

# ABSTRACTS



**WELCOME IN HERLANDIA 2013  
XIV INTERNATIONAL CONFERENCE  
OF YOUNG GEOLOGISTS  
HERĽANY 2013  
SVÄTÝ JUR, SLOVAK REPUBLIC;  
4–6 APRIL 2013**

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Ladislav VIZI, Jarek MAJKA, Maciej DWORNIK & Jakub BAZARNIK**

The XIV International conference of young geologists was organized in Svätý Jur near Bratislava from 4<sup>th</sup> to 6<sup>th</sup> April 2013. Conference was traditionally organised by members of Geological Club in Bratislava and by team from AGH University of Sciences and Technology in Krakow and Faculty BERG of Technical University in Košice. Scientific guarantee of the conference this year took over Prof. Dušan Plašienka from Faculty of Natural Sciences, Comenius University in Bratislava (SK), Prof. Maciej Manecki from AGH, University of Sciences and Technology in Krakow (PL) and Dr. Julián Kondela from Faculty BERG of Technical University in Košice (SR).

National representation of the participants extends every year. This year applied for conference more than 80 participants from Poland, Slovakia, Czech Republic, Russia, Belarus, Norway and Sweden and first time also from Latvia with their contributions from all branches of geosciences.

Opening ceremony was taken on behalf of scientific guarantees by Prof. Dušan Plašienka and Prof. Maciej Manecki and founder of ICYG conference Dr. Marianna Kováčová. Following their introductory words, the conference gradually started to fulfil its program. During two days of lectures 56 contributions were presented in several thematic blocks. All students' and Ph.D. students' presentations were evaluated by an international group of independent Earth sciences specialists according announced criteria. The best presentation was during closing ceremony the first time awarded by Rudolf Mock Award. This award is named after a famous Slovak geologist Rudolf Mock, who during his life worked at Department of Geology FNS CU in Bratislava and in 1993 founded Geological Club. The winner of this award is Sara Eklöf from Department of Earth Sciences, Solid Earth

Geology, Uppsala University in Sweden with her presentation – Analogue modelling of parasitic folds in Grängesberg, Bergslagen, Sweden. In second place was Åke Rosén with his presentation of authors team Åke Rosén, Jaroslaw Majka & Iwona Klonowska – Metamorphic evolution of the Seve Nappe complex in the Snasahögarna area, Swedish Caledonides. In third place was Barbro Andersson with her presentation of authors team Barbro Andersson, Jaroslaw Majka, Iwona Klonowska & Åke Rosén – Pressure-temperature estimates on the Tjeliken eclogite from Northern Jämtland, Swedish Caledonides. The second discussion evening enriched norwegian hydrogeologist Jon Kjetill Uppstad with his foto-presentation from expedition in Brasil. The last day of conference was traditionally devoted to excursion in Malé Karpaty Mts. Participants of the conference visited Hrubá dolina quarry near Pezinok, where Prof. D. Plašienka explained geological structure of the Malé Karpaty Mts. and after this locality had participants chance to see one of the main tourist and geological attractions of the Malé Karpaty Mts. – the Driny cave in Smolenice carst.

Organizers wish to thank the abstract reviewers, namely Martin Bednárík, Igor Broska, Slavomír Čerňanský, Renáta Fláková, Alicja Kawalec-Majka, Julián Kondela, Tomáš Lánzos, Jaroslaw Majka, Jana Michňová, Marek Osacký, Daniel Pivko, Dušan Plašienka, Jaroslav Pršek, Marián Putiš, René Putiška, Ján Schlögl, Bohuslava Sopková, Martin Števkó, Pavel Uher, Peter Uhlík, Rastislav Vojtko and Peter Vršanský.

We are looking forward to your participation next year!



The winners of Rudolf Mock Award (from right to left): 1<sup>st</sup> place: Sara Eklöf, 2<sup>nd</sup> place: Åke Rosén and 3<sup>rd</sup> place: Barbro Andersson.

**PRESSURE-TEMPERATURE ESTIMATES  
ON THE TJELIKEN ECLOGITE  
FROM NORTHERN JÄMTLAND,  
SWEDISH CALEDONIDES**

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Eclogites are important in order to understand orogenic processes, since their presence indicates high-pressure metamorphism. In northern Jämtland, Swedish Caledonides, eclogites have been found at several places in the Seve Nappe Complex (SNC). The mountain Tjeliken in the Lower Seve Nappe is one of them. Dating relates the high-pressure metamorphism to the Late Ordovician subduction of the Baltoscandian margin during the closure of the Iapetus Ocean. In this study new P-T conditions are presented for the Tjeliken eclogite. These are based on petrological studies of an eclogite sampled on the top of the Tjeliken Mt. in summer 2010. Mineral peak assemblage consists of garnet + omphacite + phengite + quartz. Peak conditions are calculated to ca. 2.7 GPa and 700°C. These P-T conditions fall into the upper part of the quartz stability field, close to the quartz-coesite transition line. The new P-T estimates indicate a deep subduction of the Baltoscandian margin already in the Late Ordovician.

## **POLYMETALLIC MINERALISATION AT HORNKULLEN, WESTERN BERGSLAGEN: A METAMORPHOSED SVECOFENNIAN FORMATION?**

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Although the Fe-Pb-Cu-(As-Ag) mineralization at Hornkullen in the classic Bergslagen ore province has been a subject of economical assessments earlier in addition of being mined intermittently during the last 100s of years, the metallogenesis of the deposit is poorly constrained. The region enclosing the deposit has experienced a rather complex geological and tectonic evolution; consequently several conceivable processes that could have influenced the mineralization need to be considered. The mineralization, which is situated in the western part of the Bergslagen province in Sweden, is hosted in ca 1.90–1.88 Ga Svecofennian metavolcanic and metasedimentary rocks. These were deposited in association with an extensional back-arc system inboard an active continental magmatic region (Allen et al. 1996). This succession subsequent underwent deformation and metamorphism during the Svecokarelian orogeny in regional greenschist to amphibolite facies (e.g. Stephens et al. 2008). At the western margin, the area was later intruded by younger granitoid rocks, (referred to as the GSDG intrusive rocks suite (Stephens et al. 2009) or the Transcandinavian Igneous Belt (e.g. Högdahl et al. 2004), locally the so-called Filipstad granite, dated at  $1783 \pm 10$  Ma (Jarl & Johansson, 1988). The metasupracrustal rocks in the Hornkullen area are enclosed as an inlier in this intrusive suite. The region has also locally been affected by the ca 1.0–0.9 Ga Sveconorwegian orogeny (e.g. Stephens et al. 2009), probably in a brittle regime. The present hypothesis is that the mineralization is syngenetic, i.e. formed in conjunction with the Svecofennian volcanic activity. However, as stressed so far, the mineralization has been affected by several thermal and deformational processes following its formation. The aim of this project is therefore to assess whether the deposit comprises of metamorphically overprinted, syn-volcanic assemblages or not. To assess this, comprehensive studies of phase and textural relations on ore minerals were conducted.

Additionally, fluid inclusion analysis is planned that would give further constrain on the ore-forming fluid. Tentative results so far suggest overprinting of brittle structures to some extent in the ore mineralogy.

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## **NEW LOCALITIES OF THE FOSSIL WOODS IN THE UPPER NEOGENE DEPOSITS OF THE TAMAN' PENINSULA (RUSSIA)**

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New collection of the Late Neogene woods from three localities was gathered during the geological field-trip in the Taman' Peninsula during the last summer period. The first locality is situated in the north coast of the Taman' Peninsula, close to the town of Taman'. The deposits are represented by the thick clay layer of the Meotian regional stage. There was found single low-petrified trunk of the wood; which was located vertically to enclosing rocks. Petrified wood from the locality of the north coast is related to Angiosperms, due to the vessels discovered in the thin section during the investigation using scanning electron microscope (SEM) CAMSCAN. The second locality is situated on the south coast of Taman' Peninsula, 2.5 km eastward the Gelezny Rog cape. There the monotonous clay layer has been intercalated by argillites. The age of the rocks has been determined to Pontian time interval. Low-petrified wood trunks of the conifers were vertically oriented in the layer. Third locality is situated near the Gelezny Rog cape. In the ferruginous sandstones of the Cimmerian regional stage, the coniferous fossil woods have been found. Two methods has been applied during the study of the wood remains – using standard SEM and microsections study. Volumetric anatomical structures of radial and tangential sections of the wood can be observed in SEM, but it is very difficult to install the cross wood section for SEM. There are six coniferous wood remains from two last localities, which were studied by using SEM. The preliminary fossil wood data from three new localities point to the presence of conifers such as *Taxodioxylon* and some of Angiosperms.

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## THE USING POSSIBILITY OF CLAY-RICH OVERBURDEN ROCKS FROM SELECTED POLISH DEPOSITS

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The objective of this work was an assessment of the possibility of utilization of selected clay-rich overburden rocks from selected rock raw material found in Polish deposits. For this purpose samples from 12 deposits in five different provinces of southern Poland (Małopolskie, Śląskie, Podkarpackie, Dolnośląskie and Świętokrzyskie) have been collected.

Exploited mineral deposits from which samples have been taken belong to wide range of materials. They are for example dolomite (Rędziny), magnesite (Brasowice), limestone (Czatkowice and Morawica), rhyodacites (Zalas), clay materials for construction of ceramics (Harasiuki, Wala Rzedzińska, Kraniec, Wręczyca) and mineral aggregates like sand (Bielany at Sole and Wola Batorska).

Main field of feasibility of using samples were components of waterproofing layers. Part of the samples was also tested for the possibility of their use in land reclamation. Mineral and chemical composition of the samples was analysed, using XRD and ICP-OAS methods, respectively. Grain size distribution was performed by using sieve analysis and by a laser particle size analyser. Exchangeable cations and cation exchange capacity were also estimated based on the concentration of displaced ions (such as  $\text{Ba}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ) by ammonium cation (from the 1 M ammonium acetate solution) and indicated cations.

Results of this study show that none of the tested samples met all the requirements for components of hydro-isolation layer, and therefore they cannot be used for this purpose. In most cases this is an effect of unfavourable mineral composition (to high percentage of non-clay minerals) and/or chemical composition. Usually the amount of examined exchangeable cations was also incorrect.

The applicability results for land reclamation showed a very large variation. Part of the samples has acquired the highest A class. However, some samples were also found to be characterized by the worst D class of reclamation utility.

## **GROUNDWATER TABLE FLUCTUATIONS IN THE DIRECT CATCHMENT OF GOCZAŁKOWICE RESERVOIR – RESULTS OF QUANTITATIVE MONITORING**

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Implementation of the Water Framework Directive (WFD) drew more attention to a problem of water quality and depended ecosystems. The strategic research project *Integrated system supporting management and protection of dammed reservoir (ZiZoZap)* which is being recently realized for Goczałkowice reservoir fulfils the mention problem. One of the important tasks of the ZiZoZap project is assessment of the groundwater-surface water interaction from both qualitative and quantitative point of view. For solving of these problems the large scale groundwater monitoring network (55 private well and 22, mainly nested, monitoring wells) has been organized within the area of direct catchment of Goczałkowice reservoir (southern Poland).

Main task of quantitative monitoring is: to identify hydrogeological conditions of the upper Quaternary aquifer in the research area, to evaluate of groundwater reaction on outer impact of such factors as precipitation and surface water level in dammed reservoir, thus, the groundwater-surface water interaction.

Groundwater table level monitoring has been carrying on since May 2011 with monthly frequency. Since July 2012 constant monitoring of groundwater level and temperature has been carrying on. Five data loggers (divers) with integrated pressure probe were installed in selected monitoring wells. Four divers have been installed in nested monitoring wells situated along the groundwater pathway at southern experimental site called Zarzecze Pumping Station. Installed divers conveniently and automatically collect groundwater level and temperature data every hour. Till the end of December 2012 the data base contained over 20,000 records. Long-term research shows large diversity of groundwater fluctuation in monitoring points. Maximum amplitude of groundwater fluctuation comes to 2.5 m in the northern side of the catchment. Groundwater fluctuations are lower in direct proximity of reservoir.

## ASSESSMENT OF STABILITY OF GROUNDWATER CHEMICAL COMPOSITION FROM NADZIEJA SPRING

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Nadzieja Spring, artesian deep well is located in confined Jurassic carbonate fissured aquifer. The well belongs to network of wells used as an emergency water supply for urban population and is open for public use. Therefore this water should be safe for health and its chemical composition should be stable in time.

Since November 1998 Department of Hydrogeology and Geology Engineering (AGH University of Science and Technology) has led up monitoring of Nadzieja Spring water quality. Average interval between samplings was ca. two weeks. Samples were collected in accordance with guidelines applied in groundwater monitoring (Witczak & Adamczyk 1994, 1995) and the procedure of groundwater sampling described in norms of PN-EN 5667 series. Chemical analyses of 13 basic elements were performed at hydrogeochemical laboratory, which implements extensive quality assurance and analytical quality control programme (PN-EN ISO/IEC 17025).

The goal of this study was to assess the stability of chemical composition of groundwater, which is intended for human consumption. Specific methodology has been proposed for this purpose (Ciężkowski 2007). According to Polish regulations (RMZ, 2010) the composition of water is stable, when the variation range is:  $\bar{x} \pm 2\sigma$ .

The assessment of stability was performed for components, which influence on the hydrogeochemical type of water:  $\text{HCO}_3^-$  and  $\text{Mg}^{2+}$ . The component influences on the hydrogeochemical type of water, when its amount in [mval] is greater than 20% (RMZ, 2006). Between November 2002 and January 2007 98 samples were collected. Detailed analysis was performed for data from 2002 to 2007. To identify and reject outliers there were used box and whisker plots. Verification of data distribution was made on the base of the results from the Kołmogorow–Smirnow Test. Due to this test it was found out, that concentrations

of  $\text{HCO}_3^-$  are characterized by normal distribution. The concentrations of  $\text{Mg}^{2+}$  are characterized by bimodal distribution. Detailed statistic analysis, in addition with observations of methods used in laboratory for  $\text{Mg}^{2+}$  determination, showed that two groups of data are result of changing methodology (change ICP-OES to ICP-MS in 2004). Separately verification of both groups distribution showed, that concentrations of  $\text{Mg}^{2+}$  are characterized by normal distribution, what is request for control charts.

Control charts (Szczepańska & Kmiecik 1998, 2005) were used to assess the stability of examined components. On the basis of this analysis the following information was derived:

- the content of  $\text{HCO}_3^-$  and  $\text{Mg}^{2+}$  in water from Nadzieja Spring in Krakow is stable (most of values are in range  $\bar{x} \pm 2\sigma$ );
- $\text{HCO}_3^-$  and  $\text{Mg}^{2+}$  influence on the hydrogeochemical type of water (their content in milival [mval] is greater than 20%);
- in case of long time series, analysis should be performed in different variants concerning factors responsible for changes of chemical components.

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## **INFLUENCE OF SAMPLING METHOD ON UNCERTAINTY ASSOCIATED WITH BROMIDE DETERMINATION IN SURFACE AND COALMINE WATER MONITORING**

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In compliance with European Union present legal state (Directive 2000, 2006, 2009) surface and ground water quality monitoring should also include identification of each source of uncertainty associated with analytical procedure. Moreover, directives (Directive 2009, RMS 2011) indicate necessity of implementation the quality assurance and quality control program (QA/QC) of research in water monitoring. They give the measurement uncertainty threshold value as well, which is assessed basing on adequate norms of environment quality and it's equal to 50% or less ( $k = 2$ ).

In this paper the empirical approach for total uncertainty and its components (geochemical, sampling and analytical) assessment was used (Witezak et al. 2006, Nordtest 2007, Kmiecik 2011, Drzymala 2012). In such approach, according to Ramsey et al. (1992), the percentage contribution of measurement variance in total variance cannot exceed 20%. Otherwise, the interpretation of hydrogeochemical data cannot be performed correctly. Moreover, the influence of sampling method on the measurement uncertainty was examined. For uncertainty estimation there were used results from analyses of normal and control (duplicate) samples, which were collected within monitoring of Upper Odra River Basin surface water and coalmine water inducted to it. The assessment of total uncertainty and its components was shown on the example of  $\text{Br}^-$  results delivered from normal and duplicate samples analyses.

The influence of container type on measurement uncertainty was determined. For this aim two procedures of samples collecting were used, concerning two types of samples containers: polyethylene containers and dark glass containers. The bromide analyses were performed using ICP-MS method in accredited Hydrogeochemical Laboratory. Each sample was analysed twice. For total uncertainty and its components assessment the ROBAN program with rANOVA technique was applied.

Basing on delivered results it was stated, that in the two groups of bromide results in samples collected neither into polyethylene containers nor to dark glass containers, the measurement variance doesn't exceed the threshold value of 20% of total variance and is equal to 0.08% and 0.02% respectively. In both cases, for two types of containers, also relative uncertainty of measurement doesn't exceed the threshold value of 50% and is equal to 5.39% and 3.05% respectively. However, the difference between values of relative uncertainty of measurement is significant and indicates the necessity of collecting samples for bromide determination into dark glass containers if possible.

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## **INVERSION OF SEISMIC TOMOGRAPHY DATA BY METROPOLIS AND SIMULATED ANNEALING ALGORITHM**

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Inversion of seismic tomography is non-uniqueness and bad-conditioned problem. Reconstruction of velocity field is a process of minimization error function between estimated and received travel times. Classical, deterministic method, like matrix decomposition or conjugate gradient, is known for finish calculation in local minimums. Other problems with deterministic methods were application of constraints to the solution.

Stochastic algorithms are methods that can be helpful in solving inverse problem in seismic tomography. This paper presents application of the following two stochastic algorithms to reconstruct velocity field: Metropolis algorithm (MA) and simulated algorithm (SA). The Metropolis algorithm is an iterative method and it was first described by Metropolis et al. (1953). This method uses Boltzmann distribution to calculate probability of replacing current solution by worse one, which is modification of current. Level of acceptance is given by value of a temperature. The simulated annealing was first described by Kirkpatrick et al. (1983) and it is a modification of Metropolis algorithm. This algorithm decreased temperature during iterative process. Both algorithms were modified by adding two dimensional median filtration in a place of modification of current velocity field. This filtration was applied with some small probability.

Estimation of travel times of primary seismic waves was performed using two ray-based methods: a straight line and a shortest path method (Moser 1991, Pięta & Dwornik 2009). The first method was very fast but nonrealistic in heterogeneous geological medium. The second method had over one hundred times longer calculation time, but provided real ray trajectories.

The algorithms were tested in series by ten independent numerical simulations for each parameter of configuration to minimize random effects of stochastic methods. Both algorithms were initialized in two ways: by random velocity fields and by velocity field obtained

by SIRT algorithm (Lo & Inderwiesen 1994). Application of median filtration and initializing by SIRT solution decreased calculation time and improved quality of inversion.

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## LOW TEMPERATURE SYNTHESIS AND THERMODYNAMIC STABILITY OF FLUORPYROMORPHITE $\text{Pb}_5(\text{PO}_4)_3\text{F}$ AT 5–65°C

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Fluorpyromorphite  $\text{Pb}_5(\text{PO}_4)_3\text{F}$  belongs to the pyromorphite group of minerals which are isostructural with apatites. Their structure allows for variety of substitutions in both cationic and anionic positions. The purpose of this study is low temperature synthesis, mineralogical and thermodynamic characterization of fluorpyromorphite (FPY) and determination of its solubility product based on the results obtained from the dissolution experiment.

