

## Characteristics of main research directions investigated at the institute and the achievements 2010–2014

Institute	Institute of Rock Structure and Mechanics of the CAS, v. v. i.
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Generally, the **Institute of Rock Structure and Mechanics of the CAS** is concerned in studies of structure and properties of rock medium, rocks, derived inorganic and organic materials and special composite materials. The subjects of investigation are natural and induced phenomena and processes affecting behaviour, development and stability of rocks in their natural location in earth crust. Advanced monitoring and laboratory methods are applied to constitute general findings and to set up conditions for their practical exploitation.

Research in the IRSM covers two main research fields according to generally used classification - Natural Sciences and Engineering and Technology. Within the field of Natural Sciences the research is mainly focused on Earth and related environmental- and geosciences. Within the field of Engineering and Technology the research is mainly focused to Materials engineering, Material science and Nanotechnology. Some of the main results presented here belong also to the field of Medical and Health Sciences.

Several new, progressive research areas have been strongly developing in the IRSM since 2010, such as paleoseismology, research of weathering of carbonates and sandstones, application of new technologies in geoscience (TLS, UAV, ERT, etc.) or study of fluid-induced micro-seismicity.

In the framework of Earth and related environmental sciences, the main research activities are focused on:

1. natural hazards: research of landslides and slope deformation (monitoring, hazard and risk assessment), monitoring and analyses of micro-movements on tectonic faults, paleoseismology and tectonic geomorphology, research on weathering of carbonate rocks and sandstones, seismological studies (seismic hazard analysis, moment tensor inversion and evaluation of possible precursors), monitoring and analyses of fluid-induced micro-seismicity, applied geophysics.
2. geochemistry: applications of coal and organic petrology and geochemistry in geology and environmental studies, application of geochemical methods from environment to medicine, sorption and texture properties of materials with significance for natural and anthropogenic processes and geochemistry and petrology of granite suites.

In the framework of Materials engineering, Material science and Nanotechnology, the main research areas are:

1. advanced composite materials: composite materials for tissue engineering and medicine, heat-resistant composites,
2. special glasses: structure of the industrial glass melting process, impact of factors on the melt flow character, bubble nucleation effects the glass melting process, special glasses for photonics and optoelectronics,
3. methods of processing of waste materials,
4. geopolymer materials: synthesis, properties and applications,
5. materials with magnetic properties: characteristics and applications.

### Research organization

The research in the IRSM is performed by 5 research departments (Department of Materials Structure and Properties, Department of Composites and Carbon Materials, Department of Geochemistry, Department of Seismotectonics, and Department of Engineering Geology), 2 joint research laboratories (Laboratory of Inorganic Materials, managed by IRSM and Faculty of Chemical Technology, University of Chemistry and Technology in Prague and Laboratory of sorption and porosimetric analysis managed by IRSM and Faculty of Science, Charles University in Prague) and in the scope of the World Centre of Excellence for Landslides Reduction (managed by IRSM and Faculty of Science, Charles University in Prague).

During the evaluation period, changes in the organizational structure of the IRSM were performed. In 2012, the Dpt. of Geodynamics was disbanded and part of its activities and young researchers were transferred to the Dpt. of Engineering Geology. In the same year, the team of Laboratory of Inorganic Materials joined the IRSM (formerly joint research centre of IRSM and UCT). By joining the LIM with the Dpt. of Geopolymer Chemistry was formed a new scientific department - Dpt. of Materials Structure and Properties. In 2013, the former department of Seismology was restructured due to lack of results. The department was renamed Dpt. of Seismotectonics, and a new head was appointed after a public competition. In 2013, the new heads were appointed also in the Dpts. of Geochemistry and Composites and Carbon Materials, in both cases young successful researchers replaced retired predecessors.

### **Summary of results**

In the period 2010 – 2014, the researchers of the IRSM worked on 57 projects (25 GA CR projects, 6 GA AS projects, 3 TA CR projects, 8 Ministry of Education, Youth and Sports projects, 9 Ministry of Industry and Trade projects, 1 Ministry of Agriculture project, 1 Ministry of the Interior project, and 2 projects by other providers). The IRSM is participating on an infrastructure project financed by Ministry of Education, Youth and Sports - project CzechGeo, as a national part of European Infrastructure Project EPOS (European Plate Observatory System).

The results of the research work were published as follows: 230 articles in IF journals, 75 in peer-reviewed journals, 5 books and 35 chapters in books were published, 63 reviewed contributions in proceedings. 7 results were patented, and 47 more applied research results were produced. 2 most significant scientific findings were published in the most impacted journals as Nature and Nature Geosciences.

### **Supporting research infrastructures**

The IRSM maintains currently 5 research infrastructures in cooperation with the Geophysical Institute AS CR, and 4 more research infrastructures alone. List of infrastructures is included in Appendix 3.3 – 5 - Administration of research infrastructures. In the scope of these research infrastructures, the IRSM performs regular monitoring in EU (CR, Slovakia, Poland, Germany, Belgium, Italy, Austria, Slovenia, Bulgaria, Greece and Spain – Canary Isles) and in Switzerland, Norway - Svalbard and Ukraine. Within the frame of the global infrastructure network cooperating with the European networks, the monitoring is being performed in USA, Peru, Iceland, Indonesia, Armenia, and Kyrgyzstan.

### **The selection of the main achievements of IRSM in period 2010 - 2014**

## **In the scope of international-based collaborations with EU research institutes**

### **Italy**

In collaboration with University of Milano-Bicocca the careful evaluation of data-driven landslide susceptibility methods identified important drawback in their use caused by strong dependency of the spatial distribution of the most susceptible zones to the type and number of predictive variables used. Empirical equations for estimation of physical vulnerability curves for debris flows were formulated using historical event from Italian Alps.

### **Poland**

Collaboration with Wroclaw University of Life and Environmental and Sciences resulted into finding that the data obtained within TecNet (fault displacement monitoring net) have shown that long periods of tectonic „quiescence“ are alternated with shorter periods of increased fault activity. This period can be characterized as a compression pulse. It was discovered that these periods of increased activity occur contemporaneously along distinct tectonic units and that they are caused by endogenous processes.

### **Slovenia**

Collaboration with Karst Research Institute in Postojna resulted into revelation of significantly high correlation between the fault displacements, measured radon flux and local seismicity.

### **Belgium**

In collaboration with colleagues from University on Mons and FNRS, a theory of cave development was suggested that speleogenesis a two stage process in which chemical weathering occurs before, and possibly long before, mechanical erosion.

### **Slovakia**

The collaboration with Faculty of Science, Comenius University in Bratislava and Czech Geological Survey resulted into the first paleoseismological research in central Europe, which showed seismogenic character of intraplate Sudetic Marginal fault in north-eastern Bohemian Massif, described tectonic phases and assessed the minimum potential magnitude for the fault.

## **In international-based collaboration with non-EU research institutes**

### **USA**

Collaboration with San Diego State University of California on the analyses of paleoseismic records lead to assessment of potential magnitude at studied faults, recurrence period and slip behaviour in several different geological environments including Trans-Mexican volcanic belt (Mexico), Dead Sea Transform Fault (Azrael), and Alhama de Murcia Fault (Spain). Also, the lateral variation in rates along the Elsinore Fault as a segment of San Andreas fault system (Coyote Mountains, Imperial Valley, California) and its constancy during Late Pleistocene, was determined by using provenance of alluvial fan deposits and their measured offsets.

## **New Zealand**

In collaboration with University of Waikato the first complex thermochronological study on the history of uplift of the Sudetes based on three modern thermochronological dating methods (zircon (U-Th)/He, apatite fission track, and apatite (U-Th)/He) gave time constraints on evolution of the Sudetic Marginal Fault and documented its activity as early as in Mesozoic and disproved historically accepted theories on larger extent of Sudetic Islands present since Permian.

## **Egypt**

In collaboration with National Research Centre in Cairo the ecological and economic use of plastic waste mixed with bituminous coal from Egyptian deposit Maghara for the production of coke for steel industry was successfully solved.

## **In the scope of national-based collaboration**

### **In collaboration with other institutes of the Czech Academy of Sciences**

Collaboration with the Institute of Geophysics of the CAS resulted into finding that the increased fault displacements reflect periods of the widespread tectonic redistribution of stress and strain within shallow crust as was proved by comparison with other geophysical methods.

Collaboration with the Institute of Geology of the CAS has for example helped to reveal that increased stress within a sandstone landform, as a result of vertical loading, reduces weathering and erosion rates, as was illustrated by using laboratory experiments and numerical modelling. The stress field is thus the primary control of the shape evolution of sandstone landforms. The results were published in Nature Geosciences.

Collaboration with the Institute of Astronomy of the CAS aiming to exploit seismic data also for non-conventional studies, has included the seismic data collected by worldwide stations and used for tracing the trajectories of some fireballs (see e.g. the well-known Chelyabinsk asteroid). The results were published in the Nature.

### **In collaboration with Universities**

Within joint research centre “Laboratory of Inorganic Materials” (IRSM & University of Chemistry and Technology) the research in material area focused mainly to glass melting processes, melt flow character and behaviour of gas phase in glasses. Among the main achievements, protected by patents, can be named a new method of glass fining by centrifuging, development of the device for glass melt fining by centrifuging, and development of glass melting furnace for continuous glass melting with controlled melt convection.

The collaboration with Czech Technical University focused on composite materials for tissue engineering and medicine. The joint research has resulted into several inventions, protected as utility models. Among the most important are for example the particulate composite bone tissue replacements with submicron bioapatite, the composite bone tissue replacements with nano calcium

deficient hydroxyapatite, or particulate composite bone tissue replacements with nano tricalcium phosphate.

Collaboration with Faculty of Science of Charles University is very wide, ranging from the research of natural hazards, landslides and tectonic history through studies of weathering history to application of the coal and organic petrology and geochemistry in geology. For example, new findings regarding to processes of coalification and maturation of organic matter, formation and migration of hydrocarbon phases in Barrandien Basin or investigation of graphite particles to a detailed characterization of tectonic structures were published in high ranking journals. Also, Paleoseismic trenching carried-out with Faculty of Science, Charles University in Prague at the Mariánské-Lázně Fault in West Bohemian Massif accompanied by several geophysical methods showed the large pre-historic earthquakes as young as Preboreal to Subatlantic, and strike-slip kinematics of the fault.

Together with the Faculty of Science of Ostrava University, the researchers of the IRSM have published several important results on the history and timing of development of vast slope deformations, mostly in Beskydy Mts.

The cooperation with Faculty of Medicine has led to an unusual application of geochemical methods has been processed in collaborative research focusing on the study of protein composition of mineralized aortic valves. It was found that it is clear evidence of the phosphor contribution in degenerative aortic valvular stenosis.

In collaboration with Faculty of Mathematics and Physics, Charles University in Prague, the IRSM researchers worked on the determination of the focal mechanisms of small earthquakes (Mw 2-3), which is notoriously problematic due to their signal-to-noise ratio. To overcome the problem, a series of related and consequent problems was worked on, resulting into a novel approach: the Cyclic Scanning of the Polarity Solutions (CSPS) which can be proficiently adopted in sparse networks where weak events are recorded.

#### **In collaboration with other subjects**

In collaboration with Czech Development Agency, new findings regarding to organominerals fertilizer were patented in 2014.

Collaboration with the Czech Cave Administration resulted to findings that the recorded anomalous carbon dioxide and radon concentration measured only a few days before the Tohoku Earthquake in the Bohemian Massif suggests that some global processes connected both phenomena.

New seismic hazard assessment for two Czech nuclear power plants (Temelín and Dukovany) was performed, which eventually served as reference document during the 2013 visit of the International Atomic Energy Agency.

The analysis of the felt seismicity induced by hydraulic injections led to development of differentiation of natural and induced seismicity, patented together with company Seismik, Ltd., in EU and USA (in approving process)

### **Without cooperation, based on national and IRSM grants**

The researchers of the IRSM have developed a method for processing of plastic waste to hydrogen-rich gas and evaluation of hydrogen production from the renewable sources was.

It was found that waste from industrial production of aluminium is an appropriate component for the geopolymerization with the matrix based on thermally treated clay materials- characteristics and use of materials with magnetic properties, using the opposing linear Halbach assemblies of NdFeB permanent magnets.

The IRSM is the only centre in the Czech Republic, which systematically focuses on organic biomarker analyses of sedimentary rock. One of the main achievements in this field is the creation of invaluable sedimentary archive of European continental environments during the Lower Miocene.

Landslide susceptibility zoning based on geomorphological mapping was verified using “wait and see” method, which proved its good ability to predict future landslide occurrence in highly variable geological conditions of Carpathian flysch.

Pioneering work in landslide risk assessment in the Czech Republic showed important local differences in landslide risk caused by different market prices of houses in geologically almost identical regions. This approach could be applied for land development planning purposes thanks to hazard definition and zoning which is missing in majority of similar works on the territory of the Czech Republic.

Study of impact of water on sorption capacity and kinetics of CO<sub>2</sub> sorption showed that the presence of water in coal can adversely influence the sorption behaviour of other molecules.

### **Popularization (more in app. 3.3)**

Each year, the researchers from the IRSM participate on several TV broadcasts, mostly in public ČT and CT24 and on Radio broadcasts, mostly in public ČRo (public radio). The researchers also performed in 21 public presentations and organized several thematic exhibitions (focused on research of IRSM in Arctic, Peru etc.). Annual event „Days of open door“ for public is organised, usually in 2 days during Academic „Week of Science“. About 100 people visit this event, mostly from secondary schools. Since 2013, IRSM published press releases announcing the most significant achievements, results or undertakings.

### **Strategy AV21**

In the scope of the Strategy AV21 (new strategy of the AS CR), 14 research programs were accepted, out of which the IRSM is participating on 5 programs (Systems for nuclear energy, Effective changes and storage of energy, Natural Hazards, New metal-, composite- and ceramics-based materials and Quality life in health and illness). The IRSM is a coordinator of the Natural Hazards research program.

## **Awards and honours**

### **2014:**

- Assoc. Prof. Jan Rybář received Gold medal of Quido Záruba, for lifelong performance in the field of engineering geology. The medal was awarded by Czech association of engineering geologists.
- Dr. Vladimír Schenk received the honorary professor title (Profesor Honorowy Uniwersytetu Przyrodniczego we Wrocławiu), for lifelong performance in the field of geoscience. The title was awarded by Wrocław University of Environmental and Life Sciences, Poland (Uniwersytet Przyrodniczy we Wrocławiu, Polska).
- Institute of Rock Structure and Mechanics of the CAS was awarded - together with Fac. of Science of Charles University - a title "World centre of Excellence on Landslide Disaster Reduction for years 2014-2017". The title was awarded for long-term research and publishing in the field of slope deformations by International Consortium on Landslides.

### **2013:**

- Dr. Miroslav Polák received Prize of Preciosa Foundation for his PhD thesis. Prize was awarded by Preciosa Foundation, Jablonec nad Nisou.
- Dr. Leo Eisner received Award "Promising innovation" for patented methodics on differentiation of induced and natural seismicity. Award was bestowed by Ceske Inovace, o.p.s.

### **2012:**

- Dr. Miroslava Vernerová received Prize of Preciosa Foundation for her PhD thesis. Prize was awarded by Preciosa Foundation, Jablonec nad Nisou.
- Dr. Filip Hartvich received Prize of the Dean of the Faculty of Science of Charles University, for outstanding performance as young researcher and lecturer. Awarded by Prof. Bohuslav Gaš, the Dean of the Faculty of Science of Charles University.

### **2011:**

- Dr. Jiří Mizera was named president of instrumental method group of Spectroscopic society J. M. Marci for publication activity in the field of radioanalysis. Named by the Spectroscopic society J. M. Marci.

## Research Report of the team in the period 2010–2014

Institute	Institute of Rock Structure and Mechanics of the CAS, v. v. i.
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Scientific team	Laboratory of Structure, Properties and Processing of Materials
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### Laboratory of Structure, Properties and Processing of Materials

Research activities of the team were concentrated into three research areas:

- Area #1. Methods of processing of waste materials into products with a high utility value.
- Area #2. Synthesis, properties and applications of geopolymer materials.
- Area #3. Characteristics and use of materials with magnetic properties.

#### Area #1.

**The main results obtained in the methods of processing of waste materials into product with a high utility value were as follows.**

##### **1. Processing of plastic waste to hydrogen-rich gas (the share of the team 100%).**

In the current state of waste production, it is necessary to find the ways of the maximum utilization of wastes. One possible way is the conversion of organic waste into hydrogen as in the near future, hydrogen will become an important fuel which could solve the local problems connected with an air quality. In our case, mixtures of waste plastics with lignite were successfully co-gasified on a laboratory scale under atmospheric pressure while the resulting tar was cracked in a thermal cracking reactor. The main product of co-gasification was hydrogen-rich gas, as by-products, soot and a solid residue were obtained. It was found that at least 20 wt.% of lignite can be replaced with waste plastics (Straka and Bičáková, 2014). This substitution does not have much effect on the composition, properties and amount of the energetic gas obtained. The higher heating value of the gas is fully comparable with that of industrial gas from lignite gasification in Lurgi generators. Further, a hydrogen production from coal/waste plastics mixtures by a two-stage co-pyrolysis was verified on macro-laboratory scale. Co-pyrolysis of these mixtures, with thermal-degradation module incorporated, produced a gas with hydrogen content up to 80 vol.% (Kříž and Bičáková, 2011). An addition of waste plastics has a significant influence on the increase of the overall hydrogen content in the resulting gas as hydrogen bound in polymer chains almost quantitatively converts in gaseous hydrogen. The solid share from pyrolysis is further usable. Through its gasification, we acquired the gas with H<sub>2</sub> content of 58 vol.%.

##### **2. Evaluation of hydrogen production from the renewable sources (the share of the team 100%).**

In the near future, biological method of hydrogen production can be used. Therefore, our work was focused on evaluating of the hydrogen production from the renewable sources by biological methods and comparison of effectiveness with the conventional methods. Our conclusions are as follows (Bičáková and Straka, 2012).



- The preferred method of hydrogen production on an industrial scale is steam reforming of natural gas for its low operational and production costs. Pyrolysis processes have acceptable investment costs and besides the production of hydrogen also satisfactory yields of oils. Two-stage co-pyrolysis is suitable considering its acquisition of a high amount of hydrogen from mixed charges. It is apparent that the co-pyrolysis of organic materials with coals is a process for hydrogen production capable of competing (Bičáková and Straka, 2010).

- With its conditions, electrolysis connected with renewable energy approaches low-emission technologies. However, for its energetic consumption, it is among the expensive technologies. In recent years, significant progress has been made in the development of systems of alternative hydrogen production including the thermochemical cracking of water and photoelectrolysis. While photoelectrolysis is currently the least expensive and most effective method of hydrogen production, thermal processes from non-renewable resources remain a less expensive method of hydrogen production.

- The methods of the biological treatment of water and biomass into hydrogen have diverse efficiencies. In both the technologies of hydrogen production and for comparison the efficiencies of the individual processes are shown synoptically. The biological processes for hydrogen production are acceptable in terms of ecology and also consume less energy as compared to thermochemical and electrochemical processes. The process of direct biophotolysis has very low efficiency and requires large areas and enough light for the production of hydrogen. It is therefore not promising for hydrogen production. Contrary, dark fermentation is a pronouncedly promising process for hydrogen production. It shows an efficiency of 60–80%, which is comparable with the most-commonly used conventional methods. Its advantage is that it does not require large areas or solar energy, which increases its market value. A still more promising process of the biological production of hydrogen seems to be the bio-electrochemically assisted microbial reactors (BEAMR) method, which can achieve efficiency of as much as 92% with the initial substrate being acetate. Figure provides an overview of the effectiveness of hydrogen production by selected biological and thermochemical processes.

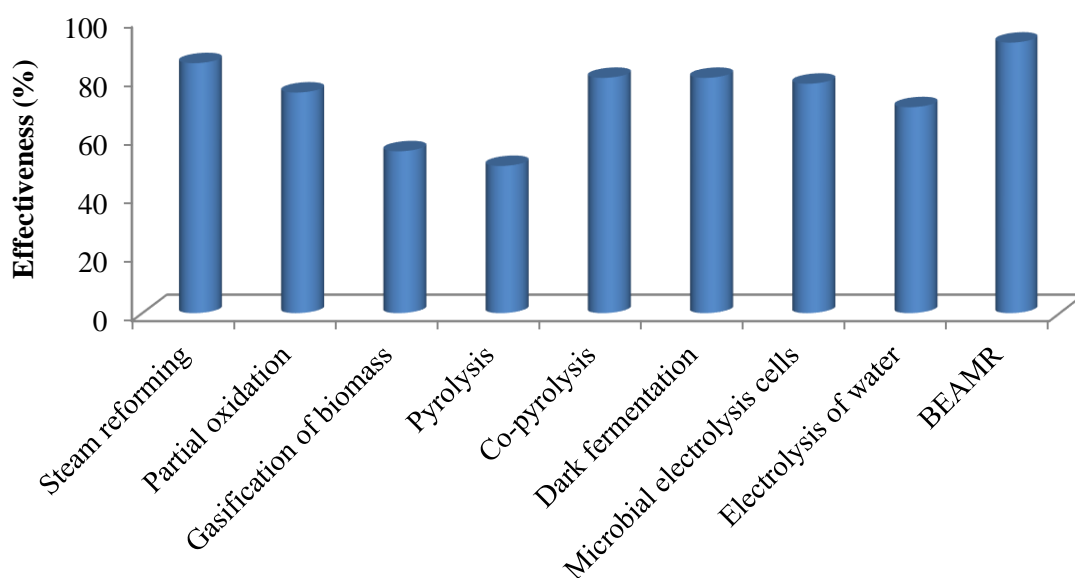


Figure: Selection of technologies for hydrogen production and their effectiveness

### **3. A novel method for the determination of unburned carbon in industrial ashes (the share of the team 80%).**

It was proposed that for the assessment of unburned (combustible) carbon, mainly in biomass-combustion ashes, one could utilize the thermogravimetric method using the strongly endothermic Boudouard reaction and making it possible to determine portlandite and carbonates. The assessment was based on the measurement of the mass loss of the sample in an inert atmosphere and subsequently in an atmosphere of carbon dioxide. The difference between the losses then determines the content of unburned carbon. The unburned carbon was hence assessed as the total organic carbon in a dry ash sample. The course of the thermogravimetric (TG) curves was confronted with the simultaneously obtained differential scanning calorimetry (DSC) curves. The method does not require acid treatment to remove the carbonates and may be used also for samples containing higher amounts of carbonate and portlandite and in the wide range of the content of unburned carbon. The proposed method has been tested on 10 contrasting ash samples from power plants burning wood chips, bark and straw and has provided correct results (Straka et al., 2014; Straka and Havelcová, 2012).

The share of the team was 80%: idea and concept of determination, TG and DSC measurements, collection of industrial ashes, interpretation of results, writing of the article.

### **4. Characterization of total and mobile element contents in ash derived from biomass combustion (the share of the team 20%).**

Seven samples of the ash derived from biomass, representing both fly and bottom ash, were analysed for a wide spectrum of total and mobile contents of nutrient and potentially risk elements. Several techniques, X-ray fluorescence (XRF) spectrometry, instrumental neutron activation analysis (INAA), proton-induced gamma-ray emission (PIGE) and proton induced X-ray emission (PIXE), inductively coupled plasma–atomic emission spectrometry (ICP-OES), and flame atomic absorption spectrometry (F-AAS) were compared. The results showed fairly good agreement between the XRF and INAA results, where the correlation coefficients ( $r$ ) varied between 0.96 and 0.98. Lower contents documenting insufficient dissolution of the ash samples in the applied acid mixture were observed for both ICP-OES and AAS. In this case, weaker correlation with the INAA results not exceeding  $r = 0.7$  were obtained. Therefore, the sample decomposition step is a bottleneck of the accurate analysis of this type of materials. For the assessment of plant-available portions of the elements in the ash samples, the Mehlich III extraction procedure and the extraction with a 0.11 mol L<sup>-1</sup> solution of CH<sub>3</sub>COOH were applied. The results showed relatively low mobility of the elements (especially micronutrients) in the ash samples regardless of their source and composition, suggesting limited immediate effect of direct ash application as a fertilizer (Száková et al., 2013).

The share of the team was 20%: sampling, determination of loss on ignition, chemical analyses by XRF.

- ✓ Bičáková O., Straka P., 2010. *The resources and methods of hydrogen production*. Acta Geodynamica et Geomaterialia, 7, 175–183.
- ✓ Bičáková O., Straka P., 2012. *Production of hydrogen from renewable resources and its effectiveness*. International Journal of Hydrogen Energy, 37, 11563–11578.
- ✓ Kříž V., Bičáková O., 2011. *Hydrogen from the two-stage pyrolysis of bituminous coal/waste plastics mixtures*. International Journal of Hydrogen Energy, 36, 9014–9022.

- ✓ Straka P., Havelcová M., 2012. *Polycyclic aromatic hydrocarbons and other organic compounds in ashes from biomass combustion*. Acta Geodynamica et Geomaterialia, 9, 481–490.
- ✓ Straka P., Bičáková O., 2014. *Hydrogen-rich gas as a product of two-stage co-gasification of lignite/waste mixtures*. International Journal of Hydrogen Energy, 39, 10987–10995.
- ✓ Straka P., Náhunková J., Žaloudková M., 2014. *Analysis of unburned carbon in industrial ashes from biomass combustion by thermogravimetric method using Boudouard reaction*. Thermochemica Acta, 575, 188–194.
- ✓ Száková J., Ochečová P., Hanzlíček T., Perná I., Tlustoš P., 2013. *Variability of Total and Mobile Element Contents in the Ash after Biomass Combustion*. Chemical Papers, 67, 1376–1385.

## Area #2.

The main results obtained in the synthesis, properties and applications of geopolymer materials were as follows.

### 1. Synthesis of a geopolymer matrix based on thermally treated shale, the waste material from ancient coal mining activity (the share of the team 70%).

