. Results of the "minimum combination" method give the most probable information about the volume of the shales within the analyzed geological formation.

*The author is thankful to Ph.D. hab. M. Stefaniuk for care and advices. The research material thanks to Ph.D. Tomasz Maćkowski.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 141–142

# Halogen substitution in synthetic lead apatite compounds Raman spectroscopy study

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Mimetite $Pb_{10}(AsO_4)_6Cl_2$, vanadinite $Pb_{10}(VO_4)_6Cl_2$ and pyromorphite $Pb_{10}(PO_4)_6Cl_2$ are minerals isostructural with apatite occurring in the oxidation zones of Pb deposits. They exhibit hexagonal structure and rod-shape morphology. To date, most published research on crystal chemistry of lead apatites concentrated on cationic substitutions in crystalline structure (Ca, Pb, Sr etc.). Little is known, however, on anionic solid solutions, particularly on systematic changes in the structure and properties due to halogen substitutions in lead apatites. Precipitation of lead apatites is often used for immobilization of toxic forms of Pb and As in the environment. More recently, immobilization of radioactive isotope $^{129}I$ in the form of lead apatites was proposed. This isotope is released as a result of accidents at nuclear power plants (Zhang et al. 2007, Stennet et al. 2011, Redfern et al. 2012). Halogen varieties of lead apatites are also used in chemical engineering as environmentally friendly catalysts (Masaoka & Kyono 2006).

The objective of this project was synthesis of halogen-substituted lead apatites in pyromorphite series $Pb_{10}(PO_4)_6(F, Cl, Br, I)_2$, mimetite series $Pb_{10}(AsO_4)_6(F, Cl, Br, I)_2$, and vanadinite series $Pb_{10}(VO_4)_6(F, Cl, Br, I)_2$, followed by characteristics of X-ray diffraction patterns and Raman spectra. This will contribute to our knowledge on mechanisms and effects of anionic substitutions in this group of mineral phases.

Based on the literature and pilot experiments we developed an efficient method of synthesis of Pb apatite solid solutions which allows for full control on stoichiometry, and results in crystalline, homogeneous precipitate. Lead apatites were synthesized at room temperatures from aqueous solutions of $Pb_{aq}$, phosphates/arsenates/vanadates, and $F_{aq}$, $Cl_{aq}$, $Br_{aq}$, or $I_{aq}$ solutions mixed in stoichiometric proportions. Solutions are mixed dropwise in large (2 $dm^3$) reactor with distilled water. Suspension is left for 48 hours for aging, filtered and air-dried. X-ray powder diffraction is used for identification of solid phases. Qualitative analysis allows also for identification of systematic shifts in diffraction patterns resulting from halogen substitutions. Calculation of lattice parameters is used to quantify the systematic effects of substitutions on unit cell dimensions. For the first time Raman spectroscopy was applied to most of crystalline phases in question. Analysis of systematic spectral shifts with anionic substitutions was performed which allowed for explanation of molecular structural reasons for spectral shifts as well as for development of identification procedures with the use of Raman spectroscopy.

All phases preserve their hexagonal crystalline structure. Both diffraction patterns and Raman spectra corresponding to each synthesized phases exhibit systematic shifts in the series. The most pronounced features on Raman spectrum are shifts of double bands resulting from phosphate stretching mode from 968/932 through 945/918 to 941/910 $cm^{-1}$ for F, Cl and Br substituted pyromorphites, respectively. Similar trends are observed for mimetite and vanadinite series. These shifts progress towards lower angles 2θ in XRD patterns and lower Raman shifts on the spectra which is consistent with the increasing ionic radius and atomic mass of the elements resulting in larger unit cell and more rigid chemical bonds. These results confirm that solid-solutions between these phases are possible and result in systematic changes in the structure and spectroscopic properties.

*This work was supported by AGH-UST statutory grant no. 11.11.140.319.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 143–144

# Upper Jurassic gravity mass flow deposit from the north margin of the Krzeszowice Graben

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In the whole Upper Jurassic succession in the vicinity of Cracow area gravity mass flow deposits are observed. They are represented mainly by debris-flows, grain-flows, and other gravity-flows, and were noted by Felisiak (1983), Koszarski (1995), Matyszkiewicz & Krajewski (1996), Matyszkiewicz (1996, 1997), Matyszkiewicz & Olszewska (2007), Ziółkowski (2007).