FPY was synthesized by dropwise mixing of solutions containing  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{K}_2\text{HPO}_4$  and NaF at 25°C. The only product of synthesis is FPY within the detection limits of X-ray diffraction. Calculated unit cell parameters are  $a = 9.7427 \text{ \AA}$ ,  $c = 7.3216 \text{ \AA}$ . Homogeneous character of the precipitate was confirmed further with the use of scanning electron microscopy. Dissolution experiments were conducted in triplicates, open to the air, at 5, 25, 45°C and 65°C and at pH = 2.0. An aliquot of about 250 mg of FPY was placed in 250 mL of 0.05 M  $\text{KNO}_3$  with the pH adjusted using 0.1 M  $\text{HNO}_3$ . Periodically taken samples were analyzed for [Pb] using atomic absorption spectrometry AAS as well as for  $[\text{PO}_4]$  and [F] using colorimetry. Calculations of solubility products were performed with the aid of computer program PHREEQC with modified MINTEQ thermodynamic database. The activities of ionic species were calculated from measured concentrations of elements (assuming stoichiometric dissolution) with application of extended Debye–Huckel equation.

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## **ANALOGUE MODELLING OF PARASITIC FOLDS IN GRÄNGESBERG, BERGSLAGEN, SWEDEN**

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The host rocks to the Grängesberg apatite-iron oxide ore boudinage show folds with opposite vergence on either side of the boudin and a strong lineation in the necks (Nilsson et al. 2012). This study aims to, by means of analogue modeling, investigate if the competence contrast between the stiff ore bodies and the host rocks could contribute in creating this deformation pattern.

The Grängesberg apatite-iron oxide deposit is located in the Bergslagen province, an area in central Sweden that is known for its numerous mineralisations of various kinds. From the 16<sup>th</sup> century up until 1989, when the largest mine in Grängesberg close due to falling metal prices, the Grängesberg ore field produced 150 Mt iron ore, to be compared with the 420 Mt iron ore that the entire Bergslagen province produced up until 1992. The Bergslagen province is located in the south-western part of the Svekokarelian orogen in the Fennoscandian shield. The dominating rocks were formed at ca. 1.9 Ga in a back-arc setting inboard an active continental margin which were later multiple deformed and metamorphosed (Stephens et al. 2009). The host rocks to the Grängesberg deposit are 1.90–1.87 Ga regionally metamorphosed and locally hydrothermally altered, manifested as felsic to intermediate volcanic rocks rich in phyllosilicates (Jonsson et al. 2011).

The ore bodies occurs as NW-trending sheet like boudins with a moderate to steep easterly dip. Both the ore and the host rock have been affected by at least two fold phases (F1, F2) and show well developed L- and S-structures. Locally, the stretching lineation associated with D2 is strong (Nilsson et al. 2012). The earlier structures have later been refolded by large scale open F3 buckle folds. Close to the ore bodies, the less competent metavolcanic rocks show F2 domical folds with opposite vergence on either side of the lenses and with a strong lineation at the boudin necks. A granitoid has been thrust over the host rocks near the ore bodies (Nilsson et al. 2012). To investigate if the competence contrast between the ore bodies and the host rock could contribute to the formation of the

opposite verging folds and the lineation at the boudin necks seen in Grängesberg, a series of analogue models were run at the Hans Ramberg Tectonic Laboratory at Uppsala University.

Analogue modelling is a way to test natural events, but over much shorter time scales. To make analogue models comparable with natural examples, scaling is needed: a faster sequence of events gives room for softer materials to be used as rock analogues. In the Hans Ramberg Tectonic Laboratory, a large centrifuge was used to simulate the force of gravity (Koyi 1997). For this experiment, acrylic glass and modeling clay was used as rock analogues. To mimic the high competence of the ore bodies, a wedge of acrylic glass was used. On the side facing the “host rock” two elongated convex downwards bulges represented the ore bodies. These convex bulges were separated by a narrow neck zone. The wedge was inclined 60° to simulate the 50–70° dip of the ore bodies. As the less competent host rock, plastilina, a soft oil-based clay, was used. Forty 1 mm thick layers of yellow, brown and white plastilina were put together in random order to create a 40 mm thick model. The top most layer was white, and on that a black marker with circles and squares was imprinted. The plastilina was then put in an acrylic glass box with the wedge and run in the centrifuge. During centrifuging, the rigid wedge indented and shortened the plastilina layers. When completed, the model had experienced 800 rpm for a total of 12 minutes, which resulted in 32.5% shortening.

After shortening, the surface circles closest to the wedge had deformed into ellipses and the surface squares closest to the wedge had become parallelograms. The long axis of the ellipses and parallelograms showed opposite vergence on the sides of the rigid bulges of the wedge. When cutting sections perpendicular to the shortening direction, the model showed patterns between the two boudins resembling those of stretching lineation. Sectioning the model horizontally revealed S- & Z-folds around the indenting boudins. During centrifuging, the wedge indented the plastilina, resembling the possible deformation during thrusting of the deep granite. These results show that the competence of the ore bodies could be sufficient to create opposite verging folds and stretching lineation between the ore bodies.

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**STRATIGRAPHIC ANALYSIS  
OF THE “URGONIAN” COMPLEX  
IN THE BUTKOV QUARRY, THE MANÍN UNIT  
(WESTERN CARPATHIANS)**

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The Manín Unit belongs to units with Central Western Carpathians affinity and was incorporated into the Paleo-Alpine Accretionary Belt. The deposits of Manín, Klape and Drietoma units originated between the PKB Zone and Peripieninic deepwater fault (Maheľ 1980). Tectonically, these units were created in the foreland of a transferring block of the Central Western Carpathians (Rakús & Hók 2005). From the lithological point of view the Manín Unit can be divided into two groups of sedimentary sequences: the first one, the Manín – Butkov Group (Rakús 1977), which is built up mostly of hemipelagic Upper Jurassic – Lower Cretaceous marly limestones; and the second one, the Podmanín Group (Kysela et al. 1982), consisting of Albian to Maastrichtian flysch and pelagic rock complexes. The most characteristic massive set of Barremian – Lower Albian Urgonian limestones is developed in Manín and Podhorie formations (Vašíček et al. 1994). The recorded Albian stratigraphic hiatus within the Manín Unit was followed by rapid deepening of this sedimentary area and onset of the pelagic deposition of dark marls of the Butkov Formation. The Manín Formation is developed in complex of mainly gray to light gray massive organogenic limestones with numerous Barremian to Albian fossils of foraminifers (Orbitolina), crinoids, echinoids, molluscs, ostracods, corals and calcareous algae. Organodetritic bituminous limestones with dark grey cherts are typical of the Barremian – Lower Aptian Podhorie Formation. In microfacies, the fragments of foraminifers (Hedbergella), molluscs and crinoid ossicles are the most frequently identified bioclasts (Borza et al. 1987). In the Butkov Quarry, within the Manín Formation three lithological sections were sampled, which were used for the biostratigraphic analysis. The lower parts of the sections consist of grainstones, pelbiontrasparites, with dominance of recrystallized peloids and intraclasts.

Fragments of foraminifers, corals and sponges are less common. Microborings of blue-green and green algae were observed in bioclasts, which indicate deposition within the photic zone (up to 75 m), (Budd & Perkins 1980). In the upper parts of the sections only biomicrite wackestones occur with dominant increase of bioclasts. Biostratigraphically important foraminifers (*Globigerina*, *Textularia*, *Miliolida*, *Orbitolina*) are common. They belong sometimes to rock-forming elements, especially in the Lower Cretaceous open shelf and deep-shelf deposits. Fragments of brachiopods, echinoids, bivalves and gastropods were also identified. The limestone sedimentation in the Manín Unit in Manín – Butkov Group ends with typical hardground (Rakús 1977), which terminates the Jurassic – Lower Cretaceous sedimentary cycle. Total thickness is variable and ranges from about 50 m (Butkov Quarry) to 120 m (Manín Strait).

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## **GEOCHEMICAL MAPPING IN THE AREA OF ĽUBIETOVÁ, SLOVAK REPUBLIC**

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Ľubietová is a village in the Banská Bystrica Region in the Slovak Republic. There is an old mining spot in its vicinity, where copper was extracted from the Bronze Age to the 19<sup>th</sup> century. Currently, the region is interesting by mineral collectors due to a copper phosphate that can be found there, called libethenite.

According to the literature (Koděra 1990, Ďud'a & Pauliš 2002) there are two areas of copper mineralization near Ľubietová, which differ in the occurrence of copper compounds formed with arsenic and phosphorus. The first deposit (Podlipa) is mainly known for its secondary-mineral paragenesis of copper phosphates, especially libethenite and pseudomalachite. On the second, (the Svätodušná deposit) diverse paragenesis of secondary arsenic minerals developed. The most characteristic of these arsenians are olivenite, euchroite and pharmacosiderite.

Many scientific works concern the Ľubietová region (Andráš et al. 2009, Rusko et al. 2009), however none of them has yet paid attention to the differentiation and the lateral distribution of copper-phosphorus and copper-arsenic mineralization and to the description of primary and secondary causes of the differentiation and the distribution.

The aim of this study was to determine these phenomena and to optimise future analytical procedures, which would allow the local copper mineralization to be examined thoroughly. The project was based on the assumption that surface geochemical mapping will help to establish the range of copper mineralization in two areas distinct from each other if regard to the copper compounds. In order to draw up appropriate methodology, it was necessary to conduct research that included terrain inspection, preliminary sampling and analysis of soil specimens and dump-field material in regard to the content of copper, phosphorus and arsenic.

The field study was based on extracting three soil specimens and two dump-field material samples along the profile line. Their chemical composition was later analysed by X-ray Fluorescence (XRF) and their mineral composition was determined by X-ray Diffraction (XRD).

The preliminary examination confirmed the existence of lateral differentiation of copper mineralization, which was proved by establishing the differentiation of samples' content of copper, phosphorus and arsenic along the profile line.

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## **METAVOLCANICS OF NORDENSKIÖLD LAND FROM SW SVALBARD AS AN EXAMPLE OF NEW OCEAN CRUST**

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This study concerns late Neoproterozoic metavolcanics from southwestern Svalbard in an investigation to trace the evolution of oceans plate rifting. A number of outcrops of these rocks are connected with the regional Torellian unconformity, which is associated with a Late Neoproterozoic orogenesis event – post 640 Ma. This unconformity divides the younger metasediments of the Sofiebogen Group from older metasedimentary sequence of the Deilegga Group. Samples have been collected from Nordenskiöld Land belonging to the Sofiebogen Group, which is situated between Bellsund and Isfjorden, to the north of Wedel Jarlsberg Land.

Field observation reveals that these metavolcanics very often occur as a pillow lavas and lavas. They contain mineral assemblages typical for greenschist facies metamorphism such as: actinolite, chlorite, epidote, albite, but some of them contain garnets and glaucophane, which is typical for blueschist facies conditions. Based on a total alkali silica diagram they are classified as tholeiitic basalts. Spider diagram shows patterns similar to MORB, where the REE are flat. The LILE except Sr are depleted, but this depletion is caused probably by metamorphism. However, the metavolcanics of Nordenskiöld Land are also relative depleted in HFSE ( $\text{Th/Yb} = 0.2\text{--}0.31$  and  $\text{Nb/Yb} = 2.9\text{--}4.4$ ) and LREE ( $\text{Lan/Smn} = 1.0\text{--}1.5$ ). Trace elements like Nd, Th, Yb and La show trends that could be associated with fractional crystallization.

The geochemical character of metavolcanics from Nordenskiöld Land, as well as, their forms (pillow lavas) suggests that they created beneath the sea level, as new ocean crust.

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## THE METHODS OF VERTICAL TIME TO DEPTH CONVERSION

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The final aim of seismic imaging is to position reflectors correctly in the depth domain. Depth imaging implies building up a velocity model of the subsurface. This velocity model must be chosen so that calculated traveltimes provide the closest approximation to real traveltimes.

A correct and accurate estimate of depth and dips is required in many instances: structural interpretation of seismic data, well placement and design, rock volume assessment. This means that after time migration interpretive step is necessary for transforming times into depths. A operation that transforms a time-domain seismic data set into its corresponding depth-domain data set is referred to as time to depth conversion.

The author is presenting an overview of different methods of converting time to depth using the set of seismic section from Wiszniów – Tarnoszyn survey and 10 number of wells with full set of borehole geophysical data and stratigraphic data. Inter alia: *Single well and analytical  $Z = f(T)$  function, Several wells and single  $Z - Z_{sf} = f(T - T_{sf})$  polynomial, Wells and average velocity maps, Wells and interpolation with seismic times, Wells and interpolation using calibrated stacking velocities, Wells and de-tended stacking velocities, Wells only and interval velocities, Wells and interpolation using calibrated interval seismic velocities, Wells and  $V_{int} = f(Z_{mid})$ , Wells and  $V_0 + kZ$ , Wells and normalized velocities.* Examples of the methods' application were performed. They used building the velocity models on the basis of time to depth transformation. The results are presented on several graphs for comparison of outputs of different models.

## OPAL MINERALIZATION FROM CIGEĽ LOCALITY (CENTRAL SLOVAKIA)

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Besides the famous precious opals from Eastern Slovakia, the Neogene volcanic field in Central Slovakia shows numerous localities with various types of opals. Unfortunately these localities contain only common opal (or potch opal), but moreover, there are only few information on mineralogical composition or genesis of such opal types in Slovakian geological literature. Common opals are bound to all types of volcanic rocks and their pyroclastics. They can be found in fissures and cracks in basaltic, andesitic as well as in rhyolitic rocks. The Cigeľ locality was chosen from the number of different opal localities based on the well preserved cross sections through the andesitic volcanic rocks and redeposited pyroclastics of Vtáčnik Formation (Šimon et al. 1997) Opals can be found in irregular nodules of variable size in weathered redeposited pyroclastic materials as well as in fissures and cracks in fresh andesitic rocks. Opals are often associated with greenish clays, which are often intimately overgrown with opal, or they create a thin crust around the opal nodules. Also they create infilling of fissures in weathered pyroclastic material.

Selected samples of opal were studied using optical microscopy, powder X-ray diffraction analyses (PXRD), scanning electron microscopy (SEM), infrared spectroscopy (IR) and electron microprobe (EMPA) in order to determine their exact mineralogical and chemical composition. Both types of opals samples (nodules and infilling of cracks in fresh andesite) shows typical PXRD pattern for opal-CT (Floerke et al. 1991, Graetsch 1994) with presence of expandable layer silicates. Etched surfaces of samples show presence of lepispheres (Floerke et al. 1975) of opal-CT in SEM. Based on IR analyses the associated clays consist mainly of nontronite, kaolinite was detected in lower amount. Chemical composition of opals is quite variable. Samples are not homogenous, they show two different phases which are either poor or rich on trivalent compounds. With increasing amount of trivalent compounds the content of SiO<sub>2</sub> is getting lower, but the concentration of divalent and monovalent impurities is significantly getting higher. As for comparison phases poor on trivalent compound shows concentration of Al<sub>2</sub>O<sub>3</sub> up to 0.01 wt. % and Fe<sub>2</sub>O<sub>3</sub> up to 0.2 wt. %.

The concentration of  $\text{SiO}_2$  in this phase reaches up to 99.2 wt. %. Phase rich on trivalent compounds shows concentration of  $\text{Al}_2\text{O}_3$  up to 2.7 wt. % and 23.3 wt. % for  $\text{Fe}_2\text{O}_3$ .  $\text{SiO}_2$  concentration reaches 64.3–83.4 wt. %. Besides the opal phases, also impurities with high concentrations of  $\text{MnO}_2$  and  $\text{Fe}_2\text{O}_3$  were identified. Sums over 100 wt. % belong to moganite, which was subsequently identified by the means of Raman spectroscopy.

Based on the field observations, detected mineralogical features and chemical composition, an infiltration-weathering formation of opal was proposed. The proposed process includes low-temperature hydration of volcanic glass (smectitization) in solid state (Šamajová et al. 1992, Velde & Meunier 2008). Access of silica is transported by descending fluids and subsequently the opal can be precipitated in fissures or in cracks (Koivula et al. 1983, Horton 2002) between the weathered pyroclastic materials or in cracks and fissures in fresh andesite.

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**GRAFTONITE-SARCOPSIDE INTERGROWTHS  
IN PHOSPHATE NODULAS  
FROM PEGMATITE AT MICHAŁKOWA,  
SOWIE MOUNTAINS BLOCK, SW POLAND**

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Sarcopside  $(\text{Fe,Mn,Mg})_3(\text{PO}_4)_2$  and graftonite  $(\text{Fe,Mn,Ca})_3(\text{PO}_4)_2$  are the dominant minerals found in the phosphate nodules from the Michałkowa pegmatite in the Sowie Mountains block. The nodules are rather small with mainly varying brown coloration and with lamellar texture visible in hand specimen. Both minerals occur with other primary and secondary phosphates in the form of nodules like triphylite or ferrisicklerite, stanekite or wolfeite, members of the arrojadite and wyllieite groups, kryzhanovskite, fluorapatite and others. Apart of typical pegmatite minerals like quartz, microcline, albite, muscovite and biotite, only black tourmaline can be found. Pyrrhotite, pyrite and chalcopyrite, occurring in the form of tiny grains or veinlets, penetrating also the phosphate nodules are common.

Standard mineralogical investigations (light and reflected microscopy, XRD), combined with SEM-EDS analyses and WDS method were carried out to characterize these phases.

Graftonite and sarcopside form massive aggregates of euhedral crystals or lamellar intergrowths. Euhedral crystals of sarcopside are typically enriched in Mn and Mg. Ca is commonly absent or present in negligible amounts. MnO usually ranges between 10.0–11.0 wt. %; only locally reaches a higher content up to 13.3 wt. %, MgO content commonly reaching 4.0–5.0 wt. %, or only about 2.0 wt. % in Mn-rich compositions. The lamellar sarcopside shows compositional characteristics similar to the variety forming the euhedral crystals. In consequence, the Mn/(Mn+Fe) ratio that informs about a degree of Mn-Fe fractionation in the parental, pegmatite forming melt, attains in both morphological varieties of sarcopside rather low values, usually 0.18–0.20.

In graftonite the CaO content is higher in crystals co-occurring with euhedral sarcopside, reaching in this variety up to 11.0 wt. %, whereas the lamellar graftonite has only 6–7 wt. %

of the component. In both types of graftonite the contents of MgO are less than in sarcopside and they do not exceed 2.0 wt. %. Graftonite richer in Ca is simultaneously poorer in Mg. FeO content is higher in graftonite forming lamellar intergrowths with sarcopside (31.0–32.0 wt. %), and slightly lower in euhedral crystals (27.0–28.0 wt. %). Manganese is close similar in both varieties, whereas Zn is undetectable or present in a small content distinctly below 1 wt. % ZnO. The lower Mn/(Mn+Fe) values (0.36–0.39) are characteristic of lamellar graftonite; only slightly higher values (0.40–0.41) attains graftonite in association with euhedral sarcopside.

Both minerals show weakly varying compositions resulted from homovalent substitutions  $(\text{Fe, Mn})^{2+} \leftrightarrow \text{Mg}^{2+}$  and  $\text{Ca}^{2+} \leftrightarrow (\text{Fe, Mn})^{2+}$  marked in varying values of Mn/(Mn+Fe) ratio. The minerals crystallized from the parental P-bearing melt exsolved from pegmatite-forming silica melt during temperature decreasing. The formation of the massive or lamellar forms depends on a relationship between amounts of the exsolved Ca- and P-bearing melt and its Ca-negligible counterpart.