A specific raw material for geopolymer synthesis was investigated. Shale, the waste material from ancient coal mining activity, was naturally thermally affected by slow and unequal burning of coal residues. The intensity of the thermal treatment has been studied by <sup>27</sup>Al magic angle spinning nuclear magnetic resonance. Despite the high content of mullite and quartz, the amorphous clay residues in the shale react with an alkaline solution and create stable solids with excellent mechanical properties. The FTIR spectra of the shale geopolymer matrix have proved the presence of geopolymer chaining (Perná et al., 2014a). The best geopolymer matrix prepared has flexural strengths of 8.9 MPa, and the compressive strengths reach the value of 60 MPa. The findings proved the shale as a new raw material for geopolymer synthesis and a possibility of waste material recycling.

The share of the team was 70%: experiments, data collecting and analyses, formulation of hypotheses, interpretation of results, and writing of the paper.

### 2. Utilization and solidification of waste materials

(a) It was found that waste from the industrial production of aluminum is a good component for the geopolymerization with the matrix based on thermally treated clay materials. The solidification of highly alkaline, generally semi-liquid red waste and gray slag from the aluminum production inhibits their toxic properties. Through the geopolymerization, both wastes were transformed to the compact and foamed materials. The compact solids have the compressive strength higher than 30 MPa and do not produce any hazardous gases when heated (Perná and Hanzlíček, 2014). The gray waste was used for preparation of the insulation material whose thermal-conductivity properties were compared to existing materials. The method answers the demand of aluminum waste solidification and recycling.



Figure: A solid product from a foamed and a compact geopolymer containing a high amount of aluminum-production waste

The share of the team was 100%.

(b) The fire resistance is one of the important behaviors of the construction and thermal insulating materials. The foamed material was made from fluidized bed ash (FBA) in combination with natural smectite having a filler function. The foaming effect was insured by addition of metallic aluminum to the FBA/smectite mixture. Study of fire resistance was a part of experiments directed on heat insulating materials and the fire-resistance test of this foamed material was acquired according to the international norm EN 1364-1 of fire-resistance control in the Czech Centre of Fire Resistance Authority at Veselí nad Lužnicí (South Bohemia region) by authorized person AO 216. The article introduces test results of this life gardening material proving a resistance to heat exposition. The hypothesis of chained alumina-silicates acting as bonding agent was presented and confirmed by infra-red spectroscopy. Poly-condensed alumina-silicates and anhydrite are responsible for physical stability of shape even attacked by direct flame. The stability of rectangular form without shrinkage or visible surfaces cracks during the exposition against open flame confirms that products made from foamed FBA/smectite mixture could be one of the best life guarding materials (Hanzlíček and Perná, 2011).

The share of the team was 100%.

(c) The ashes from biomass combustion are easily and successfully utilizable by the geopolymer technology without regard to their chemical compositions. Besides classic use of geopolymer composites it is possible to create building element with specific properties. The resulting composites are hard, stabile, heat and fire resistant. The results showed that insulating properties (sound and heat) could be modified according to the future utilization. The biomass ashes could be also used in production of board materials, combining textile, glass or carbon fibrous materials with geopolymer matrix. These results open possibility to use these composites as light insulating and fire resistant panels also in cars or airplanes (Perná et al., 2010).

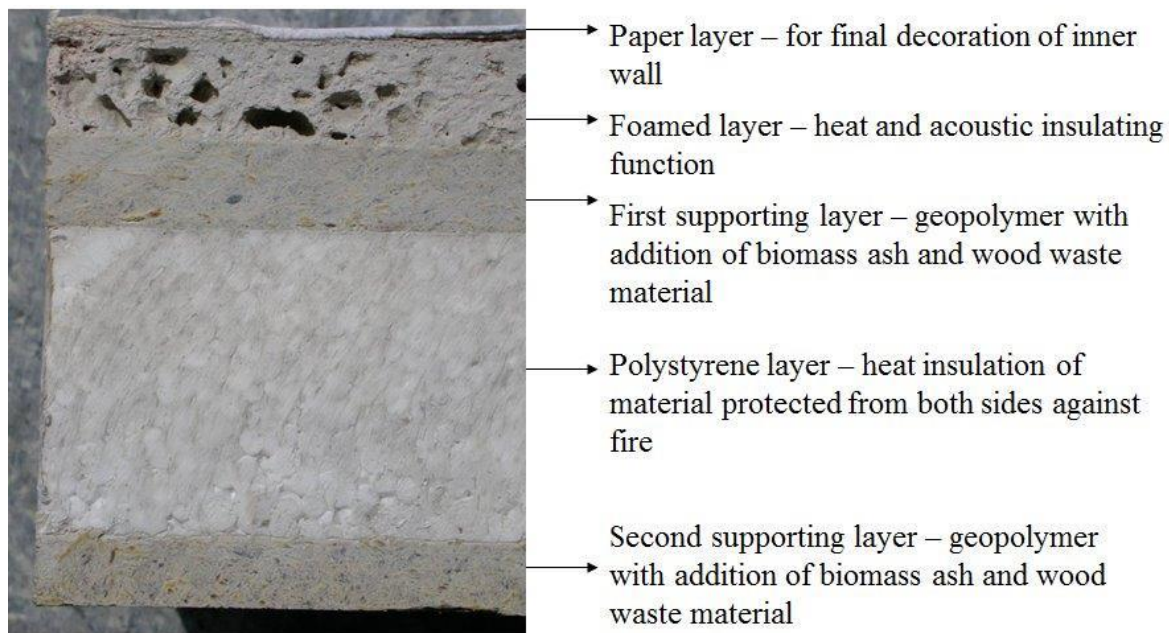


Figure: Multipurpose composite with description of layers

The share of the team was 80%: experiments, data collecting and analyses, interpretation of results, writing of the paper, and presentation at the international conference.

(d) The solidification and stabilization of coal fluidized-bed ashes (ASTM classification Class C ashes) were accompanied by the identification of the alumina-silicate residues of the burned coal. The combustion temperature seems to be responsible for the aluminum coordination level while the aqueous alkali condition used in solidification leads to the possibility that the long-term stability and water insolubility of the obtained solids reflect the creation of a new amorphous phase formed from shorter or longer chains of poly-condensed calcium alumina-silicates complementing the calcium carbonate crystals. These alumina-silicate chains are responsible for the good mechanical properties, long-term stability and insolubility of the solids in water (Hanzlíček and Perná, 2011).

The share of the team was 100%.

### **3. Mechanical properties of geopolymer composite in relation to their porous structure (the share of the team 80%).**

Mechanical properties of metakaolinite geopolymer composite with quartz sand were studied. A compressive strength, flexural strength and Young's modulus were confronted with the structure parameters given by mercury porosimetry. The maximum of the compressive strength and the flexural strength were reached up to 70 MPa and 12 MPa, respectively, at 78 wt. % of sand, confirmed by the bulk density maximum. The breaking point at 82 wt.% of sand demonstrated coarse pores evolved by the lack of geopolymer binding gel between sand grains, which was proven by a rise in porosity. Freezing resistance was confirmed due to a presence of large mesopores in the grain-geopolymer interfacial transition zone, on the amount of 35% portion in the bulk pore volume. The study showed for the first time the pore structure influence on strength of geopolymers and their frost-resistance being dependent on the interfacial transition zone mesopores (Steinerová and Schweigstillová, 2013; Steinerová, 2011).

The share of the team was 80%: experiments, data collecting and analyses, interpretation of results, and writing of the paper.

#### **4. Contributions to historical mortars identification and restoration**

(a) Chemical structure of modeled mortars prepared from the combination of lime and thermally treated clay as substitute of ceramic shreds used in the past times was compared with that of ancient mortars. The alumina-silicates, present in calcined clays or in fired ceramics with a limited temperature of firing, were identified by FT-IR as poly-condensed chains distributed among the calcium-containing substances. The possibility of aluminum-ion hydration and chaining is supported by  $^{27}\text{Al}$  magic angle spinning nuclear magnetic resonance measurements, where the shift to the aluminum ions in four-fold coordination could be seen. The netted alumina-silicates are balanced by the positive charge of calcium ion while forming a connection with the calcareous surroundings. These chained structures in which calcium is chemically bound are responsible for long-term stability of mortars. These findings could help in historical-mortar restoration (Hanzlíček et al., 2012a).

The share of the team was 95%: experiments, data collecting and analyses, formulation of hypotheses, interpretations, writing of the paper.

(b) Medieval mortars usually contain alumina-silicates in various forms, such as the remnants of weathered rocks, clays and crushed ceramics, in addition to a calcium-containing substance. As researchers have long ignored the role of alumina-silicates in historical mortars, the aluminum coordination in mortars performed by  $^{27}\text{Al}$  magic angle spinning nuclear magnetic resonance in the solid state was identified. The identification of aluminum coordination in historical mortars helps to explain the thermal treatment of clayed substances in calcareous rock or the common knowledge of the addition of ceramic shards to calcareous matrices. Aluminum and silicon ions in 4-fold coordination to oxygen form chained structures and these stable poly-condensed chains contribute to the long-term stability of historical mortars. This determination should be utilized by restorers of historical mortars (Hanzlíček et al., 2013).

The share of the team was 70%: data collecting and analyses, interpretation of results, writing of the paper.

(c) The historical background of the 20th-century technology of geopolymers in light of a literature research of the 15th to 19th centuries offers a hypothesis on why this historical knowledge was forgotten when Portland cement appeared. The recapitulation of the different cementitious calcareous matters returns all the way to the Bible builders; Ancient Vitruvius Pollio's work "Ten Books of Architecture". These books were not only read but practically proven in pre-Portland times and especially at the beginning of 19th century (Hanzlíček et al., 2012b). The long-term stability of Roman mortars and constructions was studied from the perspective of the cementitious materials, and the cited literature demonstrates the historical evolution of calcareous cements, then the reasons for the interruption of progress and return to the historical experience in the 1980s.

The share of the team was 80%: Research of historical documents, data collecting, interpretation of results, and writing of the paper.

(d) The art of mosaic in the Czech lands in the 19th century generally reflects the religious sentiment of the artists and their customers. The identification of the materials used

before the restoration work is begun is an important part of national treasure conservation. The mosaic from Jablonec nad Nisou (the region of North Bohemia) and its history were studied (Perná et al., 2014b). The chemical analyses of the mortar have not confirmed the direct Italian origin of the mortar but it was proved the use of the Italian mortar style, quite likely consisting of the local lime and the local potshards. Tesserae were imported from Italy, and the presented chemical analyses have detected the composition of sodium-calcium based glass with a rather high content of lead oxide.

The share of the team was 70%: experiments, data collecting and analyses, interpretation of results, and writing of the paper.

### **5. Transfer of technology from the laboratory to semi-industrial level**

The important points in the processes of knowledge transfer between the chemical laboratory and industrial unit were clarified. The difficulties in material selection which could be resolved by a laboratory equipped with all facilities are not effective on the industrial level, where the energy and manpower costs must be very well judged. The previous laboratory studies on the geopolymer matrix have resulted in the semi-industrial production of selected geopolymer goods - large-size polished boards for the kitchen countertops and very thin inset tiles (both with dimensions of 1,000 × 500 mm), heating and decorative panels (Boura et al., 2012). Each fabricated product needs a specific technology timing, which in the case of heating panels is converted into real production know-how. The conversion of the laboratory result to the semi-industrial level needs investment, time and the creativity of the production unit staff.

The share of the team was 60%: data collecting, interpretation of results, and writing of the paper.

### **6. Patents**

#### **(a) Organominerals fertilizer I.**

The invention relates to organomineral fertilizer for enhancing plant nutrition comprising fly ash from mixed wood chips from biomass combustion. The fertilizer is in the form of pellets containing fly ash coupled by an organic natural binding agent, with the addition of sawdust. The mixture can be complemented by solutions of humic acid sodium salts of a preselected concentration, optionally by solutions of iron sulfate of a preselected concentration (Ertl et al., 2014a).

The share of the team was 90%: creation of data, writing of the patent.

#### **(b) Organominerals fertilizer II.**

In the invention, there is disclosed an organomineral fertilizer for improving nutrition of plants comprising a fly ash from crop straw, optionally in a mixture with grate ash from crop straw. The fertilizer is in the form of pellets containing fly ash coupled by an organic natural binding agent, with addition of sawdust. Solutions of humic acid sodium salts of a predetermined concentration, optionally solutions of iron sulfate of the preselected concentration are added to the mixture (Ertl et al., 2014b).

The share of the team was 90%: creation of data, writing of the patent.

✓ Boura P., Ertl Z., Hanzlíček T., Perná I., 2012. *The Experience on Geopolymer Technology in Semi-Industrial Production*. Journal of Materials Science and Engineering B, 2, 300–305.

- ✓ Ertl Z., Hanzlíček T., Perná I., 2014a. *Organomineral fertilizer*. Patent No. 304603, Industrial Property Office, Prague. Holders: Czech Development Agency, o.p.s., and Institute of Rock Structure and Mechanics ASCR, v.v.i
- ✓ Ertl Z., Hanzlíček T., Perná I., 2014b. *Organomineral fertilizer*. Patent No. 304631, Industrial Property Office, Prague. Holders: Czech Development Agency, o.p.s., and Institute of Rock Structure and Mechanics ASCR, v.v.i.
- ✓ Hanzlíček T., Perná I., 2011. *Thermal resistance of foamed fluidized bed ashes*. *Acta Geodynamica et Geomaterialia*, 8, 115–122.
- ✓ Hanzlíček T., Perná I., 2011. *The alumina-silicates in stabilization processes in fluidized-bed ashes*. *Ceramics-Silikáty*, 55, 94–99.
- ✓ Hanzlíček T., Perná I., Ertl Z., 2012a. *The Influence of Temperature and Composition on Modeled Mortars*. *International Journal of Architectural Heritage*, 6, 359-372.
- ✓ Hanzlíček T., Perná I., Ertl Z., Miller, S.M., 2012b. *Pre- Portland cements and geopolymers*. *Acta Geodynamica et Geomaterialia*, 9, 57–62.
- ✓ Hanzlíček T., Perná I., Brus, J., 2013: *<sup>27</sup>Al Magic Angle Spinning–Nuclear Magnetic Resonance (MAS-NMR) Analyses Applied to Historical Mortars*. *International Journal of Architectural Heritage*, 7, 153-164.
- ✓ Perná I., Hanzlíček T., Ertl Z., 2010. *Utilization of biomass ashes for construction purposes*. in: *Advances in Geomaterials and Structures AGS' 10, Third Euro Mediterranean Symposium in Advances on Geomaterials and Structures, 10.5. – 12.5.2010, Djerba, Tunisko, str. 661–666, nakladatel: LGC-ENIT, Tunisia.*
- ✓ Perná I., Hanzlíček T., 2014. *The solidification of aluminum production waste in geopolymer matrix*. *Journal of Cleaner Production*, 84, 657–662.
- ✓ Perná I., Hanzlíček T., Šupová M., 2014a. *The identification of geopolymer affinity in specific cases of clay materials*. *Applied Clay Science*, 102, 213–219.
- ✓ Perná I., Hanzlíček T., Kracík Štorkánová M., 2014b. *Characterization of historic mosaic at Pfeiffer-Kral Sepulcher, Jablonec nad Nisou: A study of the mortar and tesserae origin*. *Ceramics-Silikáty*, 58, 308–313.
- ✓ Steinerová M., 2011. *Mechanical properties of geopolymer mortars in relation to their porous structure*. *Ceramics – Silikáty*, 55, 362–372.
- ✓ Steinerová M., Schweigstillová J., 2013. *Porous microstructure of the interfacial transition zone in geopolymer composites*. *Ceramics – Silikáty*, 57, 328–335.

### Area #3.

The main results obtained in the characteristics and use of materials with magnetic properties were as follows.

#### 1. Intensity distribution of strong magnetic fields created by opposing linear Halbach assemblies of permanent magnets.

For the purposes of mineral processing, creating strong magnetic fields using the latest type of permanent magnets is presented. Both the computer simulation and the realization of the test device was confirmed that by chosen opposing assemblies of NdFeB magnets with a high energy product it is possible to achieve in a defined volume of air gap the magnetic fields with high magnetic induction. When using large magnetic blocks thus appears a real possibility for creating of a strong magnetic field in a larger volume of air gap, usable for the treatment of



mineral mixtures, in instrumentation technique, and in other areas (Žežulka and Straka, 2011; Žežulka and Straka, 2012; Žežulka et al., 2013).

The share of the team was 70%: idea of the work, design and realization of the test device, measurements and cooperation in the evaluations of results.

## 2. Patents

(a) Method of forming magnetic blocks and equipment for carrying out that method.

The invention describes the method of magnetic blocks formation as follows. During formation of magnetic blocks from material with high energy product, a first permanent magnet is inserted from above to the bottom of vessel which is then filled with liquid. Further magnets are gradually inserted in the vessel in a direction perpendicular to their resulting contact surfaces, where the adjacent surfaces of the superimposed magnets have an opposite polarity. The speed of an attraction of magnets is controlled by the regulated discharge of the liquid from the space between adjacent magnets. This leads to slow attraction magnets without damaging them (Žežulka et al., 2010).

The share of the team was 67%: idea of the patent, design of the equipment for creation of magnetic blocks, practical verification of the patented method.



Figure: Equipment for assembling large magnetic blocks from magnetic plates

(b) Method of making linear assemblies of permanent magnets facing each other and apparatus for making the same.

The invention relates to a method of making assemblies of magnetized permanent magnets facing each other or from blocks of such magnets for generating strong magnetic fields and a large volume in a gap between such assemblies, wherein the method is characterized in that separate permanent magnets of at least two assemblies are forcibly inserted in a predetermined sequence and a predetermined mutual polarity into a non-magnetic hollow non-circular tube with open ends. Apparatus for making the above-described method is made of non-magnetic material and comprises at least two hollow non-circular tubes with multiple times greater length if compared with the length of the assembled magnet assembly and the internal profile of which corresponds with a certain clearance to the external contour of the inserted magnets and which have at their each open end two fixedly attached clamping bases provided each with an assembly surface for interception of a connecting element for attaching a cross piece of the magnet pushing mechanism (Žežulka and Straka, 2014).

The share of the team was 100%.

- ✓ Žežulka V., Straka P., 2011. *The suspended magnetic separator with large blocks from NdFeB magnets and its long term technological tests*. Acta Geodynamica et Geomaterialia, 8, 89–97
- ✓ Žežulka V., Straka P., 2012. *The realization of strong, stray static magnetic fields*. Acta Geodynamica et Geomaterialia, 9, 71–77
- ✓ Žežulka V., Pištora J., Lesňák M., Straka P., Ciprian D., Foukal J., 2013. *Intensity distribution of strong magnetic fields created by opposing linear Halbach assemblies of permanent magnets*. Journal of Magnetism and Magnetic Materials, 345, 7–12
- ✓ Žežulka V., Straka P., Soukup V., 2010. *Method of forming magnetic blocks and equipment for carrying out that method*. US Patent No. 7796001, United States Patent and Trademark Office. Holder (Assignee): Institute of Rock Structure and Mechanics ASCR, v.v.i.
- ✓ Žežulka V., Straka P., 2014. *Method of making linear assemblies of permanent magnets facing each other and apparatus for making the same*. Patent No. 304444, 2014, Industrial Property Office, Prague. Holder: Institute of Rock Structure and Mechanics ASCR, v.v.i.

## Research Report of the team in the period 2010–2014

Institute	Institute of Rock Structure and Mechanics of the CAS, v. v. i.
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Scientific team	Laboratory of Inorganic Materials
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### Laboratory of Inorganic Materials

Organizational changes related to the Laboratory of Inorganic Materials were adopted during the period under review and therefore the Research Report and corresponding results are presented only for the 3 years period of 2012-2014.

The developing family of special glasses and growing glass industry lead to establishing the present glass team arisen mostly from original Ph.D. students. One part of the team deals with the physical chemistry and chemical engineering of the industrial glass melting process, involving particularly the behavior of gas phase in glasses, modelling of the melting process and character of melt flow in the melting spaces. The fundamental and applied research is almost balanced in this research topic. The second research group engages in preparation and properties of the family of glasses distinguished by high transmittance in the IR region and having broad utilization in optics and photonics. The fundamental research is characteristic for the research group but the potential applicability of developed glasses is always considered.

The main activities were focused on the following research topics:

- 1. Structure of the industrial glass melting process**
- 2. Impact of factors on the melt flow character and harmonizing the optimal melt flow conditions for sand dissolution and bubble removal in the model glass melting space**
- 3. Application of optimal flow conditions in glass melting spaces with energy sources**
- 4. Bubble nucleation in glass melts and its effect on the glass melting process**
- 5. Special glasses for photonics and optoelectronics**

#### **1. Structure of the industrial glass melting process**

The intensive physico-chemical study of the glass melting process started already in the last century by laboratory crucible melts focused on the impact of fundamental melting factors, the raw materials, their composition and granulometry, melting temperature, the glass target composition and the oxidation reduction conditions of the melting process as the fundamental melting parameters [1-5]. The physico-chemical examination during the second half of the century provided fundamentals of glass melting thermodynamics and kinetic equations describing the principal melting processes [6-17]. The transfer of the results into the industrial melting process was highly desirable and there were many attempts to do that on the base of up to date results. However, the scientific effort faced the problem of detailed knowledge of melting conditions, set up naturally in the continual melting spaces, particularly the temperature and velocity distribution of the melt inside of the melting space. Such knowledge was facilitated by development of computer mathematical modeling during eighties and

nineties [18-23]. Later on, the kinetic equations of the principal melting processes were applied [24-29]. The complex mathematical models of glass melting spaces spread out all over the world, supported new melting ideas and accomplished technological tasks [30-32].

Nevertheless, the glass melting still remains a process with considerable footprint for environment owing to the high energy consumption, accompanied mostly by massive production of CO<sub>2</sub>, low specific melting performance leading to large melting spaces with high need of expensive refractory materials and owing to evaporation of harmful volatile glass components at high melting temperatures. The contemporary experience shows that the actual requirements, referring mostly to the energy consumption and melting performance (or size of the spaces), cannot be solved without new principles introduced in the glass melting process [33].

One of new hopeful approaches opened the presenting research group by the come-back from modeling industrial melting spaces to fundamentals of the glass melting process, to definition of principal processes, their general important and perspective factors and to introducing the potentially innovative principles in the partial processes [34-35]. According to this approach, the contemporary mathematical models should be applied to simplified abstract melting spaces working under precisely defined conditions instead of to the complicated industrial equipments. The effect of new factors can be thus clearly evaluated and single examined cases can be easily compared. The process structure and necessary model data should be obtained by relevant experiments. The optimal results have to be subsequently transferred to spaces with gradually increasing technical level.

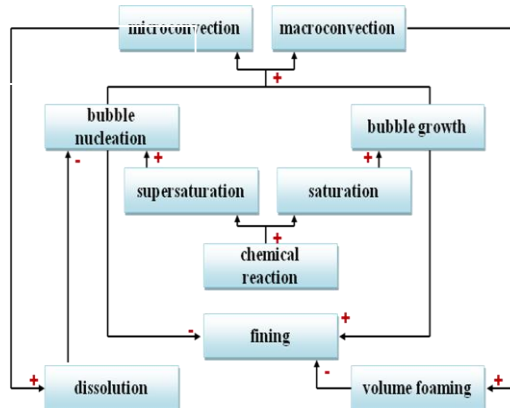
The modelling of glass melting as the complex process requires consideration of not only kinetics of the single phenomena but also their ordering in the melting space. The simplified melting model involves the serial ordering of glass batch conversion to glass and two parallel processes in the melt, hence dissolution of SiO<sub>2</sub> particles (glass sand) and removal of batch decomposition bubbles. The significant energy and performance reserve of the continuous melting process is hidden in the way how both parallel homogenization phenomena are influenced by the character of melt flow in the melting space. The arisen problem of the quantitative evaluation of the melt flow character solved the research group by introduction of the new quantity called *utilization of the space* [34-41]. Utilization of the space represents the ratio between time necessary to accomplish the given homogenization phenomenon under conditions of a quiet melt and the time necessary for accomplishing it in a continual space with the given character of the melt flow. It involves s.c. dead (non-productive) spaces and may be obtained by the mathematical modelling of the relevant homogenization phenomenon in the glass melting space. The values of the space utilization are then involved in the relations for the melting performance of the space and specific energy consumption of the melting process.

Theoretically, the optimal character of the melt flow may be estimated from the standard liquid flows, i.e. plug flow and mixer. The helical flow as the superposition of slow circular mixing perpendicular to the uniform working flow appears optimal for glass melting. This fact was proved by the detailed modelling studies [36-37, 40]. The character the melt flow resulting from the modelling was really the helical-like. The optimal character of the melt flow was determined as a function of the ratio between the preset transversal and longitudinal temperature gradients in the melt, the maximal utilization value being mostly at the gradient ratio between 5-10. These results have shown that the energetic losses can be decreased and the melting performance increased even several times if the helical-like flow would be set in the melting space. *Also other factors may, however, influence the character of the melt flow as is the total intensity of melt circulations, the melting kinetics and the size of the melting space. The impact of the mentioned factors should be in details investigated.*

Despite of the fact that the helical-like flow occurred optimal for both dissolution and bubble removal - different detailed flow conditions may result and *further research should be therefore undertaken to harmonize the flow conditions of both phenomena. In the following step, the more realistic conditions should be set up, particularly the sources of energy should be used instead of temperature gradients, to show that the optimal flow conditions would be practically realizable.*

The experimental research has nevertheless shown that still some other phenomena, occurring during the melting process, may influence the fundamental homogenization processes and the melting efficiency, particularly the phenomena evoked by chemical reactions releasing a gas into

the melt. Thus, the actual model of the melting process can be more complicated than this applied till this time. The released gas brings about the bubble nucleation, glass foaming and local melt convection [42-44]. The processes as bubble nucleation and foaming prolong the bubble separation process but the local micro-convection, evoked by bubble nucleation and growth on undissolved sand particles, accelerates particle dissolution [44]. The experimentally found relations between processes are drawn in Fig. 1. Only a qualitative or semiquantitative knowledge exists, however, about relations between these phenomena and the principal homogenization processes till this time, and no adequate experimental methods are at disposal for examination of bubble nucleation. The more detailed *study of the mentioned processes and their relevant relations, as well as development of relevant experimental methods* are needed to acquire a more detailed insight in the mentioned glass melting phenomena and to support or inhibit their effects.



