

# **ESIR Isotope Workshop XIII**

**European Society for Isotope Research – ESIR 2015**

**Zadar, Croatia**

**September 20 – 24, 2015**

## **Book of Abstracts**



**Ruđer Bošković Institute**



**University of Zadar**

Book of Abstracts: ESIR Isotope Workshop XIII  
September 20 – 24, 2015 – Zadar, Croatia

ESIR Isotope Workshop XIII  
Zadar, Croatia, September 20 – 24, 2015

Editors: Ines Krajcar Bronić, Nada Horvatinčić, Bogomil Obelić

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## Welcome

ESIR – European Society for Isotope Research – is the association of scientists engaged in isotope research, focused primarily on Central and Eastern Europe, but is open to all interested parties from around the world. Isotopic studies of interest to ESIR include various aspects and applications of natural distribution of stable and radioactive isotopes, such as isotopes in geochemical processes, geosciences, oceanography and meteorology, applications of isotopes in industry, mining, forensics, and various other areas, as well as the development of methods and measurement techniques

ESIR promotes the exchange of ideas and results of isotope research with the emphasis to isotope geochemistry by organizing regular workshops on biannual basis. The history of the ESIR starts in 1990, when during International Isotope Meeting "Three Isotopic Days" (Poland) Mariusz-Orion Jędrysek proposed establishment of a scientific isotope society with the aim to organize workshops on biannual basis. Isotope Workshops took place always in Europe with special care to minimize participation costs: 1992, Lublin, Poland, 1994, Książ, Poland, 1996, Budapest, Hungary, 1998, Portorož, Slovenia, 2000, Kraków, Poland, 2002 Tallinn, Estonia, 2004 Seggau, Austria, 2005 Leipzig, Germany, 2007, Cluj-Napoca, Romania, 2009, Złotniki Lubańskie, Poland, 2011, Budapest, Hungary, and 2013, Freiberg, Germany.

ESIR Isotope Workshop XIII takes place in the University of Zadar, Zadar, September 20 – 24, 2015. The Workshop is organized by the Ruđer Bošković Institute, Zagreb, Croatia, in cooperation with the University of Zadar, Zadar, Croatia. Ruđer Bošković Institute is the largest research institute in Croatia, that celebrates this year its 65<sup>th</sup> anniversary. Zadar, almost three thousands years old city, surrounded by historical ramparts, is full of exceptional history and rich cultural heritage, being a treasury of archaeological and monumental riches from the ancient and the early Christian period, the Middle Ages, Renaissance to contemporary architectural achievements and gives an exceptional opportunity for exchange of scientific ideas in the unique historical environment.

The Book of Abstracts contains a total of 82 submitted abstracts from 15 countries. The editors have made some technical changes and unification, while the scientific content is the responsibility of the authors. The abstracts are grouped into sections Geochemistry, Geology and Paleoclimatology, Ecology and Environmental Research, Hydro(geo)logy, Karst Environment, and Methods and Instrumental Techniques. Within the Karst Environment section a special Workshop session is devoted to the REQUENCRIM project "Reconstruction of the Quaternary environment in Croatia using isotope methods".

The ESIR2015 Isotope Workshop has been financially supported by the Ministry of Science, Education and Sports of the Republic of Croatia, and by The Foundation of the Croatian Academy of Sciences and Arts.

The Organizing Committee welcomes all the participants of the ESIR Isotope Workshop XIII. We wish you successful scientific sessions and enjoyable time in Zadar and Croatia.

Organizing Committee of the ESIR Isotope Workshop XIII

# **ESIR Isotope Workshop XIII**

**Zadar, Croatia**

**September 20 – 24, 2015**

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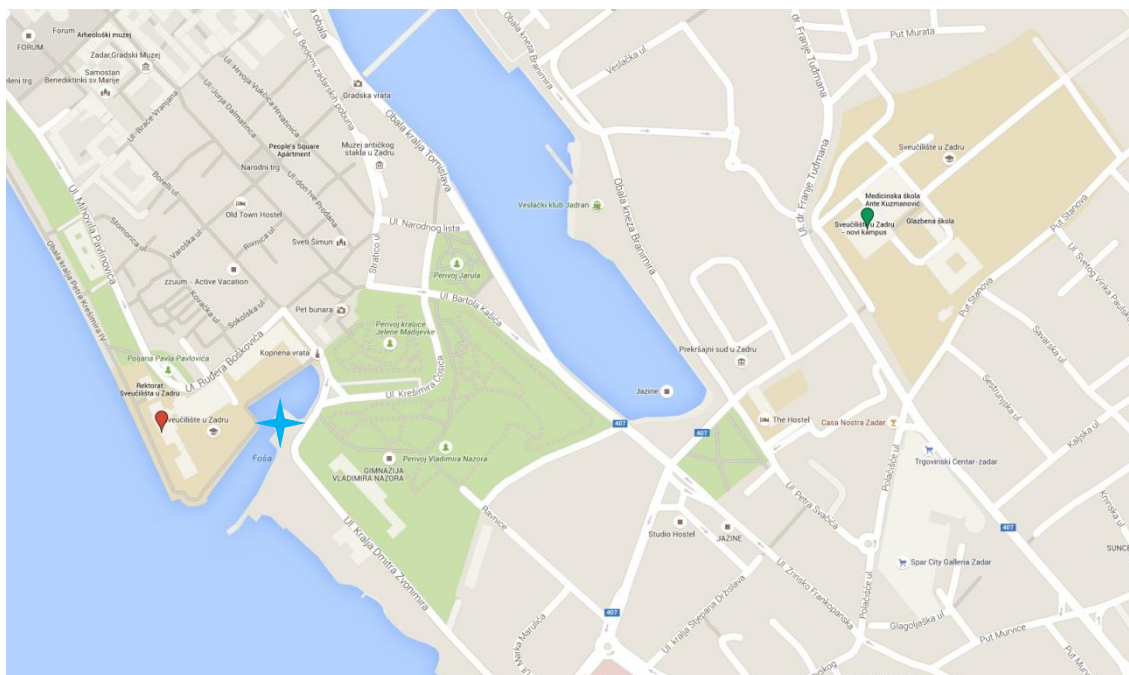
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The Book of Abstracts has been printed by the financial support of The Foundation of the Croatian Academy of Sciences and Arts.

## Conference venue

The ESIR Isotope Workshop XIII takes place at the University of Zadar. The reception and the opening ceremony will be held in the central University building (red mark, Obala kralja Petra Krešimira IV 2), while the conference sessions will be organized in the multimedial hall of the New campus (green mark, Ulica Franje Tuđmana 24).

Conference dinner will be in Restoran Foša, Kralja Dmitra Zvonimira 2.



Position of University of Zadar, Central University Building (red mark) and New Campus (green mark). Blue mark: ★ conference dinner.



## **Information**

### **Oral presentations**

Keynote lectures are 40 minutes long (30-35 minutes presentation and 5-10 minutes discussion). Oral presentations are 20 minutes long (recommended: 15-17 minutes talk and 3-5 minutes discussion). All talks should be accompanied by PowerPoint or PDF slides. Presenters are kindly invited to bring their presentations at latest during the break before the scheduled section to the person responsible for transfer to the conference computer. We kindly ask the participants to stick closely to the allocated duration of oral presentations.

### **Poster presentations**

Poster boards are allocated in the hall and the material for setting the posters up is available at the Registration desk. Poster board dimensions are 90 cm (width) by 100 – 120 cm (length). There are two poster sessions, one on Monday, 21 September afternoon and the other on Tuesday, 22 September afternoon. Posters should be set up in the morning of the presenting day and taken down after the poster session. Please, display your poster at the poster board assigned with the code number of your poster (look at the Content of this Book of Abstracts). Poster presenters should be available for discussion at their poster display during the scheduled time.

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## Keynote lecture

### Use of isotopes and selected chemical tracers to investigate the origin and fate of nitrate in aquatic systems

Albrecht Leis<sup>1</sup>, Martin Dietzel<sup>2</sup>, Pierpaolo Saccon<sup>3</sup>, Hermann Stadler<sup>1</sup>, Joel Saverino<sup>4</sup>, Jan Kaiser<sup>5</sup>

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The accumulation of nitrate in aquatic systems is a well-known and worldwide occurring phenomenon. Individual sources of  $\text{NO}_3$  and mechanisms for its accumulation depend strongly on the environmental conditions during recharge, infiltration and aquifer storage. The source of dissolved  $\text{NO}_3$  in groundwater is commonly attributed to (i) anthropogenic origin, including leaching of fertilisers or animal waste, (ii) dissolution of evaporate deposits, (iii) leaching of organic or inorganic nitrogen from soils and (iv) atmospheric deposition. Evidence for nitrate origin is traditionally obtained by measuring  $^{15}\text{N}/^{14}\text{N}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios. From respective  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  signatures the  $\text{NO}_3$  provenances can be evaluated. However pristine isotope ratios may be overprinted during nitrogen transformation processes in soils and within the aquifer (e.g. by (de)nitrification). Additionally mixing of nitrate derived from different sources might hamper the identification of nitrate origin. Some of these limitations can be minimized by including other tracers e.g. boron isotope composition ( $\delta^{11}\text{B}$ ) and / or polar organic micro pollutants. These substances are ubiquitous co-migrants of nitrate from anthropogenic origin. Combining these tracers and nitrate isotopes allows in many cases to distinguish animal manure from sewage and mineral fertilizer inputs. Moreover, the role and contribution of atmospheric  $\text{NO}_3$  are still not well understood. Recently a triple stable isotope approach using  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$  signals in  $\text{NO}_3$  was successfully applied to discover the contribution of atmospheric nitrate ( $\text{NO}_{3,\text{atm}}$ ) from different terrestrial sources.  $\text{NO}_{3,\text{atm}}$  is exclusively characterized by a  $^{17}\text{O}$  anomaly, where mass independent isotope fractionation (MIF) results in non-zero  $\Delta^{17}\text{O}_{\text{NO}_3}$  values.

Here we present some recent cases studies and novel approaches on the identification and characterization of multiple sources of nitrate in different aquatic systems (i) Mediterranean coastal lagoon, (ii) Saharan paleo-aquifer and (iii) Alpine karst aquifer.

In the lagoon environment we used beside the traditional hydrochemical analyses (major ions and nutrients) a combined isotope approach including stable isotopes of nitrate ( $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$ ), the isotopic signature of boron ( $\delta^{11}\text{B}$ ), the stable isotopes in water ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) and the stable isotopes in sulphate ( $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$ ).  $\Delta^{17}\text{O}$  analyses were used to

quantify the terrestrial and atmospheric contribution of  $\text{NO}_3$  to lagoon water.  $\delta^{18}\text{O}$  ( $\text{NO}_3$ ) data even permit us to decipher between freshwater-derived  $\text{NO}_3$  exported from inflowing rivers and marine nitrate produced from nitrification processes in the lagoon. The ammonium sources in lagoon water are originated from decay of locally occurring biomass and partly from anthropogenic sources (e.g. sewage water). Since the  $\delta^{18}\text{O}$  of seawater is higher than that of freshwater, the nitrate produced in the lagoon from nitrification of ammonium will have a higher  $\delta^{18}\text{O}$  value. This may mean that nitrate with  $\delta^{18}\text{O} > 8\text{‰}$  mainly originates from nitrification processes within the lagoon itself, especially since the small  $\Delta^{17}\text{O}$  values (mean 0.65 ‰, maximum 3 ‰) indicate an direct atmospheric nitrate contribution of less than 3 % on average (but up to 10 % locally).

In the Saharan paleo-aquifer we show that a  $^{17}\text{O}$  anomaly in  $\text{NO}_3$  is well preserved in this old Saharan groundwater reservoir. The  $^{17}\text{O}$  anomaly is caused by mass independent oxygen isotope fractionation via photochemical reactions and thus tracing atmospheric  $\text{NO}_3$ .  $\text{D}^{17}\text{O}$   $\text{NO}_3$  values clearly indicate up to 20 mol% of  $\text{NO}_3$  originated from the Earth's atmosphere besides microbial  $\text{NO}_3$ . The isotope composition of water accounts for recharge under rather cool and humid paleo climate conditions without significant evaporation. Isotope signals of  $\text{NO}_3$  indicate flood events from periodic heavy precipitation with rather instantaneous infiltration, which is documented by high  $\text{NO}_{3,\text{atm}}$  proportions at elevated  $\text{NO}_3$  concentrations.