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## MAIN GEOTHERMAL WATER RESOURCES THAT CAN BE USED IN BALNEOLOGY IN THE POLISH LOWLANDS

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Geothermal waters can be used in two ways: for direct utilisation and for indirect utilization – electricity generation. Direct utilization of geothermal waters is mainly considered for space heating. But geothermal waters could be widely use in balneology and recreation too.

The Polish Lowlands covers huge area, which is about 80% of Poland's territory. The most perspective disposable resources of geothermal waters are accumulated in the Lower Jurassic aquifers containing about  $1.88E + 18 \text{ J/year} = 4.48E + 07 \text{ TOE/year}$  (TOE – tons of oil equivalent,  $1 \text{ TOE} = 4.18 \cdot 10^{10} \text{ J}$ ) (Górecki 2006).

The two main types of water occurring in the area are chloride waters, which are the most common and sulphate-sulphide waters, both used in balneology.

Geothermal waters when used for balneology must fulfil some specific conditions. Water must contain appropriate chemical composition and TDS level. Also temperature of water for baths is very important and it is determined in connection to human's body temperature. Additionally, waters, which are labelled as healing waters must be accepted by the Ministry of Health.

In the Polish Lowlands there are a very few geothermal health resorts, such as Ciechocinek, Konstancin and Grudziądz. There are also a few geothermal recreation and spa centres. However, the possibility of geothermal waters utilization in balneology is much better. Some the most perspective localizations of waters for geothermal balneology are shown in the presentation.

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## **INTRODUCTION TO INTERFEROMETRY PROCESSING WITH DORIS: THE DELFT OBJECT-ORIENTED RADAR INTERFEROMETRIC SOFTWARE**

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Interferometric synthetic aperture radar (InSAR) is a powerful tool for mapping the Earth's land, ice and even the sea surface topography. It is based on processing of the pair of images to map out the differences in the reflected signals over the area (typically 100 km × 100 km). By bouncing signals from a radar satellite off the ground in successive orbits and looking at the differences between the images, interferometric synthetic aperture radar can detect small differences in the distance between its position and the ground as the land surface moves – whether up or down. A digital SAR image can be seen as a mosaic of pixels. Each pixel gives a complex number that carries amplitude and phase information about the microwave field backscattered by all the scatterers (such as rocks, buildings, vegetation) within the corresponding resolution cell projected on the ground. The amplitude depends on the roughness and typically, exposed rocks and urban areas show strong amplitudes, whereas smooth flat surfaces (like quiet water basins) show low amplitudes. The phase is directly linked to the distance between the observed terrain and the satellite sensor. By calculating the differences in phases (interferogram) between two sets of data, one can determine ground displacements that have occurred in the time between the data acquisitions.

One of the popular open source and free program called Doris (The Delft object-oriented Radar Interferometric software) is developed to process data obtained from SAR systems. Doris basic input are SLC (Single Look Complex) images. Due to modular structure of program (processing is performed in steps/blocks), it is possible to write own steps of processing the data. Program is distributed with some helpful scripts and additional programs developed by community, which are compatible and ready to use with Doris.



On every step of processing could be used other programs to: improve attributes of data (e.g. extra filtering), plot charts to check processed data or draw a maps. There are many possibilities for scripts wrote in Matlab or similar programs. SAGA GIS or GMT (The Generic Mapping Tools) could be used to view images or merge parts of them. All the time new programs are being developed ,which may be used with Doris or its result files. There are few other programs developed for InSAR processing like ROI\_PAC or PHOTOMOD Radar, but in this article processing only in Doris is presented. The processing is not simple and may take few hours. Processing was made using data from European Space Agency before and after earthquake in Bam (Iran). At the beginning of processing, data need to be read and attached with orbits of satellite from day, when images were taken. In next step data could be connected with Digital Elevation Model (DEM) and be resampled if needed. Next, master and slave images are computed to take offsets between images. After this interferogram is created. From interferogram reference phase and reference DEM are being subtracted. At the end are being created unwrapped interferogram, coherence map and geocoded interferogram, which is presented in geographical known reference system. Obtained products from Doris like unwrapped phase map could be helpful in earth science. Maps of terrain after unwrapping shows the terrain deformation with high accuracy of cm in resolution. The best results are shown using images which are taken before and after earthquake, but this is not the only use. Here should be again mentioned that data could be obtained even at night and through the clouds or snow caps, which cause problems in some areas of Earth. Plenty of data needed to interferometry processing is available for free.

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**REVISION OF CIRRIPEDES TYPE SPECIMENS  
DESCRIBED BY KAFKA (1885)  
AND FRITSCH & KAFKA (1887),  
EXCLUDING STRAMENTIDAE,  
DEPOSITED IN THE NATIONAL MUSEUM IN PRAGUE**

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Despite almost two centuries of palaeontological research on the Bohemian Cretaceous Basin (BCB) knowledge of cirripedes from the near-shore, shallow and pelagic facies remains poor. The first studies dealing with cirripedes from the BCB were published by Reuss (1844, 1845–1846), followed by Kafka (1885), Fritsch & Kafka (1887) and Frič (1911). Cirripedes from the BCB were revised by Withers (1935), with mention of collections of A. Frič, J. Perner and J. Šulc. Withers also listed 11 species of cirripedes (including two stramentids) from the BCB: *Zeugmatolepas cretae* (Steenstrup 1837); *Calantica* (*Scillaelepas*) *conica* (Reuss 1845); *C. (Titanolepas) tuberculata* (Darwin 1851); *Cretiscalpellum glabrum* (Roemer 1841); *C. striatum* (Darwin 1851); *Scalpellum* (*Arcoscalpellum*) *angustatum* (Geinitz 1843); *S. (Arcoscalpellum) maximum* (J. De C. Sowerby 1829); *Loriculina laevissima* (von Zittel 1885); *Stramentum pulchellum* (G. B. Sowerby 1843); *Proverruca vinculum* Withers, 1914; *Brachylepas fallax* (Darwin 1851). Withers (1935: 162) suggested that *Pollicipes striatus* belongs to *Cretiscalpellum glabrum*. But the re-examination of the material revealed that the systematic position of *P. striatus* is different and actually belongs to *Cretiscalpellum striatum*, because its carina (Fritsch & Kafka 1887: 9, fig. 16) bears both longitudinal and transversal lines in contrast to carina of *C. glabrum* with only fine transversal lines.

Most of these specimens are deposited in the National Museum in Prague, from which we examined and verified these original types: carina of *Scalpellum maximum* Sowerby var. *bohemica* Kafka from Kunětická Hora (in Fritsch & Kafka 1887: 6, fig. 7A), now belongs

to *Arcoscalpellum maximum* (J. De C. Sowerby); tergum of *Pollicipes košticensis* Kafka from Košnice (in Kafka 1885, tab. II, fig. 4), now belongs to *Cretiscalpellum striatum* (Darwin); carina, scutum, tergum, rostrum, laterae of *Pollicipes fallax* Darwin from Lhota Úhřetická (in Fritsch & Kafka 1887: 10. fig. 17 c, t, t, r') and rostrum of *P. fallax* Darwin from Choceň (in Kafka 1885, tab. III., fig. 2r), now belong to *Brachylepas fallax* (Darwin). Both scutum and tergum of *Z. cretae* were donated to the Natural History Museum in London (inv. no. 31673-4). Unfortunately, predominantly part of the original specimens from the NM collection, carinal plates (4 scuta and 4 terga) of *Z. cretae* and all specimens of *Proverucca vinculum*, which were important part of Šulc's fossil collection were lost at the end of The Second World War during bombing of historical building of the National Museum in Prague (Sklenář, pers. com., 2012).

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**OCCURENCE AND REVISION  
OF GENERA *ONCOPAREIA* BOSQUET, 1854  
(DECAPODA: ASTACIDEA: THAUMASTOCHELIDAE)  
AND *CTENOCHIELES* KISHINOUE, 1926  
(DECAPODA: AXIIDEA: CTENOCHIELIDAE)  
FROM THE BOHEMIAN CRETACEOUS BASIN**

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*Ctenocheles* Kishinouye, 1926 is a heterochelous ghost shrimp typically with pectinate major claw with long fingers and acicular teeth. Isolated chelipeds are the most common remains in the fossil record of these decapod crustaceans, with several fossil species of the genus described only on the basis of isolated cheliped fragments (Schweitzer & Feldmann 2001). This type of chelipeds evolved homoplastically in different lineages of decapod crustaceans (Tshudy & Sorhannus 2000) and can be easily misidentified as remains of other decapod crustacean taxa as shown in the case from the Bohemian Cretaceous Basin (BCB). Very similar major claw is also known in an astacidean genus *Oncopareia* Bosquet, 1854, which has been considered as relatively well represented genus in the BCB (Mertin 1941), whereas *Ctenocheles* has not been identified in the respective area until now. Part of the material attributed to the latter taxon was at the disposal since the 19<sup>th</sup> century, but because of confused taxonomy of isolated pectinate claws (Feldmann et al. 1990; Tshudy & Sorhannus 2000) its identity has not been recognized and these claws were mistakenly classified as remains of genus *Stenocheles* Fritsch in Fritsch & Kafka (1887). Later, Mertin (1941) and Glaessner (1969) questionably synonymised *Stenocheles* with *Oncopareia*. Re-examination of the Cretaceous decapods deposited in the National Museum in Prague revealed that all supposed specimens of the lobster genus *Oncopareia* Bosquet, 1854 originating from the Middle Coniacian calcareous claystones of the Březno Formation in the BCB actually belong to *Ctenocheles*. This material together with newly collected specimens

from the same locality represents one of the oldest records for this genus and simultaneously the best preserved fossil material of *Ctenocheles* reported up to date (see also Hyžný et al. in press).

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**SECONDARY MINERALS  
OF Pb-Zn STAN TERG SKARN DEPOSIT, KOSOVO –  
X-RAY DIFFRACTION  
AND RAMAN SPECTROSCOPY STUDY**

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Stan Terg deposit, one of numerous occurrences within the Vardar Zone on the Balkan Peninsula, is located in the north-eastern part of Kosovo. The formation of the deposit was controlled by metasomatic processes between carbonates and volcanic intrusive rocks. Ore bodies are located on the contact between Tertiary volcanic breccias, and Triassic metamorphic Trepça Series (represented by schists and carbonates). Significant number of ore precipitated from hydrothermal fluids in paleokarst cavities. Galena, sphalerite, pyrite, pyrrhotite and arsenopyrite are the main components of the primary ore assemblage (Forgan 1950, Schumacher 1950, Palinkaš et al. 2013).

The weathering zone is not well developed in the deposit. Development of weathering zone was stopped by tuff series overlaying the area after volcanic activity. Gossan occurs, but it is seldom (Forgan 1950). However, the circulating water through the karstic system could have dissolved sulphides, as well as neighboring rocks, which led to the precipitation and formation of secondary minerals on the galleries walls inside the mine.

The aim of the study is identification and description of secondary minerals paragenesis that is present on the corridor walls inside the mine. The knowledge about this kind of secondary minerals may led to determination of weathering conditions in the deposit. Secondary minerals described in this study occur in minor amounts and should be regarded rather as a curiosity and as a supplement of knowledge about Stan Terg deposit. Samples were collected at 6<sup>th</sup> level of the mine. 20 samples were investigated using of X-Ray Diffraction (XRD) and 5 samples by Raman spectroscopy.

Secondary minerals occur mainly in form of fine-grained crystals, dripstones or incrustations. Among them copiapite, roemerite, epsomite, bianchite, melanterite, rozenite and gypsum have been recognized.

Copiapite is present in form of yellow and yellowish fine-grained crystals. It is most common secondary mineral in the mine. It occurs together with roemerite and epsomite. Roemerite, macroscopically not visible, occurs in minor amounts. Epsomite occurs in form of fine-grained, fibrous aggregates, crusts or dripstones. It exhibits white color, but may be also orange, if mixed with copiapite. Small amounts of bianchite were found (using XRD) within fine-grained crusts of epsomite. Melanterite occurs as crusts and stalactites. It builds clear phases or occurs together with other, yet not recognized minerals. A further study of melanterite is needed for successful characterization this additional phases. Rozenite was confirmed only by XRD. This mineral occurs in greenish-white fine-grained aggregates. Gypsum is a widespread mineral in the deposit. It occurs as single phases (with fibrous, fine-grained, needle-like or tabular crystals habit) or in lesser amounts with all other secondary minerals.

Weathering of primary ore minerals is related to underground water circulating through karst cavities and fractures within the Stan Terg deposit. Recognized secondary minerals are being an effect of metal sulfides oxidation when oxygen and water are present in the environment. Highly soluble sulphates are formed in such condition. Copiapite, rozenite, melanterite, roemerite, bianchite may be caused by quickly oxidization of pyrite to aqueous  $\text{Fe}^{2+}$  and  $\text{SO}_4^{2-}$ . The source of zinc in bianchite is sphalerite, whereas the presence of the magnesium in epsomite may be linked to Mg-rich carbonates. All of described minerals precipitated from the solution.

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**NEW EVIDENCE  
FOR HIGH-PRESSURE METAMORPHIC ROCKS  
IN WESTERN SVALBARD**

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During a field expeditions to Nordenskiöld Land and Wedel Jarlsberg Land (western Svalbard), previously unrecognised high-grade metamorphic rocks were observed. These rocks are represented by blueschists *sensu stricto* and blueschist facies metapelites.

In Nordenskiöld Land, blueschists occur in form of isolated bodies/tectonic lenses of different size enclosed within metasediments. The rocks in question are dark green, consist mainly of reddish garnet porphyroblasts and greenish and bluish amphiboles (including ferroglaucophane). They also contain chlorite, epidote, phengite, biotite, pumpellyite, quartz and albite. Garnet forms euhedral to subhedral poikiloblasts containing voluminous inclusions of epidote, albite, quartz, amphibole and titanite. Garnet shows chemical compositional variation from  $\text{Alm}_{49}\text{Pyr}_1\text{Grs}_{33}\text{Spss}_{17}$  in the cores to  $\text{Alm}_{63}\text{Pyr}_2\text{Grs}_{32}\text{Spss}_3$  in the rims. Gradual changes in chemical zoning as well as bell-shaped Spss content profiles suggest one-step, progressive garnet growth. P-T estimates based on thermodynamic modeling (using *Perple\_X'07*) in the NCKFMMnASHT system suggest peak pressure conditions of ca. 20 kbar and 480°C. P-T estimates are based on garnet and phengite compositional isopleths and stability field of the paragenetic assemblage (Chl-Ph-Amp1-Amp2-Grt-Spn).

Tectonically, the whole area is characterized by a moderate, 50°-dipping of S0 and S1 (the main metamorphic foliation) to the north. Deviations from this direction are small and occur only locally. They are mostly caused by the presence of rigid metamafic bodies, around which the common orientation of the bedding and the metamorphic foliation is disturbed. The observed stretching lineations plunge towards the N-NNE and are therefore



in very good agreement with the orientation of S0 and S1. Moreover, shear sense indicators such as commonly observed sigma clasts clearly indicate a transport direction from the north to the south.

The structural observations are in good agreement with those collected south of the Nordenskiöld Land, in the northern part of Wedel Jarlsberg Land (Antoniabreen area), where high grade augen gneisses and metapelites thrust onto typical low-grade rocks of SW Svalbard occur. The metapelites contain mainly garnet, muscovite, biotite, chlorite and quartz. Most of the garnet porphyroblasts show two distinct growth zones. Garnet-I ( $\text{Alm}_{64}\text{Pyr}_6\text{Grs}_9\text{Spss}_{21}$ ) represents the inner growth zone, forming inclusion-rich garnet core and garnet-II ( $\text{Alm}_{52}\text{Pyr}_2\text{Grs}_{30}\text{Spss}_{16}$ ) builds the outer growth zone, forming euhedral garnet rims. Some of the smaller garnet porphyroblasts show only a single growth zone (representing grt-II). Preliminary P-T estimates based on thermodynamic modeling in the NCKFMMnASHT system indicate the growth of garnet-I at ca. 550°C and relatively low pressure (ca. 5 kbar), whereas garnet-II grew at ca. 500°C and 12 kbar. The P-T estimates for garnet-I are based on garnet, biotite and plagioclase compositional isopleths and stability field of the paragenetic assemblage (Bt-Chl-Pl-Ms-Grt), whereas for garnet-II on the garnet and muscovite isopleths and stability field of the assemblage (Bio-Chl-Ms-Grt-Ab). We suggest that the growth of garnet-I is connected to the Late Neoproterozoic Torellian event, while garnet-II has been growing under blueschist facies conditions, hence most probably during the Caledonian orogeny.

Tectonic observations and P-T conditions are similar in both studied areas. It suggest that vast parts of the Caledonian basement of Nordenskiöld Land and northern Wedel Jarlsberg Land were metamorphosed under high pressure conditions.

These blueschist facies rocks may be an equivalent of the high pressure unit known from Oskar II Land (Motalafjella region), occurring to the north from the research area. Further, detailed petrological and geochronological studies to verify this hypothesis are in progress.

**NEW DATA ON THE PETROLOGY  
OF METAMORPHIC ROCKS  
FROM THE KUEKVUN' UPLIFT  
(NORTH CHUKOTKA AREA)**

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Kuekvun' uplift is located within Chaun folded zone of Mesozoic Verkhoyansk-Chukchi foldbelt. Outcropped metamorphic rocks were explored here in 1960–1970s during the geological surveying. On latest geological maps (scale is 1:500,000) metamorphic rocks of Kuekvun' uplift are dated Devonian-Middle Carboniferous (based on palaeontological data).

Metamorphic rocks of the Kuekvun' uplift are represented by gneisses and schists formed from Mid-Palaeozoic sedimentary units, composed by fine-grained clastic rocks with minor carbonates. The clastic material contains an admixture from a volcanic source of mafic to intermediate composition. Almost all of the rocks were changed in the amphibolite facies.

Two samples of plagiogneisses, which represent both the marginal and the central structural zones of the uplift has been a subject of a detailed study. Metamorphism temperature estimation has been done using garnet-biotite (Perchuk & Lavrent'eva 1983) and garnet-staurolite (Perchuk 1991) geothermometers.

The mineral paragenesis and the composition of coexisting garnet, biotite and staurolite indicate the temperature of metamorphism of 560–600°C, and the pressure of 2.5–4 kbar, which corresponds to the depth of 8–12 km. Such conditions imply the relatively high geothermal gradient (nearly 60°C/km), approaching that for peri-plutonic metamorphic aureoles.

Garnets from the marginal and the central zones of the uplift reveal a similar zonation pattern. The only notable difference is the presence of compositionally contrasting Ca-enriched

rim in garnets from the central zone. Such rims could result from the evolution of the entire metamorphic complex, but they could also be related with local processes, like the crystallization of granitic plutons, which are widespread within the observed area.

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## LITHOGEOCHEMICAL CHARACTER OF MAFIC AND ULTRAMAFIC PLUTONICS IN NORTHERN SWEDEN

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Northern Sweden is dominated mainly by Paleoproterozoic rocks. Igneous activity during the Svecofennian orogeny (1.93–1.87 Ga) created vast amounts of both volcanic and plutonic rocks within and around the Archaean craton. Post-orogenic 1.80–1.77 Ga granitoids were formed later within the same region. Distinguishing between the different mafic and ultramafic members of such plutonic suites was proven problematic during bedrock mapping. Geochronology may be of use to discriminate between suites; however, it is not a cost-efficient method for dealing with large amount of samples. The mafic and ultramafic rocks have three dominating suites, the Haparanda suite (1.94–1.85 Ga), the Perthite-monzonite suite (PMS) (1.87 Ga) and the Edefors suite (1.80–1.79 Ga). This study focuses primarily on Rare Earth Elements (REE's) and trace element geochemistry to trace the distribution and distinguish between the three mafic and ultramafic suites as a tool for geochemical mapping of the northern bedrock.