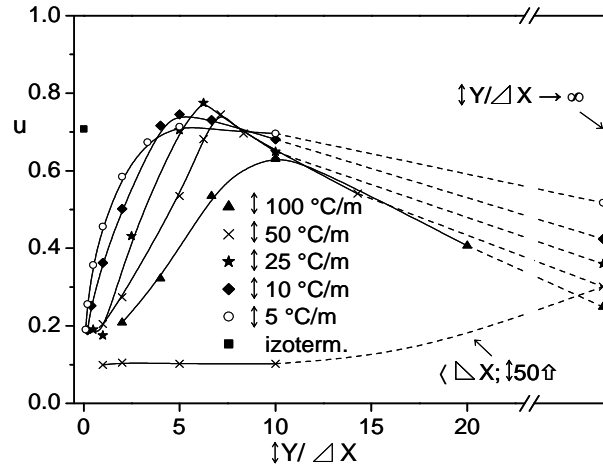
**Figure 1:** The relations between melting phenomena evoked by gases released into the glass melt by a chemical reaction (mostly by the decomposition of fining agents). + designates the acceleration, – the slowing down of the next process [44].

Taking into account the received results and emerging requirements and problems, the following research was focused on following topics:

- impact of factors on the melt flow character and harmonizing the optimal melt flow conditions for sand dissolution and bubble removal in the model glass melting space,
- application of optimal flow conditions in glass melting spaces with energy sources,
- development of a method for examination of bubble nucleation in glass melts and effect of bubble nucleation on the glass melting process.

## 2. Impact of factors on the melt flow character and harmonizing the optimal melt flow conditions for sand dissolution and bubble removal in the model glass melting space

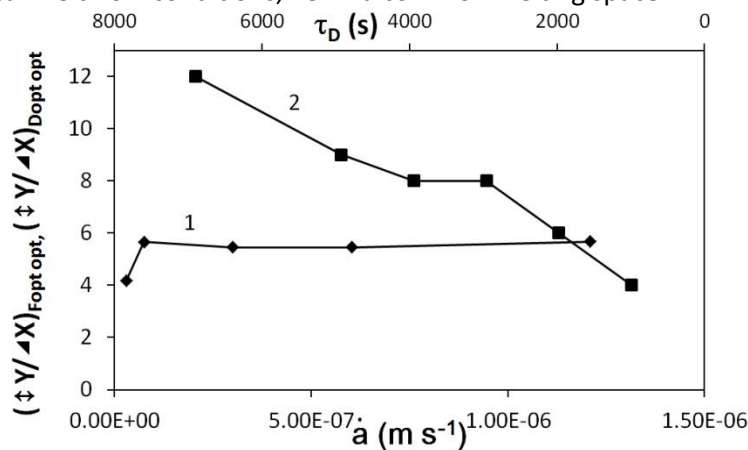
In this step of examination, the results of the mathematical modelling of sand dissolution and bubble removal [45] in a horizontal glass-melting channel were acquired when having varied the further factors influencing the space utilisation as were the total intensity of melt circulations, the phenomena kinetics (represented by the sand dissolution times and bubble growth rates) and the length of the space (channel) [46-50]. The recently found optimal class of intensive transversal circulations combined with forward working flow has been applied in the melting channel. The results of modelling were projected into the values of the space utilisation and consequently, melting performance and specific heat losses. The following Figure 2 [46] shows how the space utilization depends on the ratio between transversal to longitudinal temperature gradient at *different total intensities of natural circulations* (given here by the values of the transversal temperature gradient,  $\updownarrow Y$ ).



**Figure 2:** The dependence of the space utilisation on the ratio of the transversal to longitudinal temperature gradient,  $\Delta Y/\Delta X$ , for the case of sand dissolution [46]. The full line connects only for the reader's eyes the points with the same value of the transversal temperature gradient.

By the detailed modelling, the high values of space utilisation were repeatedly attained under examined conditions in a broad interval of melt circulation intensities, melting phenomena rates and melting channel lengths. The results of the modelling provided the maximum values of the space utilisation ranging from 0.6 to 0.8 when the ratio between the gradients was mostly between 4 and 12, the transversal temperature gradient was set between 25 and 150 K/m, the model channel length varied between 0.5 and 4 m and the rate of the dissolution and bubble removal phenomena changed at least several times. The optimal values of space utilisation were even higher than could be obtained in a space with a uniform melt flow. The relevant optimal ratio between the gradients grew with the overall intensity of the glass circulations, with the channel length and with the increasing sand-dissolution time. It almost did not change with the bubble growth rate which characterized the bubble removal kinetics. The results provided a theoretical base for the design of glass-melting segments with controlled glass flow, characterized by lower energy consumption and higher melting performance.

The comparison of optimal ratio of temperature gradients for both sand dissolution and bubble removal are presented in Figure [49]. The optimal conditions for bubble removal were comparable with those valid for the sand dissolution which fact provided a chance to operate both processes effectively under identical melt flow conditions, i.e. in a common melting space.



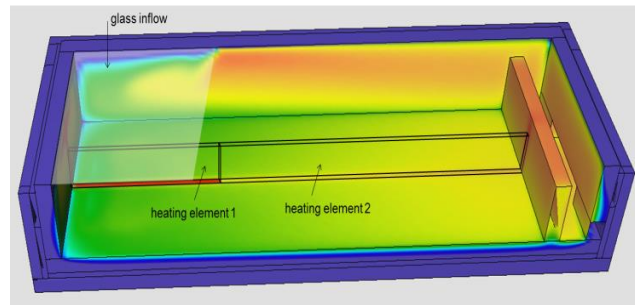
**Figure 3:** The dependence of the optimal values of  $(\Delta Y/\Delta X)_{\text{opt}}$  on the relevant growth rates of the bubble radius and sand dissolution times, respectively. The length of the channel is 1 m [49]. The lines are merely guides for eyes.

- 1:  $(\Delta Y/\Delta X)_{\text{Foptopt}}$  as a function of the growth rate of the bubble radius,  $\dot{a}$ . F - fining, bubble removal.
- 2:  $(\Delta Y/\Delta X)_{\text{Doptopt}}$  as a function of the sand dissolution time,  $\tau_D$ . D- sand dissolution.

The application of the optimal flow character in glass-melting furnaces appeared thus feasible for high performance or miniaturized melting facilities and for the process with minimalized energy losses.

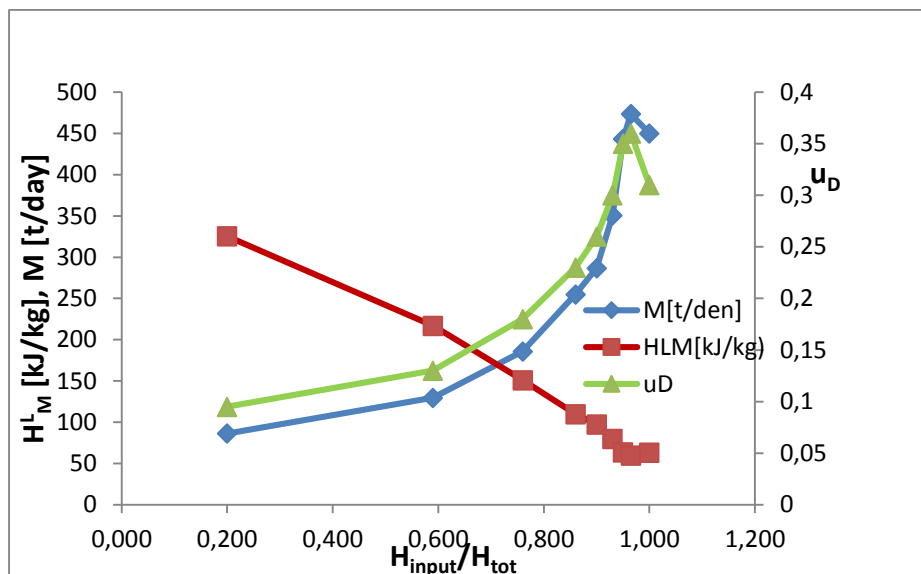
### 3. Application of optimal flow conditions in glass melting spaces with energy sources

If energy sources are applied to simulate the real melting, the resulting character of the melt flow strongly depends on local positions of the energy sources in the melting space. The horizontal distribution of the supplied energy plays here the principal role [50-51]. The space with balanced energy distribution provides the best conditions for attaining the helical-like flow in the space. The balanced state is characterized by the fact that each part of the space (input part and part with free level) is supplied just by the energy necessary for the process and heat losses coverage, so the undesirable longitudinal melt circulations are suppressed. The maximal utilization values reported in the last paragraph are theoretically available only in the balanced state. Nevertheless, the compromise including the unbalanced state and sufficiently intensive transversal circulations can bring also acceptable results. The ways should be therefore examined how to support transversal melt flows. Two model spaces were modelled to determine the relation between the space utilization (and consequently, heat losses and melting performance) and horizontal energy distribution. In the main run of calculations, the glass batch on the melt level was simulated by the inflowing melt with defined temperature and the energy supply in the space was simulated by the defined volumes of the melt, in which the relevant energy was automatically developed [52]. The principal heating element was created by the central longitudinal body of the melt having height 0.6m and being divided into part under melt inflow (heating element 1) and part under free glass level (heating element 2). The scheme of the modelled space is in figure 4.



**Figure 4:** Scheme of the model melting space ,  $l = 6.77\text{m}$  (6.225m to the barrier),  $w = 2\text{m}$ ,  $h = 1\text{m}$ . Average temperature  $1420^\circ\text{C}$  [52].

When modelling the space utilization, the amount of energy supplied below the melt inflow was increased from case to case in the direction to the balanced energy distribution. The aim of the energy transfer was to slow down the currently existing longitudinal melt circulations which prevented establishment of the helical-like flow with high space utilization. The following figure 5 shows the effect of energy transfer to the inflowing melt.



**Figure 5:** The dependence of the space utilisation  $u_D$  (dissolution phenomenon is controlling), the melting performance in t/day  $\dot{M}$  and the specific energy losses  $H_M^L$  in kJ/kg on the fraction of total energy located in the region of inflowing melt (simulating glass batch input) [52].

The almost simultaneous growth of the space utilisation and melting performance is obvious from figure 5 demonstrating the significance of the melt flow character for the melting performance. The specific heat losses sank with the increasing melting performance as expected. At very high values of  $H_{input}/H_{tot}$ , too little energy is at disposal for transversal circulations and the effect of helical flow fades. The several times increased melting performance and decreased specific heat losses are promising for practical applications of the controlled melt flow.

The mathematical modelling of melting phenomena and the flow character in the melting space resulted in application results as utility models [53-54], software [55], patents [56-58] and verified technologies [59-60].

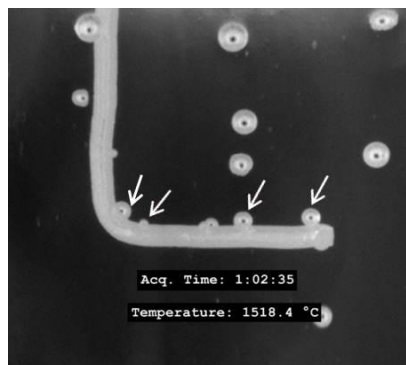
#### 4. Bubble nucleation in glass melts and its effect on the glass melting process

Several sorts of bubbles are observable and can be identified in glasses but only a part of them have their origin in the initial chemical reactions of the precursors and formation of glass melts from the initial porous and foamy material. It is well known that glass melts have a considerable ability to react with gases and form complexes in the glass melt or to dissolve gases physically [61]. The resulting glass melts behave consequently as any solution containing gases: they can be saturated or supersaturated by gases originally physically dissolved in the melt or freshly released into the melt by a chemical reaction. The secondary bubbles can then arise in glass melts by the nucleation mechanism if the melt has become supersaturated by a gas. The bubble nucleation therefore affects glass quality and plays a significant role in the production of both current commercial and special glasses [62]. In the industrial glass melting process, two massive bubble nucleations may be currently expected. The bubbles of  $CO_2$  are nucleated on the melt inhomogeneities, particularly undissolved relicts of precursors, when the basicity of the melt decreases below the  $CO_2$  saturation limit under given conditions of the ongoing melting process [63]. The bubbles of the fining gas are similarly released owing to the decomposition of chemical complexes binding the fining gas (mostly  $SO_2$  and  $O_2$ ) if the temperature of the melt is elevated to its maximum fining temperatures [64]. The phenomenon of bubble nucleation is particularly responsible for the fact that partial phenomena such as sand dissolution and the removal of nucleated bubbles are serially linked during the glass melting process and this fact should be taken into account when evaluating the melting performance and energy



consumption of the industrial melting. The decisive impulse to bubble nucleation during the melting process can be the change of temperature (temperature reboil), pressure (pressure reboil), melt composition (composition reboil) or electric potential (electric reboil). Consequently, the temperature reboil arises during glass fining or whenever the temperature is sufficiently elevated, pressure reboil arises at fining under subatmospheric pressure [65], composition reboil in the early stage of glass melting or on the interfaces melt-boundary (refractory material-melt level) and the electric reboil on electrodes or any materials acquiring the relevant electric potential [66-67].

The frequent opportunities for bubble nucleation on the one hand and the impact of bubbles on the melting process and glass quality on the other hand lead to the need for an appropriate method for the examination of bubble nucleation in glass melts. The bubble nucleation is unfortunately accompanied by negligible changes of the glass properties, even if the attention would be focused on the released gas. The visual *in situ* observation of nucleated bubbles nevertheless provides information on the existence and intensity of the nucleation process. Consequently, the method of high temperature monitoring and image analysis was developed and applied to determine the temperature at which the bubbles were nucleated on a platinum wire immersed in the melt of a float type of glass as is obvious from figure 6 [68].

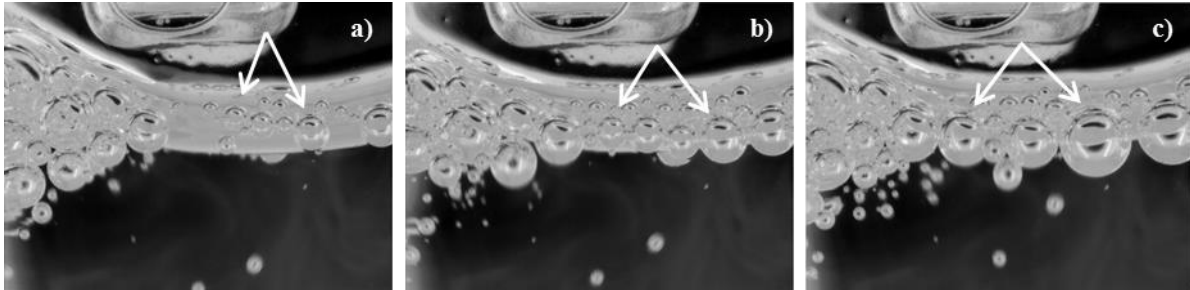


**Figure 6:** The typical picture of the melt with the Pt wire and nucleated bubbles at a temperature of 1518.4 °C [68]. The glass sample with 0.185 wt. % of chemically dissolved SO<sub>3</sub>. The nucleated bubbles marked by white arrows were evaluated.

The bubbles that rose during a slow increase of temperature were identified, monitored and subsequently, their diameter was measured and the obtained dependence between the bubble diameter and time was extrapolated to the zero size of the relevant bubbles. The bubble nucleation temperature has been determined at the temperature of bubble zero size. The obtained average value of the bubble nucleation temperature in glass with 0.185 wt. % of chemically dissolved SO<sub>3</sub> was 1502.6 °C whereas the same quantity showed the value in glass with 0.250 wt. % of chemically dissolved SO<sub>3</sub> to be 1501.4 °C. The intensity of bubble nucleation in the form of the number of nucleated bubbles and the volume of released gas versus time were also measured in both glass samples and described by a theoretical equation. The relation between the diffusion and thermodynamic barriers of the nucleation was determined and discussed in terms of transfer of the determined nucleation temperature to other types of nucleation. Consequently, the value of the bubble nucleation temperature measured on the Pt wire is transferrable to bubble nucleation on another nucleation support. The results were also discussed with respect to the literature data relating to the bubble removal process [69]. The nucleation temperature specifies the region of the intensive bubble removal from the melt.

The concept of bubble nucleation was applied when examining the reaction of water vapour with glass melt containing sulfur compounds which produces foam [70]. The soda-lime-silica glass melt was exposed to an atmosphere with a high water vapour partial pressure at temperatures of 1400-1500°C and the processes in the melt were observed and monitored using the high temperature observation method. The glass batch containing sulfates with carbon - so that the molar ratio between

the carbon and sulfate ions in the batch moved between 0 and 9 - the batch without any fining agent and the batch with the addition of antimony oxide were prepared. The foaming and bubble nucleation on the level of molten glass were observed in glasses with sulfate additions when the water vapour partial pressure in the atmosphere exceeded 0.5 bar, but the bubble nucleation in the reduced glass was observed also at a lower partial pressure (see figure 7).



**Figure 7:** The photographs of bubble-in-foam growing in the soda-lime-silica glass with a molar ratio of  $C/SO_4^{2-} = 6$  at temperature of  $1500^{\circ}C$  and  $p_{H_2O} = 50$  kPa [70]. a) 0 s, b) 108 s, c) 300 s.

The bubble nucleation intensity increased with temperature. No bubble nucleation was observed in the melts with antimony oxide or in the melt without any fining agent. The bubbles nucleated on the glass level in both the oxidized and reduced melts with sulfate additions grew by a growth rate exceeding the bubble growth rate in the volume of glass by almost one order of magnitude. The unstable but rapidly renewed foam spread subsequently over the glass level. The most intensive foaming was observed in the glass melt without carbon and in the slightly reduced glass. The mechanism of the reaction between water vapour and glass was discussed in terms of a controlling process as well as its negative impact on the glass melting process. The rapid growth of bubbles nucleated on the glass level and following glass foaming was ascribed to the Marangoni flow in the bubble lamelas.

## 5. Special glasses for photonics and optoelectronics

### 5.1.State of the art – infrared transmitting glasses

The basic intrinsic properties of glass, distinguishing it from crystals, include isotropy, homogeneity, compositional and doping flexibility, and ability to be shaped into complex forms. Its physical and chemical properties – stiffness and strength, surface quality, thermal and dimensional stability, air tightness, electrical and dielectric properties, low transmission losses, high refraction index and non-linear optical properties – allow for glasses to be used in many sophisticated applications such as optical fibres, substrates or superstrates in displays or in photovoltaics, as solid electrolytes, as a supporting materials in electronics, as a transparent materials enabling to transfer and also to manipulate transported light in optics and telecommunications applications [71-74]. It should be mentioned that also organic polymers exhibit interesting properties, but their lower optical quality, poorer mechanical properties and lower durability in comparison to inorganic glasses limit their real applications.

The general interest in the infrared transmitting materials follows from the dependence of the theoretical transmission losses of materials on the wavelength of transmitted light – in case of applications such as transmission of power and/or optical signals - and from particular requirements of specific applications (e.g. materials for infrared spectroscopy). The preparation and systematic study of new glass materials with promising optical, electrical and dielectric properties for use in optoelectronics and photonics is relevant for basic research in material science [75].

Inorganic glasses transparent in infrared region include halogenide, chalcogenide, heavy metal oxide and some phosphate glasses [76-77]. The halogenide (especially fluoride) and phosphate glasses

are extremely susceptible to humidity, which is the main hurdle to their widespread application. On the other hand, fluoride glasses exhibit highest rare-earth (RE) solubility due to the diameter of fluoride ion and its ability to compensate the field of RE ions. The chalcogenide glasses stand out with their wide transmission range reaching up to 20  $\mu\text{m}$  in case of telluride glasses [77]. They are indispensable in infrared (night) vision, because they are the only materials able to transmit the light with the wavelength of around 8-12  $\mu\text{m}$  (the maximum intensity of blackbody radiation from objects at ambient temperature falls within the interval of 8 to 12  $\mu\text{m}$ ) [75]. In addition, these materials feature the lowest phonon energies due to the covalent character of inner bonds, but also the poorest solubility of RE ions. It should be noted that the solubility of RE ions in connections with low phonon energies leads to high efficiency of RE based 4f-4f radiative transitions. The last group of inorganic glasses are heavy metal oxide (HMO) glasses, such as tellurites, antimonates and unconventional systems like  $\text{PbO-Ga}_2\text{O}_3\text{-Bi}_2\text{O}_3$  [78-80]. These materials exhibit transparency in visible and infrared region of the spectrum (up to 6-8 microns), high refraction indexes (above 2), and highly non-linear optical parameters as a function of composition. A major obstacle for their utilization is the purity of the prepared material [81].

To solve this particular problem, which itself requires a lot of effort and is time and material consuming; only partial success rather than a breakthrough can be expected for the moment. Solving the challenge of purity of quartz glass required several decades of research – and this concerned only a one-component system. So far the efforts aim to modify the existing technology to enable production of silica-based binary glasses, not to mention the multi-component ones. In the case of a more complex systems with incorporation of Sb, Ti, Al or other elements, different partial pressures of components, different melting and boiling points and different coefficients of thermal expansion need to be taken into account. These properties lead to problems with establishing and maintaining a desired glass composition and also they result in the building of stress during heat treatment that causes cracks in the obtained glass [75].

Thus, one of the key challenges that the glass scientific community faces is looking for a suitable – simple, efficient and cost-effective – methods of cleaning the source materials and of maintaining the achieved purity, and/or to develop suitable methods of preparation and fabrication of high-purity multicomponent glasses [75].

The major impurity in infrared materials is the presence of OH- groups, which reaches especially in HMO materials too high concentrations. These hydroxyl groups have their fundamental absorption band in the infrared region at around 2.9  $\mu\text{m}$ . Particular cleaning methods that are typically applicable only to a narrow group of substances have been described for the previously mentioned groups of materials (halogenides and chalcogenides), but not for the HMO glasses. In fluoride glasses OH- groups are primarily removed during the fluorination process possibly followed by melting in vacuum. The chalcogenide glasses are prepared by melting purified elements in evacuated and sealed silica ampoules. Purification of starting elements involves physical methods (sublimation, distillation) [82].

## **5.2 Research in the field of special glasses conducted in the Laboratory of Inorganic Materials**

The research in the field of infrared transmitting glasses is based on close cooperation of the Laboratory of Inorganic Materials with other partners involving the Institute of photonics and Electronics AS CR, the University of Chemistry and Technology Prague, Slovak Technical University, University of Rennes 1 (France) etc. The partners are in charge of specialized analyses and interpretation of their results, while the Laboratory of Inorganic Materials is in charge of preparation and basic characterization of investigated glasses and especially of leading the research and cooperating research groups.

Since 1993 the Laboratory was the main beneficiary of many grants of the Czech Science Foundation, the Ministry of Education, Youth and Sports of the Czech Republic or COST Association. The last grant project of the Czech Science Foundation (project No. P106/12/2384) covered partially the evaluation period 2012-2014. The secondary beneficiary of this grant was the Institute of Photonics and Electronics AS CR.

### 5.2.1 Methodology

During the period of 2012-2014 the research has been focused on two main directions: on heavy metal oxide glasses – especially on telurite, antimonate and bismuthate mixed glass systems, and on chalcogenide glasses and preparation of chalcogenide glass preforms for drawing of optical fibres.

In the field of HMO glasses research focused on preparation and characterization of new glass systems and on searching for methods of preparation of HMO glasses with higher purity (especially with regard to the concentration of hydroxyl groups). Investigated glass systems include for example  $\text{TeO}_2\text{-PbCl}_2\text{-Sb}_2\text{O}_3$ ,  $\text{TeO}_2\text{-PbCl}_2\text{-Bi}_2\text{O}_3$ ,  $\text{TeO}_2\text{-PbCl}_2\text{-WO}_3$ ,  $\text{TeO}_2\text{-PbCl}_2\text{-MoO}_3$ ,  $\text{TeO}_2\text{-PbCl}_2\text{-ZnO}$ ,  $\text{PbCl}_2\text{-Sb}_2\text{O}_3\text{-ZnO}$ ,  $\text{ZnBr}_2\text{-Sb}_2\text{O}_3$  and  $\text{PbO-Ga}_2\text{O}_3\text{-Bi}_2\text{O}_3$ . For some of them (generally for the  $\text{TeO}_2\text{-PbCl}_2\text{-M}_x\text{O}_y$  family) the glass forming areas were delimited for the first time by experiments performed in the Laboratory. The HMO glasses are generally prepared melt quench method by melting of starting mixtures in open crucibles using an electrical furnace and by pouring the melt into metallic moulds. The castings are then annealed at the temperature close to the glass transition temperature of the respective glass, then they are slowly cooled down to the laboratory temperature. Obtained samples are cut and polished to optical quality of the surfaces. The basic physico-chemical properties, such as density, thermal properties, chemical durability and optical transmission are subsequently determined.

Selected glass systems are prepared under controlled conditions in order to investigate the influence of technological conditions during preparation of samples on their physico-chemical properties. Special emphasis is given to monitoring of the final purity of the prepared glasses. Laboratory equipment allows preparing glass under various temperature regimes in different atmospheres and/or vacuuming. Crucibles used for melting of glasses may be of different materials including quartz glass, purified alumina, zirconia or periclase ceramics, glassy carbon or precious metals (Au, Pt).

Chalcogenide glasses are usually prepared by direct synthesis of purified elements in sealed evacuated quartz glass ampoules. The melting process himself involves applying the appropriate temperature regime with simultaneous mixing of the melt in rocking furnaces. The glass melt is cooled down and annealed in the melting ampoule, which is finally removed by etching in hydrofluoric acid. For the preparation of special hollow preforms for drawing of capillary and microstructure fibers the rotational melting technique is employed using a modified lathe.

The Laboratory prepares preforms for drawing of optical fibers at collaborating laboratory at the Institute of Photonics and Electronics AS CR.

### 5.2.2 Equipment

Available laboratory equipment meets the requirements of the research undertaken in the Laboratory. It includes laboratory furnaces with temperature control, apparatuses allowing control of the atmosphere around melting crucible, dry boxes. For mechanical processing of prepared samples diamond saws, micro-drill, grinding and polishing equipment are in the Laboratory. Accurate scales serve for preparation of starting mixtures and also for determining the density by hydrostatic method. Transmission spectrometers covering the spectrum from 190 nm up to 25 microns are available in the Laboratory for characterization of basic optical properties. Optical microscopes allow visual observation of prepared samples, and also allow an estimation of the refractive index of prepared glasses. Thermal analysis techniques (DTA/TG, DSC), electron microscope with the possibility of semiquantitative microanalysis and an XRF analyzer are readily available within the Institute.