At the Alpine karst spring we employed the stable isotopes of nitrate to trace dynamics of dissolved  $\text{NO}_3$  in spring water during aestival storm-flow events. Although, the  $\text{NO}_3$  concentrations were very low, a distinct signal of atmospheric  $\text{NO}_3$  could be observed during the course of the event. Our data show that a substantial portion of nitrate in the spring water is of atmospheric origin and does not undergo microbiological transformation during the transport in the karst system.

## **Isotopic composition of Permian-Triassic sulphate accumulations: examples from the Eastern Alps, Austria**

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Isotopic investigations on sulphur and oxygen from sulphate accumulations combined with mineralogical investigations may offer information regarding the origin of fluids, pH and/or eH of fluids, inflows, restricted conditions, evaporative effects, recrystallization or bacterial processes [1-5]. While sulphur isotope measurements were done on sulphates from Austrian Permian-Triassic deposits [6,7] oxygen data are missing. In this study we investigated the oxygen and sulphur isotope composition of evaporite sulphates and associated sulphides will provide additional information regarding the condition of formation and subsequent history.

The Eastern Alps are characterised by the presence of three main tectonic units, such as the Lower, Middle and Upper Austroalpine, which overlie the Penninicum [8]. The Upper Austroalpine unit consists of the Northern Calcareous Alps (NCA) overlying the Greywacke zone. The Northern Calcareous Alps are a detached fold and thrust belt. The sedimentation started in the Late Carboniferous or Early Permian, the age of the youngest sediments being Eocene. The NCA are divided into the Bajuvaric, Tirolic and Juvavic nappe complexes. The evaporitic Haselgebirge Formation occurs in connection with the Juvavic nappe complex at the base of the Tirolic units [9].

The isotope ratios of sulphates ( $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$ ) and sulphides ( $\delta^{34}\text{S}$ ) were determined by measuring the isotopic composition of resulting  $\text{SO}_2$  and  $\text{CO}_2$  gases on the IRMS with dual inlet and triple collector mass spectrometer [10,11]. Delta values were normalized to the VCDT and the VSMOW scales by analysis of the NBS-127.

Oxygen and sulphur isotopic composition were determined for anhydrite, gyps, polyhalite, blödite and langbeinite. The  $\delta^{34}\text{S}$  values vary between 10.1 ‰ to 14 ‰ (VCDT), with a few values higher than 14 ‰ and  $\delta^{18}\text{O}$  values show a range from 9 ‰ to 23 ‰ (VSMOW). The sulphur isotopic composition of sulphides as galena, sphalerite, pyrite and native sulphur ranges between -17.5 ‰ and 2.8 ‰ (VCDT).

At low temperatures, isotopic exchange between dissolved sulphate and water has slow exchange rates [12]. Accordingly, the sulphur and oxygen isotopic composition of sulphates should reflect the composition of the dissolved sulphates, and not that of water. For the investigated sulphates, the  $\delta^{34}\text{S}$  values are generally low, which are characteristic for the late Permian [13]. The broad distribution of sulphide  $\delta^{34}\text{S}$  values point toward bacterial reduction, fact also reflected by some higher  $\delta^{34}\text{S}$  values of sulphates. The  $\delta^{18}\text{O}$  values show

a larger scatter from 9 ‰ to 23 ‰, which is even larger than that found for the Zechstein anhydrites of northern Germany, north-eastern Italian Alps or western Poland [4,14,15].

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## Variability of sulphur speciation in sediments from Sulejów, Turawa and Siemianówka reservoirs (Poland)

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The aim of this study was to better understand sulphur cycle in freshwater reservoirs, particularly to: (i) assess geochemical interactions between the water column and the sediment; (ii) mechanisms of processes occurring in the sediment (iii) identification of sulphur sources in sediments. These studies were carried out in three dam reservoirs in Poland (Sulejów, Siemianówka, Turawa). These lakes differ regarding the hydrological conditions, age, sediments accumulation and organic matter content in them. The main analytical tools were chemical extraction of various sulphur compounds from samples sediment and then  $\delta^{34}\text{S}$  isotopic analysis.

In all reservoirs has been shown to speciation oxidized sulphur ( $\text{SO}_4^{2-}$ ) and reduced forms (S-org,  $\text{S}^0$ , mono- and polysulphides). The sedimentary  $\text{SO}_4^{2-}$  concentrations were in the range of 0.01 to 0.90  $\text{mg g}^{-1}$  ( $\delta^{34}\text{S}(\text{SO}_4^{2-})$  from -15.2 ‰ to 3.5 ‰ - Turawa), from 0.01 to 0.40  $\text{mg g}^{-1}$  (from 1.9 ‰ to 3.2 ‰ - Siemianówka), of 0.04 to 1.30  $\text{mg g}^{-1}$  (from -7.7 ‰ to -2.0 ‰ - Sulejów). The  $\text{S}^0$  concentrations from 0.01  $\text{mg g}^{-1}$  to 1.40  $\text{mg g}^{-1}$  (from -13.2 ‰ and -10.9 ‰ - Turawa), from 0.05 to 0.60  $\text{mg g}^{-1}$  (from -2.1 ‰ to 0.5 ‰ - Siemianówka) and from 0.01 to 1.30  $\text{mg g}^{-1}$  (from -3.8 ‰ to -2.8 ‰ - Sulejów). The S-org concentrations ranged between 0.4 and 0.9  $\text{mg g}^{-1}$  (-2.1 ‰ to 0.5 ‰ - Siemianówka), from 0.1 to 0.8  $\text{mg g}^{-1}$  (from -13.2 ‰ to -10.9 ‰ - Turawa) and from 0.3 to 0.8  $\text{mg g}^{-1}$  (from -3.8 ‰ to -2.8 ‰ - Sulejów). The recorded monosulphide concentrations in Turawa were very low, ranging from values below detection limit to 0.18  $\text{mg g}^{-1}$  sediment. In Siemianówka and Sulejów monosulphides were not found to be present in the studied sediments. The polysulphide concentrations in Turawa range from values below detection limit (<0.01  $\text{mg g}^{-1}$ ) to 1.40  $\text{mg g}^{-1}$  sediment (-14.2 ‰ and 4.0 ‰), from 0.06 to 0.70  $\text{mg g}^{-1}$  (from -3.0 ‰ to 0.9 ‰ - Siemianówka), from 0.04 to 0.30  $\text{mg g}^{-1}$  (-12.3 ‰ to -10.8 ‰ - Sulejów).

The  $\text{SO}_4^{2-}$  concentration in the water of the Mała Panew River flowing into the Turawa reservoir shows values higher by more than 20  $\text{mg/dm}^3$  compared to the concentration recorded in the reservoir. A part of  $\text{SO}_4^{2-}$  from the water column is incorporate into plants cell structures, while a part of it is deposited in the sediment, where it is reduced to sulphides.

Considerable difference in biogeochemical processes between Siemianówka and Sulejów reservoirs were observed, both in concentrations and isotopic composition of individual sulphur speciations. In both reservoirs the presence of polysulphides in sediments was revealed. In the Sulejów reservoir (probably in the sediment-water interface) probable oxidation of polysulphides to  $\text{SO}_4^{2-}$  has occurred.

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## **Correlation of stable isotope composition of carbonate precipitated in the water under different conditions**

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Composition of stable isotopes  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of fresh carbonate precipitated in the waters of the Plitvice Lakes,  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) and  $\delta^{18}\text{O}$  of waters were measured at different locations with different conditions of precipitation. For this study we collected 3 types of carbonates ( $\text{CaCO}_3$ ) precipitate in the water: 1) suspended carbonate precipitated in 4 sediment traps, 2 – 10 m below the surface in 3 lakes, 2)  $\text{CaCO}_3$  precipitated on porous plastic pads submerged in the water (surface water) at 7 locations with different water flow rates (0 to 0.7 m/s), and 3) surface lake sediments (top ~40 cm) at the bottom of 3 lakes. Carbonates were collected in different seasons in period 2011 – 2013. We also measured  $\delta^{14}\text{C}$  of  $\text{CaCO}_3$  from plastic pads.  $\delta^{13}\text{C}$  values for all carbonates are generally in the range from -10 ‰ to -6 ‰ which is typical for fresh water carbonates, but the difference between 3 types of carbonates was obvious.  $\delta^{13}\text{C}$  values for  $\text{CaCO}_3$  in 4 sediment traps were very uniform, with mean values from -8.5 ‰ to -7.5 ‰, showing stable conditions of carbonate precipitation in deep water. Difference between  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  of the  $\text{CaCO}_3$  was between 2.8 and 3.9 ‰, indicating partial equilibrium conditions of precipitation. Narrow range of  $\delta^{13}\text{C}$  values of  $\text{CaCO}_3$  of surface lake sediment in 3 lakes (mean values from -9.5 ‰ to -9.0 ‰) showed similar stable conditions of  $\text{CaCO}_3$  precipitation, also in deep water.  $\delta^{13}\text{C}$  values of  $\text{CaCO}_3$  precipitated in surface waters showed variations from -10 ‰ to -4 ‰ depending on locations. At 2 out of 7 locations the higher  $\delta^{13}\text{C}$  indicated the mixing of authigenic  $\text{CaCO}_3$  and detrital  $\text{CaCO}_3$  of mineral origin. This was also indicated by  $\delta^{14}\text{C}$  values in the same locations that were much lower (10 – 30 pMC) comparing with other 5 locations (70 – 80 pMC).  $\delta^{18}\text{O}$  values of surface water showed seasonal fluctuation (-10.9 to -9.8 ‰), while the  $\delta^{18}\text{O}$  values of  $\text{CaCO}_3$  showed more significant fluctuation depending on micro-location. Good correlation of  $\delta^{18}\text{O}$  of  $\text{CaCO}_3$  from 4 sediment traps with mean water temperature in period of precipitation was obtained.  $\delta^{18}\text{O}$  values of water and  $\text{CaCO}_3$  were used for estimation of temperature of carbonate precipitation. The best agreement of estimated with the real/measured temperatures at all deep waters/traps was obtained by the approach of Leng and Marshall [1].

The work was performed within the project with Plitvice National Park: Influence of environmental and climate changes on the biologically induced calcite precipitation in form of tufa and lake sediment at the Plitvice Lakes.

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## Temperature dependence of oxygen- and clumped-isotope fractionation in travertines and tufas in the 6 – 95 °C temperature range

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Conventional carbonate-water oxygen isotope thermometry (e.g. [1]) and the more recently developed clumped isotope thermometer [2] are widely used for the reconstruction of paleotemperatures from a variety of carbonate materials. In spite of a large number of existing studies, there are still significant uncertainties in both  $\delta^{18}\text{O}$ - and  $\Delta_{47}$ -based temperature calibrations. For this reason there is a need to better understand the controls on isotope fractionation, especially on natural carbonates. In this study we analyzed oxygen, carbon and clumped isotopes of a unique set of modern calcitic and aragonitic travertines, tufa and cave deposits from natural springs and wells. Together these samples cover a temperature range from 6 to 95°C. Travertine samples were collected close to the springs and from downstream pools. Tufa samples were collected from karstic creeks and a cave. The majority of our vent and pool travertines and tufa samples show a carbonate-water oxygen isotope fractionation comparable to the one of Tremaine et al. [3] with some samples showing even higher fractionations. No significant difference between the values of the calcite-water and aragonite-water oxygen isotope fractionation could be observed. The  $\Delta_{47}$  data from the travertines show a strong relationship with temperature and define the regression  $\Delta_{47} = (0.044 \pm 0.005) \times 10^6 / T^2 + (0.20 \pm 0.05)$ . The mineralogy and precipitation rate do not appear to significantly affect the  $\Delta_{47}$ -signature of carbonates, compared to the temperature effect and the analytical error. The tufa samples and three additional biogenic calcites show an excellent fit with the travertine calibration, indicating that this regression can be used for other carbonates as well. This work extends the calibration range of the clumped isotope thermometer to travertine and tufa deposits in the temperature range from 6 °C to 95 °C. Our results will help to improve the confidence in paleotemperature reconstructions not only from travertines, but also from cave carbonates and diagenetic cements.

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## Methanogenic biodegradation of lignite from Konin mine, central Poland

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The main challenge of lignite biogasification is understanding the role of the organic additives in the biogas production. In this work organic matter from lignite were fermented under various, lab-controlled conditions using bacterial inoculum (groundwater from lignite mine and methanogenic consortium from lake sediments), mineral medium and various supplemental components vital for microbial life. The main part of our laboratory work was geochemical analyses in substrate-product system (gases, solutions, solids).