Lithochemical data (e.g. major elements, REEs and trace elements) covering the majority of northern Sweden gathered during bedrock mapping was provided by the Geological Survey of Sweden (SGU). Plutonic rocks ranging from gabbros to quartzdiorites and monzonites comprised nearly 80 analyses. Normalized spider plot patterns of REEs and trace elements served as a basis for subdivision into groups by similarities in key identification parameters. Several patterns are characterized by a pronounced Eu – trough while the middle – to HREEs display a rather flat trend, criteria that are related to rocks from the Haparanda suite, while samples with positive Eu-anomaly ( $\text{Eu}/\text{Eu}^* > 1$ ) and a nearly flat trend from La to Pr with a marked positive peak at Sr and generally less enriched in LILE, are consistent with the Edefors suite. An approximately uniformly depleted trend throughout the HREE with a slight concave upward shape from the LREEs towards the HREEs and an

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apparent enrichment in Sr and Nd and depletion in P could relate to either the Haparanda or the PMS suite. Among the others, statistical methods will be used to compare the correlation between the REEs within the datasets to find suitable elements for further analysis and thereby assigning the groups to appropriate suites, thus, the distribution of rock based on key tracers for related suites will be presented accordingly.

## **A WEB-BASED SYSTEM FOR COLLECTING AND ANALYSING OF GEOLOGICAL OUTCROPS**

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The evolution of computer technology has created possibility to build digital catalog of geological outcrops cards – the geological data bank. In the recent times, the milestone event in the computer cartography was the release of Google Maps service (2005) and more accurately – geoservices, called web map services. These services were based on software (both commercial and open source) called map servers (Nowacki & Opach, 2009). One of these map servers is “Geoportal” – <http://geoportal.gov.pl>, acting as a broker service, that provides the digital cartographic data and spatial services for the users. Another interesting spatial service – Central Geological Database was made by Polish Geological Institute – <http://baza.pgi.gov.pl/>.

The appropriate collection and processing of data, collected as a result of geological research is a non-trivial task due to their volume and the multiplicity of formats in which they are delivered. Therefore geological databases are most miscellaneous and comprehensive, which means that they are a valuable source of information during performing of the analysis. Furthermore, data in themselves have no value, only systematization and appropriate interpretation by the user can make these data useful. To achieve this goal, spatial databases are being used, because in addition to the information received as a result of the analysis, they also have a spatial reference. This data structure forms the base layer of Geographic Information Systems (GIS) and is present in applications for analyzing and visualization of the processing of geological data results. One of this application is the Internet-based system “GeoOutcrops”, which enable collecting and analyzing data collected in the geological outcrops.

GeoOutcrops is a universal database system of geological outcrops. It was created in Department of Geoinformatics and Applied Computer Science in Faculty of Geology,

Geophysics and Environmental Protection, AGH University of Science and Technology. The GeoOutcrops database is processed, refreshed and expanded with new technical solutions version, of the geological service “GeoKarpaty 2”. Similarly to the GeoKarpaty2, the GeoOutcrops service is designed to store data of the Polish Flysch Carpathians. It can also be adapted to store data of entire Carpathians. In contrast to previous version, GeoOutcrops is a open source system, with better user interface usability and user friendly template.

GeoOutcrops is a three-tier system model, which consists of: data tier, business tier and presentation tier. The data tier represents MySQL database with spatial extension – MySQL Spatial. The business tier of system, which contains the entire functional structure of the service, has been programmed using PHP language with Kohan’s Framework 3.0 and PDO library. Interaction with the user supports JavaScript with the JQuery library. The presentation tier, including the user interface, is made with XHTML and CSS languages. The web site has been developed in accordance with the current standards, both in terms of structure, the user interface and aesthetics. The whole thing is the result of a thorough analysis of requirements and capabilities, aimed at creating a geoservice dedicated to users associated with the geological sciences. Moreover, the system also includes the implementation of Google Maps API and allows specifying the location of the various outcrops on the map.

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## **POLYMETALLIC MINERALIZATION IN THE BAYANLIG AREA, AIMAK BAYANKHONGOR, MONGOLIA**

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Since 2007, exploration works have been carried out for the metalliferous deposits in SW Mongolia (Bayankhongor province), close to the north edge of the Gobi desert.

Mongolia is subdivided into 44 fault-bounded terranes (Badarch et al. 2002). The studied area is a part of the Gobi Altai Terrane, which is a long and narrow belt, located in the south of the Main Mongolian Lineament. The terrane is genetically classified as backarc/forearc basin and mainly consists of greenschist facies metamorphosed sandstones, shallow-marine limestones, volcanic rocks and granite/plagiogranite intrusions (Badarch et al. 2002).

The presented research is based on the mineralogical samples collected during the exploration works conducted in 2012. During the fieldwork several types of rocks were identified, such as mafic and ultramafic rocks which are serpentinised to various degree and also more felsic lithologies. Both mafic and felsic rocks revealed macroscopically visible metalliferous mineralization.

The aim of the study was to identify ore minerals in all types of rocks and to determine succession of the ore minerals occurring in the serpentinised mafic and ultramafic rocks. Microscopic observations in transmitted and reflected light were conducted in the Ore Deposits Geology Laboratory of the Mining and Economic Geology Department at the AGH University of Science and Technology in Krakow.

Macroscopic observations revealed that magnetite is a dominant ore mineral in the mafic lithologies, whereas malachite and copper sulfides in the felsic rocks.

On the basis of microscopic observations two main types of ore minerals were identified: oxides and sulfides. Samples from mafic rocks revealed chromite, magnetite, other Cr-Fe spinels, hematite, ilmenite, rutile, millerite, polydymite and pentlandite. Oxide minerals



dominate in these rocks. Ore minerals identified in samples from felsic lithologies are represented by chalcopyrite, pyrite, idaite, covellite, malachite, pyrrhotite and molybdenite. Moreover, electrum and native gold have also been recognized in one set of samples from felsic rocks.

As a result of the conducted research an attempt of determining precipitation stages of ore minerals occurring in the serpentinised rocks was made. On the basis of ore structures, textures and mineral assemblages, three main phases of ore minerals succession have been distinguished. The first phase is represented by primary ore minerals like chromite and ilmenite. The second one is closely related to serpentinisation process and characterized by the occurrence of minerals like magnetite and Fe-Cr spinels, and also pentlandite, millerite, polydymite. The last stage is related to the oxidation process and represented by hematite.

The presented results are part of the research which is still in progress and is focused on better understanding of metallogenic processes which occurred in the studied area.

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## **PHASE DIAGRAM – UNIQUE METHOD FOR PREDICTING HYDROCARBON PHASE CHANGE**

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Analyzed Main Dolomite reservoirs, located in the western part of Poland, form the biggest oil fields discovered during last few years. These fields, located in fractured Zechstein formation are under high fluid pressure and does not show influence of hydrodynamic reservoir conditions. Proven recoverable reserves of crude oil in Lubiatów – Międzychód – Grotów field are 7.25 million tons, while the proven reserves of natural gas are about 7.3 billion m<sup>3</sup>. As a result of its investments, the Polish Oil and Gas Company (PGNiG) will be able to significantly increase the production of natural gas and oil production in the coming years to about 1 million tons per year.

Currently built installation is planned only for oil exploitation which may cause situation when saturated oil will reach conditions below saturation pressure. Then two phase hydrocarbon recovery will reduce energy of dissolved gas and without any second and third method of intensification it will not be possible to get high recovery factor.

Main criterion for hydrocarbon classification, normally used in reservoir engineering, is construction of phase diagram which shows current average pressure vs. reservoir temperature.

Testing of perforated interval 3,166–3,202 m bsl in Sieraków-1 well gave two phase hydrocarbon inflow – oil and gas. The measured and interpreted Horner's pressure buildup provided 41 MPa in pressure. Temperature was on the level of 105°C (Słupczyński et al. 2008).

Based on PVT fluid analysis for hydrocarbons and non-hydrocarbons composition, the authors constructed triangular graph and phase diagram (Ahmed 1989, Whitson & Brulé 2000). The phase diagram needed recombination and recalculation of p-T reservoir conditions (Well Test Analysis in Gas/Condensate Reservoirs 2004).

Described reservoirs lie in “Gas Condensate” region. The analysis of the phase behavior character show that almost all fluid samples are above bubble pressure. Only one well (Sieraków-1) shows two phase hydrocarbon inflow confirming sense of phase diagram construction.

Planned installation for oil exploitation can only reduce reservoir pressure and finally decrease recovery factor. The above results suggest changing the exploitation plan and starting enhance reservoir energy during the time of oil recovery.

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## **CORRELATION AND COMPARISON OF JURASSIC DEPOSITS IN REPUBLICS OF BELARUS AND LITHUANIA, AND RUSSIAN FEDERATION IN TRANSBOUNDARY REGION**

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Correlation and comparison of the Jurassic deposits of Republic of Belarus, Republic of Lithuania and Kaliningrad region of the Russian Federation transboundary region is an important time milestone in studying of a paleogeographical situation of the western part of the East European Platform.

The geologist Ullman began to study Jurassic deposits of the Republic of Lithuania in 1830s (Grigyalis 1958). He investigated river Venta in the town of Papilany. For the first time, geologist A.E. Gedroyts conducted research of the Jurassic deposits in the territory of Belarus. He found erratic boulders in the Białowieża forest at the beginning 1880s (Mityanina 1982). Correlations of the Jurassic deposits were repeatedly undertaken in this region. In 1922, N.F. Bliodukho discussed the similarity between “Western” and “Russian” Jurassic on basis of the mollusk analogies.

The second attempt was made within the project of UNESCO No. 86 of the International program of geological correlation *The East European Platform (southwest region)* only in 1985. Correlations were carried out within the project “Peritetis”. The newest re-search of the Jurassic deposits of Belarus revealed the series of paleogeographical and sedimentological features (Makhnach 2011).

This research revealed, a glacial exaration of the Jurassic deposits from Grodno (Republic of Belarus), Druskininkay and Premay (Republic of Lithuania) as a distinctive feature of the Lithuanian-Polish Monocline. The considered transboundary region includes (from the North to the South) following tectonic structures: Baltic Syncline, western slope of the Latvian Saddle, Mazursko-Beloruskaja Antecline and Podlyassko-Brestsky Hollow.

Descriptions and paleontological material from stratigraphic wells, which encountered Jurassic deposits were used as a research material. Data from following wells were used: stratigraphic wells Gvardeyskaja-57 and Bely Yar-1 for the Kaliningrad region, Yoty's stratigraphic well for the Republic of Lithuania, stratigraphic wells Vysokoe-77 and Brest-52 for the territory of Belarus.

The correlation of regional data and comparison of paleogeographical events showed that the most complete section of the Jurassic deposits for this area is located in the territory of the Kaliningrad region – a stratigraphic well Gvardeyskaja 57. For the territory of Belarus, the most complete section of Oxfordian is presented in the stratigraphic well Vysokoe-77, and Callovian deposits are best represented in the stratigraphic well Brest-52.

Paleogeographical reconstruction shows that the sea was absent in the territory of Belarus, but the plentiful river network drained the Polesye Saddle through the Svislochsky snap in Early Callovian. Lowland with wetlands existed in Early Callovian during the beginning of transgression in the transboundary region of Lithuania, Belarus and the Kaliningrad region. The maximum transgression from the Polish Sea occurred during the *Kosmoceras jason* time (Middle Callovian). At this time, connection through the Pripyat Passage and through the southern passage systems with the Central Russian Sea was established. The second maximum transgression in this region happened during the *Quenstedtoceras maria* time (Early Oxfordian), and the communication with the Central Russian Sea was reestablished in the period of *Cardioceras cordatum* (Early Oxfordian). Completeness of Middle and Upper Oxfordian cuts from the territory of Belarus isn't clear and requires further paleontological research.

Lithological differences and time of sediment accumulation reveal different sedimentation conditions. This fact indicates various movement directions of tectonic structures. It should be noted that unidirectional movements (immersion) effected all tectonic structures during the maximum sea transgressions.

Differences in regions, where Jurassic sediments were deposited, were also studied. In the second half of Late Callovian, the Podlyassko-Brestsky Hollow underwent immersion and a flexure towards the Strytsky Deflection while Mazursko-Belorussky Antecline was under conditions of tectonic rest. During *Cardioceras cordatum* time (Early Oxfordian), the submerging of Pripyat passage northern part was amplified. Most likely, the Polish Sea started to recede from the major part of the territory of Belarus during Middle Oxfordian, marking a new land stage of the territory. The buckling of the Latvian Saddle towards the Baltic Syncline was observed within the territory of Lithuania.

Paleontological data are also interesting. Existence of coral reefs in the territory of Lithuania (Grigyalis 1958) testifies the prevalence of northwest currents from Peritethian areas, and also does not reject the hypothesis about the Northern (Baltiyskii) Passage connecting the Polish and Central Russian seas. Biota features indicate the existence of benthonic currents in Late Callovian and difficult fauna exchange between Lithuanian and Belarusian regions.

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## PALYNOSTRATIGRAPHY OF THE UPPER VISEAN DEPOSITS FROM THE MSTIKHINO QUARRY OF THE KALUGA REGION, RUSSIA

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The Mstikhino quarry is located 8 km to the north-west of the Kaluga town in the south wing of Moscow syncline. Twelve palynological samples from the Upper Visean deposits have been collected. Updated technique of the palynological preparation was employed using hydrofluoric and hydrochloric acids to dissolve silicates and carbonates. Then the ultrasonic effect and sifting were applied for the samples. The abundant and well-preserved miospores were obtained from the bluish-grey clays of the lower part of the second quarry bank (layer No. 12). One palynoassemblage MS-6 was established. 61 species were recognized. The palynoassemblage is generally composed of the significant miospore species of the **Triquitrites comptus – Cingulizonates bialatus distinctus (CBd)** Zone of the Aleksinian regional stage: *Lycospora pusilla* (Ibrahim) Somers (60%), *Schulzospora campyloptera* (Waltz) Hoffmeister, Staplin et Malloy (8%), *S. conforma* (Kedo et Jushko) N. Umnova (4%), *Cingulizonates bialatus* (Waltz) Smith et Butterworth (5%), *Tripartites vetustus* Schemel (3%), and *Triquitrites comptus* Wilson (3%). It is so unusual to find high diversity of the scarce species such as *Auroraspora granulata* (Kedo) Oshurkova, *A. micromanifesta* (Hacqubard) Richardson, *A. rugosiuscula* (Kedo) Byvscheva, *A. granulati-punctata* (Hoffmeister, Staplin et Malloy) Turnau, *Leiotriletes inermis* (Waltz) Ischenko, *L. suintortus* (Waltz) Ischenko, *Leiotriletes ornatus* Ischenko, *L. gulaferus* Potonie et Kremp, *Trachytriletes commodus* Ischenko, *T. subintortus* Ischenko, *Cyclogranisporites punctulatus* (Waltz) Lubert, *C. aureus* (Loose) Potonie et Kremp, *Granulatisporites granulatus* Ibrahim, *G. granosus* (Ischenko) Oshurkova, *G. microgranifer* Ibrahim, *G. minutus* Potonie et Kremp, *G. pennatus* (Kedo) Mamontov comb. nov., *Procoronaspora rara* (Palyford) Oshurkova, *Jugisporis subintortus* (Kedo) Mamontov comb. nov., *I. pennatus* (Ischenko) Oshurkova, *Raistrikiya macrura* (Lubert) Lubert, *R. clavata* Hacqubard, *Reticulatisporites cancellatus*

(Waltz) Playford, *Convolutispora jugosa* Smith et Butterworth, *C. ampla* Hoffmeister, Staplin et Malloy, *Tripartites incisotrilobus* (Naumova) Potonie et Kremp, *Triquitrites trivalvis* (Waltz) Potonie et Kremp, *Diatomozonotriletes trilinearis* Playford, *Vallatisporites dictyopterus* (Waltz) Byvscheva et N. Umnova in the palynoassemblage. An additional point to emphasize is that the association of rare species is not similar to those from the adjacent sections of the Kaluga Region. According to occurrence of the significant species of CBd Zone the age of the studied palynoassemblage is assigned to the Aleksinian age. The results well correspond with the data of previous palynological research. Besides the palynoassemblage MS-6 is compared to the paly-noassemblages of **Tripartites vetustus** – **Rotaspora fracta** (VF) Zone of Western Europe by the co-occurrence of significant miospores of *Tripartites vetustus*, *Triquitrites marginatus* Hoffmeister, Staplin et Malloy, *Remysporites magnificus* (Horst) Butterworth et Williams and *Knoxisporites stephanephorus* Love. According to Kmiecik (1986) the presence of *Murospora aurita* (Waltz) Playford, *Calyptosporites arenaceus* (Neves et Owens) Oshurkova, *Schulzospora campyloptera*, *Tripartites incisotrilobus* (Naumova) Potonie et Kremp and *Reticulatisporites cancellatus* (Waltz) Playford within studied miospore association confirm the correlation of the MS-6 palynoassemblage with the similar ones of the upper part of **Diatomozonotriletes saetosus** (Ds) Zone of Poland miospore zonation. Most probably that high miospore diversity of the studied palynoassemblage is related to various palaeoecological structures of the terrestrial parent vegetation.

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## **SUBSURFACE VELOCITY MODEL IN POST-GLACIAL DEPOSITS BASED ON MULTICHANNEL ANALYSIS OF SURFACE WAVES**

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First introduced and developed in the 1990s, the multichannel analysis of surface waves (MASW) is one of the active, seismic methods created for shallow seismic imaging. Surface waves generated from a sledge hammer were used for delineation of subsurface structures. MASW is analyzing the propagation velocities for each component of surface waves by generating the dispersion curves, and then as a result produces shear-wave velocity ( $V_s$ ) profiles below the surveyed surface. A  $V_s$  distribution in the depth domain is obtained in 1-D or 2-D variant after a quite simple inversion procedure. Shear-wave velocity ( $V_s$ ) is one of the elastic constants, closely related to changes in geology. Weathering zone in post-glacial area, as one of the most complex geological forms, were chosen to check MASW ability to evaluation near-surface, folded structures. Data were acquired for typical MASW continuous profiling schema in 2 meters intervals and performed using land-streamer at the distance of about 200 m, along previously existed reflection seismic line. The analysis was supported by records from previously made reflection seismic investigations.

Image of glacial till on MASW 2-D map is characterized by appearance of mix clay-sandy layers, folded and locally discontinued. Furthermore, the most of detected middle layers from 0 m up to 30 m deep form pile of thrust slices. Application of obtained subsurface model could be considered at a two main stages. First of them has a geological background where continuous  $V_s$  distribution supporting geological and geomorphological works. The second one is connecting with prospecting seismic where 2-D  $V_s$  map could be used for static purposes.

## **INTERCALATES OF KAOLINITE WITH AMMONIUM SALTS AND THEIR INTERACTION WITH AQUEOUS Cr(VI) IONS**

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Kaolinite is a dioctahedral aluminum silicate built from linked octahedral (alumina) and tetrahedral (silica) sheets, which form an asymmetrical 1:1 layer. Kaolinite is more often used as a base for the synthesis of new hybrid materials (Dedzo et al. 2012). Kaolinites modified with selected organic molecules are studied because of their potential application as environmental remediation materials and polymer nanocomposite fillers (Matusik & Bajda 2013). Therefore the purpose of the study was to test the ability of kaolinite intercalation with ammonium salts to remove Cr(VI) from aqueous solution under different conditions. Additionally, information on the removal mechanism was obtained.