The studied quarry is situated in the vicinity of Tomaszowice, at the N margin of the Krzeszowice Graben, some 15 km NE of Krakow. The outcrop is about 30 m long and 9 m high. At the base of the outcrop, bedded limestone with cherts is exposed. The limestone is white, varying in shade, beds are 0.2–1 m thick, commonly contains cherts distributed along layer-parallel horizons and numerous dish-like and cup-shaped sponges occupying life position as well as microbial structures. The bedded limestone is overlain by a layer of greenish, plastic marl up to 15 cm thick. The marl rests on irregular top of bedded limestone with denivelation up to 1.5 m. The marl is followed by a 3 m thick layer of fragmental carbonate composed of irregularly distributed zones of massive clast-supported or matrix-supported fabric, which also contain abundant chert fragments. The clasts are irregular in shape and their maximum diameter reaches 0.4 m. The texture, structure and facies relations at Tomaszowice suggest sysnsedimentary origin of the fragmental limestone layer.

Microfacies analysis indicates that the sediment at the base of the outcrop is developed as boundstone-wackestone. Siliceous sponges Hexactinellida & Lithistida, and microbial structures represented by thrombolites are the main constituents of boundstone that dominate in thin section. Tubiphytes and Terebella lapilloides are very common. Some of the sponges reveal borings filled by internal calcareous or ferrugineous sediment. The limestone clasts from the upper part of the outcrop are represented by boundstone-packstone, locally grainstone, both microfacies containing Tubiphytes, fragments of bivalves and siliceous sponges and Terebella lapilloides. Overturned sponges, microbial structures and geopetal fillings are common in larger boundstone clasts.

Synsedimentary gravity mass flow deposits, like those observed in Tomaszowice outcrop, can be found near the northern margin of the Krzeszowice Graben (e.g. Matyszkiewicz 1996). This position suggests reactivation of a pre-existing fault zone within the underlying Palaeozoic bedrock, which occurred during the Oxfordian (Żaba 1999) as syndepositional deformation. Synsedimentary origin of these fragmental rocks, suggest the age of the margin at Tomaszowice may be dated at the Late Jurassic.

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Geology, Geophysics & Environment 2014, vol. 40 (1): 145–146

# Method of estimation brittleness for shale rocks

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The properties and response of shale are important for the petroleum industry in shale gas research. Brittleness is a common term used to describe how rocks fail and is considered a key parameter for hydraulic fracturing initiation and propagation in low permeability rock (Hucka & Das 1974, Holt et al. 2007). The aim of this study is the prediction of shale mechanical properties of the Lower Paleozoic shale rocks.

The input data include well logs with mineral content, TOC, Density, Young's modulus and Poisson's ratio and was calibrated with core lab measurements to help ensure accuracy in the estimates of mechanical rock properties. This study was performed using Petrel software from Schlumberger. Typical workflows for modelling of oil and gas reservoirs were given in Zakrevsky (2011) among others.

There are two ways to define brittleness rock index (BI). The first way is to calculate the BI in terms of the proportion of minerals (e.g. quartz, carbonates and clay content) in shales (Jarvie et al. 2007):

$$Brittleness = \frac{Quartz}{Quartz + Carbonates + Clays}\ [\%] \qquad (1)$$

The second way to define the BI is in terms of the geomechanical properties of Young's modulus (E) and Poisson's ratio ($\nu$) (Greieser & Bray 2007):

$$Brittleness_{\mathrm{avg}} = \frac{\left[\frac{100(\mathrm{E}-\mathrm{E}_{\min})}{(\mathrm{E}_{\max}-\mathrm{E}_{\min})} + \frac{100(\nu-\nu_{\min})}{(\nu_{\max}-\nu_{\min})}\right]}{2} \qquad (2)$$

where:

E – Young's modulus along a well path,

$\nu$ – Poisson's ratio along a well path,

$\mathrm{E}_{\mathrm{min}}$ – minimum Young's modulus in the interval of interest,

$\mathrm{E}_{\mathrm{max}}$ – maximum Young's modulus in the interval of interest,

$\nu_{\mathrm{min}}$ – minimum Poisson's ratio in the interval of interest,

$\nu_{\mathrm{max}}$ – maximum Poisson's ratio in the interval of interest.