An access to specialized techniques for measuring low-temperature photoluminescence (starting from 4 K), electrical and dielectric measurements (currents of the order of  $10^{-12}$  A and frequency range of Hz-GHz) and others techniques is possible by established cooperation with other institutions.

### 5.2.3 Results

The research is based on close cooperation with other institutions. The Laboratory of Inorganic Materials is in charge of leading of research projects and ensures the technological part of the research – it concentrates on the preparation of glass samples and their basic characterization.

The influence of composition on electrical, dielectric and optical properties of  $x\text{TeO}_2$ - $y\text{Sb}_2\text{O}_3$ - $z\text{PbCl}_2$  glass system prepared in silica crucibles in air, where  $x$  is in the range of 40-80,  $y$  falls in the range of 0-20, and  $z$  in the range of 10-50 has been studied in detail. The properties of the most stable composition  $70\text{TeO}_2$ - $10\text{Sb}_2\text{O}_3$ - $20\text{PbCl}_2$ , prepared in various crucibles, under various atmospheres, melted and annealed under different temperature regimes, have been studied and analyzed in more detail. It was found that the colour of glasses depends on the glass composition, material of melting crucible, atmosphere above the glass melt, and duration of annealing. A slightly yellow color of binary  $\text{PbCl}_2$ - $\text{TeO}_2$  glasses darkens with addition of  $\text{Sb}_2\text{O}_3$ . The oxidizing  $\text{O}_2$  atmosphere and especially  $\text{Cl}_2/\text{O}_2$  atmosphere result in brightening of glasses. Dark colors of glasses result from the reaction of the melt with graphite or Pt crucibles, at longer annealing near  $T_g$ , and are probably due to the precipitation of elemental Te. Temperature dependences of the DC conductivity follow Arrhenius law with a single activation energy. Yellow glasses prepared in alumina crucibles exhibit the highest and black glasses prepared in glassy carbon crucibles have the lowest DC conductivity. The static permittivity depends significantly on the technology of preparation, while its lowest values are typical for brown glasses prepared in glassy carbon crucibles; the highest values for yellow glasses prepared in alumina crucibles. Increasing concentration of  $\text{PbCl}_2$  causes an increase of DC conductivity and at a same time a decrease of conduction activation energy. Addition of  $\text{Sb}_2\text{O}_3$  in low concentrations results in a decrease of the DC conductivity [83].

The glasses from the system of  $\text{Sb}_2\text{O}_3$ - $\text{Na}_2\text{O}$ - $\text{ZnO}$  prepared in cooperation with University of Rennes 1 were investigated using transmission spectroscopy in combination with low temperature photoluminescence measurements. The optical gap varying from 3.09 to 3.15 eV has a tendency to decrease at higher  $\text{Na}_2\text{O}$  and/or  $\text{ZnO}$  contents. The attention has been concentrated on the fine structure of two photoluminescence bands at 980 and 1530 nm that represent transitions from the two lowest excited states  $4I_{11/2}$  and  $4I_{13/2}$  to the ground state manifold  $4I_{15/2}$ . A detailed measurement of these photoluminescence bands at 4 K and 300 K, followed by the de-convolution of spectra into Gaussians, enabled to deduce the schematic energy diagram of Stark levels splitting for the three lowest manifolds of  $\text{Er}^{3+}$  ions. Such a procedure enabled to assign energies to Stark levels of individual manifolds and revealed the nature of broadening of photoluminescence bands when temperature is elevated from 4 to 300 K [84].

Electrical and dielectric properties of Ge-Se-Te glasses, both undoped and doped with Ho added in various chemical forms and prepared in the Laboratory were studied. The attention was focused on the influence of doping on structure and properties of prepared glasses. Two relaxation processes appear at higher doping levels (above 2000 wt.-ppm Ho). It indicates that partial crystallization takes place in the system. For heavily doped glasses (1500 and 2000 wt.-ppm Ho), XRD experiments using high-energy photons, show distinct Bragg peaks stemming from a tiny fraction (about 0.25%) of crystalline phases. Crystallites are rather homogeneously distributed within the sample. This heavy doping influences the glass network; it shortens interatomic distances, enhances mean atomic density, and increases coordination numbers. It results in a better atomic packing. Temperature dependences of the dc conductivity are Arrhenius like; their conduction activation energy decreases and the dc conductivity increases with increasing concentration of Te. Relative static permittivity of glasses decreases with increasing Te content. Doping with 1000 wt.-ppm Ho in a metallic form decreases the conduction activation energy. This decrease is pronounced for 2000 wt.-ppm Ho what is typical for phase separated or partially crystallized glasses [85].

Pure Ge-Ga-As-S glasses and those doped with  $\text{RE}^{3+}$  ions were characterized by both electrical measurements and low-temperature PL spectroscopy. Excitation within the host glass absorption edge enabled the simultaneous observation of broad-band luminescence of the host glass with superimposed narrow features due to  $4f$ - $4f$  transitions in  $\text{RE}^{3+}$  ions. Observed narrow dips, interpreted

as due to 4f-4f up-transitions, provide direct evidence for the energy transfer between the host glass and RE<sup>3+</sup> ions [86].

Other results obtained in the field of special glasses were presented as contributions (more than 30 in the period of 2012-2014) at international scientific conferences. The most important of them concerned glass formation in several systems mentioned above in the 5.2.1 part and the characterization of glasses from these systems. Our progress with preparation of hollow preforms, drawing of fibres and capillaries and their characterization at collaborating Institute was also reported. Some of these results relate to manuscripts being prepared or already sent to the journals editors.

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## Research Report of the team in the period 2010–2014

Institute	Institute of Rock Structure and Mechanics of the CAS, v. v. i.
Scientific team	Department of Composites and Carbon Materials

### Department of Composites and Carbon Materials

The research activities of the team in the period from 2010 – 2014 were focused on modern fibrous, particulate and hybrid composite materials on the basis of synthetic or natural materials. These activities can generally be divided into two thematic groups - composite materials for tissue engineering and medicine, and heat-resistant composites.

Within this period, **advanced composite materials for tissue engineering and medicine** in the form of bone graft replacements, substitutive/filling and connective elements were designed on the basis of biocompatible and biodegradable matrices and various kinds of reinforcing phase in the form of micro- and nanofibers or particles (Šupová et al. 2011a). Individual components and composites were prepared by electrospinning, lyophilisation and other widely-used curing and precipitation techniques. Long-standing experience of isolating collagenous materials and calcium phosphates from natural precursors was applied in preparing the materials. The physico-chemical characterization and the quality of particular precursors were monitored by various techniques, e.g. FTIR spectroscopy, X-ray diffraction, chemical analyses, scanning and transmission electron microscopy, energy dispersive spectroscopy, etc. (Filová et al. 2011). The ability of the composites to form a strong connection with bone tissue was further optimized with the help of specially developed techniques enabling the formation of open, interconnected pores of suitable dimensions and density for bone cell ingrowth (Kubies et al. 2010, Kubies et al. 2011, Vagaská et al. 2010).

The team was also engaged in the development of **materials** (Šupová et al. 2012, Pabst et al. 2011, Pabst et al. 2013) **and composites designed for applications exposed to elevated temperatures** (Černý et al. 2012). The research focused on polysiloxane matrix precursors and on thermally induced conversion of the precursors to silicon oxycarbide (Halasová et al. 2012). This ceramic material has high thermal resistance and low density, and it has therefore been tested for use as a fire-resistant foam core for sandwich structures or for a matrix reinforced by ceramic or basalt fibers.

The activities of the **Department of Composites and Carbon Materials (DCCM)** can be divided into two main research areas dealing with several projects:

#### **FIRST RESEARCH AREA: COMPOSITE MATERIALS FOR TISSUE ENGINEERING AND MEDICINE**

**TOPIC#1.** Isolation and characterization of natural organic and inorganic materials, their processing into nanofibrous mats and into hybrid nanofibers

**TOPIC#2.** Biocomposite materials for bone tissue regeneration

**TOPIC#3.** High performance radiolucent composite materials providing high resistance against sterilization decomposition, for use in medicine

**TOPIC#4.** Development of resorbable collagen-calcium phosphate nanolayer with controlled elution of antibiotics for implants survival rate enhancement

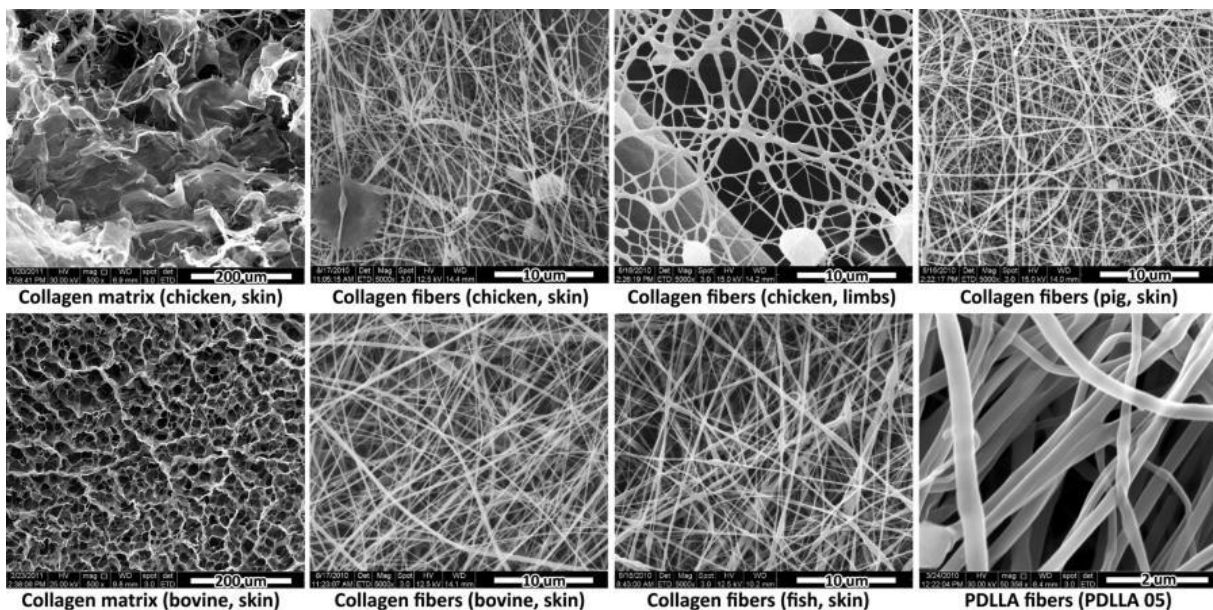
## SECOND RESEARCH AREA: HEAT-RESISTANT COMPOSITES

**TOPIC#5.** New matrix types based on pyrolysed resins for composites reinforced with ceramic fibers

**TOPIC#6.** SiOC ceramic foam from a pyrolyzed polymer precursor as the core for thermally stable composite sandwich structures

### TOPIC#1. ISOLATION AND CHARACTERIZATION OF NATURAL ORGANIC AND INORGANIC MATERIALS, THEIR PROCESSING INTO NANOFIBROUS MATS AND INTO HYBRID NANOFIBERS

A specialized laboratory for collagen preparation was developed in DCCM. Several types of collagen (mainly type I) from different animal genera and sources were isolated within the framework of this action. Various calcium phosphate nanopowders (CaPs) were assessed (Filová et al. 2014, Suchý et al. 2011a) in order to obtain a suitable filler for the studied biocomposites (Suchý et al. 2013a, Rýglová et al. 2010). Further, CaPs were prepared by precipitation and by isolation from animal bone of various genera (Šupová 2014). Isolation of bioapatite acquired from chicken femur bones was published for the very first time (Šupová et al. 2011b). These naturally derived materials were further chemically and structurally characterized. The possibilities of processing of these materials into several forms were further studied (unpublished results, utility models: Balík et al. 2013a, b, c, d). A special attention was laid on electrospinning process. Nanofibers prepared from natural and synthetic polymers were modified, e.g. with CaP nanoparticles (Novotná et al. 2014). The orientation of the nanofibers using different collectors, and by proper adjustment of the electrospinning conditions were studied. Optimization of polymer solutions for electrospinning was the main goal namely in the case of collagen. This is very often problematic because collagen is natural material and its physico-chemical properties are strongly dependent on the source (animal genera, age, gender, type of source, etc.). Co-spinning of collagen-synthetic polymers nanofibers were employed as one way to avoid this problem. Since collagen, from isolation to electrospinning, undergo various physical or chemical treatment, the unique properties of triple-helical collagen structure can be denatured to gelatine. Therefore various analytical techniques, such as infrared spectroscopy, circular dichroism, differential scanning calorimetry and second harmonic generation were used for verification of final structure of nanofibers.

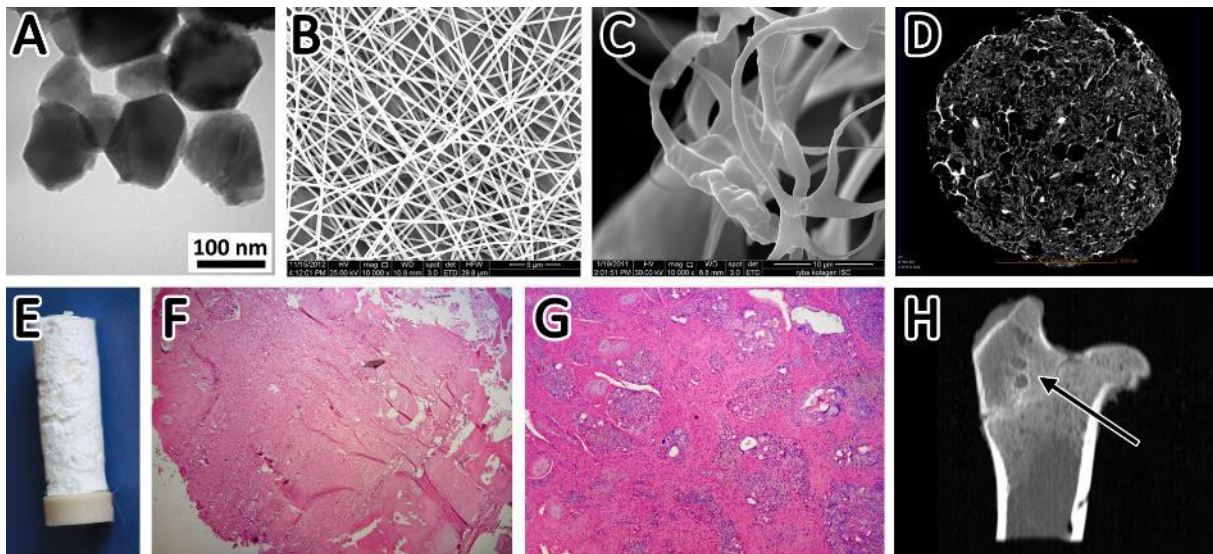


**Figure 1.** Some representative SEM images of collagenous materials and polylactide (PDLLA) fibers prepared and investigated at DCCM.

## TOPIC#2. BIOCOMPOSITE MATERIALS FOR BONE TISSUE REGENERATION

A study was made of the material properties of bone tissue engineering biomimetic materials. The composites were based on an integrated porous structure consisting of collagen (matrix), polylactide nanofibers (reinforcement) and bioapatite (acceptable dispersed filler), supplemented by hyaluronic acid. Two degradation and resorption periods were proposed, aimed at matching the healing rates for injured bone, i.e. 6 months (for a young patient) and 12 months (for an old patient). Cylindrical samples based on selected components were processed to the final design by lyophilisation. The mechanical properties of the prepared composite structures were evaluated by nanoindentation (Suchý et al. 2012a) and uniaxial tensile tests. A description of the reproducible methodology, together with results, was published (Suchý et al. 2012b, Marx et al. 2012). The mechanical properties of composites optimized by lyophilisation showed values close to the interval for human cortical bone. Using micro CT analyses the inner structure of composites was characterized. The other set of materials was used for verifying the experimental findings (exposition in simulated physiological conditions) to obtain data on swelling and on mechanical stability. The results of the exposition experiments as well as the results of *in vitro* tests proved that the prepared biocomposite is ready for use in *in vivo* biological evaluation. The performed *in vivo* tests demonstrate that composite samples were well osseointegrated. The proposed degradation periods were verified.

This study was carried out in collaboration with Elmarco Ltd., Institute of Physiology of the Academy of Sciences of the Czech Republic (ASCR) and Institute of Macromolecular Chemistry ASCR. The DCCM was the main investigator. The contribution of the team to the research involved mainly working on the proposal for basic composite components (isolation of collagen, calcium phosphates), their preparation and characterization, preparation and optimization of composite materials and implants, their characterization and cooperation on biological evaluation.



**Figure 2.** Prototypic biodegradable bio-composites prepared in the framework of the project. Basic components: (A) natural CaP isolated from bovine bone, (B) PDLLA electrospun nanofibers, (C) natural collagen isolated from fish skin. (D) a micro-CT scan of the inner structure of the composite, (E) a composite implant with a PEEK marker. An example of hematoxylin/eosin staining of a bone defect with an implanted composite (miniature pigs, femur): (F) 26 weeks and (G) 52 weeks post-surgery. (H) a CT scan of bone defects with implanted composites at 26 weeks post-surgery (unpublished results).

**TOPIC#3. HIGH PERFORMANCE RADIOLUCENT COMPOSITE MATERIALS PROVIDING HIGH RESISTANCE AGAINST STERILIZATION DECOMPOSITION, FOR USE IN MEDICINE**

This study involved fundamental research on novel radiolucent composite materials that will meet the complex and demanding requirements for materials for medical devices, e.g. surgical intra-operative guides and instrumentation, screening equipment accessories and patient support systems, ranging from hand tables and head supports to cantilevered angiography and full body CT cradles, and radiolucent tables for performing periacetabular osteotomies supported by intra-operative imaging. In the course of this project, different kinds of composite materials were prepared and analyzed (Suchý et al. 2011b). Composites were further modified by adding nanoparticles and ball milled multi-wall carbon nanotubes. Macromechanical properties were evaluated by static and dynamic three- and four-point bending tests before and after repeated sterilization (Suchý et al. 2013b). The analysis of mechanical properties was accompanied by image analysis, topography and open porosity measurements. On the basis of all the analyses, a comprehensive evaluation of the impact of the sterilization processes was made, and a group of materials with suitable resistance against sterilization decomposition was selected (Sedláček et al. 2012a, Sedláček et al. 2012b). Their compositions (selecting an appropriate volume fraction and orientation of the reinforcements) were optimized by mathematical models using finite element method. Resistance against sterilization decomposition was evaluated (shape stability, structural integrity) (Sedláček et al. 2012c). Special emphasis was laid on composites based on carbon fibers and PEEK matrix as the material showing the most appropriate properties within the analyses that were performed. The ability of composites to be formed with various orientations of the strips and to be formed into various shapes without the need for subsequent machining operations was verified. The preparation process was optimized by selecting an appropriate hardening program and by modifying the inner structure by applying various volume fractions of selected nanoparticles, and distributing and homogenizing them within the composite aiming at a higher rate of resistance against sterilization processes. Finally, the cytotoxicity of the basic components, and of the composites, was determined using cell culture techniques.

This study was carried out in collaboration with Faculty of Mechanical Engineering Czech Technical University in Prague, LETECOERE Ltd. Czech Republic and MEDIN Inc. The DCCM was the first joint investigator. The contribution of the team to the research involved mainly development and fabrication of basic composites, mechanical tests, providing sterilization tests and evaluation of shape and dimensional stability, open porosity, image and topography analyses and finally evaluation and interpretation of *in vitro* tests.

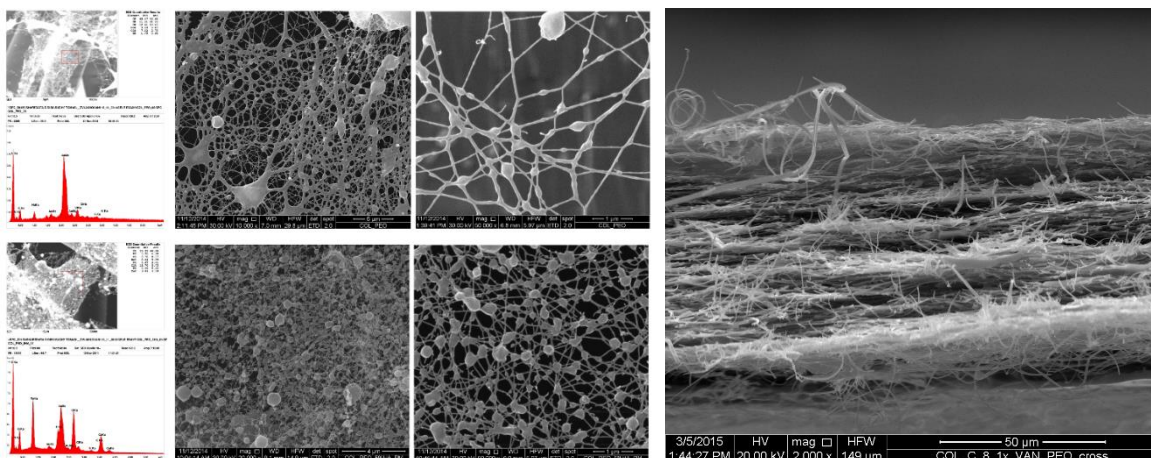


**Figure 3.** Novel carbon/PPS composite intraoperative guides for accurate targeting of the distal nail holes and accurate interlocking screws used for the treatment of diaphyseal fractures of long bones.

#### **TOPIC#4. DEVELOPMENT OF RESORBABLE COLLAGEN-CALCIUM PHOSPHATE NANOLAYER WITH CONTROLLED ELUTION OF ANTIBIOTICS FOR IMPLANTS SURVIVAL RATE ENHANCEMENT**

Since September 2014, our department has been engaged in developing resorbable collagen-calcium phosphate nanolayers with controlled elution of antibiotics to enhance the survival rate of implants. The nanostructured layers are for use especially when there is known systemic or local (joint) inflammation. This layer can provide a bone tissue/implant (titanium alloy) bioactive interface that will improve the physiological healing process and eliminate the risk of bacterial orthopaedic infections. The first prototype of this layer was composed of collagen (type I, isolated from calf skin), hydroxyapatite nanoparticles and vancomycin hydrochloride (10 wt%) (functional model: Suchý et al. 2014). The stability of the collagen was enhanced by cross-linking. In order to find the optimal cross-linking method, the mechanical and structural properties, the swelling ratio and the degradation rate of these layers were investigated and compared. The *in vitro* release of vancomycin from optimally cross-linked layers was investigated. The main aim of this stage of the continuing project was to verify whether the local concentration of released vancomycin exceeded the minimum inhibitory concentration (MIC) for vancomycin-resistant *Staphylococcus aureus* (VRSA, >16 mg/l). During the whole experimental period, the level of released vancomycin was well above the MIC for VRSA. The maximum average concentration was obtained between day 4 and day 8 (265 mg/l). At the end of the experiment (day 21), an average concentration of 104 mg/l was detected. Our study confirmed the prophylactic effects of vancomycin-loaded nanostructured layers.

This study was carried out in collaboration with Faculty of Mechanical Engineering Czech Technical University in Prague and ProSpon Ltd. The DCCM was the main investigator. The contribution of the team to the research involved mainly working on the proposal for nanofibrous collagen layers, optimization of solutions for electrospinning, their modifications by calcium phosphate nanoparticles and antibiotics, proposal of methods for crosslinking of layers and analyses of degradation behavior.



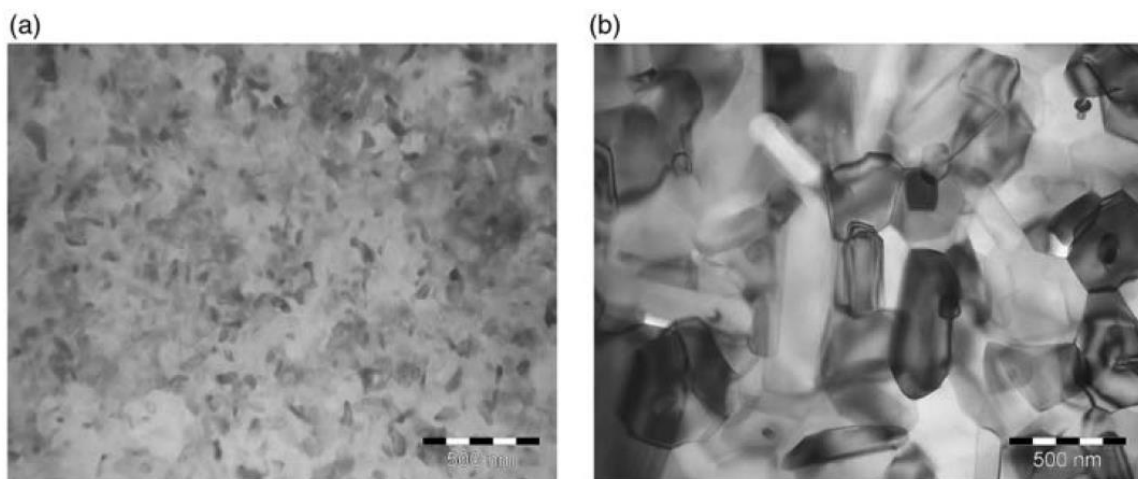
**Figure 4.** Collagen/hydroxyapatite/polyethylene oxide layers prepared by electrospinning.