Well ordered kaolinite from Polish Maria III deposit (M) was used for the experiments. The mineral intercalated with dimethyl sulfoxide (DMSO) was used as a precursor. The sample portions of 12.5 g were mixed with 90 mL of DMSO and 10 ml of H<sub>2</sub>O for 7 days at room temperature (MDS sample). The formed MDS intercalation compound was rinsed with CH<sub>3</sub>OH until all DMSO was removed from the interlayer space and the methoxy-kaolinite (KM sample) was synthesized (Matusik et al. 2012). Finally, the KM sample was centrifuged, the excess of methanol was removed and the wet KM was stirred in methanol solutions of the ammonium salts. For the experiments the following chlorides solution were used: 2M tetramethylammonium (TMA), 1M benzyldimethylhexadecylammonium (B5) and 2M benzyltrimethylammonium (B1). The formed materials were abbreviated as the salts. The TMA and B1 samples were washed with isopropanol to remove the excess of ammonium salt crystallized on the surface of the intercalates. In contrast to B1 and TMA, the B5 complex was not washed as isopropanol destroys its structure. All samples were dried at 60°C for 24 h. The products were characterized using powder XRD, IR, and CHNS elemental analysis. The sorption of chromate on the modified kaolinite was

measured spectrophotometrically using 1,5-diphenylcarbazide method as a function of Cr(VI) concentration (0.02–20 mM/L) at pH 5. The intercalates were shaken in prepared chromate solutions (ratio 20 g/L) for 24 h at 22°C. The XRD confirmed that methoxy-kaolinite was intercalated with ammonium salts, which was not possible for the raw kaolinite. The  $d_{001}$  peak (7.2 Å) increased to 14.7 Å (B1), 12.6 Å (TMA) and 38.4 Å (B5). The small molecules in the case of B1 and TMA complexes formed a monolayer in the interlayer space while the long chain B5 molecules were tilted with respect to 1:1 layers. The presence TMA, B1 and B5 in the mineral structure was confirmed by infrared spectroscopy (FTIR) as the organic bands in the 3120–2800  $\text{cm}^{-1}$  region attributed to C-H stretching vibrations were registered. The changes in the position and intensity of the bands were also observed in the Si-O vibrations region (1200–900  $\text{cm}^{-1}$ ) due to salts incorporation. Results of CHNS analyses were used to determine the chemical formulas of the derivatives:  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{3.79}(\text{OCH}_3)_{0.21}[\text{TMA}]_{0.54}$ ,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{3.79}(\text{OCH}_3)_{0.21}[\text{B1}]_{0.38}$ ,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{3.79}(\text{OCH}_3)_{0.21}[\text{B5}]_{0.59}$ .

The modification by ammonium salts enhanced the sorption capacity as compared to raw kaolinite where the sorption capacity reached only ~2 mM Cr(VI)/kg. For the TMA intercalate the maximum Cr(VI) sorption reached ~23 mM Cr(VI)/kg. For the B1 it was equal to ~73 mM Cr(VI)/kg and for the B5 it was significantly higher equal to ~979 mM Cr(VI)/kg. Two possible Cr(VI) immobilization mechanism could be distinguished: ion exchange of Cr(VI) with  $\text{Cl}^-$  and surface precipitation of organic chromate. In the experimental pH range the  $\text{HCrO}_4^-$  ionic form of Cr(VI) dominates and it can be exchanged with  $\text{Cl}^-$ . The precipitation mechanism undoubtedly dominated in the case of B5 where a yellow precipitate of organic chromate appeared. The XRD studies performed on samples after sorption indicated the lack of  $d_{001}$  values characteristic for the intercalates. This confirms that the structures are not stable in aqueous solutions.

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## GRAIN SIZE DISTRIBUTION OF THE MIDDLE GAUJA LOWLAND AEOLIAN SEDIMENTS AND THEIR SUBSTRATUM – PRELIMINARY RESULTS

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The Middle Gauja Lowland is located in the northern part of Latvia next to the border with Estonia. It is enclosed by Alūksne Upland in the north-east, Vidzeme Upland in south-west and Karula Upland in the north. Gulbene Interlobate Ridge separates the lowland from the Eastern Latvian Lowland in the south-east and Aumeisteri Interlobate Ridge separates it from the North Latvian Lowland in the north-west. The Middle Gauja Lowland has been formed by the Middle Gauja ice lobe of the Peipsijarv ice stream of the last (Weichselian) glaciation (Zelčs & Markots 2004). Ice retreated from the territory between Gulbene and Linkuva deglaciation phases (15.5–14.5 ka) (Kalm et al. 2011, Zelčs et al. 2011) forming large ice-dammed lake (Zelčs & Markots 2004). Sandy sediments of Middle Gauja ice-dammed lake form the upper part of Quaternary sediment sequence in the largest part of the lowland (Juškevičs 2002).

A total of 76 sandy sediment samples were collected at eight sites. At each site, one or two vertical outcrops, up to 5 m high, were sampled. Samples were taken from visually identifiable beds or, in cases when individual beds were very thick or had visually identifiable grading, samples were taken in approx. 10 cm intervals. Collected samples were dried at room temperature for at least two weeks. 200 g of each sample were dry sieved (mesh sizes in millimeters: 1, 0.8, 0.5, 0.315, 0.25, 0.2, 0.125, 0.1, 0.063) with mechanical shaker for 20 minutes. Each fraction was weighted on electronic scale ( $d = 0.001\text{g}$ ). The mean, sorting, skewness and kurtosis of each sample were calculated with Folk and Ward (1957) logarithmic graphic method provided by customized version of R package “rysgran” (Gilbert et al. 2012). Mean grain size verbal description was taken from GRADISTAT (Blott & Pye 2001). Frequency and cumulative frequency plots for each sample were prepared by custom R script. Obtained frequency and cumulative frequency curves were visually

compared between each other and with distribution curves published by Mycielska-Dowgiałło & Ludwikowska-Kędzia (2011).

All of sampled sites consist of moderate to well sorted medium to fine grained sand. Grain size distributions of assumed aeolian and glaci-fluvial parts of the Zelini site are similar. Presumed glaci-fluvial part has a slight increase at medium sand fraction and small amount of fine gravel. Relation between substratum and dune suggests short duration of aeolian processes.

Mustjogi 3 parabolic dune samples show almost no presence of very fine sand/silt and retain large percentage of coarser (< 2 phi) sand grains. It suggests the formation exclusively from slightly reworked underlying glaci-fluvial delta sediments consisting of medium/coarse sand as observed in Mustjogi 1 site.

Bimodal distributions of glaci-lacustrine sediments, as observed at Garengrīda and Mielupīte sites and, in lesser extent, at Mustjogi 1 glaci-fluvial delta, explain observed bimodal distributions at some of dunes (Garengrīda, Smilškalni, Mustjogi 3). Preservation of distribution maximas with only slight increase of fine sand maxima suggest only slight reworking of sandy sediment substratum in aeolian conditions before their final deposition in dunes. Similar preservation of substratum distribution characteristics has also been observed in dunes lying on fluvial and marine coastal sediments (Mycielska-Dowgiałło & Ludwikowska-Kędzia 2011).

Observed similarities between both, size distributions of aeolian sediments and potential source of sediment grain size distributions, confirm observations of other authors (i.e. McManus 1988) that granulometric analysis without assistance of other methodology is not sufficient to allow unambiguous separation of different sedimentary environments.

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## **PETROPHYSICS OF ROTLIEGEND SANDSTONES FOR UNCONVENTIONAL TIGHT GAS EXPLORATION – CASE STUDY OF POLISH PERMIAN BASIN**

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Tight gas is one of the unconventional gas accumulations. In tight reservoir, natural gas is trapped in impermeable sedimentary rock. Industry defines tight gas reservoir as a maximum 10% matrix porosity and maximum 0.1 mD permeability (excluding fracture permeability) sedimentary rock (Haines 2006). Gas is trapped by low permeability of the reservoir. Down-dip water contact and reservoir trap do not appear. Tight reservoir rock should be characterized by poor reservoir properties – low porosities, extremely low permeability and also small flow rates (Law 2002).

Tight gas accumulations are expected to originate in deeper parts of Polish Permian Basin within Rotliegend sandstones (Kiersnowski et al. 2010). Depth of burial associated with time could allow occurrence of advanced diagenetic processes amending primary porosity.

Area of research is located in the center of Polish Permian Basin – western Poland. It is a natural gas field Pxyz, where hydrocarbons are accumulated within aeolian Rotliegend sandstones characterized by low reservoir properties. Core samples from well Pxyz-2 from depth interval 3511.5–3626.0 m were selected for investigation. The porosimetric analysis (AutoPore 9220 mercury porosimeter) of 115 samples granulometric analysis of 20 samples (sieve measurements and SediGraph 5100 device) were performed in Polish Oil and Gas Company. Borehole survey revealed gas saturation in whole 172 m sandstone profile.

Obtained results allowed quantitative characteristics of samples, both grain size and pore space. Average diameter of sand grain was in the range from 0.171 mm to 0.643 mm. Based on the above results, studied sandstones were classified as fine, medium and coarse-grained (Pettijohn et al. 1972). Porosimetric studies showed poor reservoir quality of sandstones. Weak filtration of samples was proved by low values of average capillary diameter and insufficient 45% percentage of pores with diameter greater than 1  $\mu\text{m}$ . Average porosity

of samples is 7.575%, wherein samples from the upper part of sandstone complex have lower porosity values than those from the base. Total pore area ranged from 0.01 m<sup>2</sup>/g to 2.73 m<sup>2</sup>/g in whole profile. Research showed no total porosity and total pore area dependence on burial depth. It is connected with the domination of mechanical compaction in sandstones (Such et al. 2010). Changes in porosity and total pore volume showed the vertical variation in sandstones. Based on these results, zones predisposed to tight gas accumulations were distinguished.

Granulometric and porosimetric studies performed on Rotliegend samples from the area of Pxyz deposit allowed better understanding of deep buried sandstones petrophysics. Parameters received from analysis confirmed possibility of tight gas accumulations in Rotliegend sandstones in the area of Pxyz gas field.

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## **BASIN-CENTERED GAS ACCUMULATIONS IN ROTLIEGEND SANDSTONES – CASE STUDY OF POLISH PERMIAN BASIN, FIRST RESULTS**

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Permian Basin covers one of the world's largest gas-bearing clastic formation – Permian Rotliegend Group. Reservoirs are supplied by Carboniferous sources, lying directly beneath. Permian Rotliegend sandstones belong to the most important gas bearing formations in Poland. They were deposited in playa, fluvial and aeolian depositional systems (Kiersnowski et al. 2010). Both conventional and unconventional accumulations occur in those sediments. Some of unconventional accumulations occur in conditions of Basin-Centered Gas System (BCGS). Basin-Centered Gas Systems are unconventional with the greatest economical potential in the world. They are gas saturated, abnormally pressured, a low-permeability reservoirs commonly showing lack of a down – dip water contact. Two types BCGS can be distinguished – direct and indirect. Differentiation results from the attributes of the system – type of organic matter, thermal maturity, sealing and the distance of hydrocarbons migration (Law 2002). Direct Basin-Centered Gas Systems may occur in the area of the Polish part of Permian Basin. The purpose of present studies was indicating Permian Rotliegend sandstones as a reservoir rocks for direct Basin-Centered Gas Accumulations, which are associated with BCGS, according to reflectance of vitrinite measurement and permeability.

Analysis were performed on eight core samples located within the aeolian sediments of Eastern Erg (center of Polish part of Permian Basin) from the depth interval 3702–4200 m. Vitrinite reflectance measurement ( $R_o$ ) were performed on polished pellets, under oil immersion with Zeiss Axioplan microscope in reflected white 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 perpendicularly to the cylinder axis.

In each sample organic matter was dominated by vitrinite. It could indicate humic organic matter typical for gas prone source rocks. The measured vitrinite reflectance values confirmed that organic matter reached the maturation stages of hydrocarbon generation, characteristic for the gas window phase ( $R_o > 2\%$ ). Permeability results shown typical values for tight sandstones from BCGS, lower than 0.1 mD.

Performed studies on aeolian Rotliegend sandstones from Eastern Erg area confirmed the opportunity of Basin-Centered Gas Accumulations occurrence in those sediments. Humic type of organic matter and values of vitrinite reflectance corresponding to gas window phase are specific for BSGAs. Analyzed samples of aeolian Rotliegend sandstones are characterized by very low permeability, not exceeding 0.1 mD and therefore capillary sealing of the accumulation. Carboniferous source rock located directly beneath reservoir rock, confirmed short distance of hydrocarbons migration. All mentioned factors allow classifying aeolian Rotliegend sandstones as a reservoir rock within Basin-Centered Gas System.

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## **PRIMARY AND SECONDARY COPPER MINERALS FROM RĘDZINY, RUDAWY JANOWICKIE, SUDETEN, SOUTHWESTERN POLAND**

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Dolomite quarry in Rędziny is a place, which has a very rich polymetallic mineralization. It is a result of hydrothermal processes (precipitated primary minerals) or chemical weathering changes (precipitated secondary minerals). Proximity to Karkonosze Granite massif greatly influenced the variety of the mineralization in Rędziny.

Compared to numerous exploited mines located in the vicinity (for example Miedzianka, Ciechanowice, Czarnów, Radomierz), the dolostone quarry is relatively young, opencast mine. Sulfides are the most common primary minerals in Rędziny. This information appears in the study of Gołębiowska et al. (e.g. 1998, 2006, 2012). Secondary mineralization is very variable and it occurs as forms of arsenates, vanadates, phosphates, carbonates, silicates and oxides (Gołębiowska et al. 1998, 2006).

The aim of the study was to characterize primary and secondary mineralization, rich in copper compounds, which were located in northern hypergene zone of dolostones quarry in Rędziny.

Results were compared with other sampling points from the data of Gołębiowska's studies.

The chemical analysis in microscale was used to examine relationship between minerals. The presence of Cu-minerals in Rędziny is associated with brownish, greenish and reddish zones dispersed in dolostones. The classic mineralogical and chemical researches of the polymineral samples with macroscopically visible green mineralization with use of optical microscopy (transmitted and reflected light), X-ray powder diffraction (XRD), electron microscopy (SEM) and electron microprobe study (EDS, WDS) were also performed.

The main primary minerals are tennantite, chalcopyrite and less often galena or sphalerite.

In BSE there were also observed minor mineral inclusions of Ti, U, Ce, Fe and Ca phase, most probably brannerite. It was recognized in small cavities and fissures between relicts of tennantite and it forms prismatic crystals up to 10  $\mu\text{m}$ . Origin of brannerite is probably connected with decomposition of uraninite. Minerals of Ti (e.g. titanite) were also found in the Rędziny quarry.

The most common secondary mineral phases are represented by Ca-Cu arsenate (tyrolite-clinotyrolite) and Cu-silicate (chrysocolla). X-ray powder diffraction data of blue-green spherical accumulation of small crystals, correspond to the standard data of clinotyrolite and partially of tyrolite. Detailed X-Ray studies show split basic reflections: (001) CT and (002) T, and (002) CT and (004) T. These data indicated that tyrolite is intergrowths with clinotyrolite.

The analyses of Cu-Cu arsenates were normalized to a  $\Sigma$  cation = 11 ( $\text{Cu} + \text{Ca} + \text{Zn} + \text{Fe} + \text{Mn} + \text{Ba} = 11$ ) in the respective formula units of clinotyrolite:  $\text{Ca}_{1.94}(\text{Cu}_{8.99}, \text{Zn}_{0.07}) [(\text{AsO}_4)_{3.95}(\text{SO}_4)_{0.03} | (\text{OH})_{10.17}] \cdot 10\text{H}_2\text{O}$ . The amounts of  $\text{H}_2\text{O}$  were calculated by stoichiometry. Trace elements detected by EMPA are: Mn, Bi, Fe and Ba < 0.01 apfu.

Secondary minerals associations from Rędziny quarry were formed differently, which indicate various physical and chemical conditions during oxidation. Supergene phases, which occurs in the northern part of the quarry at Rędziny, were formed as a product of oxidation of primary polymetallic ores, containing sulphides, sulphoarsenides and copper-arsenic sulphosalts.

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## **SYNTHESIS AND PRELIMINARY CHARACTERIZATION OF 2-LINE FERRIHYDRITE CONTAINING DIFFERENT AMOUNTS OF Si**

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Ferrihydrite ( $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ ) is the reddish-brown, nearly amorphous hydrous ferric oxyhydroxide mineral with variable composition, widespread in various near-surface environments. Being thermodynamically unstable, it transforms with time into goethite ( $\alpha\text{-FeOOH}$ ) or hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ). Due to its low crystallinity and high surface area, ferrihydrite is highly reactive and plays, through co-precipitation and adsorption reactions, an essential role in e.g. geochemical cycling of various trace elements and capturing of contaminants from streams and groundwater in such environments as iron-laden springs, mine wastes and acid mine drainage. The environmental importance is one of the main reasons for numerous studies on ferrihydrite properties which have been carried out recently. These studies have been dealing with, among others, solubility, thermodynamic features, surface chemistry, sorption and catalytic properties etc. However, in the majority of experimental works synthetic ferrihydrite analogues with chemical composition close to ideal have been applied. Such approach might cause oversimplification, because ferrihydrite always contain substantial amounts of admixtures, with Si, C, P, As, Ca, Al being probably most common. One of the most important and the most common impurity is Si, which in the form of silicate ion has strong affinity for a hydrous ferric oxyhydroxide surface. An association of ferrihydrite with Si not only retards the rate of its transformation to the stable phases (goethite or hematite), but also seriously affects e.g. surface chemistry. Although Si-ferrihydrite was successfully synthesized in several studies, relatively little is known about its properties. The aim of this work was to fill that gap.

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  $\text{Fe}_2(\text{SO}_4)_3$  with NaOH in the presence of  $\text{Na}_2\text{SiO}_3$  at pH 8.2. The precipitates were incubated for four days at room temperature, then the suspensions were dialyzed to remove an excess of salt, and finally freeze

dried. The products were characterized using a variety of analytical techniques, including X-ray powder diffraction (XRD), inductively coupled plasma atomic emission spectrometry (ICP-AES), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and Raman spectroscopy.

The X-ray pattern of pure ferrihydrite reveals two asymmetric broad bands with maxima at 2.55 Å and 1.50 Å, characteristic for 2-line ferrihydrite. With increasing Si/Fe molar ratio, shifting in position of the first (ca.  $35^{\circ}2\Theta$ ) peak towards lower angles (up to ca.  $29^{\circ}2\Theta$ ) was observed. Gradual broadening of the peak and declining its asymmetry were noticed as well. Both the position and the shape of the second band did not shift at the same time. These features indicate reducing crystallinity and lowering grain size of Si-ferrihydrite in comparison to those for the pure ferrihydrite.

Infrared spectrum of the pure (Si-free) ferrihydrite shows a broad band at ca.  $400\text{ cm}^{-1}$ , with a shoulder at  $600\text{ cm}^{-1}$ , attributable to Fe-O stretching vibrations. Distinct bands at  $1635\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$ , related to OH stretching, are apparent as well. The presence of small peaks at  $975\text{ cm}^{-1}$ ,  $1055\text{ cm}^{-1}$  and  $1125\text{ cm}^{-1}$  is probably an effect of sulfate complex formation on the ferrihydrite surface. Increasing Si concentration strongly affects infrared spectra of ferrihydrite: additional intensive band at ca.  $990\text{ cm}^{-1}$  (Si-O stretching) appears and is getting stronger with increasing Si/Fe ratio. The position of this band is shifted slightly towards higher wavenumbers (up to  $1003\text{ cm}^{-1}$ ) at higher-Si-ferrihydrite spectra. At the same time,  $\sim 600\text{ cm}^{-1}$  shoulder and sulfate peaks disappear.