Brittleness in unconventional reservoirs is controlled by mineralogy. The presence of quartz and carbonates makes shales more brittle while the presence of more clay makes shales more ductile. Shales with higher Young's modulus and lower Poisson's ratio tend to be more brittle and vice versa for the ductile rocks that are controlled by clay, calcite and total organic carbon.

The results of this study can be successfully used to make Mechanical Earth Model (MEM).

*The Faculty of Geology, Geophysics and Environment Protection, AGH University of Science and Technology, is deeply grateful for making it possible to use the software from Schlumberger, which has been delivered within the framework* *of the University Grant Program under the Agreement no. CTT-tt-4/2012 for Software Donation.*

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# Tectonic suture of the meliata (Jaklovce) occurences – mezostructural and microstructural research application

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The study presents new paleopiezometric data of calcite marbles, contributing to a solution of principal geological and tectonic problems of autochthonous vs. allochthonous position of a carbonate succession north of Jaklovce village in the eastern part of the Northern-Gemeric zone. The Triassic-Jurassic sequences in the Kurtová skala hill are since the 1970s linked with the Meliaticum, so-called Jaklovce succession, but direct tectonic and structural evidences of its allochthonous position were not demonstrated as yet. However, due to the corresponding appearance of both, autochthonous and allochthonous carbonates, the boundary between both complexes was not clearly determined, or even both sequences were considered to be in the autochthonous position with primary lithological transitions towards the Permian bedrock.

The dymanic recrystallization of the whole volume of allochthonous calcite marbles was shown by our research. The origin of deformation twins was found in nearly each calcite grain (twinning incidence is almost to 100%). The high number of deformation twins per

1 mm of perpendicular diameter of the grain ($D$ = 173.05–646.25) at the very small size of grains (23.7–42.7 μm) resulted from their recrystallization at high differential stresses б = 347.49–429.55 MPa.

This differs the allochthonous bodies of the Meliaticum from those of autochthonous Permo-Triassic cover of the Northern Gemericum, which does not exhibit deformation twins and ductile overprint. This difference simultaneously indicates that the total plastic recrystallization of allochthonous marbles should have occurred in the conditions of subduction zone, but their post-exhumation transport occurred with kinematics of the superficial nappe and did not cause any whole-volume recrystallization. The exhumed suite (besides carbonates, radiolarites, mafic, and ultramafic rocks) was overprinted by the two principal Alpine deformation phases $AD_1$ and $AD_3$ of tectonic imbrication and horizontal shearing, causing the origin of brittle-ductile and brittle disjunctive structures. Despite the overprint, the primary bedding (gen. $S_0$ 330/55°) of allochthonous carbonates remained preserved, and contrasts to general NW–SE trending bedding and secondary foliation of autochthnous sequences.

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# Regional studies of flint characteristic properties

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Searching of flint sources and localization of places where once the Stone Age people obtained this raw material for tool making is an important subject of research not only in archeology, but in broader sense when exploring the ancient civilizations lifestyle, human migrations and interaction between ancient archaeological cultures, as well as tracing cognitive development, that covers not just simple geological observations and orientation in space, but also the first notions of material properties and their determination.

Flint and its formation conditions are not the focus of particular attention in traditional geological studies today, since most of relevant studies have been carried out (Rykart 1989, Sieveking & Hart 1986), and their quality is still very high. In turn, the knowledge level of detail required for the results interpretation in ancient cultures studies is insufficient. Diversity of analytical measurements and divisive results so far failed to give reliable and convincing answers, because natural variations of flint properties cover significantly wider range of values than those identified in relevant artefacts. As a result, the current approach allows to relatively reliably detect only the local flint sources; in other cases just a general evaluation is possiblie.

In the research of flint samples of different geological ages from several Northern Europe countries, as well as flint tools, material of artifacts collection from excavations of the Institute of History of Latvia were studied. This flint is mainly derived from the Jurassic and Cretaceous sediments, less Carboniferous and Devonian rocks, but an unique and distinct group consists of samples that cover chert and chalcedony saturated rocks. Such formations are quite widely known and are found in tectonic fractures and crack spreading zones in almost all rocks exposed in earth's surface, regardless of their geological age.