#### **TOPIC#5. NEW MATRIX TYPES BASED ON PYROLYSED RESINS FOR COMPOSITES REINFORCED WITH CERAMIC FIBERS**

The fifth study involved developing new matrix types based on pyrolysed resins for composites reinforced with ceramic fibers (Chlup et al. 2011a, b). The transformation of an organic-inorganic oligomeric resin into a cured infinite polymer network and subsequently into the final fully pyrolyzed inorganic state (black-glass ceramics) was investigated using TGA, GCMS and indentation techniques (Černý et al. 2010, Strachota 2011). Based on the knowledge that was acquired, manufacturing procedures for Si-O-C, Si-O-N-C, Si-N-C, Si-B-O-C and Si-B-O-N-C resins as precursors for matrices of composites reinforced with ceramic fibers were developed (Strachota et al. 2012). These precursors were intended for high-temperature applications. A method for dissolving iron compounds in these

resins was also developed. These manufacturing procedures were continuously modified according to the material and technological properties of the precursor. The resins that were developed can be used easily in the wet-winding technology of prepreg preparation. Temperature – pressure regimes for composite curing in a heated mold and heating programs for pyrolysis at temperatures up to 1100°C were designed. Laboratory manufacturing of composites reinforced with Nextel720 ceramic fibers demonstrated that the best technological properties are found in siloxane resins with a molecular ratio of components T and D equal to 3:1 and 4:1 and in Si-O-N-C resins (Černý et al. 2013). Pyrolyzates of these resins revealed excellent oxidation resistance beyond 1300°C (which is the ultimate application temperature recommended by the producer of Nextel720). In addition, processes for thermal treatment of the composites - annealing at 1500°C - were designed, with increased the flexural strength by 15% and reduced the creep deformation rate measured at 1300°C by 50%.

This study was carried out in collaboration with the Institute of Physics of Materials ASCR and the Institute of Macromolecular Chemistry ASCR. The DCCM was the main investigator. The contribution of the team to the research involved mainly working on the proposal for material technologies for producing long-fiber composites. In addition, DCCM carried out some basic experiments to evaluate the materials that were developed (measurements of mechanical properties at elevated temperatures, thermogravimetry, GC-MS).



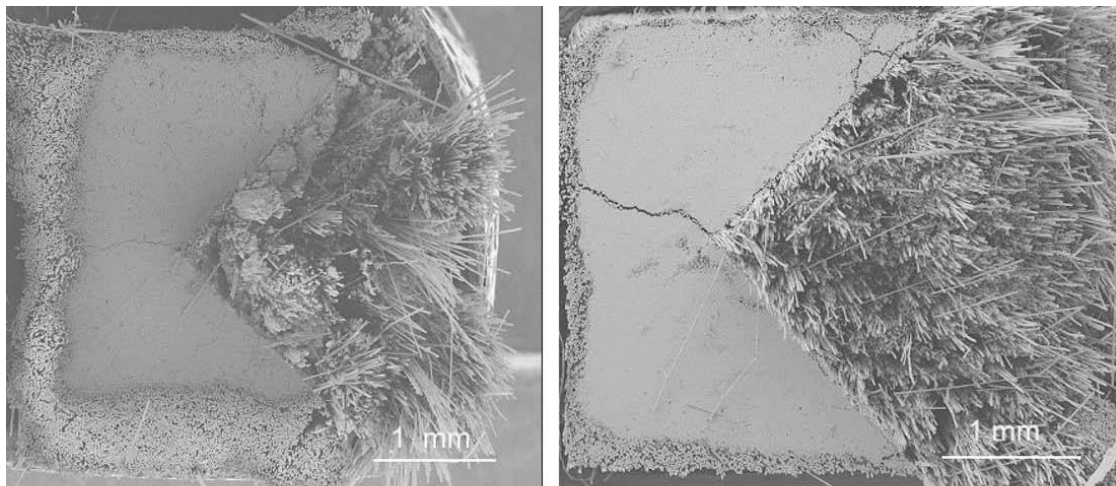
**Figure 5.** Transmission electron microscope images showing microstructure development in the fiber-matrix region of studied composites for (a) pyrolyzed stage and (b) annealed at 1500 °C stage

#### ***TOPIC#6. SiOC CERAMIC FOAM FROM A PYROLYZED POLYMER PRECURSOR AS THE CORE FOR THERMALLY STABLE COMPOSITE SANDWICH STRUCTURES***

The sixth study involved developing an SiOC ceramic foam from a pyrolyzed polymer precursor as the core for thermally stable composite sandwich structures. The goal of this project was to develop a way to prepare Si-O-C ceramic foams that will enable them to be used as cores for high-temperature-resistant sandwich structures. These foams were to be obtained via pyrolysis of polysiloxane pre-ceramic polymers. The team designed and carried out experimental tests on several preparation procedures. The best results were obtained by foaming a polysiloxane precursor resin with starch while the resin was being cured. Very promising results were also obtained by pyrolysis of a polysiloxane composite filled with epoxy powder as a sacrificial filler. The foams that were prepared display favorable mechanical properties, as well as low apparent density - these are the main attributes needed for application as a sandwich core. It was found that the foam properties can be tuned to a considerable extent by varying the preparation conditions. The dependence of the mechanical strength on the apparent density that was obtained can be used to prepare a suitable foam for a given application. The foams that were developed were used to prepare sandwich structures with CMC skin layers, which were connected with the Si-O-C foam core by a suitable high-temperature-resistant

sealant. The CMC composite skin was optimized for use under biaxial loading. Additional important project results involved acquiring knowledge about changes in mechanical properties in the course of polysiloxane pyrolysis, and also knowledge about the technology for preparing partly pyrolyzed composites with a basalt woven fabric reinforcement (Chlup et al. 2014, Černý et al. 2014).

This study was undertaken in collaboration with the Institute of Physics of Materials ASCR and the Institute of Macromolecular Chemistry ASCR. DCCM was the main investigator. DCCM designed the basic technology for Si-O-C black glass foams, the precursor for which was the resin modified by cornstarch. These foams were then used for preparing the resulting sandwich structure.



a) composite 650c

b) composite 750d

**Figure 6.** Partly pyrolysed composites with basalt fiber reinforcement, SEM micrographs of the fracture surfaces after the chevron-notch test (material treated at 600 °C and 750 °C).

All projects mentioned here were supported by the Czech Science Foundation (*TOPIC#2, #3, #5 and #6*) and the Technology Agency of the Czech Republic (*TOPIC#4*).

#### **RESEARCH PLAN OF THE TEAM FOR 2015–2019**

The DCCM activities and personnel structure will be partly re-organized aiming at broader utilization of chromatographic and electrophoretic separation methods for qualitative and quantitative analysis of the prepared nanofiber and nanoparticle composite materials based on natural or synthetic polymers. In addition to better chemical characterization of biopolymer carriers themselves, these methods will allow also selectively and sensitively monitor the content of minor components added to the matrix, and also to test the influence of different physico-chemical conditions on the kinetics of their release to the biological tissues. Last but not least, these approaches will enable control of the homogeneity of individual batches of the material prepared in terms of the composition, degree of cross-linking of the carrier matrix or their degradation to the smaller fragments. In connection with research plan for next years joined the ranks of the team (since 2015) specialist on analytical separation methods in biochemical analysis, and specialist on designing and engineering of medical implants (in part-time employment). Finally, since 2015 two students (in master's and doctoral programmes) work on two research projects of DCCM. In addition to institutional policy, the partly re-organization of the team, team multidisciplinary step-up and reduction of team average age was facilitated by long-term cooperation with universities and also by financial support of grant agencies. In the near future it will be necessary to create conditions for new post-docs and recent graduates, e.g. recently involved in our projects.

The DCCM team intends to continue its investigations of bone tissue engineering materials and biodegradable composites or composite layers. The team intends to continue its investigations of

fundamental aspects of hybrid composites with a basalt fiber reinforcement prepared by partial pyrolysis. The planned activities of the team can be divided into two main research areas:

**FIRST RESEARCH AREA: COMPOSITE MATERIALS FOR TISSUE ENGINEERING AND MEDICINE**

**SUBAREA#1.** With increasing demand for artificial replacements, there is a need for constant innovation in the field of biomaterials and therefore a special focus will be on isolating collagen and bioapatite from several natural precursors. It has been proven that some wastes often contain materials that are beneficial for fabricating bioceramics and for isolating collagen. The discovery that bioapatite ceramic generated partially or entirely from biogenic sources is better accepted by living organs, owing to its physicochemical similarity to human bone apatite, began to make this route more attractive. Collagen and bioapatite has been obtained from a wide range of natural sources (bones, skin, scales etc.). The utilization of waste biomaterials has high potential for this purpose not only because they are accumulating to a problematic extent, but also because natural raw materials are being exhausted and it would be very advantageous to reuse wastes. Biogenic sources are available worldwide, and are very inexpensive. Their attractiveness has been recognized particularly in the past decade. The potential of natural materials and their applications as basic constituents of biocomposites will be investigated, and ways and methods for processing them will be studied. Special attention will be paid to the use of the electrospinning process for preparing sub microfibers and nanofibers based on collagen and collagen fibers incorporating bioapatite nanoparticles. Several investigations will be carried out, aimed at preserving the typical and advantageous unique biological properties of collagen and at imitating this major part of extracellular matrix.

**SUBAREA#2.** The team will continue to develop resorbable collagen-calcium phosphate nanolayers with controlled elution of antibiotics to enhance the implant survival rate. The main aim of this project is to extend our knowledge of the properties of multiphase nanostructured materials and to improve the technology for preparing the materials through applied research and experimental development of a new collagen-calcium phosphate nanolayer that can be applied to the surface of medical metal alloy implants. This electrospun nanolayer will provide a bone tissue/implant bioactive interface. It will improve the physiological healing process and will eliminate the risk of bacterial orthopaedic infections. Implants with collagen-calcium phosphate-antibiotics nanolayers could be the solution of first choice in future therapy, because no simple and successful solution is currently available for dealing with septic failure of implants. They are likely to be used especially for systemic inflammation (endocarditis) or for local inflammation (of a joint). Multidisciplinary research leading to the development of specific resorbable nanolayers, with controlled elution of antibiotics, is now being carried out. Work on this project has been carried out in collaboration with ProSpon, one of the biggest Czech companies working on developing and manufacturing implants and instruments for orthopaedic surgery and traumatology. Since July 2014 is this project financially supported by the Technology Agency of the Czech Republic.

**SUBAREA#3.** The team will also continue to prepare and characterize nanocomposite scaffolds with suitable structural and mechanical properties for colonization with mesenchymal stem cells, aimed at promoting the regeneration of defective bone tissue with the required rate of safe biodegradation. The proposed composition of the scaffolds will combine the advantages of biodegradable polylactide electrospun nanofibers, natural collagen matrix supplemented with sodium hyaluronate, and natural calcium phosphate nanoparticles. The preparation process will be optimized, aiming at an interconnected and homogeneously porous material with a nano/microstructured surface, outstanding mechanical properties and a controlled rate of biodegradation capable of withstanding dynamic culture conditions and encouraging homogeneous mesenchymal stem cell colonization. Since May 2015 is this project financially supported by the Ministry of Health of the Czech Republic (Agency for Medical Research).



**SUBAREA#4.** The aim of a further planned project is to design and prepare resorbable bandings on the basis of biocompatible polymeric nanofibers and matrices. Recent reports have pointed out that pulmonary artery banding (PAB) for the treatment of complex congenital heart disease in infants is problematic, as there is a need to reoperate and reconstruct the arteries when debanding is performed (4-10 months). The development of biodegradable pulmonary artery banding would overcome the need for repeated surgical or transcatheter treatments in children with congenital heart defects. Biodegradable PAB would enable a single surgical treatment to be made in many cases, leading to a much lower risk of fatalities, complications, suffering and, last but not least, much less expensive treatment. Newly prepared composite bandings will be physically, chemically and mechanically characterized to verify their short-term and long-term mechanical properties in a simulated body environment, in the living organism, and after sterilization processes. A thorough interdisciplinary approach will be systematically applied in this project to develop and characterize the properties of these bandings and to prepare them for clinical application.

#### **SECOND RESEARCH AREA: HEAT-RESISTANT COMPOSITES**

**SUBAREA#5.** Special attention will be paid to an investigation of the effect of long-term temperature exposition on microstructure and on mechanical behavior of hybrid composites with a basalt fiber reinforcement prepared by partial pyrolysis. The aim of the project is to explain the changes that occur during thermally-induced conversion of aromatic and aliphatic siloxane resins into Si-O-C ceramics. The topic of the research will be Si-O-C precursors in the transitional state between organosilicon polymer and an inorganic material. The effect of pyrolysis on the adhesion between the matrix and the silicate (basalt and glass) fibers in composites with partially pyrolyzed Si-O-C precursor matrices will be investigated, in order to optimize these composites. The optimization will be aimed at increasing the stability of the composites during long-term heat exposure, while maintaining their mechanical strength. To this end, the pyrolysis process will be elucidated and optimized, and improvements to the surface layer of the composite will be tested. An important goal will be to minimize the pyrolysis shrinkage by incorporating powdered Si-O-C into the preceramic polymer.

#### **MAIN COLLABORATING PARTNERS OF THE TEAM**

University of Vienna, Institute of Materials Physics, Vienna, Austria  
National University of Singapore, Singapore  
Indian Institute of Technology Madras, Medical Materials Laboratory, Chennai, India  
AGH University of Science and Technology, Krakow, Poland  
Institute of Macromolecular Compounds, Russian Academy of Science, St. Petersburg, Russia  
Czech Technical University in Prague (Prague, CZ)  
Institute of Chemical Technology Prague (Prague, CZ)  
Technical University of Liberec (Liberec, CZ)  
Institute of Inherited Metabolic Disorders 1st FM, Charles University in Prague (Prague, CZ)  
Faculty of Medicine in Pilsen, Charles University (Pilsen, CZ)  
Institute of Anatomy First Faculty of Medicine Charles University in Prague (Prague, CZ)  
Institute of Physiology AS CR, v.v.i. (Prague, CZ)  
Institute of Animal Physiology and Genetics AS CR, v.v.i. (Liběchov, CZ)  
Institute of Macromolecular Chemistry AS CR, v.v.i. (Prague, CZ)  
Institute of Organic Chemistry and Biochemistry AS CR, v.v.i. (Prague, CZ)  
Institute of Physics of Materials AS CR, v.v.i. (Brno, CZ)  
Elmarco, s.r.o. (Liberec, CZ)  
ProSpon, s.r.o. (Kladno, CZ)  
Contipro Group, s.r.o. (Dolní Dobrouč, CZ)  
MEDIN, a.s. (Nové Město na Moravě, CZ)  
MEDIN Orthopaedics, a.s. (Prague, CZ)  
LA Composite, s.r.o. (Prague, CZ)

LATECOERE Czech Republic s.r.o. (Prague, CZ)  
National Radiation Protection Institute, v. v. i (Řež, CZ)

#### **INTERNATIONAL COOPERATION OF THE TEAM**

Indian Institute of Technology Madras, Medical Materials Laboratory, Chennai, India, group of prof. Sampath Kumar, preparation of bioactive calcium phosphate nano materials;

National University of Singapore, Singapore, group of prof. Seeram Ramakrishna, cooperation on biological evaluation of biocomposites on the model of a miniature pigs and rats;

Institute of Macromolecular Compounds, Russian Academy of Science, St. Petersburg, Russia, group of Dr. Vladimir E. Yudin, structural investigation and physical properties of novel graphite-like nanocomposites based on inorganic particles with a different morphology. In 2015 the mutual joint project proposal „Development of Bone Tissue Engineering Composite Scaffolds based on Natural and Synthetic Polymer Matrices and Nanofibers and Calcium Phosphate Nanoparticles” was submitted at Ministry of Education, Youth and Sports, CZ.

AGH University of Science and Technology, Krakow, Poland, group of prof. Stanislaw Blazewicz, preparation of carbon-carbon composites and composite materials for bone tissue engineering.

## Research Report of the team in the period 2010–2014

Institute	Institute of Rock Structure and Mechanics of the CAS, v. v. i.
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Scientific team	Department of Geochemistry
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### Department of Geochemistry

In the period 2010-2014, research at the Department of Geochemistry has focused on four main research topics:

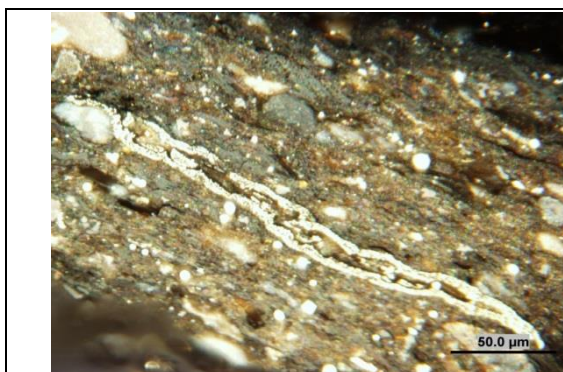
- **Topic 1:** Application of the coal and organic petrology and geochemistry in geology
- **Topic 2:** Application of geochemical methods from environment to medicine
- **Topic 3:** The sorption and texture properties of materials
- **Topic 4:** Geochemistry and petrology of granite suites

The Department of Geochemistry has extensive experience relating to the characterisation of the composition, structure, and properties of rocks and derived materials by surface chemistry, geochemistry, and petrology. During the evaluated period, the department activities focused on several areas and many problems were solved in the framework of projects funded by grants or supported thanks to long-term conceptual research plan of the Institute of Rock Structure and Mechanics.

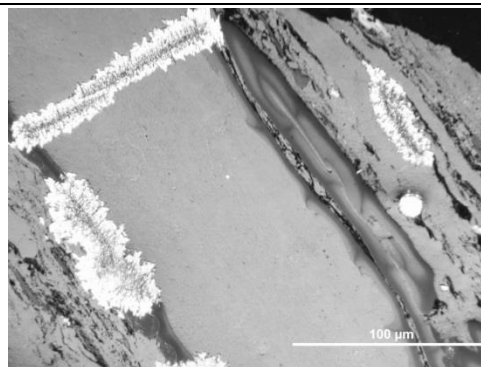
#### **Topic 1: Application of coal and organic petrology and geochemistry in geology (evaluation and utilisation of coal and organic matter dispersed in sediments, restoration of original vegetation, and palaeoenvironmental reconstruction)**

The Department of Geochemistry is the only workplace in the Czech Republic that deals with the detailed petrographic study of the properties and classification of coal, peat, and dispersed organic matter. Results in rank, maceral and chemical composition, including the occurrence of sulphur and distribution of selected trace elements in a wide range of lignite and subbituminous coal have been included, together with palynological and palaeobotanical characteristics and the conclusions of geological, hydrological, mining and technology studies, in new comprehensive overviews of mined and already closed Tertiary and Cenomanian deposits in the Czech Republic. With the assistance of leading Czech experts, the overview was published in books in both the Czech and English languages (Elznic et al., 2014; Honěk et al., 2014; Opluštil et al., 2014; Pešek et al., 2014; Pešek and Sýkorová, 2014; Rojík et al., 2014; Spudil et al., 2014; Spudil et al., 2014; Pešek et al., 2010; Pešek and Sýkorová, 2010; Spudil et al., 2010). Rank, composition of coal matter and occurrence and distribution of selected trace elements and sulphur in bituminous coals and anthracites from the Czech Palaeozoic deposits determined and evaluated in the Department of Geochemistry were summarised by Pešek et al. (2010). An interesting aspect was the cooperation with Chinese and American geologists and geochemists on the evaluation of samples with a high content of selenium in anthracite, bituminous coal from waste piles, and surrounding soil collected from the Chinese Yutangba site, when the

distribution of selenium was studied using electron microscopy by experts from the Department of Geochemistry (Zhu et al., 2012).

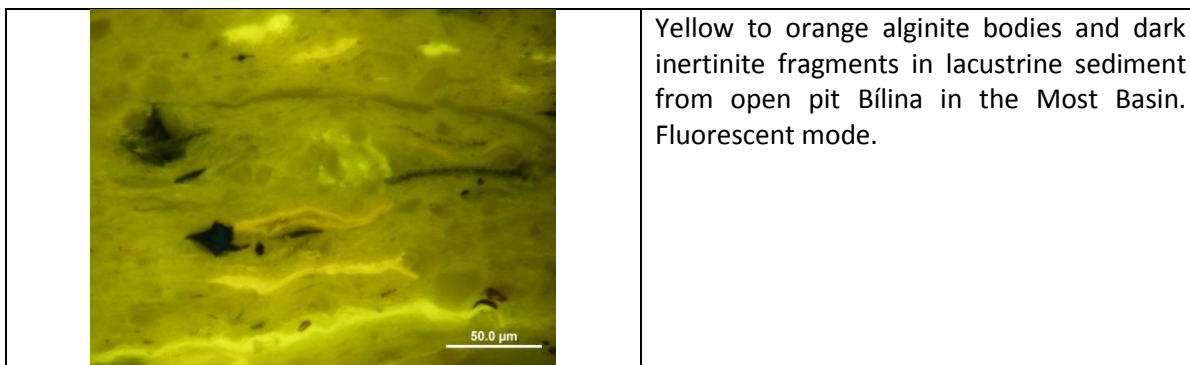


Pyritized sporinite in mineralized humic detritus in the mineral rich lignite from the Libouš mine in Most Basin. Reflected light, oil immersion.

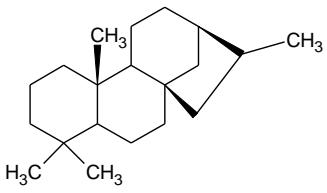
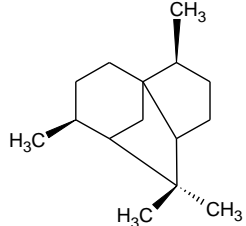
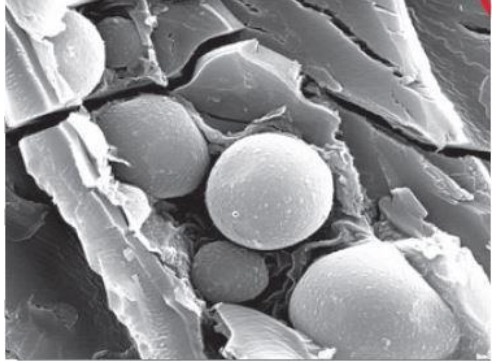


Microphotograph of pyrite with chalcopyrite and sphalerite admixture in bituminous coal from the Krkonoše Piedmont Basin. Reflected light, oil immersion.

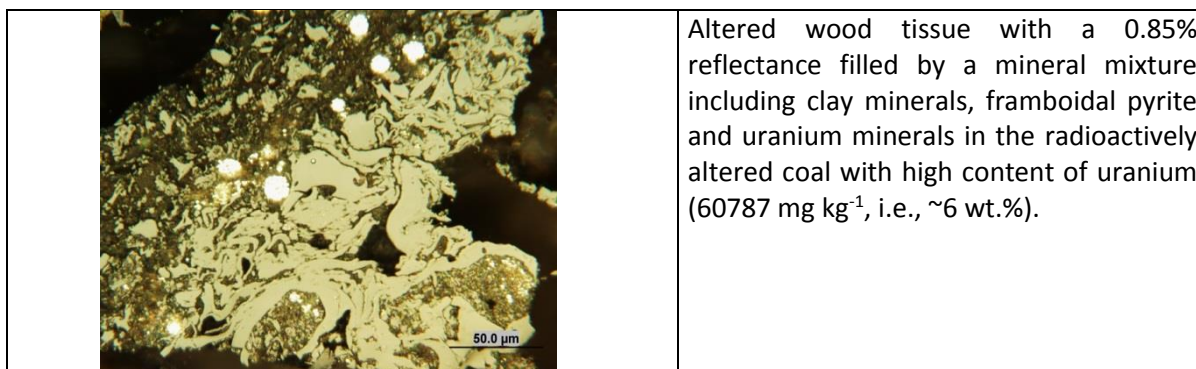
The organic petrological research in the Department of Geochemistry is focused on more details of morphology and structure of cellular tissues, debris of biological materials, and carbonaceous particles with close attention to the size, frequency, morphology, and optical properties of residues of other plant parts and organs including roots, leaves, bark, pollen, spores, fire debris, and products of microbial decomposition. On the basis of their presence and abundance in nature, vegetation conditions, the type of sediment, type of sedimentation environment and peat bogs were assessed. In lacustrine and marine sediments, the incidence of residual water plants, algae, zooclasts, plankton, and particulate terrestrial vegetation, which were transported into the sedimentary environment by water or air, was ascertained. The studies have been carried out in collaboration with experts from the Faculty of Science of Charles University, VŠB-Technical University of Ostrava, the Czech Geological Survey and other geologically-oriented institutes not only from the Academy of Sciences of the Czech Republic but also from abroad. The petrographic data including detailed maceral composition and reflectance values as a parameter of rank became part of palaeo-ecological and climatological studies of the Miocene coal seam in the open pit mine Bílina (Mach et al., 2013), bituminous coal seams of the Žacléř Formation in the Intrasudetic Basin (Opluštil et al., 2013), Carboniferous sediments from the Mšec Formation in Central Bohemia (Lojka et al., 2010), the stratigraphically significant Main Ostrava Whetstone (Jirásek et al., 2013), and Krásné Loučky locality with high matured organic matter in the Upper Silesian Basin (Jirásek et al., 2014). The identification and petrographic investigation of graphite particles dispersed in sediments contributes to a detailed characterisation of tectonic structures, studied together with employees of the Department of Engineering Geology (Štěpančíková et al., 2010). Special attention has been paid to the processes of coalification and maturation of organic matter (Sýkorová, 2011) and formation and migration of hydrocarbon phases in Barrandian Basin (Suchý et al., 2012).



The Department of Geochemistry is also the only centre in the Czech Republic which systematically focuses on organic biomarker analyses of sedimentary rock. Generally, biomarkers are specific organic compounds that can be used as indicators of geological and environmental processes. By assembling the analytical data and assessment of contexts with petrographic composition, there are appropriate criteria in biomarker analysis being sought, focusing on very complex environmental systems. Although combined methods of organic petrology and geochemistry are applied in stratigraphic and palaeoenvironmental studies around the world, studies of coals from the Czech Republic have been rare and only partial. Biomarkers of basic lignite lithotypes from Miocene deposits of the Czech Republic were characterised for the first time. These lignite basins are unique with respect to different rank, petrological, and organic geochemical composition of lithotypes reflecting differences in the peat-forming vegetation and palaeoenvironment. The biomarker fingerprints and petrographic-based indices showed that the majority of the xylite rich, matrix and sapropelic coals, liptobioliths and shale originated from mixed forests, formed by arborescent and herbaceous communities, aquatic plants and macrophytes, under wet and slightly dry and slightly oxic-anoxic conditions (Havelcová et al., 2012; Havelcová et al., 2010). Detailed characterisations were performed on coalified tree stumps with the aim of their taxonomic determination as well as on samples of the lacustrine sediments with the aim of their detailed palaeoenvironmental reconstruction. The results are a part of systematic research on the Most Basin – a valuable sedimentary archive of European continental environments during the lower Miocene (Havelcová et al., 2013). The article was prepared in cooperation with the Faculty of Science of Charles University in Prague and with Dr. Achim Bechtel who is Chair of Petroleum Geology at the Universitaet Leoben. Except for data collection, most of the analysis, data processing, and interpretations have been formulated by the team from the Department of Geochemistry.