Results of Raman spectroscopy are in general consistent with those of FTIR and gave more specific information about the band at ca.  $400\text{ cm}^{-1}$ , which is quite indistinct on infrared spectra and attributed to Fe-OH unsymmetrical-stretching vibrations. The band is getting broader and is slightly shifted to higher wavenumbers with increasing Si/Fe ratio but its intensity decreases drastically for the highest-Si samples (Si/Fe  $\geq 0.75$ ). At the same time, characteristic  $720\text{ cm}^{-1}$  peak and ca.  $500\text{ cm}^{-1}$  shoulder become hardly visible and the spectra are getting dominated by broad but intensive band of ca.  $1500\text{--}1700\text{ cm}^{-1}$ , typical for amorphous silica. Additionally, sharp peak at  $980\text{ cm}^{-1}$  present on lower-Si spectra is probably an effect of relic sulfate ion adsorption onto ferrihydrite surface.

Preliminary results indicate that silicate ions not only cause decreasing crystallinity and retard ferrihydrite transformation but also strongly affect its surface properties. To verify this hypothesis and to enhance characteristics of Si-ferrihydrite, additional analyses are planned, including solubility, surface area and  $\text{pH}_{\text{PZC}}$  determinations, thermal analyses and electron microscopy. Sorption/desorption studies involving cations and anions binding are planned as well.

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## GEOCHEMISTRY OF ORDOVICIAN BLACK SHALES FROM THE LENINGRAD REGION

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The black shales zone is located in southern periphery of the Baltic Shield and forms part of the Vendian-Paleozoic platform cover. This zone, together with the Sablino, Koporye, Mozhaiskoe, Popovka, Izhora, Ust-Luga, represents a potentially large noble metal and rhenium resource in the Leningrad region. This paper presents mineralogy and geochemistry of black shales that are important estimating the potential for possible future mining.

Sampling was carried out at seven points in the Leningrad region, where samples were collected from different parts of the strata. X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), inductively-coupled mass spectrometry (ICP-MS) and scanning electron microprobe (SEM) analyses were mainly used to identify the mineral species and estimate metal contents.

Illite, kaolinite, chlorite, quartz, and feldspar were identified as main silicates with minor amount of iron oxides such as jarosite and goethite.

Pyrite in black shale typically occurs in framboidal form and as euhedral crystals. Framboidal pyrite was found in the black shale samples from Sablino, Koporye and Ust-Luga. Such form of occurrence is typical for pyrite that is formed during early diagenesis.

The content of organic matter in the studied black shale samples is 1.3–16.5 wt. %. The total rare earth elements ( $\Sigma$ REE) content of black shale samples ranges from 65.67 ppm to 262.95 ppm. The average REE content of 15 samples from different parts of the Leningrad region is higher than 134.19 ppm for the world black shale calculated by Ketris and Yudovich (2009). The content of rhenium in the samples is 0.14–0.25 ppm. The concentration of Re is higher in the western part of the studied area. XAS shows that concentration of the palladium group elements is higher in western part of the region, where the Pd content varies from 0.45 ppm to 0.77 ppm. Additionally, the results of this study also yield contents of U (286 ppm), V (2140 ppm), Mo (1260 ppm). Therefore, black shales as a perspective source of critical metals demand further detailed study.

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**METAMORPHIC EVOLUTION  
OF THE SEVE NAPPE COMPLEX  
IN THE SNASAHÖGARNA AREA,  
SWEDISH CALEDONIDES**

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The Middle Seve Nappe in the Snasahögarna mountains, western Jämtland, Sweden, is composed of high grade metamorphic rocks emplaced in far-travelled nappes. The investigation of these paragneisses, derived from the Baltica margin, can contribute information about the subduction and exhumation processes, which controlled the formation of the Seve Nappe Complex (SNC) in the Scandinavian Caledonides.

Recent studies in other parts of the orogen have shown that the rocks of the SNC likely have experienced pressures higher than what was previously described (Janák et al. 2012, Klonowska et al. in press). These latest PT studies along with geochronological dates available suggest that the collision between Baltica and Laurentia has commenced c. 30 m.y. earlier (at ca. 450 Ma) than generally accepted.

Samples of kyanite- and garnet-bearing meta-sediments were collected along a profile at Tväraklumparna (Snasahögarna area) and investigated in thin sections using light microscopy followed by BSE imaging, WDS analysis and Raman spectroscopy.

Preliminary results show that dominant garnet reaches up to 7 mol. % of Grs content. The garnet commonly contains inclusions of quartz surrounded by radial cracks and grains of polycrystalline quartz. More rare are inclusions of kyanite and white mica with a Si-contents reaching 3.34 a.p.f.u. Detailed studies of garnet revealed dense areas of micrometer size inclusions exhibiting negative crystal shape present in the core regions. Raman studies suggest these inclusions are at least partly formed by microdiamond.

Textural evidence of peak metamorphic conditions reaching the stability field of coesite together with microdiamonds preserved in garnet cores confirms that the Seve Nappe crustal rocks of the Snasahögarna area has undergone ultrahigh pressure metamorphism.

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## THE FIRST PALYNOLOGICAL DATA OF THE MIDDLE JURASSIC DEPOSITS FROM BOREHOLE 16, ELEKTROUGLI (MOSCOW REGION, RUSSIA)

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The palynological analysis of the Middle Jurassic deposits has been carried out for the borehole No. 16 and No. 5 located in Elektrougli west of Moscow region (Russia). Twenty samples have been macerated from clays of these two boreholes. Only one of them contained palynomorphs (spores and pollen) in sufficient amount. As a result the single palynological assemblage was established. Pollen grains are abundant (over 55% of the total of the assemblage). The grains of *Alisporites similis* (Balme) Dettmann, and *A. lowoodensis* de Jersey dominates among the pollen reaching to 22% of the assemblage. It should be noted that a lot of different coniferous pollen grains from ancient deposits were found here, as such as: *A. parvus* de Jersey, *A. robustus* Nilsson and *Pseudopinus textilis* Bolchovitina. There were also the pollen grains of *Cycadopites* sp. (6%), and *Sciadopityspollenites mesozoicus* Couper (4%). A few pollen of *Vitreisporites pallidus* (Reissinger) Nilsson with affinity to Caytoniales, *Perinopollenites elatoides* Couper and *Ephedripites* sp. were rarely discovered. There are a lot of spores (45%) in the studied palynoassemblage. Spores of Filicopsida (12%) are represented by *Dictyophyllidites harrisii* Couper, *Leiotriletes magna* (de Jersey) Norris, *Deltoidospora juncta* (Kara-Murza) Singh with affinity to the genera *Dicksonia*, and *Matoniasporites* related to Matoniaceae. There are a few spores (10%) of Cyatheaceae (*Cyathidites minor* Couper). The spores of hydrophilic ferns are represented by *Osmundacidites jurassicus* Couper, *Baculatisporites comaumensis* (Cookson) Potonie, and *Todisporites minor* Couper. There are various lycopods (5%): *Uvaesporites verrucosus* (de Jersey) Helby in de Jersey, *Densoisporites velatus* Weyland & Krieger, *Lycopodiumsporites clavatoides* Couper; *Lycopodiumsporites subrotundum* (Kara-Murza) Pocock and moss spores of *Polycingulatisporites crenulatus* Playford & Dettmann (2%) which are

typical for the Bajocian deposits. There are very common the tuberculous forms such as *Leptolepidites* sp. and *Camptotriletes cerebramiformis* Maljavkina. The acritarchs are represented by *Leiosphaeridia* sp. This assemblage can be compare with palynological assemblage of the Bajocian age from Denmark (Nielsen et al. 2010) by comparable quantity of Cyatheaceae and presence of Caytoniales pollen. Thus studied palynological assemblage has the Bajocian age documented by presence of *Polycingulatisporites crenulatus*, *Alisporites similis*, *A. lowoodensis* and also ancient forms of *A. parvus*, *A. robustus*, *Uvaesporites verrucosus*, *Baculatisporites comaumensis* which are typical for the Aalenian Age. The quantity of lycopods, moss and ferns of Osmundaceae indicates the lake-mire continental conditions of the studied region.

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## **ORGANIC MATTER ASSOCIATED WITH Zn-Pb ORES FROM THE SILESIA-CRACOW REGION, POLAND**

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The Silesian-Cracow lead and zinc deposits are occurring mainly within the so-called ore-bearing dolomites of the Middle Triassic (Muschelkalk) and by the most authors are classified as Mississippi Valley-type deposits (Sass-Gustkiewicz et al. 1982, Wodzicki 1987, Leach et al. 2001, 2010). Coaly accumulations within the Zn-Pb deposits of the Silesian-Cracow region such as so-called dopplerite – a black, amorphous organic matter (OM) macroscopically resembling gelificated detrital lignite (see Sass-Gustkiewicz & Kwiecińska 1994, Kwiecińska et al. 1997), brown and matte-black intercalations in the clayey rocks of the internal sediment type (Sass-Gustkiewicz 1996) and organic matter present in inclusions of the sulfide minerals (Karwowski et al. 1979, 2001, Kozłowski 1995) are well known, but the problem of their origin is the subject of numerous discussions and to present day has not been clearly resolved. There is an agreement among investigators that the above-mentioned OM has an allochthonous origin, but the controversy raises the question of the potential source of OM and its age (Kołcon & Wagner 1983, Sass-Gustkiewicz & Kwiecińska 1999, Karwowski et al. 2001).

Preliminary tests using gas chromatography coupled with mass-spectrometry (GC-MS) and total organic carbon (TOC) measurements were carried out. First results show that studied samples (dopplerites, internal sediments and sphalerites) from various locations of the Silesian-Cracow Zn-Pb ore districts are organic matter-rich rocks/minerals. Dopplerite OM content varies from 35% to over 50% TOC, internal sediments contain up to 14% TOC, while sphalerites usually have 0.1–0.2% TOC (although there are some samples with over 1% TOC). The contents of total sulfur (TS) are highly variable and depend on the degree of sulfides mineralization. For dopplerites, TS is in the range of 2–8%, while the internal sediments usually containing more sulfur (5–20% TS) because of their association with the ore minerals. The study of coaly matter extracts from the various localities of the Silesia-Cracow Zn-Pb ore districts using GC-MS revealed its immature nature.

Although hopanes distribution differs quite considerably between samples, all of them contain hop-13 (18)-ens, hop-17 (21)-ens and 17 $\beta$ , 21 $\beta$  (H)-hopans compounds typical for an immature OM, unstable in temperature exceeded 50–60°C (Karwowski et al. 2001). It is interesting, that the pilot investigations of OM using pyrolysis and off-line derivatization showed only the presence of small amounts of fatty acids, which did not confirm the proposed origin of these organic accumulations, according to which they were precipitated with humic acids due to the presence of Ca ions (Sass-Gustkiewicz & Kwecińska 1999).

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## THE RESULTS OF MULTISTAGE LIMING AND LACUSTRINE CHALK APPLICATION IN AMD WATER RESERVOIR IN THE MUSKAU ARCH NEAR ŁĘKNICA, W POLAND

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The Muskau Arc is a 40 km long moraine belt bent into a horseshoe-like shape pushed by the Mid Polish Glaciation, located in west Poland. Pyrite-bearing Neogene lignite deposits were mined there until the 1980s. The abandoned open pits filled with groundwater are forming a set of reservoirs called “Anthropogenic Lake District”. It consists of more than 100 reservoirs on the total area of more than 1500 square kilometers. Oxidation process of iron sulfide-containing lignite left in mining pits or deposited in dumps, exposed to atmospheric oxygen and water results in formation of acidic waters and precipitation of ochreous sediments. The water is characterized by high Fe and  $\text{SO}_4^{2-}$  content. This chemical association with low pH waters is causing the main environmental waste problem in this region, which is typical for most Acid Mine Drainage (AMD) areas.

The main goal of conducted experiment has been to examine the abilities of acid mine water remediation on the example of Muskau Arch lake named Africa. The chemical neutralization of acidic pH and removal of high salinity by precipitation was made by various substances application. The objective of this study was comparison of the potential effects of this treatments applied in several steps.

Africa is one of the largest and deepest reservoirs of Muskau Arch. This meromictic lake has constant vertical stratification characterized by diversity of physicochemical parameters and content of major ions. Water contained in the mixolimnion at the top (down to about 10 m depth from surface) is well mixed by air currents and saturated with oxygen. It has lower pH (pH = 2.75) and lower ion concentrations (the average TDS amounts to 2000 mg/L) than the bottom layer. Monimolimnion in the bottom part (below 10 m from

the surface) is anoxic, poor in oxygen, with higher pH (pH = 4.75) and salinity (TDS up to 6000 mg/L). Water in both layers is not mixing due to significant density difference preserving the geochemical stratification.

In the set of laboratory experiments samples of waters from both layers were mixed with different doses of lime and lacustrine chalk. The application was carried out over half a year in several steps, because of the ability of this water to acidify itself. In all cases, especially in second stage, the treatments lead to rapid increase of pH and to precipitation of different secondary phases, mostly gypsum and iron hydroxides (ferrihydrite, goethite and rare green rust). This results in removal of ferric and ferrous ions and reduction of sulfates content by close to 80%.

However effects was varying and depends on kind of treatment, layers, which have different acid neutralizing capacity, and step of dosing. pH of upper layer is lifted to about neutral value (7–8) by chalk dosing or slightly basic (9) in the case of liming. These treatments are successful already in first step application.

Hydrogen ion releasing in iron hydroxides precipitation process in bottom layer, due to occurring specific pH-Eh conditions, restrains neutralization effectiveness. Therefore next application steps are necessary to reach neutral pH (6–7) after chalk treatment or even alkaline (11–12) by liming.

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**PALAEOCLIMATE  
AND PALAEOENVIRONMENTAL RECORDS  
AT THE NEANDERTHAL LOCALITY GÁNOVCE –  
PRELIMINARY RESULTS**

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The best known and the the most important of Neanderthal sites in Slovakia is the travertine mound of Gánovce-Hrádok (49°01' N 20°19' E) with the sedimentary record from the Saalian termination up to the Holocene. A scientific research at the site was realized since 1880s, but the complex systematic research was realized only during 1955–1960, conditioned by the famous record of Neanderthal braincase in 1926. The research results have been published in the final report and within a monograph. The basic analysis of palaeontological findings of mammals was realized by Fejfar, who divided them into 6–7 groups, providing together with fossil molluscs (V. Ložek) and plants (V. Knebllová) a basic picture on both the climate and the palaeoenvironment in the vicinity of Gánovce during the formation of the travertine mound. Apart from remains of mammals, birds, and reptiles, the most important record at the site is represented by fossils of Neanderthal Man. The age of the place, where Neanderthal fossils have been found, was determined as 105,000 BP.

The environment of Neanderthals was distinctly changed during the Late Pleistocene in the whole area of their occurrence because of severe climatic changes. Differences found in the composition of fossil assemblages reflect those in the terrestrial environment. Based on the definition of the taxonomical diversity of extinct organisms, the palaeoenvironmental reconstruction, and the exact age determination of the fossil record, a definition of individual events is possible from the evolutionary-phylogenetic and the climatic-environmental viewpoints.

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## **GEOLOGICAL FACTORS INFLUENCING THE POSSIBILITIES OF DEFORMATIONS IN THE SHAFTS OF THE LEGNICA-GŁOGÓW COPPER AREA (LGOM)**

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On 23<sup>rd</sup> March 1957 the information appeared that in the Sieroszowice region copper rich shale had been discovered. Probably nobody realized how difficult the conditions of copper ores exploitation would be. On 4<sup>th</sup> April 1959 the team lead by Jan Wyżykowski presented the first geologic documentation of the Lubin-Sieroszowice deposit. Based on the results from 24 boreholes, the reserves of the deposit were estimated as more than one billion tons of the ore (Błądek et al. 2005). Decision to build a mining enterprise, consisting of four mines, was taken immediately. Nowadays the exploitation in the region of the Legnica-Głogów Copper Area (LGOM) is carried out by three units – Mining Enterprise (ME) ME “Lubin”, ME “Polkowice-Sieroszowice” and ME “Rudna”.

The deposit of copper ore is localized within a large structural unit – the Fore-Sudetic Monocline. The deposit rocks were formed in the Permian on the border between Rotliegend and Zechstein. They were formed as sandstones, carbonate rocks (limestones and dolomites) and shales (Kłapciński 1971, *Monografia KGHM...* 2007).

Mining areas are large. Geological conditions of subsequent parts of the deposit show diversity. This causes that the area of LGOM can be divided into two parts – northern and southern.

The southern part is characterized by a lower depth of the exploitations of the copper ore (ca. 600 m). The deposit is dipping in the angle of several degrees in the NE direction and its outcrops are in the southern part of the copper area (Stupnicka 1997, *Monografia KGHM...* 2007).

The southern part is situated on the border of two tectonic units (Fore-Sudetic Monocline and Fore-Sudetic Block). The dislocation system of central Odra River, of NW-SE direction (Oberc 1972, Tomaszewski 1978) forms the border of these units. Complicated tectonics of the area influences the possibility of making deformations in the rock mass and consequently in the shafts of KGHM Company.

Although faults occur in the whole area of LGOM, within the southern part they have additional meaning – make a potential way for migration of ground waters. This is significant for the discussed region because of the possibility of joining water-bearing horizons (contacting hydraulic layers of Buntsandstein, limestones and dolomites W-1). Water-bearing properties of the north region are much weaker. This is related to the occurrence of isolation layers (Wilk & Bocheńska red. 2003). Pores and caverns are filled with gypsum and calcite, and sometimes silt, which significantly limits the possibility of water migration.

Hydro-geological dichotomy of the area is also confirmed by the observations carried out during the exploitation. They show that 95–97% of general inflow to LGOM mines comes from the region of the south deposit (Wilk & Bocheńska red. 2003). Thus in the south the biggest depression funnels of subsequent water-bearing horizons (Zechstein, Cenozoic) are observed. The biggest subsidence troughs caused by mining exploitation and related drainage are also present there (Popiołek et al. 2009).

The factors mentioned above have a strong influence on the spatial distribution of the rock mass deformation. The described dichotomy of LGOM also refers to the surveying of the effects of exploitation. The results of the monitoring indicate the increased values of subsidence of vertical strains in the shafts located in the southern part of the area. Of course, the distribution and intensity of the carried out exploitation should be taken into account. Nevertheless, in majority of cases, the thesis that in the southern region the accumulation of unfavourable geologic, hydrogeologic and other conditions results is confirmed. What is the most important for the studies, these cause increased deformation in mining shafts of LGOM.