In this study, the focus was on research methodology that would allow to find an approach to a more reliable flint source localization. The accumulated experience indicates the importance of sample macroscopic analysis and evaluation, including notes about characteristic inclusions, structural heterogeneity, typical fractures. The latter is particularly important because it contains a direct reference to rock cryptocrystalline structure properties, and was a relevant indication for ancient man about the possibilities to use such material for making tools. Without evaluation of the heterogeneity, the more detailed results of chemical and physical analysis may characterize variations of values rather than characteristic properties.

In next stage of the research, it is appropriate to evaluate the sample in ultraviolet light (calibrated wavelength 365, using additional emission filter (485–655 nm). In this UV light it is possible to assess heterogeneity and to identify areas for future research. It is appropriate to study the selected areas of the samples additionally under microscope with a magnification of approx. 50 times. This allows to describe samples microscopically and to obtain more detailed data on inclusions, cracks, layers changes, etc., which can be saved in digital image format for further analysis. Only after this assessment, it is optimal to make detailed chemical and chemical-physical examinations, as the data obtained will be safely comparable. By following such a procedure, it is possible to identify many characteristics which allow to distinguish flint samples from different sites. However, it should be noted that the research carried out is still regional and it will require several more years of study to collect data on naturally occurring flint compositions and to create a corresponding database.

At the same time, it should be noted that flint tools characterising the Stone Age archaeological cultures are made from different quality source material. The found material at many sites has been obtained quite remotely and not necessarily such "distant" material is of higher quality than the known local material. Perhaps, there had been sort of reserves or stocks that were carried, taking into account that not always it would be possible to find a suitable raw material.

The choice of suitable raw material is the knowledge that was acquired very gradually, and therefore often rejects and mistakenly made tools can be found. However, although the knowledge about material properties was increasing, there was no tendency to use higher-quality flint raw material. Rather the opposite appears true – with more skills it was becoming increasingly possible to create higher quality tools from worse quality (less appropriate) materials. Additionally, it should be taken into account that in the historical course of time stone tools and their diversity was significantly changing, which required to search for a various quality raw materials. The overall tendency points to more pronounced symmetry of the tools, that are derived from cryptocrystalline flint types with small fractures, a material with very few inclusions and hidden cracks.

The research results indicate that, following the proposed composition and properties, the investigation procedure (methodology) can identify characteristic and distinct features of flint samples, and they are indicative of to certain corresponding flint mining regions.

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Geology, Geophysics & Environment 2014, vol. 40 (1): 150–151

# New data on boundary-stratotype (limitotype) of the Vyatkian stage, Upper Permian, East European Platform

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The International Chronostratigraphic Chart (ICC) of the Permian system is based on marine sections. The Middle and the Upper Permian deposits in Russia are mainly represented by continental sediments, and that fact complicates the usage of the ICC because of global problems of detailed correlation of the marine and the continental deposits. The general stratigraphic scale (GSS) is used for subdivision and correlation of the Permian system in Russia. It is based on sections on the East European platform (Fedonkin et al. 2013). The most numerous and widespread group of fossil organisms from the Permian continental deposits of the East European platform is represented by freshwater ostracods. Active research on this group has been carried out by Russian micropaleontologists for more than 80 years. As a result, a huge material on ostracods was collected (Molostovskaya & Lukin 1998). At this point revision of all this materials was conducted. Specific, generic and familial features were marked. Sexual dimorphism, ostracod ontogeny and phylogeny were studied. The stages of ostracod development were reconstructed. On this basis the Middle and the Upper Permian deposits were subdivided into six Assemblage Zones that form the baseline for the determination of stages and substages of the GSS (Molostovskaya 2005). The boundary between the Severodvinian and Vyatkian stages of the Upper Permian (Tatarian) was fixed at the base of the *Wjatkellina fragilina – Dvinella cyrta* Assemblage Zone. Section Mutovino on the Sukhona River (Vologda region) was selected as the boundary-stratotype (limitotype) of the above-mentioned boundary. We obtained new data on the ostracod distribution in the boundary deposits of the Severodvinian and Vyatkian stages of this section. *Prasuchonella stelmachovi* (Spizharskyi, 1939), *Pr. ex gr. stelmachovi* (Spizharskyi, 1939), *Suchonellina parallela* Spizharskyi, 1939, *S. cf. parallela* Spizharskyi, 1939, *S. inornata* Spizharskyi, 1939, *Sinusuella vjatkensis* (Posner, 1948) were found just below the boundary. *Prasuchonella cf. stelmachovi* (Spizharskyi, 1939), *Pr. cf. stelmachovi var. ovalis* (Kotschetkova, 1970), *Suchonella cf. blomi* Molostovskaya, 2001, *S. ex gr. auriculata* (Schneider, 1948), *Suchonella sp.*, *Suchonellina inornata* Spizharskyi, 1939, *S. cf. inornata* Spizharskyi, 1939, *S. cf. parallela* Spizharskyi, 1939, *Darwinuloides cf. svijazhicus* (Sharapova, 1948), *Sinusuella vjatkensis* (Posner, 1948) occur at the base of the Vyatkian. The occurrence of *Prasuchonella stelmachovi* and *Suchonella blomi* is particularly noteworthy because these species are the members of an evolutionary lineage of *Prasuchonella nasalis – P. sulacensis – P. stelmachovi – Suchonella blomi – S. auriculata – S. typica*. Thus, the lower boundary of the Vyatkian stage which was established as a boundary of an assemblage zone could be fixed by the first appearance of *Suchonella blomi* which is an element of the evolutionary lineage.