<div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;">  <p>16α(H)-phytylocladane</p> </div> <div style="text-align: center;">  <p>α-cedrane</p> </div> </div> <p>The structures of the most abundant compounds found in coalified tree stumps. Results of the chemical composition analysis show that the studied samples belong to one order and appear to be representatives of the family Cupressaceae s.l.</p>	 <p>SEM microphotograph of the microscopic structures of the wood tissue preserved in the coalified tree stumps. Detail of spherical and irregular particles of resinite or corphuminite with relative smooth surface, which are discretely located in cell.</p>
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Petrological knowledge of different types of lignite and morphological and optical changes of thermal altered organic matter was also used for the geochemical study of changes in structure and properties of altered lignite from Tertiary deposits from Western Bohemia and Northern Moravia with high uranium content because in many sedimentary uranium deposits close relationships between uranium and organic matter can be observed. Investigation of these changes has been an interesting topic, mainly in geological research but also in nuclear research and its industry, in connection with the effects of radioactive materials and waste in the environment (Havelcová et al., 2014). All the authors of the above-mentioned studies were members of the Department of Geochemistry and they were responsible for article preparation, as well as language and graphical editing of the final manuscript.

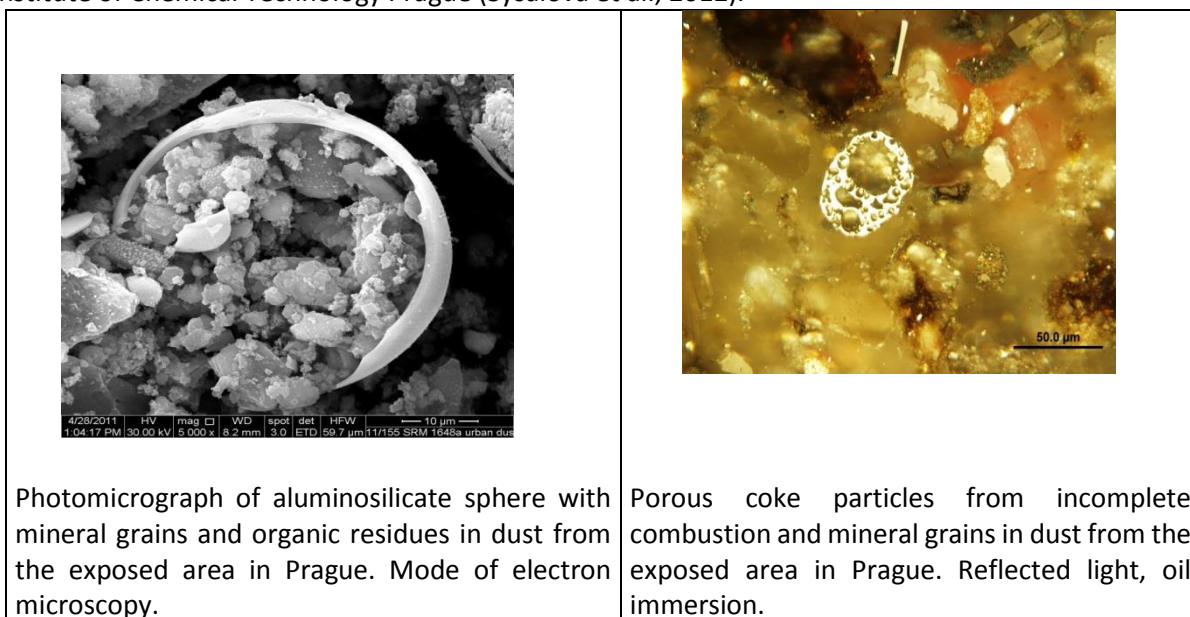


The samples of sand and peat from the Great Dune of Pilat in France were also found to be an interesting source of organic compounds. The samples have been locally impregnated with a dark brown to black amorphous organic substance of humate composition and black pebbles have been formed. Until now very few examples of these organically-impregnated lithoclasts have been described from modern siliciclastic depositional environments (Suchý et al., 2013). A collection of samples of fossil resins of different ages and from different locations was also compiled. The collection included historic and modern samples, museum specimens, and also samples of fossil resins from Malaysia and samples of amber from the Baltic. The obtained results are interesting with regard to the range of the set of samples which had been collected, and also due to the scarcity of previously published results of such samples (Havelcová et al., 2014). A majority of the experts from the Department of Geochemistry have been involved in the multidisciplinary study of forms, properties, and composition of bitumen in the Barrandian Basin to assess the petroleum charge history of the basin (Suchý et al., 2010). The role of the researchers from the department, within the processing of these samples, was essential and included microscopic and chemical analysis of studied samples, results evaluation, and article preparation. The author was responsible for language and graphical editing of the final manuscripts.

## Topic 2: Application of geochemical methods from environment to medicine

Environmental processes at the Earth's surface are affected by human activities and have caused changes that reach local, regional, and global levels. Research was conducted in order to monitor these changes in morphology, properties, and composition of and anticipate the reaction of natural systems to anthropogenic variations (Sýkorová et al., 2010; Havelcová et al., 2010; Klika et al., 2010). Self-heating and self-combustion of coal and coal wastes is one of the most dangerous environmental problems. Experts from the Department of Geochemistry, together with scientists from across the globe, participated in the development of an evaluation of the changes and intensity of the transformation of organic and mineral matter in both uncontrolled oxidative and thermal processes in coal seams, coal dumps and landfills, and to develop classification of forms of altered coal matter

(Misz-Kennan et al., 2010). This classification can be used when studying incomplete combustion of biomass. A product of either imperfect combustion of fuels and biomass or weathering is referred to as Black Carbon that occurs in the atmosphere, soil and marine sediments. The summary of findings on its origin, properties, occurrence and exposure in the biosphere, methods of measurement, impact on human health as well as its positive properties were published in a review (Blažek et al., 2014). Urban particulate matter, an important carrier of inorganic and organic pollutants, collected near a busy highway in the most exposed area of Prague, was also studied by the team to find differences in composition of compounds and particles collected during two years. This environmental problem associated with the incidence and forms of carbonaceous particles and chemical compounds, particularly toxic substances and components was solved in cooperation with experts from the Institute of Chemical Technology Prague (Sysalová et al., 2012).



As a documentation of negative human activities, thin black surface layers or black coloured gypsum crusts on stones of buildings and sculptures can be seen around the world. The black weathered stone and mortar surface from selected sections of the Prague Castle were studied with the aim to identify the sources of the carbon particles. A diverse mix of particles of organic origin was identified, of which dominated the remnants of incomplete combustion of fuels and biomass, such as soot, and char coke residues, as well as biological materials, including fragments of plant tissues, pollen, spores, but also the remains of insect wings and other organs, mites, and germs (Sýkorová et al., 2011; Popișter, et al., 2013; Sýkorová et al., 2010). The presence of carcinogenic polycyclic aromatic hydrocarbons was documented in ashes after biomass combustion (Straka and Havelcová, 2012) and in samples collected in the El-Tabbin area in the industrially affected part of Greater Cairo in Egypt. The latter study was initiated by Professor Ahmed Melegy, Head of the Geological Sciences Department at the National Research Center, Egypt, during a collaborative research project (Havelcová et al., 2014). In addition to this project, research with Professor Melegy solved a second collaborative research project aimed at the ecological and economic use of plastic waste mixed with bituminous coal from Egyptian deposit Maghara for the production of coke for steel industry (Melegy et al., 2011).

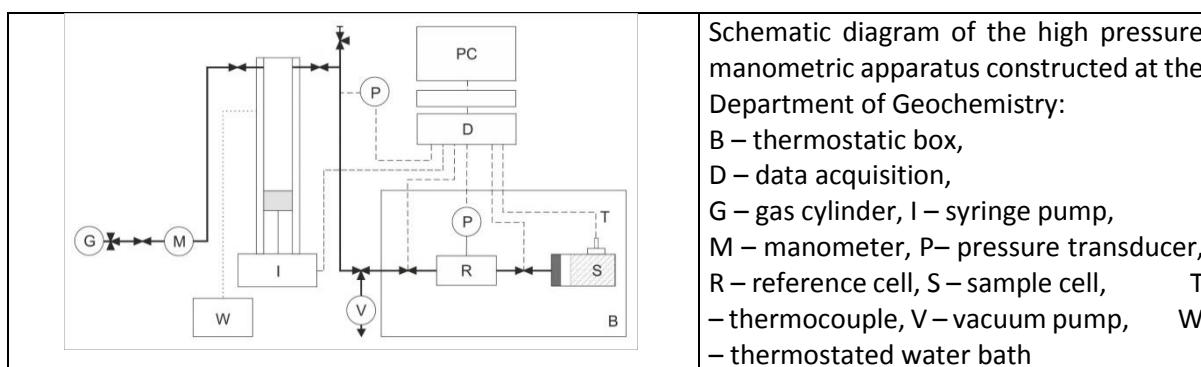
Not only do carbonaceous particles and polycyclic aromatic hydrocarbons represent a potential threat to humans, plants, and animals but so does environmental contamination with heavy metals. To remedy these harmful effects, properties of sorbents based on oxidised coal and chitosan pertinent to their metal ion sorption ability were investigated. Optimisation of these properties by physical and chemical modification of the sorbents for use in waste/groundwater treatment and construction of active geochemical barriers was studied (Havelcová et al., 2013; Havelcová et al., 2011; Mizera et al.,

2010). The studies brought together most members of the department and their contribution in the studies was essential including analysis, data processing, interpretations, and article preparation.

As an unusual application of geochemical methods, a study has been processed, focusing on the study of protein composition of mineralised aortic valves. The study of aortic valve mineralisation on the molecular level will contribute to understanding this process, which should consequently lead to effective prevention as well as to new ways of treating this grave disease. The role of the researcher from the Department of Geochemistry was in applying chemical analysis using gas chromatography/mass spectrometry including finding the optimal conditions for the methods. For the first time, such a clear evidence of the cholesterol contribution in degenerative aortic valvular stenosis was published. This work formed one quarter of the all works of all participants (Coufalová et al., 2013; Zeman et al., 2013).

### Topic 3: The sorption and texture properties of materials: significance for natural and anthropogenic processes

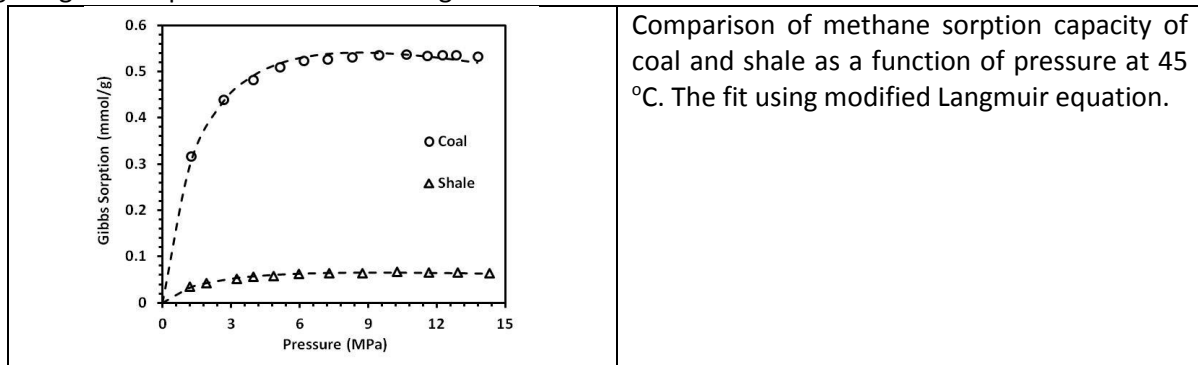
Due to increasing atmospheric carbon dioxide concentrations, its sequestration in coal seams is being actively considered as a means of reducing greenhouse gas emission. The suitability of coal seams for the use as carbon dioxide repositories is based on exceptional textural properties of coal. As the Czech part of the Upper Silesian Basin is also a locality with a carbon dioxide-enhanced coal bed methane recovery (CO<sub>2</sub>-ECBM) potential, the research was aimed at the basis of a detailed petrographic and textural analysis in order to evaluate the effect of the rank and maceral composition on the carbon dioxide low pressure sorption capacity of the coal from this basin. The tendency of carbon dioxide sorption capacity to depend on maceral composition, and also to some extent on coalification, observed for studied coal, may be related to higher microporosity due to the coalification process or oxidative processes leading to the formation of pseudovitrinite (Weishauptová et al., 2010; Weishauptová and Sýkorová, 2011). The impact of water on both the sorption capacity and the kinetics of carbon dioxide sorption were also studied because the presence of water in coal can adversely influence the sorption behavior of other molecules (Švábová et al., 2011; Švábová et al., 2012). A high pressure sorption technique was developed and used for the simulation of the carbon dioxide and methane deposition processes in the laboratory by measuring the amount of carbon dioxide and methane captured in a coal sample at a pressure and a temperature corresponding to supercritical conditions *in situ*. The potential gas-bearing and potential gas-yielding were evaluated (Příbyl et al., 2011, Weishauptová et al., 2015). The Department of Geochemistry is the only workplace in the Czech Republic which deals with high pressure sorption of carbon dioxide and methane on coal. The authors of all contributions are from the Institute of Rock Structure and Mechanics, so they were responsible for all presented results, conclusions and editing of the final manuscripts.



Shale gas is a new source of fossil energy that is of great interest at the present time. The Czech Republic has been characterised only superficially from the standpoint of potential shale gas deposits

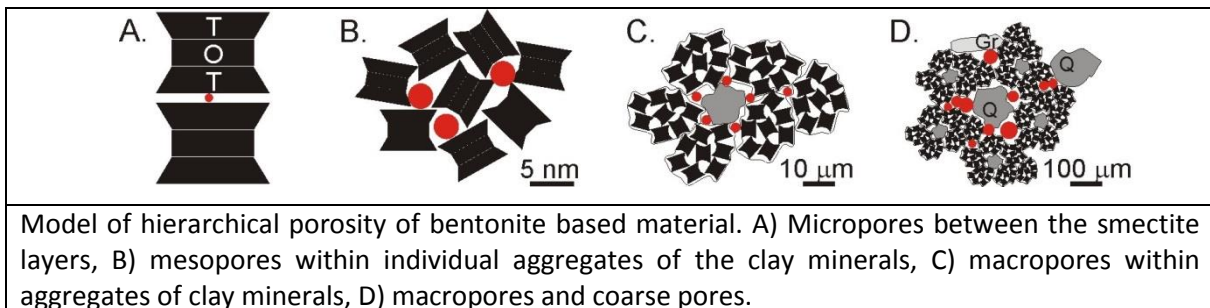


and therefore experimental equipment and procedures that were developed for studying the deposition of carbon dioxide into coal are used for determining the amount of sorbed methane in geological samples of shales from Prague Basin under conditions similar to those found *in situ*.



Comparison of methane sorption capacity of coal and shale as a function of pressure at 45 °C. The fit using modified Langmuir equation.

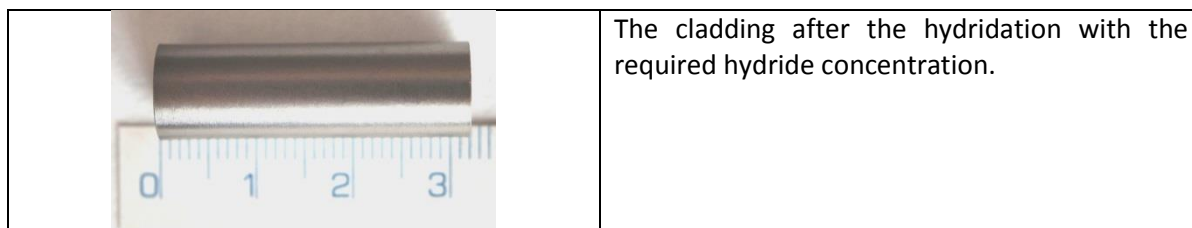
Bentonite raw material is planned to be used in artificial engineering barriers of radioactive waste disposal in deep repositories. Therefore, detailed analysis of pore microstructure of the bentonite-based buffer was performed. Its changes during the heating and hydration experiment were described. The observed changes were explained by a newly proposed model of hierarchical arrangement of porous structure of the bentonite-based buffer, which can describe the effect of burdening and the role of individual pore categories on their function (Přikryl and Weishauptová, 2010; Pusch et al., 2012). The members of the scientific team from the department were responsible for the textural analyses and their interpretation.



Physical and mechanical properties of the repaired sandstone ashlars in the facing masonry of Charles Bridge in Prague and an analytical study for the causes of its rapid decay were studied. The hardened Portland cement paste binding sandstone ashlars was also analysed (Přikryl et al., 2011). The part of the research realised at the department was focused on the detailed investigation of textural properties of porous sedimentary rocks (various types of sandstone, clayey-calcareous silicates, and bioclastic limestones) which have been modified by applying some conventional conservation agents (lime water, water glass, esters of silicon acid) used for consolidation and/or hydrophobisation treatments of natural stone by means of mercury porosimetry. Data obtained confirm the importance of the detailed trials of the effect of specific conservation agents on respective stone types before their final application in real scale. Mercury porosimetry is method which provides information about porosity and pore size distribution of samples, but as any other method, it has its own limitations. X-ray microtomography was used as a complementary method enabling another "view" into the pore space within the study of sandstone weathering (Kovářová et al., 2012). The complete textural analysis (micro, meso, and macropores determination) was used to characterise the development of porous structure of phenol-formaldehyde resin in the dependence on pyrolysis temperature (Šupová et al., 2012). Members of the scientific team from the department were responsible for the textural analysis and the interpretation.

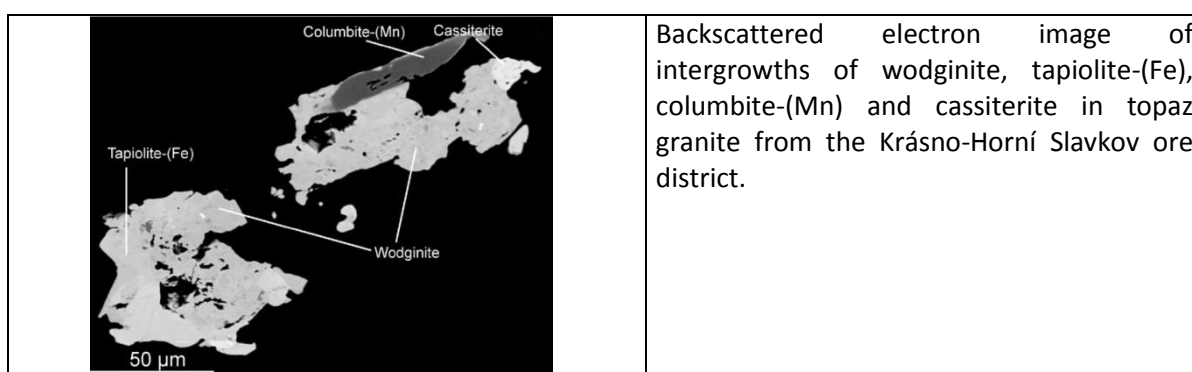
The long-term subject of research is corrosion of cladding tubes of nuclear fuel made of zirconium

alloys, which has been promoted by enhanced economical and safety requirements on the operation of nuclear power plants. New data contributing to elucidation of the corrosion mechanism have been obtained. The origin of the gel structure of the corrosion layers on samples of Zr1Nb cladding tubes after the exposure to subcritical water, pressurised steam and supercritical water was appraised (Weishauptová et al., 2012). An original method for hydriding the zirconium alloy using the gravimetric sorption of hydrogen was developed. The effect of hydrogen on high temperature oxidation at temperatures corresponding to a hypothetical LOCA-type accident (Loss of Coolant Accident) was studied in hydridated samples. The findings were covered in technical reports and have been applied in ongoing research of the corrosion layer properties and corrosion kinetics at the laboratory of UJP Prague, a.s.



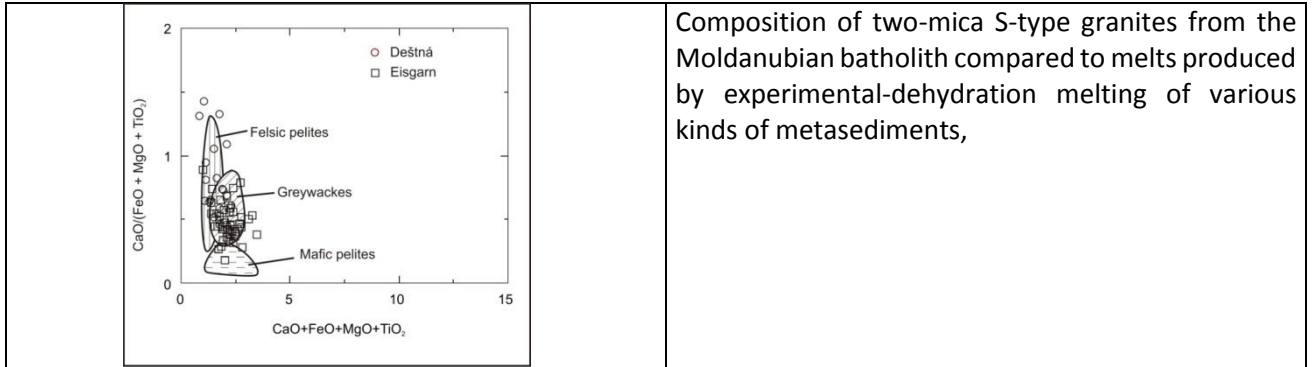
#### Topic 4: Geochemistry and petrology of granite suites

Another part of our scientific activities concentrated on the geochemistry and petrology of selected Variscan granite suites in the Bohemian Massif, especially the topaz granites from the Krušné Hory Mountains, the two mica granites of the Moldanubian Batholith, and the ultrapotassic granitoids of the Třebíč Pluton (René, 2014a; Machek et al., 2013; René, 2013b; René, 2013c; René, 2013d; René and Hájek, 2012; Dolníček and René, 2012; René, 2012a; René, 2012b; René, 2011a; Dolníček and René, 2011; René and Hájek, 2011a; René and Hájek, 2011b; René and Hájek, 2010; René, 2010c). In the topaz granites Nb-Ta-Ti oxides were studied from the Krásno-Horní Slavkov ore district along with selected accessories from two contrasted groups of topaz granites (xenotime, zircon), namely from P-rich and P-poor topaz granite (René and Škoda, 2011; René, 2014a). Rare Nb-Ta-Ti oxides (ixiolite, wodginite, tapiolite) were newly identified in the Krásno-Horní Slavkov ore district.

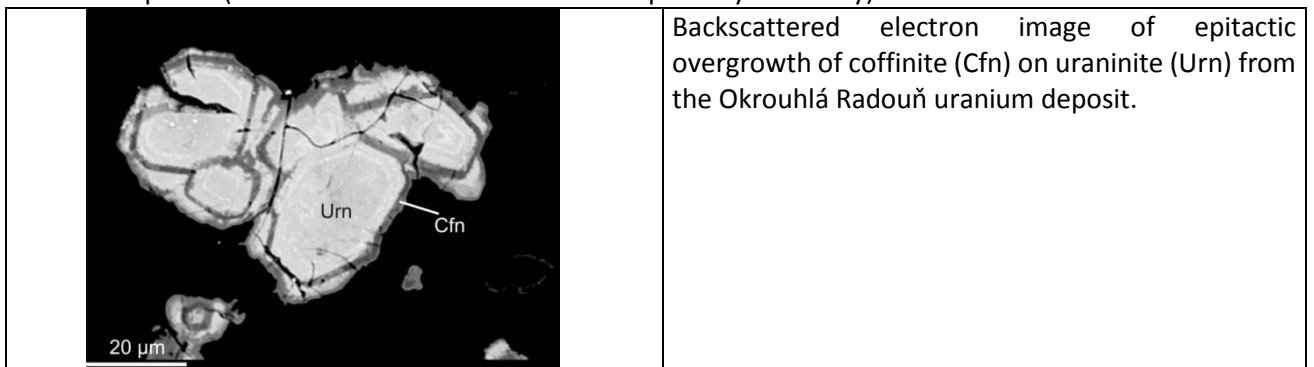


Seeing that this ore district is a very important representation of rare-metal granites, these new data are important for the petrology of rare-metal granites across the globe. Zircon from P-rich granites displays a significant enrichment in P, whereas zircon from P-poor granites has a lower P and higher Y. Xenotime from P-poor granites displays a considerable enrichment in heavy rare earth elements compared to xenotime from P-rich granites. The occurrence of ytterbian and dysprosian xenotime-(Y) in P-poor granites from the Cínovec cupola is unusual and has so far only been reported from granitic pegmatites. Another significant result was geochemical discrimination criteria of P-rich granites from the Hub stock and P-poor granites from the Cínovec cupola. In the case of topaz granites from the Krušné Hory Mountains, the best discrimination between S-type (P-rich) and A-type (P-poor) granites

include the use of Zr and Y concentrations (René, 2012e). Two mica granites from the Moldanubian Batholith are represented by two important varieties, the Eisgarn and Deštná Granites. Temperatures of granite melts and original rock sources of these melts were recognised for both granite varieties. The Eisgarn Granites were probably derived from metagreywackes and/or mafic metapelites whereas the Deštná Granites were derived from felsic, muscovite-enriched metapelites (René, 2012a, d, 2013b, 2014b; René and Hájek, 2010, 2011b). For both granite groups, also significant are their contrasted association and composition of accessory minerals (monazite, xenotime, zircon, apatite) (René, 2012d). The results offer new data sets and interpretation of the origin of the important represents of granitoids from the European Variscan Granite Belt.