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**PYRITE FRAMBOID STUDY  
OF IREVIKEN EVENT –  
EXAMPLE OF WILKÓW BOREHOLE,  
HOLY CROSS MOUNTAINS**

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The Ireviken Event was a minor extinction event at the Llandovery-Wenlock boundary. Whole event took place during regression, after the onset of global sea-level fall and finished before the maximum lowstand (Calner 2008). The mechanism responsible for the event originated most probably in the deep oceans, and made its way into the shallower shelf seas. Accordingly, shallow-water reefs were scarcely affected, while pelagic and hemipelagic organisms were hit hardest. Subsequent to the first extinctions, excursions in the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  records are observed;  $\delta^{13}\text{C}$  rises from +1.4‰ to +4.5‰, while  $\delta^{18}\text{O}$  increases from –5.6‰ to –5.0‰ (Munnecke et al. 2003). Here, identification of redox conditions was carried out using pyrite framboid diameters. The size distribution of framboids supplies information about ancient redox conditions at a fine scale resolution (Wignall & Newton 1998). Measurements of pyrite framboid diameters were carried out using Scanning Electron Microscope (SEM) in backscattered electrons (BSE). Twenty seven samples of sedimentary rocks from Wilków IG1 borehole were analysed. Based on graptolite stratigraphy, the Ireviken Event, in the described borehole, starts at a depth of 585 meters and finishes at ca. 581 meters. Almost 10 m before this Silurian event, framboids are not observed. It may suggest rather oxic conditions during sedimentation. The beginning of Ireviken Event is characterized by presence of tiny framboids with a mean diameter of 4.55  $\mu\text{m}$  (minimum value of 2.77  $\mu\text{m}$ , maximum value of 9.27  $\mu\text{m}$ ). After that euxinic pulse, anoxic conditions have changed gradually to more oxic/disoxic, which is expressed by larger pyrite diameters. The average values of framboid diameters for the central part of the extinction event are ranging from 5.35  $\mu\text{m}$  to 8.7  $\mu\text{m}$ . Euxinic conditions in water column returned at the end of Ireviken Event and were again characterized by small pyrite framboid diameters. The fluctuations during this extinction event are clearly seen and may suggest intensive sea level oscillations.

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## **CALCITE VEINS IN THE TEREBOWIEC SYNCLINE, THE SILESIA NAPPE, SOUTHEASTERN POLAND**

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The Terebowiec syncline is a part of the Zatwarnica fold which is located in the SE part of Silesian Nappe in the Polish Outer Carpathians. The Krosno beds (Late Oligocene) – thick-bedded sandstones and thin-bedded flysch consist of claystone alternating by mudstones and thin-bedded sandstones that occur in the axial part of the syncline. In the Wołosaty stream valley which crosses the syncline, two outcrops (Bereżki 1 and Bereżki 2) of thin-bedded Krosno sandstones and shales with calcite mineralization have been studied near village of Bereżki. The aim of the study was to recognize and compare calcite mineralization occurring in the Terebowiec syncline. Structural, petrographic, and isotopic ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) investigation have been carried out.

In the Bereżki 1 outcrop, calcite mineralization occurs in a fault zone. Blocky, fibrous, and stretched crystals form veins which contain numerous claystone inclusions. Fibrous calcite with these inclusions shows curved shape. Blocky calcite shows twin lamellae. For fibrous calcite the  $\delta^{18}\text{O}$  value is  $-9.23\%$ , and the  $\delta^{13}\text{C}$  value is  $-1.56\%$ .

In the Bereżki 2 outcrop, calcite mineralization occurs in several faults and joint fractures. Joint fracture (20 cm thick) filled by blocky calcite vein has been the main object of analysis. Three generations of calcite were recognized. The oldest, first generation is formed by small crystals (to 0.3 cm) with twins, growing directly on the fracture wall. The second generation is formed by big transparent crystals (up to 1 cm) with twins. These crystals show the zonality based on the cathodoluminescence study. The youngest, third generation is composed of small (to 0.1 cm) crystals without twins, growing directly on crystals which form second generation with observed hydrocarbon inclusions. In veins from the Bereżki 2 the  $\delta^{18}\text{O}$  values are between  $-9.88\%$  and  $-6.81\%$  and  $\delta^{13}\text{C}$  values vary from  $-0.24\%$  to  $0.11\%$ . Values of oxygen isotopes in the second generation are little higher than in other generations. One value of oxygen isotope ( $-6.81\%$ ) in the third generation is also distinct from other values. Two samples of host sandstone and shale have been

investigated and the results of isotopic studies are different than in veins. Both C and O values are higher (for sandstone  $\delta^{18}\text{O}$   $-4.59\text{‰}$  and  $\delta^{13}\text{C}$   $0.97\text{‰}$ , for shale  $\delta^{18}\text{O}$   $-4.12\text{‰}$  and  $\delta^{13}\text{C}$   $0.96\text{‰}$ ).

Values of O and C isotopes suggest that in both studied sites filling of veins started in similar temperature and salinity conditions. However, the higher oxygen isotope values in sandstone and shale are probably connected with high contents of primary  $\text{CaCO}_3$ .

In the Berezki 1 site, the fibrous calcites are synkinematic, related to faulting. Numerous claystone inclusions indicate that calcite veins were formed in soft sediment. In the Berezki 2 site, the veins are related to brittle deformation. Based on the relationship between types of deformation and isotopic composition of calcites it seems that mineralization started in sediments showing differentiated lithification.

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## QUALITY OF GROUNDWATER IN THE GROUNDWATER BODY SK1000600P

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The accession of Slovak Republic to the European Union created a commitment and a duty to implement the European Parliament Directive 2000/60/EC that sets the framework for the Community action in the field of water policy. Within the scope of this implementation, 101 groundwater bodies were established, 16 are in the Quaternary sediments, 59 in of pre-Quaternary sediments and 26 in geothermal settings. Seven Quaternary bodies were classified during evaluation chemical analyses as having a bad chemical state (Kuníková et al. 2005, Kullman et al. 2006). We focus on one of these groundwater bodies, namely on SK1000600P. SK1000600P is located in the South-Eastern part of the Podunajská nížina and covers an area of 515 km<sup>2</sup>. The groundwater collection in the SK1000600P body consists of alluvial and terrace gravels, sandy gravels and sands. Fluvial sediments of river floodplains and terraces belong to the most water-saturated beds. Hydrogeological character depends on the granulometric composition, width and position in regards to the surface flow. The rest of Quaternary sediments belong to low impermeable aquifers. The hydrogeological collectors possess predominant intergranular permeability. The average width of aquifer is < 10 m (Vaškovský et al. 1982). The general direction of flow of underground water in the alluvial floodplain of the Quaternary body is more or less parallel with the main flow (Malík et al. 2005).

The quality of groundwater SK1000600P formation was analysed based on chemical analyses from seven observatory boreholes (Hurbanovo-Malý Vek, Iža-Bokroš, Komárno-Komočín, Iža, Moča and Kravany) of the Slovak Hydrometeorological Institute network, during the 2002–2010 time period. The current state was evaluated based on threshold values (the Decree of the Government of the Slovak Republic 282/2010) and limit values (the Decree of the Government of the Slovak Republic 496/2010).

The basic chemical composition of the groundwater varies. The calcium and magnesium are considered dominant with sodium also having a significant presence. In the anion

spectrum carbonates can be considered dominant, the influence of the secondary pollution is reflected in a significant share of sulphates. According to the Palmer-Gazda classification, the groundwater body contains groundwater of the basically distinct Ca-Mg-HCO<sub>3</sub> type up to the basically indistinct Ca-SO<sub>4</sub> type. The overall TDS falls into the range from 0.6 g·L<sup>-1</sup> to 1.4 g·L<sup>-1</sup>. When analysing the parameters of the groundwater quality we found out, that the most polluted groundwater comes from the boreholes Iža-Bokroš and Iža that feature an increase over the threshold limit values for Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Fe, Mn, Cl<sup>-</sup> a SO<sub>4</sub><sup>2-</sup>. It should be noted, that for example the primary origin of sulfates cannot account for such high concentration which means that it was most probably caused by anthropogenic activity.

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## **SORPTION OF SELECTED ORGANIC COMPOUNDS ON ORGANO-ZEOLITES**

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Zeolites are microporous, aluminosilicate minerals that are characterized by cage-like structures, high surface areas, and high cation-exchange capacities. They are widely used as commercial adsorbents: in industry for water purification; as catalysts, for the preparation of advanced materials and in nuclear reprocessing. Zeolites are used to extract nitrogen from the air in order to increase oxygen content for both industrial and medical purposes and they are also used in agriculture. Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Currently, the world's annual production of natural zeolite is about 3 million tonnes. Demand for zeolites is extremely high, with their usage continually on the increase. Unfortunately, natural zeolites contain an admixture which reduces the purity of their composition. Furthermore, natural zeolites' properties (CEC, charge, size of cavities etc.) make it difficult to implement them in specific chemical processes – further perpetuating the demand for synthetic zeolites. Sorption of apolar substances on zeolites is low because the process takes place only on the outer surface of the crystallites. To increase the chemical affinity of the zeolite's surface to the apolar organic compounds, organic ions from quaternary ammonium salts such as hexadecyltrimethylammonium bromide (HDTMA) and dodecyltrimethylammonium chloride (DDTMA), replaced the natural cations on their exchangeable positions. HDTMA and DDTMA have a strong affinity for the zeolite's surface and replace positively charged inorganic counter-ions and neutralize the negative surface charge of the zeolite. The aim of the study was to determine the effectiveness of sorption for organically modified zeolites produced from fly ash for benzene, toluene, ethylbenzene, xylene, phenol, aniline, naphthalene, gasoline, phenanthrene, anthracene and pyrene.

Material used in this study was an X-type zeolite prepared from coal fly ash. As a result of alkaline reaction of fly ash with NaOH, experimental cases bring zeolitic materials that are rich in a Na-X phase. The synthesis was performed by pouring 400 mL of an aqueous solution of NaOH onto 20 g of fly ash. This process was carried out for 24 hours at 75°C. After a series of reactions, the material was washed twice with distilled water to remove the excess NaOH solution. The result of this process was to ultimately obtain a product containing 60% zeolite. HDTMA and DDTMA were adsorbed on a synthetic zeolite in amounts of 1.0 and 2.0 of the external cation exchange capacity (ECEC) in quantities of 24.4 mmol and 48.8 mmol per 100 g of zeolite respectively. In order to select the optimal conditions for modification, the test was performed with different ratios of the solid product (zeolite) to the solution (aqueous solution of ammonium salts). Ratios used were: 1:10, 1:20, 1:30, 1:40, with modification temperature: room temperature, 40°C, 60°C and 80°C. On Surfactant-Modified Zeolite (SMZ) sorption of apolar compounds was performed. 200 mg of the organo-zeolite was placed in a tube and 10 cm<sup>3</sup> aqueous of benzene, toluene, ethylbenzene, xylene, phenol, aniline, naphthalene, gasoline, phenanthrene, anthracene and pyrene was added.

After modification with the HDTMA and DDTMA surfactans, the zeolite used in this work shows a significant ability to remove organic contamination from aqueous solution. As a result of this, the maximum sorption capacity of organo-zeolites and zeolites in terms of these compounds was ultimately determined. Synthetic zeolites exhibit very good sorption properties and HDTMA proved to be a better surface modifier than DDTMA. Sorption efficiencies of apolar compounds were observed at greater than 80% for all compounds in solutions. The results of this research can be used in environmental protection as well as for further study on the properties of SMZ and their potential industrial applications.

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## CELLULAR AUTOMATA FOR SEISMIC TRAVEL TIME ESTIMATION

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In this work, the application of the cellular automata for the seismic first breaks time estimation is presented. Cellular automata (CA) algorithms are usually described by set of simple rules applied onto the grid of cells, which can represent one of the few different discrete states. In spite of this simplicity, these algorithms can still simulate variety of complex physical processes, i.e. model the fluids or gases behavior, but also simulate and predict forests fire or the spread of diseases (Turcotte 1997). What is more, these algorithms are easy to accelerate using one of the most advanced parallelization techniques, like graphics card programming – the calculation can be then performed even 1000 times faster.

In this work one of the popular CA, presented by Hardy et al. (1973), was modified, according to Rothman (1987), to perform the simulation of the seismic wave propagation in geological medium. This CA was initially designed to simulate gas behavior in a reservoir, but it was modified in the following way: each cell of the grid contains set of values, which represents particles – positive and negative – that describes expansion and compression, respectively, of that cell. Then, both particle sets are calculated separately in two steps: the first is the propagation, when each particle is moved to next cell according to its movement; the second is collision, when rules are applied on each particle, if there is more than one particle in the cell. The collision rules can be divided into categories that represent their complexity, i.e. more complex behavior can be achieved if static particles are implemented, but this requires additional rules of collisions with moving particles. All the rules have to preserve the principle of conservation of mass and momentum.

The major modification of the algorithm described by Rothman (1987) is the implementation of the Boltzmann lattice method (Huang 2007), which changes the regular rectangular cellular grid for the triangular network. This modification provides more option when implementing algorithm, especially the collisions rules. On the one hand, triangular grid requires slightly different approach to represent it in computer memory, just like

the implementations of the rules. On the other hand, triangular grid can produce better simulation results compared to the classical rectangular grid.

The results of this simulation can be used in further calculations, i.e. to solve the inverse problem. To make this CA useful, it has to provide either better than similar methods errorless results or significantly shorter computation time with comparable errors. In this work the CA is compared with mathematical wave propagation solution and the Shortest Path Method (SPM).

SPM uses graph theory to reconstruct seismic ray trajectory in a real, geological medium. This method was first described in Moser (1991). As it is more time-consuming than linear method, for large model the parallel approach is necessary (Pieta et al. 2013). One of the major advantages is the possibility of optimization of the modeling quality and calculation time by adjusting number of accessory nodes. This method is easily extendable to cover the anisotropy case.

This work describes, verifies and validates the CA algorithms to check the potential of use in further calculations for solving the forward problem in seismic modeling. The research shows that the presented CA method, in spite of its speed and parallelization options, can not be applied if high precision is required.

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**MODELING OF SEDIMENTATION  
IN JURASSIC BASIN  
BASED ON ANALYSIS OF MAPS OF THICKNESSES  
(CENTRAL PART OF THE BARENTS SEA  
MEGADEPRESSION)**

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Stratigraphic subdivisions of deposits in the Barents Sea is often based only on rare cores, which usually does not allow distinguishing facies of the stratigraphic units, and possible facies zoning of coeval strata. Thus, the facies zonation in the Barents Sea, reconstructed at intervals of geologic time, can be considered as arbitrary. Usually this zoning was determined by means of available data on the adjacent land and general trend of the evolution of sedimentation in the Barents region. In this regard, within the oil and gas prospects scientists were asked not to use the classic facial analysis but to use modeling of sedimentation and as a consequence – identifying patterns of distribution of sediments with improved reservoir properties.

The materials from marine wells and analysis of maps of thicknesses were used for modeling sedimentation in Jurassic time in the Barents Sea megadepression. Maps were built on the seismic materials of MAGE (Murmansk Arctic Geological Expedition). According to the interpretation of seismic profiles three stages of sedimentation were considered: Early Jurassic, Middle Jurassic and Late Jurassic. Every stage is characterized by its environment of sedimentation and therefore by its own characteristics of hydrodynamic conditions.

**Early Jurassic stage.** For the most complete characterization of sedimentation of this stage we must be aware about environment of sedimentation in Late Triassic. In 2010, the author did a report which name was *Sequence stratigraphy for studying of oil and gas potential of Triassic deposits of the Eastern part of Barents Sea*. Biolithostratigraphical correlation scheme used in that work helped to identify sequence of the second order.

This sequence begins with transgressive tract in Induan and ends with lowstand system tract on boundary of Carnian and Norian. This information allows us describing transgression in Early Jurassic time. Analysis of the model of sedimentation for Early Jurassic stage which consists of map of thicknesses and 3-D visualization clearly confirms this description.

**Middle Jurassic stage.** Analysis of the model of sedimentation for Middle Jurassic stage allows making conclusions about the active development (peak) of transgression. The increase of the alluvial fan graphically shows this development. Stokman, Ledovoe and Ludlovskoe fields as well as many local structures like Akhmatovskaya, Severo-Nadezhdinskaya and others belong to proximal part of the alluvial fan. Also we can see gas and gas-condensate productive horizons in this interval of x-section of Shtokman, Ledovoe and Ludlovskoe fields determining favorable conditions for reservoirs.

**Late Jurassic stage.** Analysis of the model of sedimentation for Late Jurassic stage allows making conclusions about the beginning of regression. We can see decrease of depression which graphically shows this fact. Two small depocentres of depression and significant decrease of proximal part of alluvial fan show favorable conditions for cover rocks.

Analysis of maps of thicknesses, in particular models of sedimentation, can show us maximum thicknesses of reservoirs and cover rocks, so we can make conclusions about oil, gas and condensate traps and deposits in prospect areas.



## DISSOLUTION OF MIMETITE $Pb_5(AsO_4)_3Cl$ IN MALIC ACID SOLUTIONS

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Pentavalent arsenic and lead are presently considered to be one of the major soil pollutants. These and widespread elements occur in very low concentrations. Their natural concentrations in soils and waters are the results of leaching from rocks containing Pb and As(V) minerals. However, concentration of these elements in environment can be drastically raised by anthropogenic processes, such as coal combustion, mining, metallurgy, pesticides application or glass manufacturing. Leaching of Pb and As(V) from soils and residues containing lead arsenates may cause contamination of the pedosphere.

Arsenic and lead minerals are relatively numerous but in nature occur occasionally. The most common secondary As(V) and Pb minerals are schultenite ( $PbHAsO_4$ ), mimetite ( $Pb_5(AsO_4)_3Cl$ ), hydroxymimetite ( $Pb_5(AsO_4)_3OH$ ) and sahlinitite ( $Pb_{14}(AsO_4)_2O_9Cl_4$ ), though mimetite is considered to be prevalent (Bajda 2011). Mimetite, as a slightly soluble and thermodynamically stable mineral, especially at pH above 5 characteristic to natural waters and soil solutions, is considered to have great possibilities to be applied in remediation procedures (Bajda 2010). Mobility and bioavailability of lead and arsenic can be controlled by mimetite crystallization at mentioned pH range, then important aim arises, to determine stability of  $Pb_5(AsO_4)_3Cl$  at pH below 5. Solubilization of extremely insoluble apatite through efficient ligand-promoted organic complexation of metals has been observed before, which suggests that mimetite dissolution may be similarly enhanced by low-molecular-weight organic acids (LMWOAs) (Bajda 2011). The influence of LMWOAs on mimetite stability was investigated, but malic acid was not included in these experiments, which is a purpose of this research.

Batch dissolution experiments were carried out with use of mimetite synthesized of  $Na_2HAsO_4 \cdot 7H_2O$ , KCl and  $Pb(NO_3)_2$ . Malic acid concentrations selected to these experiments were 0.1 mM; 0.5 mM; 1 mM; 5 mM; 10 mM. As a control there were used three

non-organic solutions with pH set using  $\text{HNO}_3$  to be similar to the primary pH measured in certain organic acid solutions. The purpose of performing non-organic samples was to compare effect of pH on mimetite dissolution at parallel pH value in organic and inorganic acid solutions. Duration of the experiment was 120 hours and samples were taken after 24, 48, and 120 hours. The total Pb concentration was determined by atomic absorption spectroscopy (AAS) and pentavalent As concentration were determined colorimetrically by the molybdene blue method (UV-Vis).

Data obtained for the experiment allowed to notice that the state of equilibrium was reached before 24 hours regardless of pH and organics concentration. It was found that lower values of pH enhance mimetite dissolution, which is confirmation of previously run studies (Bajda 2011, Magalhaes & Silva 2003). Solubility of mimetite expressed by the amount of As(V) and Pb released to the solution was significantly higher at low pH. Similar correlation was observed investigating solubility and acid concentration: the higher the acid concentration is, the more elements were released to the solution. The total concentration of As(V) in 10 mM acid solution was about 20 times greater than in 0.1 mM. For lead this ratio was lower and equaled 11.4.