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# HP metamorphism recorded by kyanite-garnet gneisses in the Kåfjord Nappe, Northern Norway – preliminary results

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Scandinavian Caledonides are Himalaya-type mountain belt consisting of allochthons that are a result of the Ordovician-Silurian collision of Baltica and Laurentia (Gee et al. 2008). The Skibotn Nappe Complex, traditionally ascribed to the Upper Allochthon (but possibly being a part of the Middle Allochthon) is situated in northern Norway. It consists of the Normandsvik, Kåfjord and Vaddas nappes (Anderson et al. 1992). The Kåfjord Nappe has not been fully examined, so the information about the age and metamorphic conditions are lacking. The main goal of this project is to provide a new data about peak metamorphic conditions to which the Kåfjord Nappe has been exposed and to compare them with possible equivalents within the Scandinavian Caledonides.

Three samples of kyanite-garnet gneisses from different parts of the Kåfjord Nappe have been studied. All of them contain similar mineral assemblage. Progressive paragenesis occurs in lenses and contains garnet, kyanite, quartz, white mica, biotite, plagioclase, rutile and opaque minerals. Retrogressive paragenesis contains similar minerals with additional presence of chlorite. Two generations of garnet, white mica and biotite are present. Garnet I occurs as large poikiloblasts up to 6 mm in diameter with abundant variably sized inclusions, whereas garnet II is smaller (up to 1 mm) with less numerous inclusions. Biotite and white mica appear as flakes conformable with the main foliation and as transversal blasts. Kyanite occurs as transversal blasts up to 5 mm in size, with moderate number of inclusions. All the observations mentioned above suggest that these rocks were probably subjected to at least two metamorphic events, one of which could have happened under high pressure conditions.

On the basis of chemical composition of minerals and rocks bulk chemistry, thermodynamical modeling will be performed and peak temperature and pressure as well as the retrogressive paths will be determined. Similarities in lithologies and the inferred grade of metamorphism suggest that, in contrast to the previous correlations, the studied gneisses from the Kåfjord Nappe may be an equivalent of the Seve Nappe Complex described by Hacker & Gans (2005).

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Geology, Geophysics & Environment 2014, vol. 40 (1): 154–155

# Pińczów limestone in the architecture of Cracow, Poland

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The Pińczów limestone is as well-known building material commonly used in Poland as building stones, facing slabs, etc., but the most for carved details and sculptures.

These limestones occur within the area of the Nida Trough, with Pińczów, a small town distant about 70 km to NE of Cracow, being the most known place of their exploitation.