The coupled uranium mineralisation in the Okrouhlá Radouň uranium deposit represents mineralisation with anomalous rare-earth, yttrium and zirconium mobility (René, 2012f, Dolníček et al., 2014). The results are important for the deposition of high-level radioactive waste in geological formations, especially in granite plutons, proposed for their deposition by a government institution in the Czech Republic (SÚRAO - The Radioactive Waste Repository Authority).



Ultrapotassic magmatic rocks of the Třebíč Pluton represent one of the crucial rock types for understanding the magmatic history of the European Variscan Belt and offer a unique opportunity to address the question of the origin of K-rich magmatism. The experimental fractionation trend recognised by the research team from the Leibniz University, Hannover, Germany indicates that K- and Mg-rich magmas in the Bohemian Massif may have been generated from partial melting of a phlogopite-clinopyroxene-bearing metasomatised peridotite (Parat et al., 2010). Experimental melt compositions also suggest that felsic durbachites can be generated by simple fractionation of a more mafic parent and mixing with mantle-derived components at mid-crustal pressures. However, for these experiments, the team from the Institute of Rock Structure and Mechanics has performed field studies, selected rock samples, recognised petrology of selected samples and cooperated on the interpretation of experiments (approximately 15% of the entire research of ultrapotassic rock) (René, 2011b).

**Summary of the results of the team:**  
Peer reviewed papers in IF journals: 45

Peer reviewed papers in other journals: 19  
Chapters in monographs: 17  
Conference proceedings: 15

During the past years, Department of Geochemistry established fruitful cooperation with a number of Universities, Research Institutes and private companies

**MAIN PARTNERS**

- Charles University (Praha, CZ)
- Brno University of Technology (Brno, CZ)
- Masaryk University (Brno, CZ)
- Technical University – VŠB (Ostrava, CZ)
- Palacký University (Olomouc, CZ)
- Nuclear Physic Institute ASCR, v.v.i. (Řež, CZ)
- Institute of Chemical Technology (Praha, CZ)
- Institute of Theoretical and Applied Mechanics ASCR, v.v.i. (Praha, CZ)
- Geological Institute ASCR, v.v.i. (Praha, CZ)
- Czech Geological Survey (Praha, CZ)
- National Research Centre (Cairo, Egypt)
- North Bohemia Coal Mines (Severočeské doly a.s.) (Bílina, CZ)
- UJP Praha a.s. (Praha, CZ)
- Sokolovská uhelná a.s. (Sokolov, CZ)
- Leibniz University (Hannover, Germany)
- University of Salzburg (Salzburg, Austria)

## Research Report of the team in the period 2010–2014

Institute	Institute of Rock Structure and Mechanics of the CAS, v. v. i.
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Scientific team	Department of Seismotectonics
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### Department of Seismotectonics

In the period 2010-2014, research at the Department of Seismotectonics has focused on four main research topics:

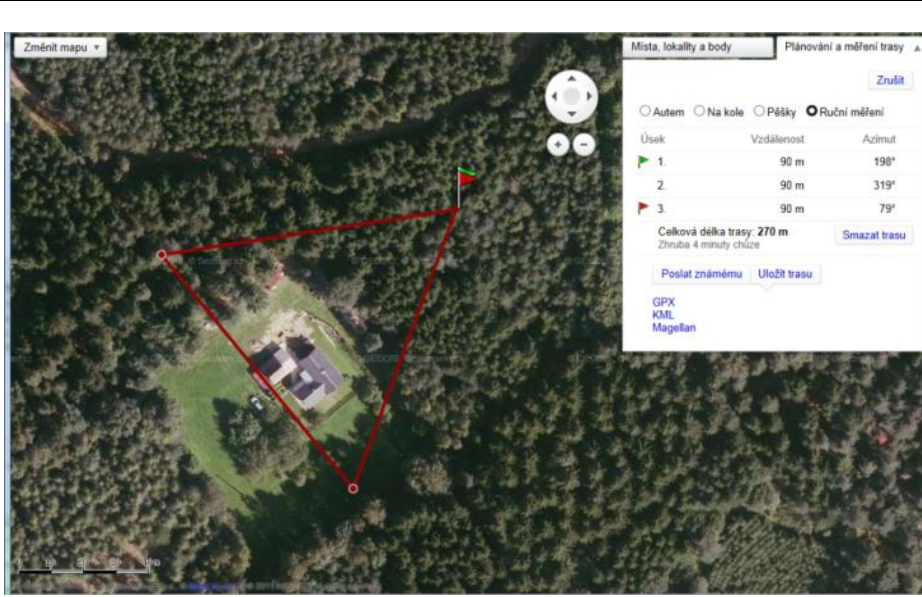
- **Topic 1:** Seismological studies including seismic hazard analysis, moment tensor inversion, evaluation of possible precursors, and palaeoseismological studies
- **Topic 2:** The monitoring of fluid-induced microseismicity and its risk assessment
- **Topic 3:** Applied geophysics including the acquisition and analysis of resistivity, gravity, and seismic data
- **Topic 4:** Prototyping and implementing novel sensors and devices for the acquisition of seismic data

In all these areas, the research activities span from basic research to its final implementation, thus determining a congruent system capable of properly addressing a number of aspects of geophysical research. Seismic, resistivity, and gravimetry data acquisition and analysis are widely adopted for a number of near-surface applications including environmental monitoring, archaeological studies, geological mapping, seismic-hazard evaluation, and geotechnical applications.

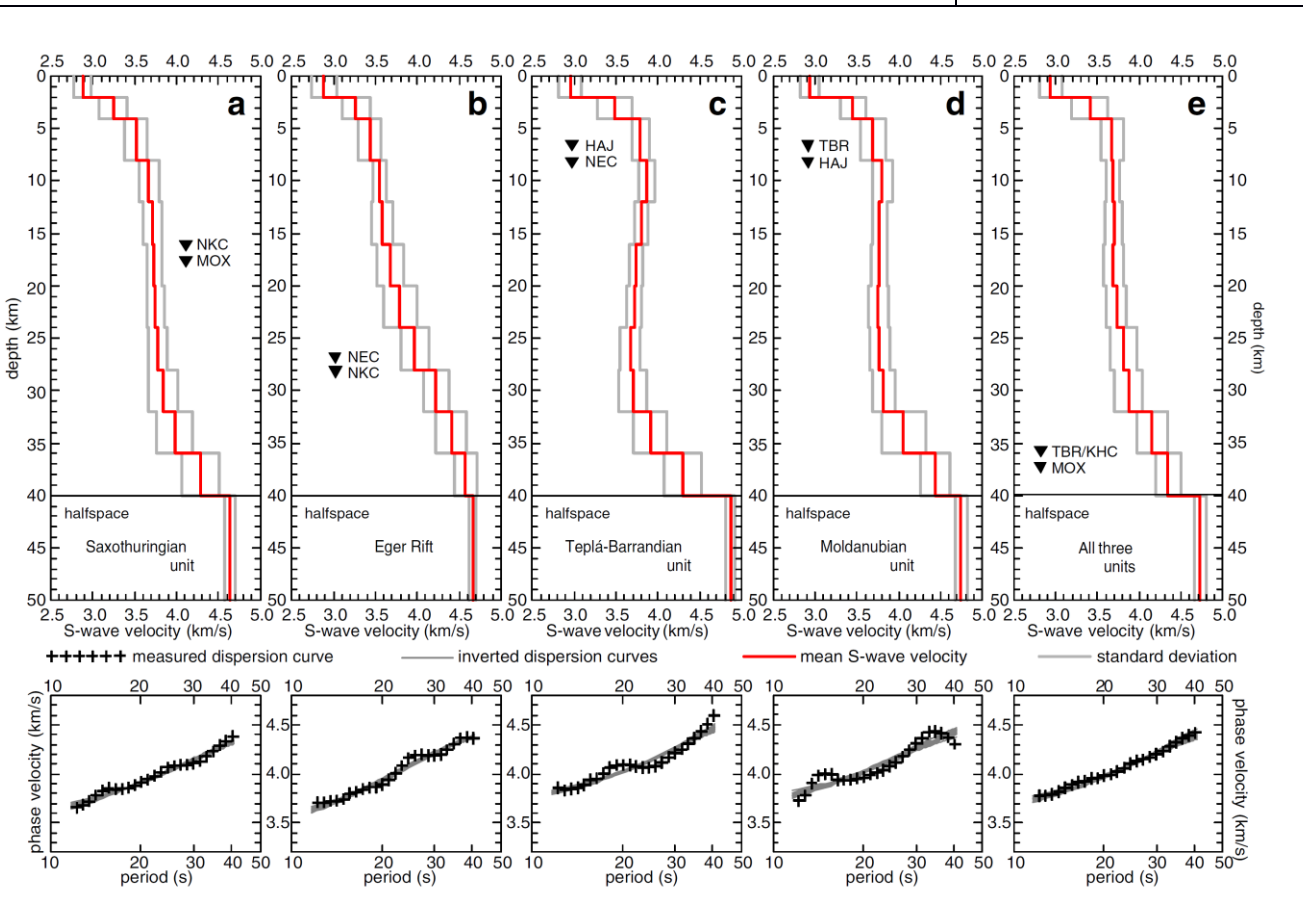
#### **Topic 1: Seismological studies including seismic hazard analysis, moment tensor inversion, evaluation of possible precursors, and palaeoseismological studies**

In the framework of CzechGeo ([www.czechgeo.cz](http://www.czechgeo.cz)) and through cooperation project with the Slovak Academy of Sciences, permanent and temporary seismological stations have been deployed across the Czech and Slovak Republics. These aim to monitor regional seismicity as a part of the European Plate Observing System (EPOS). The collected data are used both for basic academic research as well as for monitoring seismic activity and the related seismic-hazard issues associated with important infrastructure located within in two countries (e.g. the nuclear power plants of Temelín, Dukovany, Mochovce, and Bohunice, or the underground gas storage near Příbram). Furthermore, after the Fukushima disaster in March 2011, greater attention has been paid to the analysis of the seismic hazard related to nuclear power plants. Members of the Department of Seismotectonics conducted a new hazard assessment for two nuclear power plants in the Czech Republic, Temelín and Dukovany, which eventually served as reference document during the visit of the International Atomic Energy Agency in 2013. The Department of Seismotectonics, in cooperation with other institutions, is constantly monitoring real time signals recorded by these stations with the dual purpose of creating a high-quality database available to the international seismological community and for studying seismic activity in West Bohemia. Data are used both for analysing the European seismic regime and for determining the crustal structure of central Europe (e.g. Kolinsky et al., 2011; Valenta et al., 2011; Novotny et al., 2013;

Coubal et al., 2014). Groundwater levels are also monitored together with the seismological data and this allows us to study relationships between these two phenomena (Gaždová et al., 2011; Kolínský et al., 2012). Although some correlations between anomalous groundwater changes and seismicity have been observed, the specific local geological conditions seem to play a fundamental role. This prevents possible generalisations regarding the observed behaviour. With the aim of monitoring the microseismic activity in the Czech and Slovak Republics, the 2009-2013 Advanced Industrial Microseismic Monitoring (AIM) EU-FP7 project promoted synergies between academic institutions from the two countries (the Institute of Geophysics ASCR, the Institute of the Rock Structure & Mechanics ASCR, Charles University in Prague, and the Geophysical Institute SAS) and industrial partners from Norway (NORSAR Innovation, Kjeller), South Africa (the Institute of Mine Seismology, Stellenbosch), Slovakia (PROGSEIS, Trnava), and Canada (the Engineering Seismology Group, Kingston). Three seismological stations for the monitoring of seismic activity in the Little Carpathians, close to the Bohunice Nuclear Power Plant, were installed. In addition to these central European stations, several temporary stations and field campaigns took place across the globe such as those in Iceland and Bulgaria. In the framework of GAČR Project P210-12-2336, the Department of Seismotectonics, together with the Institute of Geophysics ASCR, established a temporary local seismic network in the Reykjanes Peninsula of southwest Iceland. This region is a typical earthquake-swarm area at a contact of two tectonic plates. The performed analyses focused on the Krýsuvík volcanic zone where fifteen autonomous stations were deployed (nine broadband and six short period). Besides numerical seismology, some palaeoseismological studies were also performed for mapping palaeostress evolution and analysing past seismicity (Nováková, 2014; Špaček et al., 2011). Furthermore, the influence of some meteorological factors and crustal deformation evolution on the observed microseismicity is carefully considered through the analysis performed on the data collected from the aforementioned seismological stations (e.g. Holub et al., 2013). Special efforts have been made to determine the focal mechanisms of small earthquakes (Mw 2-3), which represent a notorious problem as their signal-to-noise ratio is only good at frequencies above the microseismic noise peak ( $\sim 0.2$  Hz), waveforms can be modelled only up to  $\sim 1-2$  Hz, and they can only be detected by relatively close stations (up to a few kilometres). To overcome this series of related problems, the Department of Seismotectonics worked on a novel approach: the Cyclic Scanning of the Polarity Solutions (CSPS), which can be proficiently adopted in sparse networks where weak events are recorded (Fojtíková & Zahradník, 2014). In order to also exploit seismic data for non-conventional studies, seismic data have also been used to trace the trajectories of some fireballs (see, for example, the well-known Chelyabinsk Asteroid - Borovička et al., 2013; Kalenda et al., 2014).



A Small Aperture Array (permanent station) in Nový Kostel (CZ). Data collected during a period of apparent quiescence (2008) showed that the levels of seismic activity were up to fifteen times greater than the levels recorded by the pre-existing seismic network. This demonstrated that the installed seismic stations are a valuable tool for the detection of small-magnitude events.



Shear-wave velocity profiles in the Western Bohemian Massif. From Kolínský et al. (2011).

Coubal M., Adamovič J., Málek J., Prouza V., 2014. *Architecture of thrust faults with alongstrike variations in fault plane dip: Anatomy of the Lusatian Fault, Bohemian Massif*. Journal of Geosciences, 59, 183–208.

Borovička J., Spurný P., Brown P., Wiegert P., Kalenda P., Clark D., Shrubený L., 2013. *The trajectory, structure and origin of the Chelyabinsk asteroidal impactor*. Nature 503, 235–237 (14 November 2013).

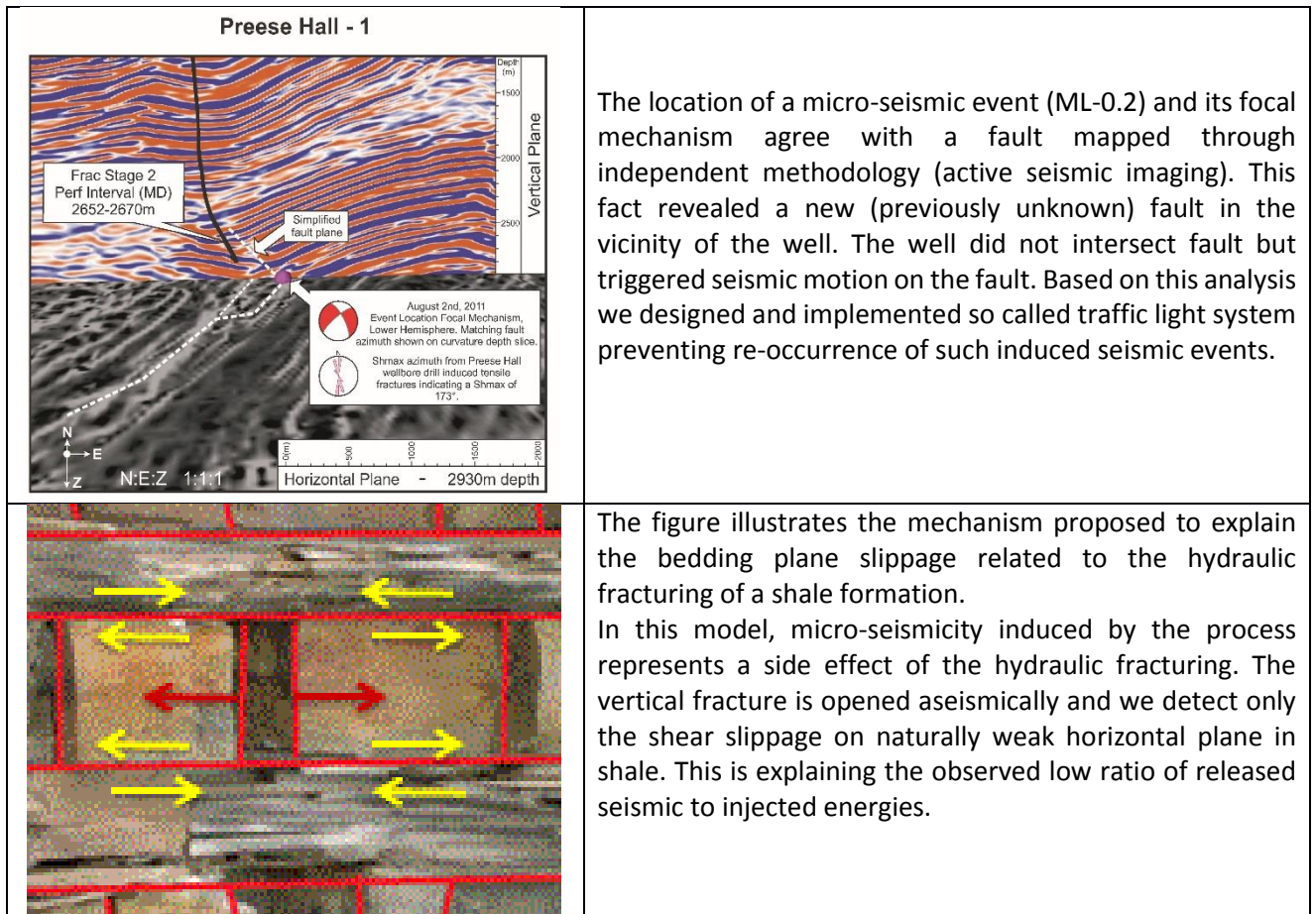
Fojtikova and Zahradnik, 2014. *The new strategy for weak events in sparse networks: the first-motion*

- polarity solutions constrained by single-station waveforms*. Seismological Research Letters, 85, 1265-1274.
- Gaždová, R., Novotný, O., Málek, J., Valenta, J., Brož M., Kolínský, P., 2011. *Groundwater level variations in the seismically active region of Western Bohemia in the years 2005–2010*, Acta Geodynamica et Geomaterialia, Volume 8, No. 1, 17–27.
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## **Topic 2: The monitoring of fluid-induced microseismicity and its risk assessment**

Microseismic monitoring has become the method of choice for mapping fracture propagation during stimulation of either unconventional or geothermal reservoirs. The Department of Seismotectonics has developed a strong research program in passive seismic monitoring which focuses on microseismic monitoring induced by hydraulic fracturing, large volume injections, or reservoir production carried out in the oil and gas industry (with a strong focus on unconventional resources and gas storage) and for geothermal energy. A dedicated effort has been spent on the assessment of the hazard related to induced felt seismicity, i.e. seismicity induced by injection felt on the surface by humans, associated with fluid injections. Members of the Department of Seismotectonics have developed a new general methodology for simultaneous inversion of source mechanism and location of microseismic events, attenuation of the media, determination of magnitude of induced events, and stability of inverted source mechanisms. The analysis of the inverted source mechanisms on real dataset enabled the development of a new geomechanical model describing the interaction between injected fluids and seismicity (Eisner et al., 2013; Stanek et al., 2014; Anikiev et al., 2014). The analysis of felt seismicity induced by hydraulic injections led to development of differentiation of natural and induced seismicity (Opsal and Eisner, 2014). Dr. Leo Eisner, one of the researchers working on these topics, was invited for his expertise in relation to the analysis of seismicity induced in Blackpool (UK) in 2011 (Clarke et al., 2015). Furthermore, a recent publication on the maximum magnitude of events induced by hydraulic injection has received considerable attention (Hallo et al., 2014).





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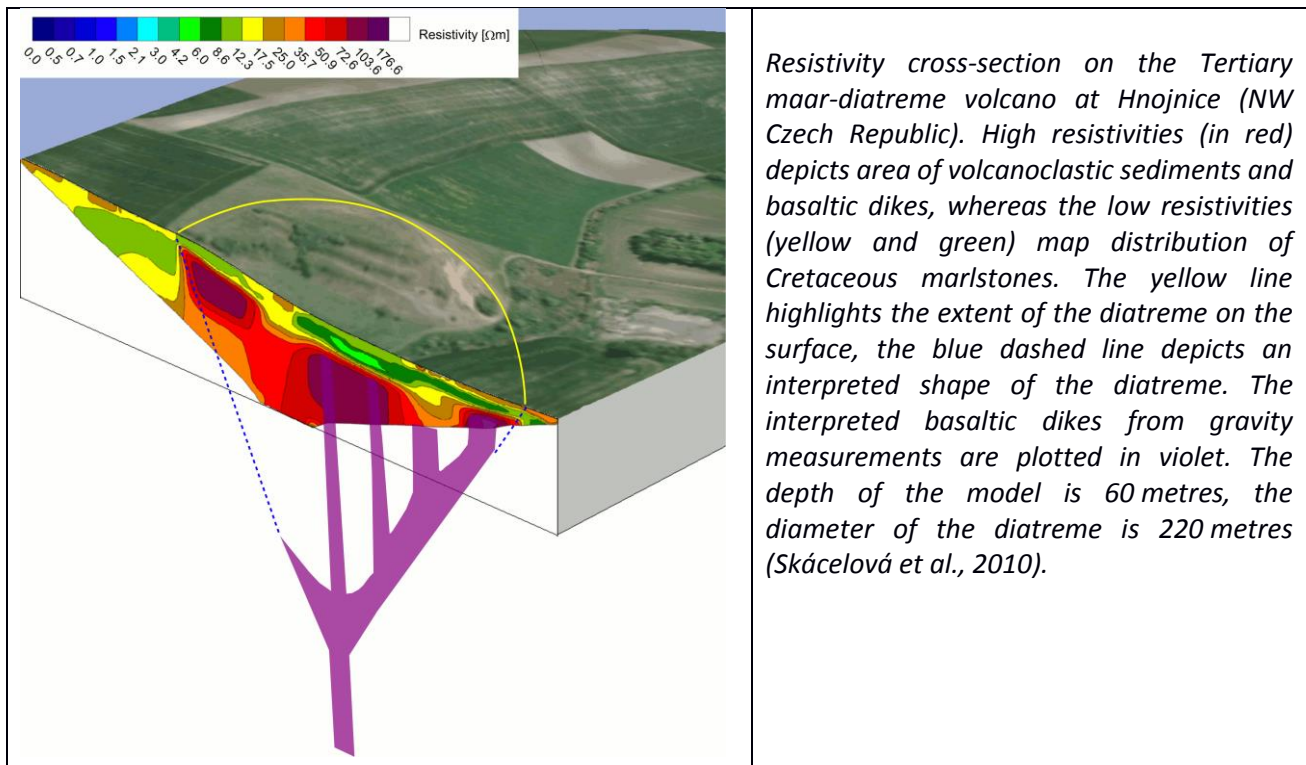
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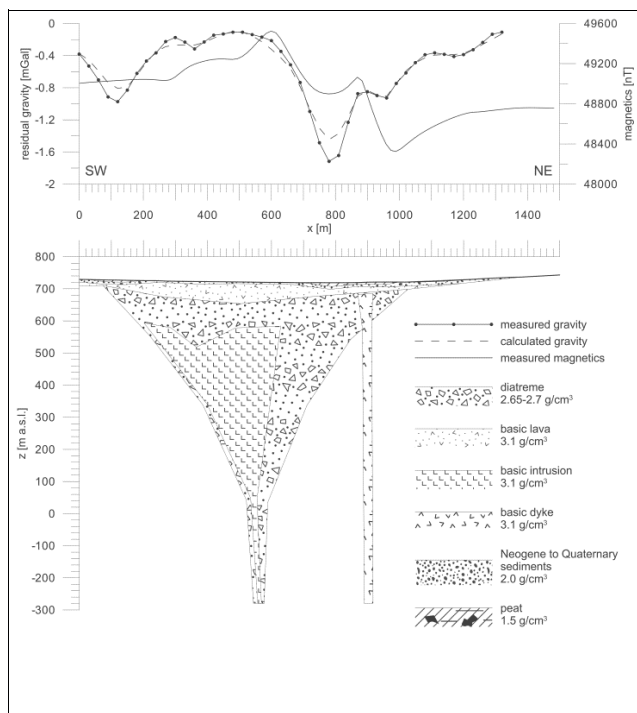
### Topic 3: Applied geophysics including the acquisition and analysis of resistivity, gravity, and seismic data

The Department of Seismotectonics actively uses all classical methods (seismic, electromagnetic, and gravimetric) to image near-surface conditions for applications as diverse such as geological mapping, geotechnical investigation, archaeological investigations, seismic hazard assessment, and environmental monitoring. Researchers from the department have been working on the implementation of new and/or improved techniques as well as in their application in a number of practical applications/problems. For instance, surface wave analysis has been applied in the

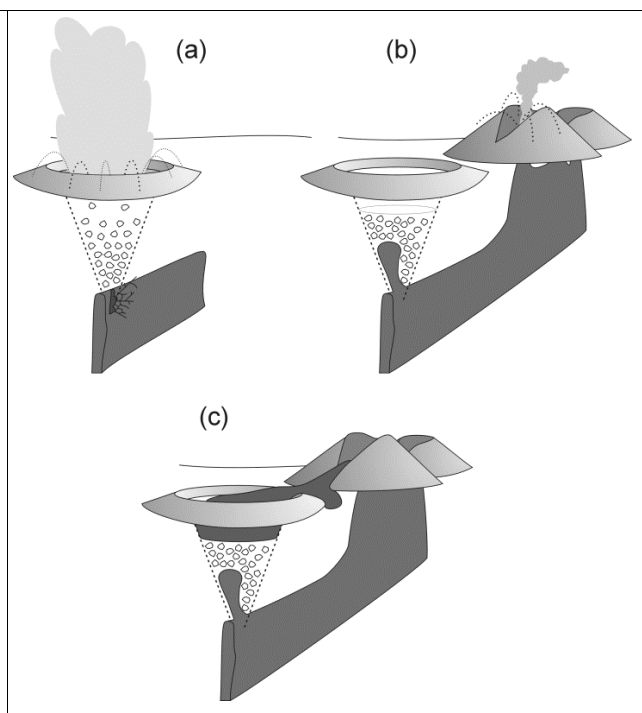
characterisation of a velocity model for the Hronov-Poříčí Fault Zone (Kolínský et al., 2014) while multidisciplinary approaches have been adopted for the identification and study of recent tectonic features (Hartvich and Valenta, 2013), for the assessment of conditions for landslide reactivation (Burda et al., 2013), and to image the inner structure of maar diatreme volcanoes (Skácelová et al., 2010; Valenta et al., 2014a, b).