Our results show that biogenic methane is present in groundwater from Konin mine, central Poland. Thus, methanogenesis is natural, recent process in lignite beds. Simulation and especially enhancing of these natural processes under laboratory conditions are very difficult. In long-term (up to 19 months) experiment in anoxic conditions methane production was below the detection limit. General conclusion was that methanogenesis can be affected or even inhibited by activity of sulphate reducing bacteria.

In experiments with lignite inoculated with methanogenic consortium from lake sediments and organic compounds such methanol, acetate, glucose, nutrient A, nutrient B, 160 samples of biogas were obtained. Volume of biogas samples varied from 8 to 555 ml. Concentration of methane varied from 0.01 to 85.93 %. Concentration of carbon dioxide was in the range from 0.01 to 32.65 %. The  $\delta^{13}\text{C}(\text{CH}_4)$  value varied from -70.2 to -6.6 ‰. The  $\delta\text{D}(\text{CH}_4)$  value varied from -396.6 to -290.5 ‰. The  $\delta^{13}\text{C}(\text{CO}_2)$  value ranged from -55.16 ‰ to surprisingly high value of 44.98 ‰.

Generally, biogas emission varied with time and depended on the availability of carbon sources in the solution. Various carbon compounds, including carbon-bearing nutrients, could be degraded by microorganisms with different rates. It caused high variation of the  $\delta^{13}\text{C}$  of methane and carbon dioxide and suggests mixing of gases from different carbon sources along incubation. Understanding of the  $\delta\text{D}(\text{CH}_4)$  variation is even more difficult, because many substrates contain often exchangeable hydrogen (e.g. water, lignite, elements of nutrients). Glucose, acetate and methanol significantly increased biogas production. Biodegradation of these organic compounds influenced isotopic composition of carbon in methane and carbon dioxide. Simultaneously, additional compounds, nutrient A and nutrient B, were not a source of organic carbon to methane formation, but their presence has magnified biogas production.  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^{13}\text{C}(\text{CO}_2)$  values combined allowed to state that the dominant methanogenesis pathway in experiments was acetate fermentation.

The main achievement of this work is identification of experimental series in which methanogenic decomposition of lignite took place (components: lignite, glucose, nutrient A, nutrient B). Comparative analysis of the efficiency of methane production from lignite and agricultural wastes showed that potential of methane production from lignite was one order lower than from agricultural wastes.

## **Geochemical and isotopic characterization of coalbed gases in active excavation fields at Preloge and Pesje (Velenje Basin) mining areas**

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Coalbed gases in excavation fields of mining areas in the Velenje coal basin have been subjected to geochemical and isotopic monitoring since the year 2000, with the aim of obtaining better insights into the origin of coalbed gases. Results from active excavation fields in the mining areas Pesje and Preloge in the year 2013 and 2014 are presented in this study. Composition and isotopic composition of coalbed gases were determined with methods utilizing mass spectrometry. The chemical and isotopic compositions of coalbed gases in the Velenje Basin vary and depend on the composition of the source of coalbed gas before excavation, advancement of the working face, depth of the longwall face, pre-mining activity and newly mined activity. The basic gas components determined in excavation fields are CO<sub>2</sub> and methane. The isotopic composition of deuterium in methane has been determined and used to characterize the origin of methane. The isotopic compositions of carbon and hydrogen in methane in the excavation fields show its biogenic origin, while a high Carbon Dioxide Methane Index indicates the bacterial and endogenic origin of CO<sub>2</sub>.

## **Stages of uranium mineralization in the Kola-Karelian region (Russia): Sm-Nd, Rb-Sr and U-Pb data**

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Processes of uranium mineralization are typically multistage, complicating the investigation and revealing of their evolution and suggests the involvement of isotope-geochronological studies. Metasomatic uranium-bearing rocks of South Pechenga zone and Litsa district of the Kola Peninsula and Ozernoe area of the Salla-Pana-Kuolajarvi zone of the Northern Karelia (Russia) have been studied by Sm-Nd, Rb-Sr and U-Pb methods. The obtained Sm-Nd mineral ages are within 1886 - 1750 Ma, which is responsible for the manifestation of metasomatic processes at the regressive stage of regional metamorphism of the Baltic Shield and fully justify the assumption of [1] on the formation of Fe-Co-Au-U deposits after the peak of Svecofennian metamorphism. Rb-Sr data define the lower age limit for metasomatic processes at  $1730 \pm 40$  Ma. Low closure temperature for Rb-Sr system of biotite which defines isochrones indicates that during growth of uranium minerals the temperature did not rise above 300 - 350 °C. A change of the Nd initial isotopic composition ( $^{143}\text{Nd}/^{144}\text{Nd}$ ) from 0.51032 at 1.89 Ga to 0.51022 at 1.75 Ga, and thus, variations in the  $\xi\text{Nd}$  values from +1.2 to -3.4 indicates mantle origin of fluid flow and lack of significant interaction with crustal rocks at 1.89 Ga with the subsequent contamination of fluid by crustal material to 1.75 Ga. Variations of initial strontium ratio ( $^{87}\text{Sr}/^{86}\text{Sr}$ ), characteristic for fluid-saturated ore-bearing metasomatites [2], from low (0.7027) to high (0.7156) also indicate a significant interaction of metasomatizing fluid with crustal rocks. U-Pb rutile age of ore-bearing albitites from the Ozernoe area is  $1756 \pm 8$  Ma which allows estimating the temperature of rocks at that time since the known closure temperature for U-Pb rutile system is about 400 – 450 °C. Chemical dating of uraninite gave an age of  $1627 \pm 42$  Ma, U-Pb brannerite age is  $385 \pm 2$  Ma. These ages are also known for uranium mineralization in other parts of the Kola Peninsula [3]. Thus, the isotopic systems showed the two-stage formation of ore-bearing metasomatites in the Kola-Karelian region, which were associated with mantle fluid that was contaminated by crustal material with time.

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## **Variations of $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and sulphate content in water from precipitation to groundwater drainage in Tylicz area (Beskidy Mountains, SW Poland)**

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The area of Tylicz, located in Poprad River Valley, a part of the Polish Carpathians Massif (Beskidy Mountains) is a particularly important region as a place of exploitation and bottling of therapeutic, mineral and fresh groundwater, where groundwater exploitation have been started in the mid '70s last century. Hydrochemical and hydrodynamical processes of forming groundwater resources of this area, relations between fresh and medicinal groundwater and water pumping impact are still the subject of discussion. The main goal of this study was to explain the relationship between surface water, fresh and medicinal groundwater, precipitation and infiltration water based on selected research ground observations using chemical and isotopic analysis.

Sulphur isotopic ratio of dissolved sulphate ions  $\delta^{34}\text{S}(\text{SO}_4^{2-})$  and sulphate content were measured in surface water from Muszyna River, groundwater from two wells (P-IVa – fresh  $\text{HCO}_3\text{-Na-Ca-Mg}$  type water and P-VII – medicinal mineral  $\text{HCO}_3\text{-Na}$  type water), infiltration (from lysimeter) and precipitation water. Samples were collected from April 2014 to October 2014 in monthly intervals and analyzed using HPLC Waters (ions content) and Mass Spectrometer Thermo Scientific Delta V Advantage ( $\delta^{34}\text{S}(\text{SO}_4^{2-})$ ). The results showed considerable differences in sulphate isotopic composition in studied water suggesting its strong chemical and isotopic transformation from recharge by precipitation, through infiltration and flow, to surface and groundwater drainage. Sulphate contents and  $\delta^{34}\text{S}(\text{SO}_4^{2-})$  values varied from < 0.01 to 2.30 mg/l and from 2.81 to 5.95 ‰ in precipitation, from 0.43 to 4.21 mg/l and from -4.77 to 30.80 ‰ in infiltration water, from 14.51 to 24.14 mg/l and from -11.49 to -4.32 ‰ in surface water, from 37.70 to 54.27 mg/l and from -18.15 to -15.39 ‰ in groundwater from well P-VIa, from 42.70 to 78.61 mg/l and from -17.68 to -16.41 ‰ in groundwater from well P-VII respectively. Observed temporal variation of  $\delta^{34}\text{S}(\text{SO}_4^{2-})$  in water from P-VII and P-IVa wells suggest the existence of different flow systems and intensification of groundwater mixing processes in autumn season. Wide range of  $\delta^{34}\text{S}(\text{SO}_4^{2-})$  values in infiltration water probably indicates very intensive biochemical processes in unsaturated zone with great significance of microbiological sulphate reduction.

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## **Deposition and sources of sedimentary organic matter in the Neretva deltaic plain and coastal area: its relation to the sediment surface properties**

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The deposition and distribution of sedimentary organic matter (SOM) in surface sediments of the Neretva River in the delta and the adjacent coastal region were investigated. These processes were studied in relation to the sedimentological characteristics of the deposits and their surface physico-chemical properties, i.e. specific surface area (SSA) and cation exchange capacity (CEC). The concentration of sedimentary organic matter and its C and N stable isotopic composition ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) were determined. The sources (terrestrial vs. marine) of OM were estimated using a mixing model from the  $\delta^{13}\text{C}_{\text{org}}$  values of the sediments and estimated end-members.

The presence of the seawater intrusion in the deltaic section of the river indicates that SOM in the watercourse originates from mixing of marine and river-borne particulate OM. The mixing model revealed that the fraction of terrestrial organic matter varied from up to 80 % in the river and decreased to about 60 % in the sea at the river mouth. The spatial distribution of organic matter content (TOC) in the coastal sea illustrates the reduction of riverine influence towards the open sea, despite the relatively uniform granulometric composition of the surface sediments. The strong negative correlation between TOC and its  $\delta^{13}\text{C}$  values and a lack of correlation with sedimentological parameters, such as clay content, SSA or CEC, clearly points toward the input of the river-borne  $^{13}\text{C}$ -depleted terrestrial organic matter as the dominant source of marine sedimentary  $\text{C}_{\text{org}}$ . Based on the  $\delta^{13}\text{C}$  values of TOC, it was estimated that the fraction of terrestrial component in the marine SOM decreases from about 35 % in the area at the river mouth to about 6 % at the furthestmost sampling sites. No statistically significant correlation between TOC and SSA was found nor in the river, neither in the marine sediments. The TOC:SSA ratios in the river sediments and related wetlands and lakes, as well as at most marine sites, exceed the monolayer equivalent values. This implies that the sorption of organic matter is unlikely as a predominant mechanism of its transport and preservation; a considerable fraction of organic matter must be present in discrete particles, such as plant debris, while leaching of soils contributes only a minor fraction of OM. This is also confirmed by the sedimentary  $\delta^{13}\text{C}$  values in the delta area, which are consistently lower than those of soils along the eastern Adriatic coast.

## **Isotopic and palynological signatures of the paleoclimatic conditions of peat bog from the polar region (south-western Spitsbergen)**

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In the recent years, global warming and climate changes issue is more and more popular. Wetlands and peat bogs studies can be helpful to follow tempo of changes. Bogs from polar regions give information about paleoclimatic past periods thanks to their specific and unique forming conditions. In the studies of paleoclimatic conditions reconstruction, carbon isotopic analyses ( $\delta^{13}\text{C}$ ) are very important. Thanks to isotopic analyses, it is possible to follow climate changes and important environmental episodes. Complementary to geochemical studies, palynological analyses of bog profiles are very useful.

Analyses were carried out on bog profiles gathered in Hornsund located in the south-western part of Spitsbergen (Norwegian Svalbard archipelago, Arctic Ocean). For the analyses three profiles were selected: two located near the sea (T1 or T2) and one (T4) located near the mountain range.

72 peat samples (every two centimeters) were taken for palynological and isotopic analyses.

All stable isotope analyses were carried out using an off-line vacuum preparation technique. For palynological analyses samples were treated with 30 % perchlorate, and then macerated with Erdtman's acetolysis. Frequency of pollen material was variable, hence the total sum fluctuated in the range from 50 to 300 pollen grains of trees, shrubs and herbaceous plants. POLPAL palynological software was used to create the percentage pollen diagram and histogram.

The isotopic composition varied from -28.0 to -23.8 ‰, from -30.5 to -16.3 ‰ and from -29.2 to -22.6 ‰ for profile T1, T2 and T4, respectively.