This mechanism mainly depends on free protons concentration and the process of protonation, which is proved by released curves for controls where samples containing inorganic nitric acid instead of malic also exhibit higher solubility of mimetite at low pH. However, because of Pb-malate complexes formation, presence of organic anions can noticeably increase the scale of mimetite decomposition. Complexation and protonation of mimetite surface are complementary and additive processes, which speeds up and intensifies mimetite dissolution. The difference between total As(V) in samples and controls was 12.5% for 5 mM and 26.5% for 1 mM while for Pb it was respectively 5.6% and 8.6%. This suggests that soil organic acids can potentially liberate Pb and As(V) from mimetite and thereby comprise a probable risk to the groundwater quality.

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**PRELIMINARY HYDROLOGICAL FORECAST  
FOR THE MAJES-SIGUAS PROJECT  
AND PROBLEMS ASSOCIATED  
WITH WATER MANAGEMENT  
IN THE AREQUIPA REGION IN SOUTHWESTERN PERU**

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The hydrotechnical project Majes-Siguas, started in 1973 and its aim is to direct waters flowing out from under the Nevado Mismi glaciers as also the rivers Apurimac and Colca to the desert plain Majes-Siguas westward from Arequipa. The situation was caused by diminishing sources of waters in this area. Little precipitation, weaker and weaker supply of the waters coming from the melting glacier mantles on the nearby volcanoes and additionally, the El Nino phenomenon, made the government ready to undertake the realization of this project in order to find a solution to the problems. Main goal is to provide people with water and increase the number of cultivable grounds supplying food for the rising amount of people in Arequipa as well as surrounding villages and towns.

Peru is a country where the water resources are disproportionately spread. More than 97% of the water resources occur in the less urban areas with scarce population. The smaller part of the resources is placed in the much more urbanized regions such as: Lima, Arequipa, Trujillo and Chiclayo with a majority reaching 65% of the population of Peru. 80.4% of GNP of this country also comes from these areas. Currently, 1,280,000 km<sup>2</sup> is being irrigated, which accounts for about 30% of the whole Peru ([www.ana.gob.pe](http://www.ana.gob.pe)). The goal of such countries policy is to increase the alimentary safeness and to develop agrarian policy. The electoral slogans such as: “Agua por todos”, meaning: “water for everyone”, attract more and more settlers to the regions of Majes, only making the problem worse, because the irrigation project Majes-Siguas, which disturbs the water relations in Arequipa, can lead to catastrophic changes in the future.

The whole investment is going to replace the well-prospering arable terrace system that formerly existed in the Colca Valley. Nowadays only 40% of the area of the terraces is being used. However, the ecological results of this project have already made their impact on the environment, it seems to be certain, that it would be much more difficult to encourage settlers to work in the high Andes, on a small and almost inaccessible fields. The substantial reduction of waters flowing into the Rio Colca is also noticeable, and in time this trend will be increasing because of the fact that the brooks from Altiplano, supplying the river, are directed to Rio Chilii from which water is extracted for Arequipa, a city of 800,000 people, struggling with a deficit of drinking water (Galaś 2008).

Another possible problem can be increasing salinity and contamination of soil, caused by enormous evaporation in this area, which in turn can contribute to making growing crops and farming virtually impossible.

According to the initial analysis of project Majes-Siguas, it can be concluded that it would be impossible to predict interchangeable results of this project without the development of a monitoring system. That is why, further research aimed at defining the exact hydrological forecast for this region appears to be justified. Soon, water balances for the mountain areas that supply the project Majes-Siguas as well as for the areas being subjected to direct irrigation will be performed. Moreover, the analysis of the changes in the chemical composition of soils will be carried out as well.

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**PALEOSTRUCTURAL AND SEDIMENTARY  
PROVENANCE ANALYSIS  
OF LOWER DEVONIAN-UPPER PERMIAN  
OIL AND GAS COMPLEXES  
OF THE TIMAN-PECHORA BASIN PROVINCE**

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Paleostructural analysis is based on well log data, the results of recent seismic work and also previous geological works of the Timan-Pechora Basin Province. The main purpose of this investigation is to define the main stages of the structural and tectonic development of the study area. Sedimentary basin analysis is a geologic method by which the history of a sedimentary basin is revealed, by analyzing the sediment fill itself. The results show the formation of sedimentation depocenters, the formation of barrier reefs and other features of a sedimentary basin. According to this analysis several sedimentary complexes were distinguished: Middle Ordovician-Lower Devonian, Middle Devonian-Sargaevskiy, Domanic-Tournaisian, Middle Visian-Lower Permian, Lower Permian, Upper Permian.

**Middle Ordovician-Lower Devonian.** Paleostructural surface of this oil and gas complex (OGC) have a complicated structure. In the central part of the study area is situated a large paleo-high bounded from the west, north and east by several deep depressions. Northern and eastern depressions in Ordovician time perhaps originated as aulacogens formed by deep faults.

Analysis of the thickness map allowed identifying three depocenters. It should be noted that in the Middle Ordovician-Early Devonian time there are two types of sedimentation. During the Early Ordovician and the first half of the Middle Ordovician terrigenous sedimentation prevailed (Severo-Zapadnaya-202 and B Ugrinskaya wells). During the Late Ordovician, Silurian and Devonian terrigenous sedimentation type changes to carbonate.

**Middle Devonian-Sargaevskiy.** Paleostructural surface of this complex contrasts with the previous one. In the Early and Middle Devonian tectonic structural alteration of

the surface happened. West depression in all probability was filled with deposits of Ordovician-Devonian and the end of time is formed by a large high, the central part of which is land. The eastern depression was significantly reduced in size. Two depressions in the Varandey-Azdvinskaya and Severo-Preduralskaya areas were separated by large arched high, the southern part of which was perhaps located outside of sedimentation area. The rest of the territory is a monocline, gradually deepening in the north-east. Analysis of the thickness map allowed identifying three depocenters. It should be noted that the formation of is OGC was in two stages: regressive and transgressive.

**Domanic-Tournasian.** Paleostuctural surface varies slightly. Western part of the study area is still a monocline complicated by two small uplifts. The eastern part has undergone tectonic reconstruction. The result is a large, complex depression, divided in the northern part by the small uplift.

Analysis of the thickness map allows identification of only one sedimentation depocenter, located in the land area of the Timan-Pechora Basin Province. Only the northern end of Domanic depression shows marine sedimentation.  $D_{3fr}$ - $D_{3fm}$  time is characterized by the accumulation of carbonate-terrigenous sediments, which by the end of early Famennian fill the Domanic depression. In the shallow-water part of the shelf, the carbonate phase of sedimentation begins. In the land area of the Timan-Pechora Basin Province reef rock and biostromes were formed.

**Lower-Middle Visean.** Tectonic reorganization divided the study area into two parts: a large uplift was elevated in the west and south-west part while in the east and north-east part shallow depression with marine type of sedimentation was formed.

**Middle Visean-Lower Permian.** Paleostuctural surface is characterized by the development of major depression in the central part of the study area. Depression is complicated by two cavities. In the south-west and south-east of the study area two major uplifts were formed. Late Visean is characterized by transgressive stage of development. Marine type of sedimentation covers the whole territory. Two depocenter of sedimentation were formed; one in the central part of the territory, the other – outside the study area. In both depocenters accumulation of terrigenous or carbonate-terrigenous sediments is possible. Early Permian period is characterized by calm tectonic conditions and, therefore, carbonate type of sedimentation.

**Lower Permian.** Paleostuctural surface changes. Artinskian-Kungurian time is characterized by a sharp shallowing marine basin, evidenced by small power complex. Relatively deep sea is preserved only in the east area. Accumulation of terrigenous (clay) material represent the type of sedimentation **Upper Permian.** Paleostuctural surface is characterized by fragmentation of the tectonic area, affected by several major fault zones, which formed depressions and uplifts. Based on this, we can assume that this process represent a fundamental tectonic reorganization, which controlled the sedimentation in the basin. The tectonics caused change in the type of sedimentation.

## **MATURITY OF MENILITE SHALES FROM POLISH OUTER CARPATHIANS BASED ON VITRINITE REFLECTANCE AND ROCK-EVAL PYROLYSIS DATA**

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Maturity of organic matter is one of the most important parameters characterizing the source rock. The maturation process depends on organic matter properties (kinetic parameters of kerogen) and burial history (temperature and time). The vitrinite reflectance measurements and Rock-Eval pyrolysis are widely used to characterize the maturity of organic matter occurring in the source rock. The purpose of the present study is to determine the thermal maturity of organic material present in Oligocene Menilite Shales from Polish Outer Carpathians based on vitrinite reflectance and Rock-Eval pyrolysis data. These organic-rich rocks are considered as a main source of oils accumulated in Outer Carpathian sequence (Kotarba & Koltun 2006).

Analysis has been performed on eleven claystone samples collected from outcrops of Dukla Unit. Part of them was taken in tectonic windows of Dukla Unit within Magura Unit: Świątkowa, Grybów and Ropa. Microscopic analysis of organic matter in reflected white light and fluorescence has been carried out for each sample. Macerals have been characterized and classified according to their optical properties and morphology.

Rock-Eval pyrolysis has been used to determine: a) the amount of free hydrocarbons present in the sample ( $S_1$ ), b) the amount of residual hydrocarbons generated during pyrolysis of organic matter ( $S_2$ ), c) the amount of  $\text{CO}_2$  generated during pyrolysis of organic matter ( $S_3$ ), d) the temperature of maximum of  $S_2$  peak ( $T_{\text{max}}$ ), e) the amount of  $\text{CO}_2$  received during oxidation of residual, carbon ( $S_4$ ). Based on received parameters the source-rock indices were calculated: a) total organic carbon  $\{\text{TOC} = [0.83(S_1 + S_2) + S_4]/10\}$ , b) hydrogen index ( $\text{HI} = 100S_2/\text{TOC}$ ), c) oxygen index ( $\text{OI} = 100S_3/\text{TOC}$ ), d) production index  $[\text{PI} = S_1/(S_1 + S_2)]$ .

Reflected white light optical research methods of organic matter enable to find in each studied sample macerals from vitrinite and inertinite group. Two generation of vitrinite has

been noticed during the studies. The first type has been represented by vitrinite *in situ*. The second one has been recognized as a dark, gelified vitrinite, filled in with some mineral or organic association. Inertinite macerals have been represented mostly by detritus material. Macerals from liptynite group have been recognized using fluorescent microscopy. These macerals occur commonly in each sample, what could indicate domination of oil-prone kerogen Type II.

The vitrinite reflectance measurements have been carried out for both types of vitrinite. The random reflectance  $R_r$  of organic matter varies between 0.45% and 0.9% for first type of vitrinite and from 0.2% to 0.66% for the second one.

Measurements of reflectance of vitrinite *in situ* have indicated that organic matter has reached the maturation stages of hydrocarbon generation corresponding to *oil window* phase. Values of selected parameters and indices received from Rock-Eval pyrolysis vary: TOC from 1.73 wt. % to 6.4 wt. % (median 4.3 wt. %), HI from 197 mg HC/g TOC to 681 mg HC/g TOC (median 342 mg HC/g TOC) and  $T_{max}$  from 421°C to 456°C (median 440°C). These data indicate that analysed samples are rich in organic matter, predominantly of oil-prone kerogen Type II. Rock-Eval  $T_{max}$  temperature values correlate well with reflectance of organic matter for vitrinite *in situ*; for dark vitrinite this correlation is not visible.

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## HALLOYSITE-BASED MATERIAL WITH IMPROVED CATION SORPTION PROPERTIES

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Halloysite is 1:1 layered, dioctahedral phyllosilicate. It belongs to kaolinite subgroup of kaolinite-serpentine group. Halloysite is often defined as a hydrated phase of kaolinite. Two types of this mineral are distinguished: hydrated 10 Å-halloysite, with water molecules in the interlayer space and dehydrated 7 Å-halloysite. Widely conducted research on modified kaolin group minerals, either intercalates or grafted compounds with selected organic molecules opened many possibilities for using this layered aluminosilicate in industry and environmental protection. One of the possible applications is the sorption of heavy metals. For the raw halloysite the sorption exclusively takes place on the particles surface. The interlayer space of the mineral is not accessible for cations. Thus the research goal was to provide the access of cations to the interlayer using organic modifications with selected aminoalcohols (Letaief & Detellier 2007). Moreover, the sorption properties of the new material towards selected cations were examined.

Dehydrated type of halloysite from Polish deposit Dunino located near Legnica, which is still exploited was used for the experiments. Halloysite-dimethyl sulfoxide (DMSO) complex was used as a precursor. For this purpose 12.5 g of halloysite was reacted with a solution containing 90 mL of DMSO and 10 mL of H<sub>2</sub>O at room temperature for 7 days. Afterwards the sample was centrifuged and dried at 65°C for 24 h (HDMSO sample). In the next step, the HDMSO was reacted with diethanolamine (DEOA) or triethanolamine (TEOA) at 180°C under argon for 24 h. Finally, it was washed with isopropanol (HTEOA-I sample) and subsequently with water (HTEOA-W sample). The samples were examined by X-ray diffraction (XRD), infrared spectroscopy (IR) and CHNS elemental analysis.

The XRD diffraction patterns of HDMSO with  $d_{001}=11.3$  Å confirmed the intercalation of halloysite with DMSO. The  $d_{001}$  peaks for the HTEOA-I and HTEOA-W samples were found at 11.3 Å and 10.8 Å, respectively. In turn, the  $d_{001}$  peaks for the HDEOA-I and HDEOA-W were found at 11.3 Å and 10.3 Å, respectively. The  $d_{001}$  decrease after water

washing was due to removal of the DMSO remnants and intercalated however not grafted aminoalcohol molecules from the interlayer space. The difference between the  $d_{001}$  values for the HDEOA-W and HTEOA-W results from the size of the organic molecules. The IR bands related to hydrogen bonds between DMSO and kaolinite OH groups were observed at  $3539\text{ cm}^{-1}$  and  $3504\text{ cm}^{-1}$ . The formation of HDEOA and HTEOA was confirmed by the disappearance of peaks characteristic for the HDMSO and the presence of C-H stretching vibrations in the  $3000\text{--}2800\text{ cm}^{-1}$  region. As the structure of the obtained materials was resistant to water washing they can be named as grafted compounds (Letaief & Detellier 2007, Matusik et al. 2012). The CHNS analysis allowed to calculate the theoretical sorption capacity of the materials (HDEOA: 264 mmol/kg, HTEOA: 355 mmol/kg) assuming that the center, which attracts cations was connected with nitrogen electron pair of aminoalcohols. The materials were tested towards lead sorption. The equilibrium experiments were carried out in the Pb concentration range 0.005–5.0 mmol/L at pH 5. The materials were shaken in Pb solutions (20 g/L ratio) for 24 hours at room temperature. The concentration of Pb was measured using atomic absorption spectroscopy method (AAS).

Sorption of Pb on unmodified halloysite reached  $\sim 37$  mmol/kg for its highest concentration and is relatively high as for the minerals from kaolinite group. However, the sorption for the halloysite modified with aminoalcohols is significantly higher. It was equal to  $\sim 57$  mmol/kg for the HTEOA and  $\sim 62$  mmol/kg for the HDEOA. It seems that the structure of molecules determines the sorption capacity. The TEOA has three alkyl chains linked to the nitrogen and the DEOA has two chains. This may cause reduced availability of nitrogen for cations due to steric effects. Therefore, the HDEOA complex achieves higher sorption values. The pH after sorption on the modified halloysite increases rapidly in contrast to raw halloysite which is probably due to adsorption of protons to nitrogen and their competition with lead. This affects the sorption capacity and will be the subject of further study.

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## **STATIC 3D MODEL OF THE ROTLIEGEND DEPOSITS – CASE STUDY FROM NATURAL GAS FIELD AREA, FORE-SUDETIC MONOCLINE, WESTERN POLAND**

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The “Z” natural gas field is located in the southern part of the Fore-Sudetic Monocline, in the western part of Poland. Rotliegend sandstones, characterized by good reservoir properties are located in the Polish part of the Southern Permian Basin (Gast et al. 2010). The “Z” gas deposit was discovered in 1978. Reservoir “Z” structure is a regular, oval brachyanticline. The culminations are separated by a shallow depression in which the top of Rotliegend complex is located at depth somewhat less than – 1275 m bsl. Massive type accumulation covers about 25 km<sup>2</sup> and shows a height up to about 105 m (Karnkowski 1999).

3D static modelling was performed using Petrel software from Schlumberger. Typical workflows for modelling of oil and gas reservoirs were applied (e.g. Zakrevsky 2011). Structural model was created by 100 m × 100 m grid increment. Ten proportional layers of reservoir zone were set resulting in model composed of over 1,000,000 cells. The base case model assumed gas/water contact at 1345 m bsl. These models were result of geostatistical simulation based on Kriging technique.

The quality and number of the input data used to develop parametric models play a major role.

The most important parameters characterizing the reservoir rocks are: porosity, permeability and shale volume (vshale). Average petrophysical parameters based on base case model in the area are: 15% for porosity, 45 mD for permeability and 14% for vshale.

Performed structural-parametric models of the Żuchłów gas field can be successfully used for dynamic simulation and reserves estimation.

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## STRUCTURE AND MESOZOIC TECTONICS OF THE SOUTHEASTERN TAIMYR FOLD AND THRUST BELT

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The Taimyr fold and thrust belt (FTB) consists of several zones that show evidence for Precambrian, late Paleozoic (Hercynian), and Mesozoic tectonic events. Most scientists point to Precambrian and late Paleozoic compression as the most intense event, although Zonenshain et al. (1990) argued for a strong Mesozoic tectonic event. Our studies of the Central and Southern Taimyr done in 2005–2012 in the frame of projects supported by the State geological mapping program and by TGS-NOPEC Company also points to important role of the Mesozoic tectonics. The main results are summarized in the following points:

1. The only clear angular unconformity in the sedimentary succession of the Central and Southern Taimyr is between Vendian and underlying rocks. Vendian-Triassic succession does not contain unconformities, although some hiatuses may occur.
2. Pre-Rhaetian unconformity (previously interpreted as pre-Jurassic) may be related to extension event as well as to compression event.
3. Folds in Cambrian up to Upper Permian rock units have very similar geometry.
4. In the eastern part of Southern Taimyr (Tsvetkova Cape area) Permian to Jurassic rocks show similar structural style.
5. Stress axes orientation estimated from the fracture study in Riphean rocks in the Central Taimyr and Permian up to Upper Jurassic sediments in the eastern part of Southern Taimyr (Tsvetkova Cape area) is very similar.
6. Apatite fission track study of samples from the Tsvetkova Cape area point to ca. 150–125 Ma and 75–60 Ma uplift/erosion events
7. In the eastern part of Southern Taimyr all compression-related structures were affected by a younger extension.

In summary, our observations do not show evidence for a strong late Paleozoic compression in the Central and Southern Taimyr. Granite intrusions, previously interpreted as Carboniferous, are ca. 250 Ma and may be presumably linked to the Norilsk trap LIP magmatic event. Also worth noting is that there are no Paleozoic ophiolite complexes within Taimyr FTB.

Similarity in fold geometry and stress axes orientation shows that Vendian and younger rocks up to Permian in the Central Taimyr as well as Permian and Mesozoic rocks of the Southern Taimyr were mainly deformed during Mesozoic (Early and/or Late Cretaceous) compressional event, also recognized by brittle fractures in the Riphean rock units. These events are approximately synchronous to major collisional processes occurred in latest Jurassic-Cretaceous time in the northeast Asia and may reflect a connection between Southern Taimyr and Mesozoic fold belts of the northeast Asia. The final extension best documented in the Tsvetkova Cape area likely reflects tectonic relaxation processes right after the compressional event and opening of the Laptev Sea rifted sedimentary basin in Late Cretaceous-Cenozoic.