The occurrence of the Pińczów limestone is associated with the NE margin of a postorogenic sea, extending within the foreground trough north of the Carpathians from the vicinity of Miechów to NE towards Pińczów and Sandomierz, then to E towards Biłgoraj and further towards Lvov and the Podole area (Peryt & Peryt 1994). This rock is from the Lower Badenian stage and diversified lithologically sediments of this trough, whose thickness reaches 50 m. The Pińczów limestone is a phytogenic calcarenite or calcilutite with the calcite contact cement. It formed from accumulated detritus of the algae *Lithothamnium* sp., contains a subordinate admixture of quartz grains and clay, as well as the fragments of bryozoans, molluscs, brachiopods, corals, barnacles, crabs, crayfishes, echinoids, crinoids, and others.

The Pińczów limestone belongs to the rocks self -hardening after excavation from the source quarry. The porosity of this limestone is usually high, ranging from above 35% in coarse-grained rock to ca 25% in fine-grained rock and a bulk density of 1.5–2 g/cm$^3$ (Bromowicz 2001). Compression strength of this stone is 70-150 MPa, abrasion resistance on Boehme's disk – 2–2.5 cm and water absorption is about 12-18%. The fresh Pińczów limestone is soft and can be easily worked even with the help of carpenter's tools. Under influence of natural atmospheric factors, the limestone is covered by a natural protective layer – a patina. During dressing the stone does not take polish and always displays a dull lustre.

This *Lithothamnium* limestone is not only associated within Świętokrzyskie district and Roztocze, but similar rock could be finding in Austria. The most widespread unit along the Leithagebirge and the Rüster Höhenzug, as well along the western margins of the Vienna Basin, is the Leitha limestone, also well-known as *Nullipora* or *Lithothamnium* limestone. The southern tip of the Leithagebirge is the best-developed of this rock, where the limestone reaches the greatest spatial extent and the thickest sequences about 50 m.

The Pińczów limestone has been used in Poland since the 10th century and in the Cracow architecture since the 12th century, with the peak of its popularity in the Renaissance, forming the cultural heritage of Krakow, spread all over the city.

One of first places, where the Pińczów limestone was used in masonry, is the large, Gothic window situated between two towers of St. Mary's Church. Also it was used by Wit Stwosz to curve a huge crucifix in this church and the figures of the Gethsemani chapel of St. Barbara's Church. The Pińczów limestone was used in the finest stone masonry, 14th-century portal with floral ornamentation and dragons hiding among the plants, in the church of Dominican Fathers. As well this limestone was used to the rosette and outer wall facings of the Renaissance Myszkowskis' chapel executed (1613) by the church of Dominican Fathers. We can find the Pińczów stone in the 16th-century Renaissance canopies over the sarcophagi of kings Ladislaus Jagiełło and Casimir the Great in the Wawel cathedral. An excellent Renaissance sculptor and architect Jan Maria Padovano curved in these stone ornamental masks of the Cloth Hall attic. Regarded the most beautiful in Poland is the attic of the Boner family mansion in the Main Market Square, curved by Santi Gucci. Another characteristic element of the Cracow landscape can be seen outside the church of saints Peter and Paul in Grodzka Street. These are figures of twelve apostles standing at the front of this church, curved by David Heel (1715) in the Pińczów limestone. The current statues are replicas of the original ones, dating back to the beginning of the 18th century, damaged in the second half of the 20th century by environmental changes.

The Pińczów limestone represents an architectonic stone still used in Krakow, mostly limited to revaluation works and small replacements during reconstructions. Still it is the stone-of-choice for sculptors: in the lay and graveyard sculpture, as well as in a small municipal and garden architecture.

*Research is supported by the AGH University of Science and Technology, Faculty of Geology, Geophysics and Environment Protection in Krakow as the grant no. 11.11.14 0.17.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 156–157

# Diagenetic impact on reservoir quality in deeply buried tight Rotliegend Sandstones – case study of Polish Permian Basin

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During burial, sediments and rocks undergo physical and chemical changes due to temperature and pressure growth. All these processes are known as diagenesis (Boggs 2009). These changes play an important role in postedpositional modification of reservoir parameters, such as porosity, permeability and filtration. Primary porosity of rock may be reduced by cement precipitation, mechanical compaction, mineral reactions or pressure solutions, and moreover increased (secondary porosity) during burial, as a result of grain and cement dissolutions, mineral reactions or fracturing (Bjørlykke 1983). Permeability is controlled mainly by pore – throat size (Pittman 1992) and its loss corresponds to the decreasing volume of primary porosity (Pittman 1992, Dutton & Loucks 2010). The aim of presented work was investigation of diagenetic changes within deeply buried tight Rotliegend Sandstones from Polish part of Southern Permian Basin and their impact on reservoir properties of rocks.