Palynological and isotopic data show temperature fluctuations in profiles. Colder and warmer periods were found, but the deeper into profile the lower average temperature was obtained.

## **Gammaspectrometric determination of radionuclides in soil**

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Ability to predict consequences of accidental release of radionuclides depends mainly on the level of understanding of the mechanisms involved in the interaction of radionuclides with different components of agricultural and natural ecosystems and their shaping into models of assessment.

This study is based specifically on time-limited contamination and is the first step, followed by the effect of different concentrations of contaminants on the development of plant species that is planted in soil contamination.

The experiment used wheat crops, seeds the “Winter wheat” variety “Renaissance”, Category C-1. After graduating from the early stages of the vegetative period, samples of earth, roots and above-ground parts of plants were measured from the vertical coaxial HPGe POP-TOP detector p-type producer ORTEC model GEM 30P4 with relative efficiency of 30 %.

The results show that the <sup>238</sup>U activity in the soil increases in proportion to the addition of higher concentrations of the contaminant uranyl acetate. Its <sup>40</sup>K activity was lower than the <sup>238</sup>U activity due to permeation and chemical composition of the soil. Based on these results it can be concluded that the plant in the process of self-preservation performs a selection of macro and trace elements from the soil, ie. takes the most necessary elements for optimal development.

## **Carbon, hydrogen and sulphur isotopic analysis to trace migration of natural gas in the enhanced gas recovery system**

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One of the first CCS (Carbon Capture and Storage) installation based on the EGR (Enhanced Gas Recovery) in Europe works in south-central Poland. This gave an opportunity to gather experience in the development of CCS on an industrial scale. Due to the small size of the deposit it can still be a great research opportunity to develop Enhanced Gas Recovery and all processes associated with injection of CO<sub>2</sub> and H<sub>2</sub>S are possible to observe in the experimental short time scale.

Isotopic analysis of injected and exploited gases is a potential tool to observe migration in the deposit. These studies, carried out since 2009, showed that the gases in the deposit are a complex system with a wide variation in the isotopic composition. Variations of the carbon, hydrogen and sulphur isotopic compositions depend on several physico-chemical factors strictly connected with injection and exploitation processes.

Carbon and hydrogen stable isotopic composition from methane was determined by manually preparation of gas samples on vacuum lines. Methane was separated from other hydrocarbon gases and CO<sub>2</sub> by means of cryogenic purification using molecular sieves, a dry ice/ethanol mixture, and liquid nitrogen. The methane passed through a copper oxide furnace (850 °C), where it was completely combusted to CO<sub>2</sub> and H<sub>2</sub>O, which were then separated cryogenically. H<sub>2</sub>O was reduced with zinc. Carbon stable isotopic composition of methane was analyzed off-line on dual inlet system (Finnigan MAT delta E IRMS) and hydrogen stable isotope composition of methane was analyzed off-line on Delta V Advantage IRMS. Carbon stable isotopic composition from carbon dioxide was determined by online measurements on mass spectrometer Europa 20-20 with trace gas preparation module ANCA TG. Sulphur stable isotopic composition from hydrogen sulphide was determined by online measurements on mass spectrometer Europa 20-20 with ANCA SL separation module for solid and liquid samples.

Isotopic composition of carbon in methane (n = 92) varied from -46.93 to -17.87 ‰ (average -35.22 ‰) and isotopic composition of hydrogen (n = 63) in that methane varied from -159.3 to -85.2 ‰ (average -114.6 ‰). Isotopic composition of carbon in carbon dioxide (n = 88) varied from -23.33 to -3.11 ‰ (average -13.35 ‰). Isotopic composition of sulphur in hydrogen sulphide (n = 13) varied from 2.46 to 7.65 ‰ (average 4.99 ‰). Spatial and temporal variations in stable isotopic ratios in methane, carbon dioxide and hydrogen sulphide show that the system is very dynamic. Namely, the carbon, hydrogen and sulphur isotopic ratios show that the gases movement is marked by the lowest isotopic ratios.

The studies are supported by the owner of the deposit and Lower Silesian Marshal Department, project „Entrepreneurial PhD student – an investment in the innovative development of the region”, Operational Programme Human Capital and also COST Action Number ES0806 Stable Isotopes in Biosphere-Atmosphere-Earth System Research (SIBAE).

## **The effect of non-carbonate soil components on the measured isotopic composition of carbonate**

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When the carbonate component of soil or other types of samples is not separable, the stable isotopic composition (C and O) of carbonate is determined on the bulk sample. It is a common practice that after pre-treatment of samples (removal of organic matter; drying), carbon dioxide is liberated by addition of phosphoric acid to an aliquot of sample in vacuum. Theoretically 100 % of the C content of the carbonate phase is released, while 2/3 of the O is released, and 1/3 remains in water formed during the acid-carbonate reaction. The effect of isotope fractionation between the liberated O and O in water is eliminated by application of laboratory standards treated in the same way as the samples. Since clay minerals may contain some interlayer water even after drying, this water may alter the oxygen isotope fractionation, and as a consequence alter the measured  $\delta^{18}\text{O}$  value of the carbonate.

To check the possible effect of soil components other than carbonate on the measured  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of carbonate phases a series of measurements have been carried out on mixtures of clay minerals, quartz and calcite. Since, if there is any effect, it is expected to be caused by clay minerals and not by quartz, the first series of measurements was accomplished on mixtures of different ratios of clay minerals and calcite. Four different types of natural clays were used: montmorillonite, Ca-montmorillonite, illite and bentonite. The calcite content varied from 50 % to 90 % and not any effect on the measured stable isotopic composition was observed. In the second series mixtures of clay, quartz and calcite were used with calcite content varying from 20 % to 2 %. In the case of carbon no shift in the measured  $\delta^{13}\text{C}$  values was observed. In the case of oxygen a positive shift of 0.3 ‰ – 0.5 ‰ was observed in the measured  $\delta^{18}\text{O}$  values at 2 % calcite content, but at higher calcite contents no shift was found.

## Keynote lecture

### Speleothems as archives of Quaternary palaeoenvironmental changes in Croatian karst – isotopic approach

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Speleothems, as secondary carbonate deposits precipitated within the caves, record series of data related to the changes in the atmosphere, biosphere, hydrosphere and lithosphere during their deposition. Reconstruction of many of those environmental changes is based on speleothems' isotopic compositions, particularly on their temporal variations. Both stable and radioactive isotopes are used to provide insight into past events either for chronostratigraphic purposes (U-Th series,  $^{14}\text{C}$ ), for the interpretation of varying temperature and rainfall composition ( $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ), for the vegetation changes ( $\delta^{13}\text{C}$ ) or as palaeothermometer ('clumped isotopes', i.e.  $\Delta_{47}$ ). Speleothems stand out among other archives, e.g. ice cores, deep sea cores, lake sediments etc., due to their: i) very precise chronology; ii) high-resolution proxy records; iii) geographical distribution in regions omitted by ice and marine cores; iv) precipitation reflecting mean annual climate conditions; v) cave environment well protected from exogenic impacts; vi) simplicity of preservation for future studies, etc. However, there are still some weaknesses of the dating methods (unknown initial  $^{14}\text{C}$  activity or presence of initial  $^{230}\text{Th}$ ), and of arguable reliability of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  signals due to their dependence of many different variables. Nevertheless, isotope-based speleothem studies are worldwide accepted and Croatia, with its classical Dinaric karst and thousands of caves, offers exquisite potential for such researches. From the late 1990's on, speleothems were used for the reconstruction of the palaeoenvironments above and below sea-level. Ten submerged caves (18 speleothems) have been encompassed into the sea-level reconstruction, while 15 subaerial caves (>30 speleothems) have undergone researches aimed to the reconstructions of the palaeoclimate changes. In order to provide insight into contemporary geochemical settings and hydrogeological behaviour of the rain- and dripwater, and modern carbonate deposition, recent studies are complemented with thorough monitoring program.

In spite of relatively small surface area, Croatia occupies important geographical position in terms of distribution of the air masses between continental Europe and Mediterranean. Thus, the main objectives of these researches are evaluation of dominant influences throughout the Quaternary and estimation of the resulting climate and overall environmental settings which should be starting point for the projections of the changes to come.

## **Last Glacial palaeotemperatures: A new proxy provided by oxygen isotopic signature of earthworm calcite granules in loess context**

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Earthworm calcite granules are composed of rhomboedric calcite crystals, organized in a radial crystalline structure. These granules are secreted by various earthworm species, mostly *Lumbricus terrestris* and *Lumbricus rubellus*, and are excreted at the surface and in the soil upper part. As biogenic carbonate is produced in equilibrium with its environment, calcite granule  $\delta^{18}\text{O}$ -VPDB composition is assumed to derive from soil water isotopic composition buffered by the mean soil temperature. In this study, we explored, for the first time, the potential of this new bio-indicator as a climatic proxy for temperature. We extracted 30 earthworm granules from eleven samples extracted from three tundra gleys and two brown soil horizons from the Nussloch sequence P8 previously dated between 45 and 23 ka. This 17-m-thick loess profile is considered as one of the most complete record of the Last Glacial in Western Europe and is chronologically well characterised.  $\delta^{18}\text{O}$  measurements were performed on each granule and duplicated or triplicated when possible. Throughout the studied section,  $\delta^{18}\text{O}$ -VPDB values range from -14.8 to -0.9 ‰ for tundra gley layers and from -10.7‰ to -0.3‰ for boreal brown soils. To generate quantitative climatic parameters from the granules  $\delta^{18}\text{O}$ -VPDB record, we first estimated the  $\delta^{18}\text{O}$ -VSMOW of meteoric water from modern values corrected with paleo-records data. We also considered that, in permafrost environment, ground temperature is generally 3°C warmer than air temperature and that earthworms are inactive during the winter period (from October to April). We thus estimated a mean annual air temperature of  $12 \pm 4$  °C for the interstadial warm seasons of the last glacial period in Nussloch. This value is in agreement with the few other reconstructions generated from different proxies in Western Europe (diatom assemblages, coleopteran, botanical remains). This original preliminary study highlights both the potential of earthworm calcite granule  $\delta^{18}\text{O}$ -VPDB measurements as proxy for absolute mean air temperature during the warm season of Last Glacial interstadials in continental environments as well as the first estimate for the Rhine Valley.

## **Stable isotope palaeoclimatology using speleothems: a progress report from the Alps**

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The stable isotopes of O, H and C are among the most widely used proxies in palaeoclimate research, exemplified by the long, continuous records from high-latitude ice cores and the deep sea. In the last two decades speleothems have been recognised as a key climate archive in mid- to low-latitude continental settings and increasingly complete and detailed stable isotope records of millennial and shorter time scales have been published in recent years. In contrast to many other archives the chronology of speleothem records is tightly anchored by high-precision  $^{230}\text{Th}$ -dates. This presentation provides a concise overview of recent and on-going research by the Innsbruck Quaternary Research Group focussing on caves in the Alps. Highlights include a nearly complete O isotope stack covering the last glacial period including the Last Glacial Maximum, detailed insights into Dansgaard-Oeschger cycles mimicking those identified in Greenland ice cores, a record of Termination II showing centennial-scale events, and the first quantification of temperature changes across the Younger Dryas based on both calcite and fluid-inclusion stable isotopes.