Novel techniques for efficiently acquiring and analysing surface-wave propagation have been implemented, always considering their analysis in a joint perspective. The fundamental focus was in fact to overcome all the problems related to the standard approach of surface wave analysis (fundamentally based on the interpretation of the modal dispersion curve(s) of the vertical-component of Rayleigh waves). The improvement of such a classical and simplistic approach was achieved by considering multicomponent data whose inversion is then capable of overcoming the otherwise inevitable problems connected to non-uniqueness of the solution and to possible data misinterpretations as well as in the determination of 2D vertical profiles (Gaždová et al., 2015). Joint data inversion was addressed via unconventional methods based on the *dominance* (Pareto) criterion. Unlike standard methods, this approach avoids problematic data normalisation and properly accounts for the different nature (*incommensurability*) of the different objective functions, also providing, through the evaluation of the Pareto-model symmetry, a way of evaluating the overall consistency of the performed inversion. In this area, accomplished research activities determined the *optimal components* and the design of *efficient procedures* for a non-ambiguous determination of the  $V_S$  vertical profile. By “optimal components” we mean all (and only) those data which are necessary for an unambiguous analysis, while by “efficient procedures” we mean that the field acquisitions should be as simple as possible and the inversion scheme robust and capable of providing evidence about the consistency of the inversion itself.



Possible density model of the Tertiary maar-diatreme volcano at Rájov (western Bohemia). The model is constrained by geophysical data and geological assumptions (Valenta et al., 2014a).



Schematic reconstruction of the evolution of the Rájov – Podhorní vrch volcanic system: (a) The first phase, when the magma reached water saturated sediments and a volcanism started with a phreatomagmatic eruption; (b) Second phase, when the available water has been already used, eruption type changed to the Strombolian and the nearby scoria cone Podhorní vrch Hill is formed. Part of the basaltic lava also intruded into the already formed Rájov diatreme; (c) The last phase of the eruption, when a lava flow from the Podhorní vrch Hill filled the upper part of the Rájov diatreme (Valenta et al., 2014a).

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#### Topic 4: Prototyping and implementing novel sensors and devices for the acquisition of seismic data

During the past few years, researchers from the Department of Seismotectonics have designed and implemented 28-bit data-loggers (Strunc and Broz, 2011) which have then been used in the framework of both international (e.g. Advanced Industrial Microseismic Monitoring) and national projects (Czech and Slovak Regional Seismic Networks). The designed data logger was adopted for a number of small-aperture arrays in the Czech Republic (Strunc and Broz, 2011), for evaluations into the stability evaluation of historical buildings, and as an accurate acquisition system for the Rotaphone. The Rotaphone is a patented six-component short-period seismic sensor developed by the Department of Seismotectonics in collaboration with the Faculty of Mathematics and Physics at Charles University in Prague. This innovative device is capable of acquiring both the translational and rotational components of the ground motion induced both by natural and artificial events. The rotational components of seismic waves were mainly studied thanks to the GAČR Project P210-10-0925 (2010-2013). Two instruments were developed and tested: (i) a six degree-of-freedom seismic sensor (Rotaphone) capable of recording the rotational and translational seismic motions in the 2-50 Hz frequency range, with a high dynamic range which allows to detect rotational motions in the  $10^{-1}$  to  $10^{-7}$  rad/s range; and (ii) an S-wave and rotational-component seismic source, capable of producing *repeatable pulses* with a dominating frequency of about 35 Hz. Both devices were registered as *functional prototypes* (RIV/00216208:11320/13:10189296 and RIV/00216208:11320/13:10189301) and are now ready for routine use. Compared with other, much more expensive, devices for acquiring the seismic rotational components, one of the most relevant aspects that characterises the Rotaphone is its highly-efficient *in-situ* calibration method which is applied during each measurement and which allows the acquisition of highly-accurate data. The project also focused on the challenging issue of measuring the seismic rotational components for weak and shallow local earthquakes, thus eventually proving their existence, measurability, and potential to better understanding both the characteristics of the seismic source and the subsurface structure. Equations describing the translation and rotation at small hypocentral distances have been derived and their validity was verified while analysing data collected in different seismotectonic regimes: an active rift in the Gulf of Corinth, a seismic swarm area in West Bohemia, induced seismicity at Provadia in Bulgaria, and volcanic seismicity in Iceland.



The rotational source (bottom) and the *Rotaphone* (top) developed at DoS.

Total mass of the rotational source: 100 kg

Radius of the flywheel: 0.25 m

Mass of the flywheel: 23 kg

Maximum revolving rate: 15 Hz

Maximum angular velocity:  $94 \text{ s}^{-1}$

Kinetic energy at 15 Hz: 3200 J

Stopping time: 0.01 s



Testing of *Rotaphone* at the USGS laboratory in Albuquerque (New Mexico, USA): special rotary shock table facilitates a detailed determination of the *Rotaphone* parameters.

Main facts:

frequency range 2 - 60 Hz

sampling frequency 250 Hz

LSB (Least Significant Bit) for translational components 0.647 nm/s

LSB (Least Significant Bit) for rotational components 2.16 nrad/s

maximum translation velocity 86 mm/s

maximum rotation rate 287 mrad/s

dynamic range 120 dB

Brokešová J., Málek J., 2010. *New portable sensor system for rotational seismic motion measurements*. Rev. Sci. Instrum., 81(8):084501.

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During the past 4 years, DoS established fruitful cooperation with a number of Universities, Research Institutes and private companies working in the broad field of Geosciences.

#### **MAIN PARTNERS**

Academy of Sciences of the Czech Republic (Geophysical Institute and Geological Institute)

AGH (University of Science and Technology) Krakow (Poland)

Arcadis Geotechnika a.s. (Czech Republic)

Czech Geological Survey

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Charles University in Prague - Faculty of Mathematics and Physics

Czech Technical University in Prague - Faculty of Electrical Engineering

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Isatech, Ltd. (Czech Republic)

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Petroleum Institute - Abu Dhabi

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NORSAR (Norway)

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Stanford University (USA)

Slovak Academy of Sciences - Geophysical Institute

University of Brasilia (Seismological Observatory) - Brazil

United States Geological Survey (USGS)

University of Patras (Department of Geology; Seismological Laboratory) - Greece

University of Stuttgart - Institute of Geophysics

# Research Report of the team in the period 2010–2014

Institute	Institute of Rock Structure and Mechanics of the CAS, v. v. i.
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Scientific team	Department of Engineering Geology
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## Department of Engineering Geology

In the period 2010-2014, research at the Department of Engineering Geology has focused on four main research topics:

- **Topic 1:** Slope deformation and landslide monitoring, hazard and risk assessment
- **Topic 2:** Monitoring of micro-movements on tectonic faults
- **Topic 3:** Palaeoseismology and tectonic geomorphology
- **Topic 4:** Weathering of sandstones and carbonate rocks

### Topic 1: Slope deformation and landslide monitoring, hazard and risk assessment

In the field of landslide research, during the last five years a significant proportion of our achievements are reflected by the verification and improvement of the landslide susceptibility zoning methodology which represents the main measure for mitigating against the possible negative effects of landsliding in the Czech Republic. The application of new methods (e.g. geophysical measurements) and improved instrumentation (optical-mechanical crack gauge) for landslide monitoring now offers an opportunity for a far more comprehensive interpretation of the monitoring data with respect to important environmental factors (e.g. groundwater levels). Moreover, significant steps toward applicable landslide risk assessments were made with the aim of bridging the gap between academic research and praxis.

- Landslide susceptibility zoning based on geomorphological mapping was verified using the “wait and see” method and this proved to be good in its ability to predict future landslide occurrence in the highly variable geological conditions of Carpathian Flysch (Rybář et al., 2011).

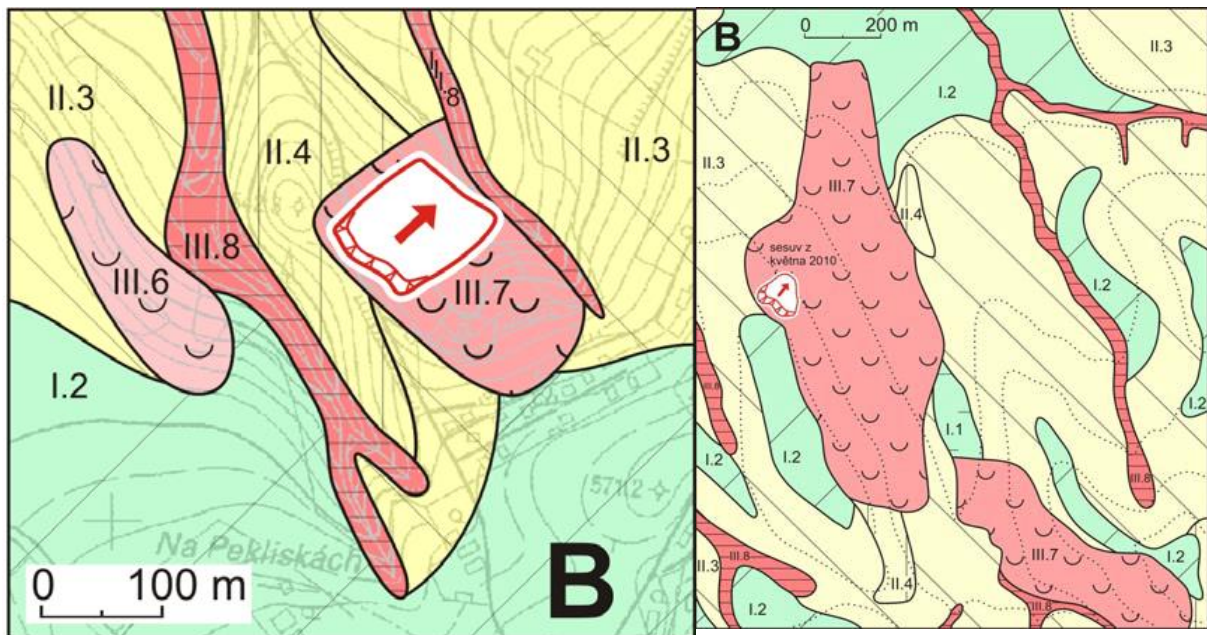


Fig. 1: Two examples show results of “wait and see” verification method of the landslide susceptibility maps. The new landslides are shown with white background and red arrow in the middle (Rybář et al. 2011).

- Careful evaluation of data-driven landslide susceptibility methods identified an important drawback in their use caused by a strong dependency on the spatial distribution of the most susceptible zones to the type and number of predictive variables (Sterlacchini et al., 2011).
- Multi-disciplinary approaches including, for example, the construction of extremely long geophysical survey profiles have been used to identify the real extent of deep-seated slope deformations far beyond their morphologically defined borders (Pánek et al., 2014). It provided arguments for more “optimistic” field mapping of landslide susceptibility zones, showing that while the older landslide accumulations may already be erased from the morphology, they may still be present below the ground surface and could possibly adversely affect conditions for construction.
- Typical geological and geomorphological conditions were defined for regions with highly active recent and present day geomorphological processes in generally stable areas (e.g. Bohemian Forest Mts.). They prove the importance of material supply thresholds for occurrence frequency of slope deformations in such conditions (Hartvich and Mentlík, 2010). This concept is important in landslide susceptibility and hazard assessment as it explains irregular and relatively infrequent occurrence of slope deformations in highly susceptible regions.
- It was shown that field geophysical measurements provide necessary information when evaluating ground surface kinematics of landslides based mainly on surface movement monitoring (Prokešová et al., 2014). Information about the surface setting is crucial for the interpretation of ground movements and their causative relationships with, for example, hydrogeological conditions.
- The optical-mechanical crack gauge TM-71 was updated with new data reading, storing, and transmission units which enable the collection of high frequency deformation measurements and their remote access. These new capabilities have substantially broadened applicability of the crack gauge and increased quantity of data, which may allow observations of more



detailed, short-term processes, which were impossible to observe before (Klimeš et al., 2012; Marti et al., 2013).

- Empirical equations for the estimation of physical vulnerability curves for debris flows were formulated using a historical event from the Italian Alps (Quan Luna et al., 2011).
- Pioneering work on landslide risk assessment in the Czech Republic showed important local differences in landslide risk caused by different houses market prices in nearly identical geological regions (Klimeš and Blahůt, 2012). This approach could be applied for land development planning purposes thanks to hazard definition and zoning which is missing from the majority of similar work in the territory of the Czech Republic.

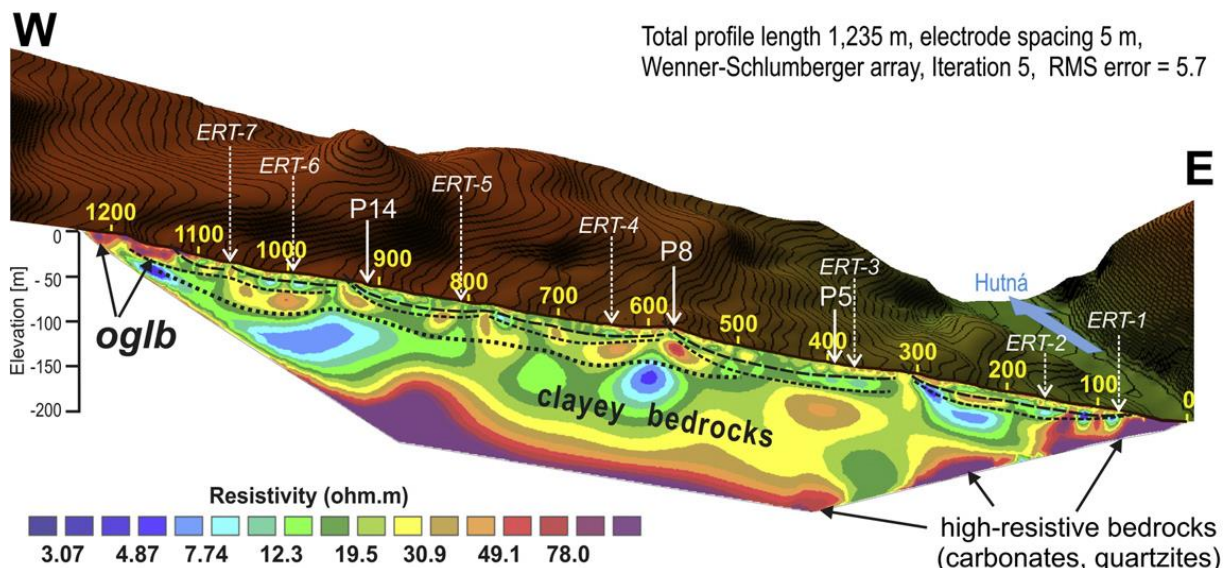


Fig. 2: Electric resistivity pseudosection with topography and groundwater surface monitoring points (P) illustrate advantages of the geophysical information for landslide movement interpretation (Prokešová et al., 2014).

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## **Topic 2: Monitoring of micro-movements on tectonic faults**

Based on data provided by TecNet monitoring net (see [www.irms.cas.cz](http://www.irms.cas.cz)) some new findings were published:

- The data obtained have showed that long periods of tectonic „quiescence“ are alternated with shorter periods of increased fault activity. These periods can be characterized as a compression pulse. It was discovered that these periods of increased activity occur contemporaneously along distinct tectonic units and that they are caused by endogenous processes (Stemberk et al. 2010; Stemberk and Hartvich 2011; Petro et al. 2011; Briestenský et al. 2014)
- The increased displacements reflect periods of widespread tectonic redistribution of stress and strain within shallow crust as was proved by comparison with other geophysical methods (Košťák et al. 2011)
- Analyses of fault displacements and comparison with gas flux show high correlation between radon emanation and displacements (Briestenský et al. 2011) as well as among radon, displacements and local seismicity (Šebela et al. 2010). The recorded anomalous carbon dioxide and radon concentrations measured only few days before the Tohoku Earthquake in the Bohemian Massif suggest some global processes are in play (Briestenský et al. 2014).

References:

**Briestenský, M. , Stemberk, J., Rowberry, M.D.** (2014): The use of damaged speleothems and in situ fault displacement monitoring to characterise active tectonic structures: an example from Západní Cave, Czech Republic. *Acta Carsologica*. 43 (1): 129-138.

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### Topic 3: Palaeoseismology and tectonic geomorphology

Neotectonic activity and palaeoseismicity have been studied on morphologically pronounced tectonic structures in the Bohemian Massif, Carpathian Foreland, Dead Sea Fault, and Alhama de Murcia Fault by using the multidisciplinary approaches of tectonic geomorphology, structural geology, applied geophysics, geochemistry, sedimentology, thermochronological dating alongside several other dating methods and palaeoseismology, a young branch of the earth sciences first implemented in central Europe by our research team. Reconstruction of faulting history helps to assess the tectonic hazard in the studied areas and several times the results have contributed to seismic hazard (re)assessment. Several achievements in palaeoseismology and faulting history reconstruction have been fulfilled:

- The first palaeoseismological research in central Europe showed the seismogenic character of the intraplate Sudetic Marginal Fault in the northeast Bohemian Massif, described tectonic phases and assessed the minimum potential magnitude for the fault (Štěpančíková et al., 2010). Its late Pleistocene activity and fast slip-rate due to ice-loading during Last Glacial Maximum were proved and modelled (Štěpančíková et al., 2013, 2014a). Several geophysical methods showed their potential for tracing the fault during studies (Štěpančíková et al., 2011; Hartvich et al., 2014).



Fig. 1. Bílá Voda trenching site at Sudetic Marginal Fault where late Pleistocene faulting was proved.

- Paleoseismic trenching across the Mariánské-Lázně Fault in the west of the Bohemian Massif was accompanied by several geophysical methods. This research showed large pre-historic earthquakes as young as Preboreal to SubAntlantikum, as well as the strike-slip kinematics of the fault (Fischer et al., 2012, Štěpančíková et al., 2014b).
- The first detailed thermochronological study in the Sudetes employed three modern thermochronological dating methods (zircon (U-Th)/He, apatite fission track, and apatite (U-Th)/He) to give time constraints on the evolution of the Sudetic Marginal Fault and documented its activity as far back as the Mesozoic. This work disproved historically accepted theories on the persistence of the Sudetes since the Permian (Danišík et al., 2012).
- Palaeoseismic records, the potential magnitude of faults, the recurrence period and slip behaviour in several different geological environments were determined. These not only related to plate boundaries but also to such faults in the Trans-Mexican Volcanic Belt, the Dead

Sea Transform Fault, and the Alhama de Murcia Fault, (Ortuño et al., 2012, Lacan et al., 2013, Wechsler et al., 2014).

- The lateral variations in slip rates along the Elsinore Fault, a segment of San Andreas Fault System, and their constancy during Late Pleistocene were determined using the provenance of alluvial fan deposits and their measured offsets (Masana et al., 2013).

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#### **Topic 4: Weathering of sandstones and carbonate rocks**

Recent research into sandstone weathering has lead to a considerable number of results:

- Different types of rock crust and the underlying unweathered sandstone have been sampled. Two types of rock crust were distinguished on a morphological basis: patterned crust with a variety of weathering forms (i.e. honeycombs and wall karren) and armoured rock crust with a relatively smooth, hardened layer.
- Speleothems in six sandstone caves in the Český ráj were dated by means of <sup>14</sup>C and U-series methods. The sandstone caves probably evolved rapidly during or at the end of the Last Glacial period.
- The study of the Čertova kazatelna massif with extreme retreat rates of overhang ceiling demonstrated that sandstone overhangs may potentially develop within a few hundred years in case of favourable conditions.
- The underground conduit network in Střeleč Quarry developed over five years as a result of groundwater flow in Cretaceous marine quartz sandstone. Natural landforms were probably formed very rapidly by overland flow, piping, and possibly fluidisation during or at the end of the glacial periods when the sandstone was not yet protected by case hardening.
- The underground conduit evolution is described in two phases in Střeleč Quarry. Mass wasting in the second phase is responsible for > 90 % of the mobilised sandstone.
- Three distinct kinds of sandstone surface were defined based on the field appearance, erodibility, and tensile strength (erodible sandstone, sub-vertical fracture surfaces, and case hardened surfaces).
- Case hardened surfaces of sandstone have the most of the pores filled with kaolinite clay reinforced by lichen hyphae. Measuring of the tensile strength and relative erodibility confirmed that these surfaces play a key role in the stabilisation of the sandstone landscape.
- The hardened surface of fractures in sandstones was achieved the underground spaces propagating upward contrary to the existing model for the origin of rock cities.
- Gravity-induced stresses had been assumed to not play a role in landform preservation and to instead increase weathering rates. It was proved that increased stress within a landform as a result of vertical loading reduces weathering and erosion rates, using laboratory experiments and numerical modelling. The stress field is the primary control on the morphological development of sandstone landforms. For additional information please see the references: Adamovič et al. (2011), Bruthans et al. (2012a, 2012b, 2013, 2014)

Recent research into the weathering of carbonate rocks has concentrated on understanding the mechanisms responsible for dissolution in the Carboniferous Limestone of south Wales (Rowberry et

al., 2012, 2014). The results of such studies help to inform geotechnical engineers and reservoir engineers as well as providing insights for natural hazard mitigation planning in karst terrains (Dubois et al., 2015). Systematically selected samples of residual alterite have been obtained from a number of study sites and these were then subjected to a range of geochemical techniques in order to characterise their petrophysical, mechanical, and hydrological properties. So far these analyses have not only demonstrated that dissolution took place early in the geological history of the limestone, soon after diagenesis but before burial by the overlying terrestrial mudstones during the Namurian (Rowberry et al., 2014), but also provided the first evidence for hypersaline depositional environments within a generally open carbonate platform - the latter forms the basis of ongoing research. A protracted hiatus between the first stage, represented by chemical dissolution and removal of the soluble species, and the second, represented by mechanical erosion of the undissolved particles, is characteristic of the process of ghost-rock karstification (Dubois et al., 2014). The transition from the first stage to the second is driven by the amount of hydrodynamic energy within the thermodynamic system. Our research provides the first report of this process from anywhere in the British Isles (Rowberry et al., 2014) and its significance is twofold: it demonstrates that the geomorphological development of karst topography is far more closely related to that of siliceous topography than generally supposed and it implies that it is now necessary to reconsider the origin of many karst features in light of this research (Dubois et al., 2014).

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### **Summary of publications in 2010-2014**

During the evaluation period the team published:

- **67 papers in IF journals** (So far they obtained 204 citations on WoS, 302 on Scopus and 457 on Scholar Google.)
- 22 other peer-reviewed papers
- 11 chapters in monographs
- 12 conference proceedings full papers

### **International cooperation**

**Austria:** University of Vienna, Museum of Natural History, Vienna

**Bulgary:** Institute of Geology of the Bulgarian Academy of Sciences, National Institute of Geophysics, Geodesy, and Geography of the Bulgarian Academy of Sciences

**Ethiopia:** Arba Minch University, Ethiopian Geological Survey

**France:** Institute de Physique du Globe de Paris

**Germany:** Karlsruhe Institute of Technology, Technical University of Darmstadt, Geologisches Amt Baden-Württemberg Freiburg, Friedrich-Schiller-Universität Jena, Institut für Geowissenschaften, Ludwig Maximilian University of Munich, University of Leipzig

**Israel:** Tel Aviv University

**Italy:** Institute for the Dynamic of Environmental Processes, CNR-IDPA, Milan, Institute for Geo-Hydrological Protection, CNR-IRPI, Padova, University of Florence, University of Camerino

**Japan:** University of Kyoto

**Kyrgyzstan:** Institute of Seismology, Central Asian Institute for Applied Geosciences

**Mexico:** Universidad Nacional Autónoma de México, Querétaro

**New Zealand:** University of Waikato, Hamilton

**Norway:** Det Norske Veritas, Oslo

**Peru:** Institute of Seismology

**Poland:** Institute of Geophysics PAS, Polish Polar Station Hornsund, Wrocław University of Environmental and Life Sciences, Polish Geological Institute – Lower Silesian Branch in Wrocław, Polish Academy of Sciences, Research Centre in Kraków, Institute of Geological Sciences, Kraków, Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Kraków

**Russia:** Russian Academy of Sciences, Institute of the Geospheres Dynamics, Moscow

**South Africa:** Council for Geosciences

**Slovakia:** Comenius University, Bratislava, Matej Bel University, Banská Bystrica, Geological Institute of the Slovak Academy of Sciences, State Geological Institute of Dionýz Štúr, Slovak Caves Administration

**Slovenia:** Karst Research Institute ZRC SAZU Postojna, University of Ljubljana

**Spain:** Institute of Earth Sciences “Jaume Almera”, CSIC, Barcelona, Department of Civil Engineering, University of Las Palmas de Gran Canaria, Las Palmas, National Geographical Institute (IGN, Santa Cruz de Tenerife, Institute of Geology and Mining (IGME), Las Palmas, Universitat de Barcelona

**Switzerland:** NAGRA, University of Bern, GAMMA Remote Sensing Research and Consulting AG

**USA:** Brigham Young University, San Diego State University

**Cooperation within Czechia:** Charles University in Prague, Faculty of Sciences, Czech Technical University, Technical University in Brno, Faculty of Electrotechnics, Masaryk University, Ostrava University, Palacký University in Olomouc, SÚRAO, Czech Geological Survey, Cave Administration of the Czech Republic, Chemcomex a.s., Strix Chomutov s.r.o., RockNet s.r.o., Gestra Sedloňov a.s., 1. Litoměřická a.s., Diamo s.p., Geological Institute of Czech Academy of Sciences, Geophysical Institute of Czech Academy of Sciences, State Office of Nuclear Safety (SÚJB), Energoprůzkum Praha, s.r.o.