For the research were selected 26 core samples from 16 wells and depth interval 3439.8–4284.7 m. All wells are located within the aeolian sediments of Eastern Erg (central part of Polish part of Permian Basin). Samples are represented by medium – and fine – grained quartz arenites and wackes. Qualitative examination of samples included petrographic analysis of thin sections in polarizing microscope in transmitted light and scanning electron microscopy. Numerical characterization of pore space was obtained during petrophysical analysis on 11 samples, usingmercury porosimetry.

Diagenetic processes strongly amended reservoir parameters of rocks. The greatest impact on the decrease of primary porosity had mechanical compaction. It resulted in the development of long grain contacts. As the main cement component were identified clays, with subordination of carbonate, ferruginous and anhydrite minerals. Porosity of analyzed samples does not exceeded 6%, permeability – 0.1 mD.

Reservoir properties of Rotliegend Sandstones were affected by diagenesis, forced by temperature and pressure growth during burial. Primary porosity of sandstones was decreased by mechanical compaction and cement precipitation. Observed evidence of secondary porosity was created due to dissolution of less stable minerals – feldspars. Precipitation of authigenic clay minerals also highly reduced permeability and filtration of sandstones.

*The research was financed by the AGH University of Science and Technology grant no. 15.11.140.350.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 158–159

# Application of the high resolution lidar data for detection of the mass movement's landforms at the Podhale area (southern Poland)

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Light Detection and Ranging (LiDAR) is a modern remote sensing technique, which provides accurate and precise topographical information. LiDAR method, also known as Airbone Laser Scanning (ALS) uses electromagnetical radiation in the optical range. This system consists of a transmiter and receiver of a laser beam, a scanning device and a real-time positioning system. The transmitter emits pulses of light that reflects from the ground surface (including natural surface, buildings and vegetation) and goes back to the receiver. The measurement of the time between sending and registration of the beam is used to calculate the distance to the points located on the Earth (Wehr & Lohr 1999). These points form a "point cloud", which is positioned in 3D spatial coordinate system. The density of these points could reach even 100 pts/m$^2$ (Jaboyedoff et al. 2012). Points corresponding to the forest canopy or buildings could be removed in post-processing. It allows to create Digital Elevation Model (DEM), which reflects morphology very accurately. Through this, application of the model facilitates searching and interpretation of morphological forms, including those hidden under the forest canopy (Van Den Eeckhaut et al. 2007).

The aim of this study is to test the application of the LiDAR technique as a support in mapping of the mass movement's landforms, for instance: landslides, debris slides, etc. This landforms were observed at the Podhale Flysch Area by Mastella (1975). The basic research method was to analyse the terrain model generated from the LiDAR data in comparison with the older cartographic sources and field verification. The laser scanning was carry out in the 2010 and the acquired data was used to derive the DEM. This model was compared with the topographic map at a scale 1:10 000, detailed geological map of Poland at a scale 1:50 000 and the ortophoto at a scale 1:5 000. DEM's horizontal resolution is 1 m and this model covers almost 100 km$^2$ of the area among the villages of Biały Dunajec, Jurgów, Trybsz and Poronin. Analysing of the area was based on different ways of displaying. This allowed selection of three test areas (3 km$^2$ each) as examples of the territory where morphological forms are associated with mass movements occur.

The obtained results allows precise delimitation, determination of surface and morphology of forms resulting from mass movements, which enabled more accurate mapping of these landforms, particularly in the area of dense vegetation cover. Moreover, a comparative analysis of LiDAR model with older cartographic sources can confirm or exclude the existence of areas considered as endangered of mass movements occurence. Airbone Laser Scanning method is therefore a perfect complement to the field studies in geology and geomorphology.