## Recently forming stalagmites from NE Hungary as recorders of regional climate conditions

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Actively forming stalagmites were collected from the Baradla Cave, NE Hungary. The cave entrance is situated in a forested area, the system stretches between 300 and 450 m a.s.l. in the host rock which is the lagoon facies Triassic (Ladinian) Wetterstein Limestone. The cave temperature was  $10.2 \pm 0.3$  °C in 2013 – 2014. The annual precipitation in 2013 was 723 mm, dominated by rain falling in early summer. Two stalagmites were collected from the collection site cca. 1100 m from the main entrance. The thickness of the overlying rocks is about 150 m. Along with temperature measurements dripwater samples were collected and their H and O isotope compositions determined ( $\delta D = -66.2 \pm 1.3$  ‰ and  $\delta^{18}O = -9.52 \pm 0.18$  ‰,  $n = 8$ ). The two stalagmites (~5 and ~7 cm in height) are composed mainly of columnar calcite and show well developed seasonal lamination. Based on  $^{14}C$  activity measurements and fitting to the Northern Hemisphere atmospheric  $^{14}C$  bomb-peak curve (1955 – 2000), the couplets of dark-light laminae represent annual growth layers and hence could be used for the establishment of age-depth models. Lamina thickness was determined in thin sections under optical microscope. Trace element and stable C and O isotope compositions were determined on the carbonate using ICP-MS and continuous flow IRMS techniques. C isotope compositions showed significant fluctuations (-11 to -8 ‰) in correspondence with lamina thickness values as well as with  $\delta^{13}C$ - $\delta^{18}O$  correlations, indicating that enhanced degassing caused faster growth and stronger kinetic fractionation. Mg and Sr contents do not vary in line with the C isotope compositions, suggesting that prior calcite precipitation did not play a significant role. The O isotope compositions range from -8.7 to -6.5 ‰ with no apparent systematic variation. The isotope compositions were correlated with local temperature and precipitation data, but no systematic relationship was detected. On the other hand, the C isotope data yielded a good negative relationship with precipitation–evaporation (P–E) values obtained for the region of the Baradla Cave from the 20<sup>th</sup> Century Reanalysis database of the NOAA (U.S. National Oceanic and Atmospheric Administration), which represents the net water budget. The data were compared with other stable isotope records of recently forming European stalagmites that indicated good correspondence. Hence, the stalagmite records obtained for the Baradla Cave were not only determined by site-specific processes but can be regarded also as climate proxies for a wider region. Interestingly, the data showed pronounced relationships with large-scale synoptic meteorological systems of the Atlantic region that will be presented.

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## Temperature and humidity changes at the beginning of the last interglacial reflected by combined H and O isotope compositions of inclusion-hosted water

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Inclusion-hosted water may provide direct information on the isotopic composition of the dripwater from which cave deposits formed. We have developed a technique to analyse  $\delta D$  and  $\delta^{18}O$  values in inclusion-hosted waters using a Los Gatos Ltd. laser spectrometer (LWIA-24d) and a preparation line [1]. The method applied here is slightly modified to conduct vacuum crushing in helium flow to reduce the possibility of  $H_2O$ - $CaCO_3$  oxygen isotope exchange during the extraction. The accuracies of  $\delta D$  and  $\delta^{18}O$  data were tested by analysing recently forming stalagmites where dripwater compositions are known and calcite samples whose isotopic compositions had been determined by independent mass spectrometric measurements. The technique was applied to study inclusion water compositions in a double stalagmite that covers a large part of the period of the last interglacial. The stalagmite actually comprises two columns that grow beside each other and show strikingly similar internal textures. U/Th age dating revealed that the stalagmite formation started at about 127.4 ky BP and ended at about 110.1 ky BP with a hiatus. The studied stalagmite section was dated by 7 U/Th age dates, all in stratigraphic order. An age-depth model was established using the StalAge program [2]. The stalagmite columns were correlated using textural characteristics and analysed for C and O isotope compositions of the calcite as well as H and O isotope compositions of inclusion-hosted water. The calcite C and O isotope compositions decrease and increase, respectively, with time, indicating development of warm and humid climate at about 120 ky, then drying and warming at about 116 – 118 ky, and a strong cooling after 116 ky. This scheme is similar to the climate evolution suggested by other records. H and O isotope compositions of inclusion-hosted water, however, indicate additional effects. The 120 ky climate optimum and the cooling at 116 ky is clearly reflected by both records, but between 127 and 124 ky – when the calcite  $\delta^{13}C$  and  $\delta^{18}O$  values show fluctuations – both a  $\delta D_w$  and  $\delta^{18}O_w$  values show strong negative excursions. The negative shifts can be well correlated with Mediterranean and North Atlantic records. Compilation of high-resolution records revealed that a sudden cooling event in the North Atlantic was associated with a warm and humid event in the Mediterranean. These data may point to the change in meteorological circulation regime during the last interglacial with stronger Mediterranean influence in the early part and a domination of Atlantic moisture transport to the Carpathian Basin in the middle to the late period of the interglacial.

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## **Stable isotope records of the speleothems from the eastern Adriatic islands caves**

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There are many systematic studies of stable isotopes in speleothems used to get proxy records of past climate changes in the Mediterranean region, as well as in Europe. Croatia encompasses a large part of Eastern Adriatic region and therefore has an important role in understanding the paleoenvironmental changes in the Adriatic and Mediterranean region. Despite that fact, there are not many investigations on reconstructing the paleoclimate and paleoenvironmental changes using the speleothem records in Croatia. Here we present the results of stable isotope variations in speleothems collected from Strašna peć, located on Dugi otok Island in the central part of the Croatian Adriatic, and Mala špilja cave and Vela špilja cave, located on Mljet Island in southern part of the Croatian Adriatic. High resolution oxygen and carbon isotopic record of U-Th dated stalagmites provided an insight to Holocene period from 9.8 to 1.5 ka along with interruptions in growth. Stable isotope measurements conducted on speleothem subsamples, revealed frequent fluctuations and abrupt changes in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values expressed in a number of peak values. Periods of relatively rapid growth are associated with relatively low  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values. Mid-Holocene climate is characterized by fluctuations between relatively wet and relatively dry conditions. The general trend of increasing  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  and reduced growth rate in Late Holocene indicates warming trend and/or the occurrence of dry climatic conditions in the paleoenvironment of the eastern Adriatic. In addition saw tooth pattern of high and low  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values indicate alteration of wet and dry periods that are characteristic for late Holocene speleothems from Europe and the eastern Mediterranean.

## **Late Glacial to Early Holocene climate change recorded by calcite-aragonite and calcite speleothems in an inneralpine dry valley (Vinschgau, northern Italy)**

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The Vinschgau is an inneralpine valley in the Southern Alps. The area is characterized by anomalously low precipitation today, but local climate archives (including debris-flow fans, speleothems) suggest that periods of a distinctly more humid climate occurred during the Late Glacial and the Early Holocene. The region is built up by metamorphic rocks characterised by a high degree of tectonic deformation. Although karst is not known in the Vinschgau, calcite-aragonite flowstones are deposited from the saturated groundwater along the South-facing mountain slope as a result of strong evaporation [1]. Inactive calcite-aragonite and calcite flowstones were analysed by various petrographic methods in order to identify fabrics and diagenetic alteration features (replacement of aragonite by calcite). In addition to stable carbon and oxygen isotope measurements, high-resolution U-series dating was performed. Preliminary data show that flowstone deposition occurred intermittently since ca.  $14.1 \pm 0.1$  ka and that these speleothems provide a local climate record of decadal to annual resolution. Even though petrographic analyses of calcite-aragonite speleothems revealed the presence of secondary calcite, U/Th analyses of the successive layers yielded ages in stratigraphic order, providing strong evidence that any mineralogical alteration occurred very early and within less than a few decades of deposition. The stable analyses of most samples show a strong co-variation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , implying kinetic isotope fractionation during carbonate precipitation.  $\delta^{18}\text{O}$  of both polymorphs shows significant (e.g. 2 ‰) variation, suggesting changing hydrological conditions. Although local factors, such as strong evaporation, amplified the primary climate signature, Vinschgau speleothems show similar  $\delta^{18}\text{O}$  pattern as other isotope records in the greater alpine realm, such as the ostracod record from Ammersee in southern Germany [2].

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## **Tsunami deposits record past climates**

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Earthquakes or explosive eruptions generate tsunami waves at the origin of thick and chaotic coastal sediments. These commonly fossiliferous deposits are formed instantaneously at the historical or geological timescale and therefore have the potential to provide snapshot records of past climates. In Crete, near the city of Palaikastro, crops out a 1 to 9 m thick sedimentary layer deposited by huge tsunami waves of about 10 m high. The presence of volcanic ash, the geometry, the archaeological and faunal contents of the sedimentary deposit along with radiocarbon dating converge altogether for interpreting this tsunamite as coeval with the Minoan Santorini (Thera) eruption 3,350 years BP. During its drawback, the devastating tsunami wave has deposited large rocky blocks and a muddy matrix containing mollusc shells dredged from the seabed as well as cattle skeletal remains and various artefacts (e.g. ceramic sherds, wall plaster) belonging to the contemporaneous Minoan civilization. Oxygen isotope measurements of both marine mollusc shells and terrestrial vertebrate teeth and bones revealed that sea surface and air temperatures were about 2 °C higher than nowadays. This result compares with the 2.5 °C temperature difference already estimated according to both  $\delta D$  and  $\delta^{18}O$  values of Greenland ice cores. Investigation of seasonality through incremental sampling of marine gastropods and bovid teeth suggest that the summers were as warm as today (26 °C) whilst winters were mild with temperatures of about 16 °C instead of 12 °C. If the eastern Mediterranean basin suffered the major climatic climax of the Holocene, the tsunami produced by the explosion of the Santorini volcano largely contributed to the fall of the Minoan civilization.

## **Cave sediments as time capsule: The Aeneolithic and Early Bronze in Poiana Ruscă Mts. (Romania)**

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The investigation of archaeological sites has revealed important information about the life of ancient people and continues to be an attractive research area. In Romania the interest is generally focused on potsherds, tools or other objects. Still, the study of the sediments is important as they may contain other elements (e.g. charcoal, pollen, particular minerals) which are useful for radiocarbon dating and describing the environment in which the people have lived. The aim of our research is to analyze the sediments from an archaeological site located in the Cerișor Cave from Poiana Ruscă Mts. (Southern Carpathians). The excavation has revealed a 39 cm thick sediment profile containing ceramics and hearths. Using the potsherd information and by comparison with the equivalent cultures from adjacent regions, the archaeologists distinguished three cultural groups that inhabited the cave and estimated their ages as follows: Turdaș (around 4250 BC) and Coțofeni (around 3150 BC), included in the Aeneolithic period and the Wietenberg culture (around 1575 BC) placed at the beginning of the Bronze Age. We have collected 7 mineralogical samples, 8 charcoal fragments for stable carbon isotope analysis and 3 charcoal samples for <sup>14</sup>C dating (awaiting for the results). Quartz, carbonates, hydroxylapatite, clay minerals and feldspars are the main mineral phases. The  $\delta^{13}\text{C}$  values range from -7.63 ‰ to -1.76 ‰. As shown by the isotopic profile, the Aeneolithic is characterized by a shift toward a drier climate followed by a wet period towards the end which extends to the Early Bronze Age. The results are similar to those from the POM2 stalagmite (Ascunsă Cave, Romania). Coțofeni culture is very common in the archaeological sites from Romania and the favourable climate may have contributed to the success of this population, but further research on this subject needs to be carried out and confirmed by other results.

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## **Stable isotopes in tree rings from Southern Poland and Eastern Carpathian: temporal stability of climatic signal versus pollution emissions**

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Trees are interactive monitor of environment. Because of their prevalence and the relative ease of dating, tree rings seem to be an excellent archive of past climatic and environmental change. Tree growth, photosynthesis, and the degree of carbon and oxygen isotope fractionation as preserved in the tree rings, is influenced by defined climatic conditions like temperature, precipitation, humidity, light intensity and change in soil moisture. Isotopic measurements in tree rings can be very useful in reconstructing past climate. However, such reconstructions may encounter some problems. One of these, especially at the present time, is environmental change caused by anthropopression, which also affects the stable isotope ratios. Since the beginning of industrial revolution, the  $\delta^{13}\text{C}$  of the atmospheric  $\text{CO}_2$  has decreased due to emission of  $^{13}\text{C}$ -depleted  $\text{CO}_2$  from human activities such as fossil fuels burning and land clearing. The so called Suess effect is reflected in tree rings  $\delta^{13}\text{C}$ . Emissions of  $\text{SO}_2$ ,  $\text{NO}_x$ , and other phytotoxic compounds lead to serious disturbances in tree physiology and metabolism and therefore change also isotopic composition of plant tissue. For example gaseous  $\text{SO}_2$  can cause the closure of stomata and reduce negative carbon isotope composition. It can also affect oxygen isotope composition.

The selected research areas: Sudeten, Tatras, Eastern Carpathians and Silesia region represent various forms of topography and diverse intensification of anthropopression. Sudeten and Silesia are examples of areas with significant human impact on the environment. Even for those areas air pollution emissions were not continually monitored and data is only available for the last 20 years.

We present the results concerning measurements of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in tree rings  $\alpha$ -cellulose of pine for Silesia and spruce for mountain region.

Isotopic composition of  $\alpha$ -cellulose samples was determined using the continuous flow isotope ratio mass spectrometer coupled to the elemental analyzer.