*The research was financed from the AGH UST grant no. 11.11.140.175.*

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Geology, Geophysics & Environment 2014, vol. 40 (1): 160–161

# The influence of silicate content on thermal stability of 2-line ferrihydrite and properties of its transformation products

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Naturally occurring ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$) is a poorly ordered iron (oxyhydr)oxide mineral, with non-stoichiometric composition and not fully understood structure. Because of its unique chemical and physical properties, such as low crystallinity, high surface area and surface reactivity, ferrihydrite plays significant role in e.g. inorganic weathering processes, biochemical cycling of iron and as a sorbent in various near-surface environments. Ferrihydrite is a metastable phase and transforms with time into stable oxides: goethite and/or hematite, through dissolution-reprecipitation and dehydration-rearrangement mechanisms, respectively.

Ferrihydrite structure provides numerous sorption sites and for this reason substantial amounts of admixtures are present in its chemical composition. The most common and well documented impurities include silicate, phosphate, arsenate, sulphate, calcium, aluminum and organic compounds. These ions affect ferrihydrite composition, surface molecular structure and sorption properties. Silicate, probably the most important impurity, causes decreasing crystallinity of this nanomineral, modifies magnetic ordering and solubility. Thus, natural ferrihydrite distinctly differ from synthetic pure analogue. As it was previously shown, the association of Si with ferrihydrite surface hindered thermal transformation to hematite. The implications of this observation for the understanding of Si-ferrihydrite stability in geochemical systems are obvious. The aim of this work was determining of the influence of the Si/Fe ratio in ferrihydrites on its thermal transformation processes and the properties of the products.

Ferrihydrite samples having different Si/Fe molar ratios: 0.00, 0.05, 0.10, 0.20, 0.25, 0.50, 0.75, 1.00, and 1.50, were obtained by reaction of $Fe_2(SO_4)_3$ with NaOH in the presence of $Na_2SiO_3$ at pH 8.2. After four-day incubation, dialysis and freeze-drying, the precipitates were characterized using X-ray powder diffraction (XRD), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), Raman spectroscopy, and scanning electron microscopy (SEM). Then thermal analyses (DTA/DTG/TG) were performed. All of the ferrihydrites were heated from 30°C to 1000°C, at 10°C $min^{-1}$ in flowing air, using hematite as inert material. After heating all the samples were again characterized by XRD and SEM-EDS methods.

DTA curve of pure ferrihydrite shows typical dehydration endotherm at 160°C and. sharp exotherm at 350°C, attributed to hematite formation. Additional weak peaks at 550°C and 710°C were probably originated form decomposition of relic sulphate. The presence of Si in ferrihydrite appears to stabilize its structure and prevents conversion to hematite: the ferrihydrite-hematite transformation peak weakens and broadens and is shifted towards higher temperatures, up to ca. 900°C for high-Si materials. However, no simple linear relationship between silica content in ferrihydrite and the position of this peak has been found.

X-ray diffraction patterns indicate that the main product of thermal transformation of all ferrihydrites is hematite ($\alpha$-$Fe_2O_3$). For low-Si samples (Si/Fe < 0.20), a gradual broadening of 104, 214, 300, 110 hematite reflexes has been noticed, indicating the decrease of its crystallinity. On the other hand, for high-Si materials the broadening appears to be less distinct. Increasing Si/Fe molar ratio (≥0.10) in the initial material took an effect also in the appearance of a cristobalite-type oxide, the content of which increases drastically for the highest-Si samples. Additionally, the XRD pattern of the Si/Fe 0.10 sample reveals the presence of some spinel phase.

Hematite originating from the heating of Si-free ferrihydrite forms quite large (up to 1 mm in size) isometric and prismatic crystals, often exhibiting pseudohexagonal shape. In contrast, the oxide particles become tenfold smaller even in the lowest-silicate material (Si/Fe = 0.05) and reveal pseudospheric morphology. In higher-silicate products (Si/Fe > 0.10) the crystallites are getting elongated and the elongation increases with increasing Si/Fe ratio.

This preliminary study demonstrates that silicate content causes the retarding of ferrihydrite (thermal) transformation to hematite and affecting crystallinity of the latter. Even small Si admixture in the precursor reduces crystal size of the product. During roasting of low-Si ferrihydrites some Si probably enter the hematite structure, but higher-Si hematites cannot form and for this reason heating of high-Si ferrihydrites produces two-phase composition.

*This work was supported by AGH UST statutory grant no. 11.11.140.319.*