Testing the temporal stability of climate - stable isotopes relationships has fundamental implications not only for reconstruction of natural climate variability, but also for estimating changes associated with anthropogenic activity. Relationships between isotope values and monthly climate data were modelled using bootstrapped correlation function in DendroClim2002. Using a moving interval technique, the temporal stability of correlation between isotope chronology and climate was investigated. These studies showed no climate signal stability for the years of the maximum industrial human activities.

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- “Trees as isotope archives of climate and human impact on environment in Central Europe mountain areas” funded by the National Science Centre allocated on the basis of decision number 1557B/P01/2009/37.

## **The 8.2 kyr event in Central Europe recorded by combined H-C-O isotope compositions of calcite and inclusion-hosted water of a stalagmite**

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Among the climate events during the Holocene the 8.2 kyr event was the most pronounced. Here we present new isotopic data of calcite and inclusion hosted water of stalagmite from Béke Cave (NE Hungary, Carpathian Basin) that covers the time interval from 10500 to 4500 yr BP. The oxygen isotopic composition of the stalagmite calcite recorded the 8.2 kyr event by elevated  $\delta^{18}\text{O}$  values between 8000 and 8400 yr BP, while the carbon isotopic compositions do not show significant changes during this period. Beside the C and O isotope compositions of the speleothem calcite, hydrogen and oxygen isotopic compositions of the inclusion hosted water of the studied stalagmite have been determined by using vacuum crushing and cavity ring-down spectroscopy. The relatively high water content allowed us to achieve ~5 mm sampling (and hence ~50 year age) resolution. Both hydrogen and oxygen isotopic compositions of inclusion hosted water show positive excursions around 8.2 kyr where the host calcite yielded elevated oxygen isotope compositions. The observed positive anomalies in O isotopic compositions in both the host calcite and its fluid inclusion content is in contrast to other western European speleothems which recorded this cooling event by marked decreasing of  $\delta^{18}\text{O}$  values of the calcite. The different response to this event in the Carpathian Basin might be caused by 1) decrease of the amount of winter precipitation and summer temperature resulting relatively more infiltration of summer precipitation leading to enhanced annual isotopic composition; 2) increased influence of air masses originated Mediterranean delivering precipitation with enhanced  $\delta^{18}\text{O}$  values (i.e. relative decrease of Atlantic air masses that is characterised by lower  $\delta^{18}\text{O}$ ).

Relatively drier and cooler conditions have been inferred from other paleoclimate archives in Europe for the 8.2 kyr event. The dataset presented in this paper would be in agreement with these observations, if the relative amount of winter precipitation decreased along with temperature drop resulting in lower evaporation rate during the warm seasons. This would increase the relative contribution of warm season precipitation – and hence elevated  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values – in the dripwater from which the stalagmite was formed. This model would be consistent with the constancy of carbon isotope composition indicating that soil activity was not affected significantly.

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## **Paleoenvironmental reconstruction of the "Gazda" travertine quarry based on sedimentological and geochemical studies (Süttő, Gerecse Hills, Hungary)**

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Tentative reconstruction of the depositional environment of a Pleistocene "Gazda" travertine complex (Süttő, Gerecse Hills, Hungary) is presented. Samples were analysed using integrated sedimentological, petrographical and geochemical methods. Gazda quarry is part of the Süttő travertine system that occurs in the NW part of Hungary, where the travertine body is exposed by active quarrying.

On the basis of macroscopic and microscopic observations four major lithofacies were distinguished. They are supposed to correspond to the *palustrine*, *pond*, *slope* and *reed mound* depositional environments. Stable oxygen and carbon isotope analyses show that the carbon isotope values are ranging from -3.38‰ to 0.44‰ (V-PDB) (mean value  $-0.42 \pm 0.97$  ‰), whereas the oxygen isotopes values (ranging from -12.44‰ to -10.41‰) show a mean value of  $-11.59 \pm 0.67$  ‰ (V-PDB). Examining separately the mean values of micrites and cement phases show that both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  signatures of the micrite phase possess a slight enrichment in the heavy isotopes (-11.52 ‰ in  $\delta^{18}\text{O}$  and -0.27 ‰ in  $\delta^{13}\text{C}$  values), whereas the cement phase is characterized by somewhat more depleted  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values (-11.75 ‰ and -0.79 ‰ in V-PDB, respectively). The stable oxygen and carbon isotope values of the Gazda travertine compared with those of the samples collected in the neighbouring quarries (Újharaszt - Diósvölgy – and Hegyhát) indicate that they all precipitated from the same waters [1]. Using the equation of Kim & O'Neil [2] it becomes clear that the Gazda travertine precipitated from luke-warm fluids of about 25°C temperature. It is interesting to note that based on the recalculated original carbon isotopic signature of the dissolved CO<sub>2</sub> in the water, the Gazda travertine qualifies as a meteogene travertine (*sensu* [3]).

Based on the sedimentological and petrographical investigations, the geometry of the travertine beds of the Gazda quarry seems to follow the antecedent land-surface, i.e. a NE-SW striking pre-Pleistocene valley. To the north of the quarry, in a relatively higher elevated position, there is another open-cast operation, called Hegyhát quarry, the travertine of which was supposed to have been deposited in a large carbonate pond according to [4]. The geometry of the travertine sequences exposed by the two quarries displays obvious continuity, suggesting simultaneous formation. Due to lake-level fluctuations, water could episodically overflow from the Hegyhát area thus providing water for travertine precipitation along the gently sloping terrain. The overflowing water encountering a supposed topographic "obstacle" formed a shallow pond which became colonized by hydrophilic plants (e.g. reeds) stabilizing a

gradually evolving mound. Plant growth was apparently able to keep pace with the progradation of the mound which thus became gradually asymmetric. Field observations suggest that after passing through the mound, the overflowing water may have encountered another topographic “obstacle” thus providing for the formation of another pond.

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## Uranium isotope disequilibrium as an indicator for interaction ore matter with enclosing sediment rocks of Arkhangelski kimberlite tube from Lomonosov field

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The theoretical model of radioactive decay for ancestor and its daughter products foresees the oncoming of the secular equilibrium consisting in nuclide activity equation after a lapse of time (in comparison with duration of geological processes). For under consideration uranium series (isotopes  $^{238}\text{U}$  and  $^{234}\text{U}$ ) this period is about 1 million years. Accordingly, in natural compounds occurred more than 1 million years ago in uranium series the secular equilibrium should be observed. Numerous studies of the isotopic composition of uranium of various rocks and minerals demonstrate significant deviation ratio of  $\gamma = ^{234}\text{U}/^{238}\text{U}$  from equilibrium [1]. As a rule, recent beds, such as peat, bottom sediments, soils, are significantly enriched by  $^{234}\text{U}$ . This is due to the fact that the  $^{234}\text{U}$  atoms remote from bed rock accumulate in the re-deposited rocks exposed to natural waters [2,3].  $^{234}\text{U}$  enrichment is also characteristic for the recent volcanic deposits. For the ancient rocks the activity ratio of even uranium isotopes for the above reasons, comes close to the equilibrium. The research of the uranium isotopic composition of solids within the Northern Tien Shan ore beds allowed to reveal the spatial trends of  $\gamma$ -value, consisting in excess reduction of  $^{234}\text{U}$  from the center in a distal direction of the ore fields, to background levels closed to 1 [4]. We studied the uranium-isotopic composition of sample series of diamond and enclosing rocks of Arkhangelski kimberlite tube from M.V. Lomonosov field of the Arkhangelsk diamond province. The purpose of this study was to analyze the isotopic composition of uranium in diamond and enclosing rocks and to estimate degree and potential reasons of fractionation in „ores- enclosing rocks“ system. The total uranium isotopes of samples were studied for this. Uranium-isotopic data point at significant differences in the uranium content and  $\gamma$  value ( $\gamma = ^{234}\text{U}/^{238}\text{U}$ ) in the studied samples. For all samples relatively low concentrations of uranium are characterized. Mainly, the data indicate a significant deviation of the isotopic ratio of uranium upward bias of light isotope  $^{234}\text{U}$ , in such case  $\gamma$ -value changes from  $0.96 \pm 0.03$  to  $1.60 \pm 0.02$ . Most of the studied samples are characterized by  $^{234}\text{U}/^{238}\text{U} > 1$  values. The explanation of the high  $\gamma$  values in the total uranium faces difficulties, when the rock is viewed as a completely open geochemical system. The measurements of alpha activity even isotopes of uranium have established significant violations of radioactive equilibrium for very ancient rocks Arkhangelski kimberlite tube. The obtained values are anomalous for this type of rock. The non-equilibrium uranium of solid phase accompanies all ore deposits. Apparently this picture is explained interaction ore matter with enclosing sediment rocks at the present geological stage.

It is shown that in radiochemical total uranium samples from Arkhangelski kimberlite tube there is a significant value deviation of uranium isotope alpha activity from equilibrium as  $^{234}\text{U}$  upward bias. The obtained anomalous values can testify about modern processes of the ore material transformation.

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## **Carbon and hydrogen isotopic composition (GC-C-IRMS) of natural gas acquired from Polish shale formations**

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Polish shale formations are varied and their evaluation based on chemical and isotopic composition analyses may be very useful. On the basis of the  $\delta^{13}\text{C}$  value of methane, ethane and propane estimation of source rock (from which the gas was generated) thermal transformation degree can be performed. This may lead to recognition of the areas within basin with high hydrocarbon potential.

Analysis of the chemical composition of the gas samples were made using the Agilent model 7890 A chromatographs, equipped with TCD and FID detectors. Carbon and hydrogen isotopic composition of individual gaseous hydrocarbons was determined using isotope Delta V Advantage spectrometer with chromatograph Trace GC Ultra from Thermo Scientific.

Analyses of chemical and isotopic composition were performed for gas samples from cores degassing. Total amount of 23 samples was acquired during the drilling of two wells located in north (well A – Baltic basin, 9 samples) and south (well B – Lublin basin, 14 samples) of Poland. Both wells were exploring Silurian and Ordovician shale formations.

The isotopic composition of methane carbon from well A samples corresponds to the beginning of the oil window and from well B samples corresponds to the gas window. In order to accurately determine the type of gas  $\delta^{13}\text{C}$  and  $\delta\text{D}$  values were plotted on Peters diagram [1]. Respective data of gases from well A are located in the fields of mixed and oil related gases, while from well B they are located in the fields of condensate and oil related gases. Gases from well located in north of Poland were generated on considerably lower thermal maturity level of organic matter than gases from well located in south of Poland. Data from well A correspond to 0.8 to 1.0 % vitrinite reflectance thermal maturity and from well B (four samples without roll-over effect) correspond to 1.0 to 1.3 % vitrinite reflectance thermal maturity. Ten samples from well B, has inverted isotopic composition – roll-over effect. Polish shale formations are varied and natural gas composition analyses can be helpful for correct prediction of type and amount of natural gas in shale formation.

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## **Opposite carbon isotope discrimination during dark-respiration in leaves versus roots - A review**

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Leaves in general are <sup>13</sup>C-depleted compared to all other organs (e.g. roots, stem/trunk and fruits). Different hypotheses are formulated in the literature to explain this difference. One of these states that CO<sub>2</sub> respired by leaves in the dark is <sup>13</sup>C-enriched compared to leaf organic matter, while it is <sup>13</sup>C-depleted in the case of root respiration. The opposite respiratory fractionation between leaves and roots was invoked as explanation for the wide-spread between-organ isotopic differences. After summarizing the basics of photosynthetic and post-photosynthetic discrimination, the recent findings on the isotopic composition of CO<sub>2</sub> respired by leaves (autotrophic organs) and roots (heterotrophic organs) compared with respective plant material (i.e. apparent respiratory fractionation), as well as its metabolic origin will be reviewed [1]. The potential impact of such fractionation on the isotopic signal of OM will be discussed. Some perspectives for future studies will be proposed as well.

- [1] Ghashghaie J, Badeck F-W. Opposite carbon isotope discrimination during dark-respiration in leaves vs. roots – A review. *New Phytologist* 201 (2014) 751-769.

## **Qualitative distinction of autotrophic and heterotrophic processes on the leaf level by means of triple stable isotope (C-O-H) pattern**

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Foliar samples were harvested from two oaks (*Quercus robur*), a beech (*Fagus sylvatica*) and a yew (*Taxus baccata*) at the same site in Bern, Switzerland in order to trace the development of the leaves over an entire vegetation season in 2012. The investigated trees live next to each other therefore the atmospheric (weather, ambient CO<sub>2</sub>, etc.) and soil moisture conditions were identical for all trees. Consequently, the leaf cellulose formation of the studied species can be compared by investigating the isotopic composition of all elements (C-O-H) of cellulose molecules. Therefore, cellulose yield and stable carbon, oxygen and hydrogen isotopic compositions ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) were analysed on extracted leaf alpha-cellulose. All parameters unequivocally define a juvenile and a mature period of the foliar expansion for each species. The accompanied shifts of the  $\delta^{13}\text{C}$  values are in agreement with the transition from remobilized carbohydrates (juvenile period) to newly assimilated photosynthates (mature phase). While the opponent seasonal trends of  $\delta^{18}\text{O}$  of blade and vein cellulose are in perfect agreement with the state-of-art mechanistic understanding, the lack of this discrepancy for  $\delta\text{D}$ , is unexpected. For example, the offset range of 18 permil (oak veins) to 57 permil (oak blades) in  $\delta\text{D}$  may represent a process driven shift from autotrophic to heterotrophic processes. The shared pattern between blade and vein found for both oak and beech suggests an overwhelming metabolic isotope effect on  $\delta\text{D}$  that might be accompanied by the proton transfer linked to the Calvin-cycle. In addition, yew needle formation is driven by heterotrophically formed carbohydrates therefore it represents the seasonal  $\delta\text{D}$  and  $\delta^{18}\text{O}$  variability of local precipitation. These results provide strong evidence that hydrogen and oxygen are under different biochemical control even at the leaf level.

## The evidence of anthropic events in the sedimentation processes of the Uzlina and Isac Lakes, Danube Delta, Romania

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The second largest delta in Europe is the Danube Delta, having surface of 4152 km<sup>2</sup>. Natural factors lead to its continuous change on different time-scales. Therefore the analysis of the sedimentation processes is of great importance. Moreover, the anthropogenic interventions and the construction of the Iron Gate hydroelectric power plant (1972) have the same effect. The objective of the present study is to assess the sedimentation rates and the dynamics of the sedimentation processes in the Uzlina and Isac lakes after identifying the anthropogenic influences of the Iron Gate using the <sup>210</sup>Pb radiometric dating method (usable for 0 – 200 year old samples). The method was verified using the <sup>137</sup>Cs radionuclide concentrations corresponding to 1963 (Nuclear weapon tests) and 1986 (Chernobyl).

Three cores were analyzed from the Isac-lake and one from Uzlina-lake (both lakes being situated between Sulina and Sfantu Gheorghe branches). The sediment cores were sub-sampled into 1 – 3 cm layers and physical parameters (porosity, water content and bulk density) were determined. The sub-samples were put into aluminum boxes and each was stored for 30 days. The *in situ* <sup>210</sup>Pb was measured through <sup>226</sup>Ra (<sup>214</sup>Bi, <sup>214</sup>Pb) and the <sup>137</sup>Cs activity concentration was measured with high resolution gamma spectrometry, using an HPGe detector. The total <sup>210</sup>Pb content was measured via its alpha emitting progeny, <sup>210</sup>Po. The <sup>210</sup>Po content of each sediment sample was determined using 0.5 g of dry sample; <sup>209</sup>Po tracer was used for determining the chemical yield. The dry sediments were digested by a series of acids (HNO<sub>3</sub>, HCl and H<sub>2</sub>O<sub>2</sub>), after which they were deposited on high nickel content stainless steel discs, interferences (Fe<sup>3+</sup> ions) being eliminated by ascorbic acid. The alpha spectrometric measurements were carried out using a PIPS detectors system. The geochronology of the sediments and their sedimentation rates were calculated using the CRS model.

The <sup>226</sup>Ra (*in situ* <sup>210</sup>Pb) activity concentration of the sediment cores was 14 – 25 Bq/kg, with an average of 19 Bq/kg (this activity concentration is typical of Danube Delta sediments), while the total <sup>210</sup>Pb activity concentration ranged from 17 to 81 Bq/kg. The mass sedimentation rate maximum was 1.896 g/cm<sup>2</sup>y between 1993 and 1989. These data is corresponding with the major floods from 1993 and 1981 being visible in all sediment cores. In case of the linear sedimentation the highest value (1.991 cm/y) was reached in 1985, year until which the linear sedimentation had an average of 0.362 cm/y. The sedimentation shows a decreasing tendency from 2005, while the period between 2005 and 1980 was consisting of many substantial floods proven by the average sedimentation rate of this period being 0.594 g/cm<sup>2</sup>y; before 1980 these values were nearly three times lower (0.192 g/cm<sup>2</sup>y). After 1973 (Iron Gates construction) the sedimentation rates were one third lower (0.237 g/cm<sup>2</sup>y) than in the years before (0.344 g/cm<sup>2</sup>y) meaning 31 % decrease.

## **Seasonal variations of bacterial input to sulphur turnover and its isotopic signatures in sediments of dam reservoir**

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The aim of the study was to assess the role of bacterial processes in sulphur turnover in sediments of freshwater dam reservoir. The study area was located on Turawa dam reservoir (Mała Panew River, SW Poland) with capacity of  $92.5 \times 10^6 \text{ m}^3$ , which is stated as an eutrophic waterbody. Sediments and water for analyses were collected twice (May and September 2011) from 5 points randomly distributed on the area of the reservoir. Following parameters have been analyzed: 1/ sulphate concentration in sediments, water-sediment interface and water column; 2/ sulphides concentration in water-sediment interface and water column; 3/ arylsulphatase activity in sediments (the enzyme that leads to release of sulphate ion from organic matter), 4/ dehydrogenase activity (indicator of bacterial metabolic activity) in sediments, 5/ total number of bacteria, 6/ number of sulphate reducing bacteria and 7/  $\delta^{34}\text{S}(\text{SO}_4^{-2})$  value in sediments, 8/  $\delta^{34}\text{S}(\text{S}^{-2})$  value in monosulphides and polysulphides and 9/  $\delta^{34}\text{S}(\text{S})$  value in sediments. The results showed significant seasonal and spatial differences in sulphate and sulphides isotopic composition in sediments due to seasonal change in organic matter delivery from water column. Average organic matter content in sediments recorded in May 2011 was 6.4 %, while in September 2011 was on the level 29.2 %. Total bacterial number was higher in September ( $2.97 \times 10^{13} \text{ g}^{-1}$ ) than in May ( $1.07 \times 10^{13} \text{ g}^{-1}$ ), with considerably lower arylsulphatase activity in September ( $99 \mu\text{gg}^{-1}\text{dwh}^{-1}$ ) comparing with May ( $270 \mu\text{gg}^{-1}\text{dwh}^{-1}$ ). The increase of number of sulphate reducing bacteria was noted in September ( $4422 \text{ CFU g}^{-1}$ ) when referring to May and ( $256 \text{ CFU g}^{-1}$ ). Sulphate concentration in sediments in May ranged between 0.04 and 0.51  $\text{mg g}^{-1}$  and in September between 0.01 and 0.72  $\text{mg g}^{-1}$ .  $\delta^{34}\text{S}(\text{SO}_4^{-2})$  value in May was fluctuating between -15.17 and 3.51 ‰ and in September between -11.15 and -3.36 ‰.  $\delta^{34}\text{S}(\text{S}^{-2})$  value in monosulphides in May ranged between -6.09 and -7.39 ‰ and in September between -13.48 and -15.29 ‰.  $\delta^{34}\text{S}(\text{S}^{-2})$  value in polysulphides in May was recorded between 4.02 and -9.77 ‰ and in September between 1.31 and -13.25 ‰. The results suggest that sulphate released due to bacterial decomposition of organic matter undergoes immediate bacterial reduction to sulphides in sediments. Bacterial activity possibly explain underestimation of  $\text{SO}_4^{-2}$  in sulphur balance in sediments of the Turawa Reservoir. Particular areas of intensive bacterial sulphate ion production as well as areas of intensive bacterial sulphates reduction to sulphides were indicated in the bottom of the Turawa Reservoir.

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## **Trees' response to climatic and anthropogenic environmental changes: Application of stable isotopes and $^{14}\text{C}$ analysis in monitoring of industrial area**

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Tree rings are a very useful tool in analysis of ecosystem changes. The tree-ring chronologies, wood components and their physical and chemical properties provide information about the ecosystem in which the tree grew. The aim of research is monitoring the influence of human activities related to industrial development and the introduction of pro-environmental policy since 1975. The monitoring and reconstruction of atmospheric pollution is essential in order to evaluate the impact of environmental regulations on the forest ecosystem and human health. Similarly to most countries of the world, the systematic long-term monitoring of air pollutants in Poland is generally restricted to rural point-source regions in urban areas and this was limited only to the last decades. To reconstruct the ecosystem changes, caused by the climate changes and the human activities, different natural archives providing long-term data are used, such as lake sediments, peat and trees. However, there is an obvious lack of analysis concerning short term changes in the ecosystem in the area near emitters of pollutants in the contemporary environment which are responsible for this gradient of the changes in order to establish a valid relation between the climatic factors and the anthropogenic effects signal, which are known to vary in time and space. This lack of short term changes analysis is fundamental for the analysis of long-term data, especially throughout choosing the references, representativeness stand and sampling sites. We present the first results concerning short-term interannual variations in stable isotope and radiocarbon concentration in different parts of tree (wood and its component, needles) as bioindicators. The challenge is to establish, with respect to climate changes and environmental conditions, the significance of the variations from one year to another in the observed isotope fractionation. In this study, stable carbon, nitrogen and oxygen isotope ratios and radiocarbon concentration in the samples of pine collected from heavily urbanized area in close proximity to large point source pollution emitters, such as a heat and power plant, nitrogen factory and steel mill in Silesia (Poland), were analysed as bioindicators of contemporary environmental changes. The measurement of stable isotopes was carried out using the continuous flow isotope ratio mass spectrometer coupled to the elemental analyzer, whereas radiocarbon concentration was determined by liquid scintillator counter (Quantulus) and accelerator mass spectrometry (AMS) techniques. Not only climate factors, but also diffuse air pollution caused the variation in isotope concentration. The influence of air pollution depended on the localization in the space (distance and direction) from factories and some local effects of other human activities. This study indicates that isotopic fractionation data can reflect the responses to environmental changes and that the combination of stable isotopes and radiocarbon compositions analysis is a powerful tool for ecological and dendrochronological research.

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## **Stable isotopes as proxies for food sourcing in alpine streams undergoing glacial recession**

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Because of contemporary global warming and glacier shrinkage, alpine streams have received increased attention as sensitive indicators to climatic change. The ecological functional characteristics (e.g., food sourcing and consumption) of alpine streams are vastly influenced not only by thermal and hydrological regimes, but also by structure and activity of benthic communities (i.e., macroinvertebrate fauna), and inputs of primary food sources (i.e., autochthonous and allochthonous organic matter) within streams. Here we highlight the use of carbon and nitrogen stable isotope methods in tracing food source changes and feeding plasticity of macroinvertebrates within alpine streams undergoing rapid glacial recession. Our goals were to investigate the response of macroinvertebrate assemblages to changes in food resources regarding: 1) the glacial recession, 2) differences among various alpine stream types that display contrasting riparian development along their longitudinal gradients, and 3) year-round seasonal differences in food sourcing along alpine stream gradients. The sampling was conducted seasonally from November 2013 to July 2014 within the glacial stream network at the base of Roseg and Tschierwa glaciers (Bernina Massif, Switzerland), which have decreased in size rapidly with climate change (on average 40 m per year during the period 1997-2007 according to the Swiss Glacier Monitoring Network). The sampling sites were selected based on an earlier study of food webs in the same catchment in 1997. At each of the 4 sampling sites, we collected the most common macroinvertebrate taxa and their potential food sources, including primary producers (algae, biofilms, detritus) and riparian vegetation (grasses, shrubs, leaf material). The variability in isotopic signatures (i.e., carbon and nitrogen isotope ratios;  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) for macroinvertebrates and their potential food sources was then analyzed across seasons and sites. The spatial (between-site) and temporal (seasonal) differences in isotopic signatures provide information on year-round changes in macroinvertebrate feeding habits along the longitudinal alpine stream gradients, thus allowing a better understanding of functional shifts in these ecosystems. Furthermore, by showing potential shifts in macroinvertebrate food acquisition during the glacier recession, our results reveal how alpine stream macroinvertebrates could change their feeding habits in response to climate-induced environmental changes.

## **Radionuclides in drinking water of Slovenia**

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EU Drinking Water Directive 98/83/EC sets out parametric values, frequencies and performance characteristics for analytical methods for monitoring radioactive substances in water intended for human consumption. However, this Directive does not mean the beginning of public concern about radioactivity in drinking waters. Collection of values for radioactive emitters started many years before, especially in the countries with nuclear facilities. Slovenian data base with radiological results from regular monitoring programs for drinking waters consists of information on gamma ray emitters, tritium and radiostrontium. The measurements started in early eighties of 20<sup>th</sup> century. Results are evaluated in regular annual reports in the sense of radiological impact and dose rate calculation. We will present the schemes of monitoring programs for radionuclides in drinking water of Slovenia from early days till nowadays. In 2015, for example, the drinking water is sampled at 15 different locations. In previous years, the number of sampling points was the same, but on different locations. The gap between the reality of monitoring and newest EU Directive 2013/51/Euratom will be shown as well, together with possible solutions and suggestions for near future. Some strategies regarding radiological monitoring of drinking waters from other countries will be commented and compared. The values and trends from Slovenian data base and other available data worldwide will be presented and evaluated as well. We will try to go even further, searching the answer to the following question: is it possible to extract any new hydrological information from existing radiological data base? Especially tritium results are promising in this sense.

## **Stable isotope composition of human fingernails from Slovakia**

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Stable isotope composition of human fingernails is useful for documenting geographical patterns and human dietary information in archaeological, forensic and anthropological studies. Detection of all factors influencing the stable isotopic composition in the certain regions is important for these scientific fields. In this study, carbon, nitrogen and oxygen isotope ratio data of human fingernail keratin from 52 individuals from Slovakia were reported. The online combustion for combined N/C analyses and high temperature conversion for O analyses and continuous flow isotope-ratio mass spectrometer Delta V Advantage were used to examine the isotope ratio composition of fingernail keratin samples from 24 vegetarian and 28 omnivorous individuals. Samples were prepared at Faculty of Mathematics, Physics and Informatics Comenius University in Bratislava. Isotope analyses were performed at State Geological Institute of Dionyz Stur in Bratislava. We reported expected significant differences between vegetarian and omnivorous groups. Moreover, we examined the tendency of significant differences between smokers and non-smokers in both  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values. The oxygen stable isotope ratio composition of fingernail keratin mirrored the isotopic information of local meteoric water. These data were compared to previously published information on isotopic composition of fingernail from across the globe. We provided the information on the stable isotope signature of individuals from Slovakia, a Central European region, for the first time [1].

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## **The use of stable isotopes and metal concentrations for discrimination between conventional, hydroponic and organic vegetable production regimes**

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Organic farming has rapidly grown over last few years because of general concerns regarding the safety and ethics of conventionally produced foods. Because of the higher market prices of organic products, mislabelling and adulteration have become the most serious problems in many areas of food industry since they threaten honest traders and infringe the rights of consumers. Thus the development of robust analytical methods to differentiate between organically and conventionally grown products is needed. The nitrogen isotopic composition ( $\delta^{15}\text{N}$ ) can be used to differentiate between some sorts of vegetables grown with inputs of synthetic fertilisers under conventional regime and vegetables grown under organic regime. The application of synthetic nitrogen fertilizers with low  $\delta^{15}\text{N}$  values (close to 0 ‰) shall result in the  $\delta^{15}\text{N}$  values of plants grown under organic production systems being higher than of those grown under conventional conditions. The use of  $\delta^{13}\text{C}$  values in combination with elemental composition could give us information about environmental impact on plants and their geographical origin. In our study the use of  $\delta^{15}\text{N}$  in lettuce (*Lactuca sativa* L.), sweet pepper (*Capsicum annuum* L.) and tomato (*Solanum lycopersicum* L.) as a potential marker for determining differences between organic, conventional and hydroponic production was tested. The soil samples from conventional and organic production practices for every type of vegetables were analysed for  $\delta^{15}\text{N}$ . The  $\delta^{13}\text{C}$  value in vegetables and soil and the content of Mn, Fe, Zn, Br, Rb, Sr, Mo, P, S, Cl, K and Ca in vegetables and soluble fraction of soil samples were determined to find out information about given environmental signal. To determine the bulk  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of selected vegetables and soil samples elemental analysis - isotope ratio mass spectrometry (EA-IRMS) was used, whereas the content of 12 elements was determined using the X-ray fluorescence (XRF) elemental analysis. The differences in  $\delta^{15}\text{N}$  values between production regimes occurred. The highest  $\delta^{15}\text{N}$  values were determined in organically grown vegetables, but some  $\delta^{15}\text{N}$  values in vegetables grown under conventional and hydroponic production overlapped. The differences in  $\delta^{13}\text{C}$  values occurred between lettuce, in which the lowest values were determined, and sweet pepper and tomato, in which the  $\delta^{13}\text{C}$  values overlapped. Both,  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  were found to be lower in soil samples from organic in comparison with conventional production regime. Inside the plant types, soil samples where lettuce was grown had lower  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values than soil samples where sweet pepper and tomato were grown. Metal concentrations were higher in conventional (Mo) or hydroponical regimes (Fe, Zn, Mo, K) or overlapped with concentrations obtained from organic production (Mn, Sr, Ca). The concentration of Rb was found to be higher in organic production regime. Inside the plant types the content of almost all elements was found to be higher in lettuce.

## Quality of Mediterranean mussel *Mytilus galloprovincialis* at mariculture locations from NE Adriatic (Croatia): insights from condition indexes, stable isotopes and selected elements

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Condition indexes, selected elements and As speciation were used to estimate the quality of marine mussel *Mytilus galloprovincialis* and ecological conditions of the marine costal environment in North Eastern Adriatic, Istria Region at following mariculture locations: S1) Vabriga, S2) Lim channel, S3) Pomer, S4) Budava and S5) Raša bay. All condition indexes confirmed that mussels from all locations are of good quality with the content of the meat of about 15 %. Comparing sampled mussels in the winter period, we ranked mariculture locations from the highest condition index value to the lowest: S3 > S1 > S5 > S4 > S2, with the highest value for S3) Pomer (25 %). During the summer period locations were ranked differently: S4 > S2 > S3 > S5 > S1, with the highest value for S4) Budava. Higher values of condition index/meat content indicated that the most suitable environmental conditions for mariculture are Pomer and Budava locations. Using nuclear marker Me 15/16 to distinguish *Mytilus edulis* complex species, all sampled mussels were identified as *M. galloprovincialis*. Alkalinity of seawater seasonally ranges from 3.2 to 3.7 mM.  $\delta^{13}\text{C}_{\text{DIC}}$  in our study seasonally ranged from -13.4 to 0.0 ‰.  $\delta^{13}\text{C}_{\text{DIC}}$  values enriched with  $^{12}\text{C}$  indicate fresh water input. We obtained a good regression ( $r = 0.69$ ) observed between salinity and  $\delta^{13}\text{C}_{\text{DIC}}$ . Based on selectivity equation regarding isotopic composition of carbon in soft tissue ( $\delta^{13}\text{C}$ ), isotopic composition of carbon in particulate organic matter ( $\delta^{13}\text{C}_{\text{POC}}$ ) and isotopic composition of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ), it was estimated that mussels assimilate their carbon primary from phytoplankton. Sewage sludge pollution was not confirmed in *M. galloprovincialis* tissue, because  $\delta^{13}\text{C}$  ranged from -24.5 to -20.8 ‰ and  $\delta^{15}\text{N}$  varied from 3.8 to 6.1 ‰. The bioaccumulation of the metals measured in this study decreased in Zn > As > Mn > Cu > Se > Cr > Ni > Co > Pb > Cd order indicating that essential metals tend to accumulate in higher and faster rate than non-essential and possibly toxic elements. Based on all measured metals (expresses on dry weight) Zn concentrations range from 28.3 to 72.1 mg kg<sup>-1</sup>, Mn concentrations from 1.52 to 7.40 mg kg<sup>-1</sup>, Cr concentrations from 0.17 to 11.3 mg kg<sup>-1</sup>, Se concentrations from 1.16 to 4.84 mg kg<sup>-1</sup>, Co concentrations from 0.17 to 3.13 mg kg<sup>-1</sup>, Ni concentrations from 0.20 to 3.13 mg kg<sup>-1</sup>, Cu concentrations from 1.44 to 3.99 mg kg<sup>-1</sup>, Cd concentrations from 0.21 to 0.58 mg kg<sup>-1</sup>, Pb concentrations from 0.20 to 2.50 mg kg<sup>-1</sup>. The highest concentrations of metals (Pb and Cd) were observed at S3) Pomer and S5) Raša bay. Total As in mussels ranged from 12.2 to 27.5 mg kg<sup>-1</sup> dry weight (d.w.). Main As compound identified was osmolite arsenobetaine indicating its abundance in food and possible concentration to salinity and not to pollution. Arsenosugar phosphate ribose originating probably from phytoplankton and minor amounts of inorganic arsenic, arsenocholine, methylarsonic acid and unknown compounds were found as well.

## Isotopic studies of nitrates ( $\delta^{15}\text{N}$ , $\delta^{18}\text{O}$ ) and phosphates ( $\delta^{18}\text{O}$ ) in the assessment of the eutrophication reasons in Zemborzycki Lagoon

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The Zemborzycki Lagoon is a small retention reservoir (approx. 280 ha), formed on the Bystrzyca River in the southern part of Lublin (S-E Poland). Due to rapid progressive eutrophication, the quality of water is extremely deteriorated. In last years, in water blooms was observed several cyanobacteria taxa, eg. *Anabaena spp.* and *Aphanizomenon spp.*, potential producers of neurotoxic anatoxin-a, threatening also for humans [1].

The main reason of eutrophication is increasing content of nutrients in water, mainly nitrogen and phosphorus compounds [2,3]. The maximum phytoplankton growth is observed for the C:N:P = 106:16:1, where for critical nutrients concentration is presently considered: 0.3 g N/m<sup>3</sup> H<sub>2</sub>O and 0.01 g P/m<sup>3</sup> H<sub>2</sub>O [4]. Chemical methods can provide information about the processes occurring in this reservoir, but only isotopic analysis can determine the main sources of nitrates and phosphates in Zemborzycki Lagoon. Measurements of NO<sub>3</sub><sup>-</sup> concentration and analysis of their isotopic compositions ( $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ ) can determine whether nitrates are derived from atmospheric deposition, fertilizers or manures applied on nearby agricultural areas or formed during nitrification process in soil [5]. Similarly, in the case of the analysis of  $\delta^{18}\text{O}$  in PO<sub>4</sub><sup>3-</sup> ions, we can determine whether the phosphates are of natural or anthropogenic origin [6].

The concentration measurements of nitrogen and phosphorus compounds are performed in Chemical Laboratory of Department of Hydrology UMCS. For extraction of nitrate from water the method described by Silva et al. [7] was used and the next step was simultaneous preparation of CO<sub>2</sub> and N<sub>2</sub> from silver nitrate [8]. Phosphates extraction from water was completed by the method described by Gruau et al. [9] and the next step the obtained Ag<sub>3</sub>PO<sub>4</sub> is prepared by Pelc & Hałas method [10]. In both cases, gaseous products of conversion are analyzed on a dual inlet and triple collector isotope ratio mass spectrometer.

Results presented here will be the first data of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  in NO<sub>3</sub><sup>-</sup> and  $\delta^{18}\text{O}$  in PO<sub>4</sub><sup>3-</sup> in Zemborzycki Lagoon. We hope that the long-term studies will allow as to identify the main pollution sources in Zemborzycki Lagoon, and also will allow deeper understanding of biogeochemical processes taking place in the ecosystem.

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## Isotopic signatures of methane and carbon dioxide from mixed maize silage and manure fermentation

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Application of methane fermentation into the treatment of agriculture waste is an excellent way to convert organic compounds simultaneously gaining energy rich biogas. Methane – the main compound of biogas - is either produced via the cleavage of acetate (aceticlastic pathway) or by reduction of CO<sub>2</sub> with hydrogen (hydrogenotrophic pathway). Methane obtained by each of these pathways is distinguishable based on its isotopic fingerprint. Tracing methane fermentation pathways is essential for the process of optimization with potential industrial applicability. Therefore, determination of stable isotope characteristic of methane and carbon dioxide can be an alternatively rough estimation on the predominant methanogenic pathway in anaerobic digesters.

The main goals of the study were to: (1) evaluate the influence of temperature on biogas production, (2) determine the optimal condition for biogas production, (3) assess the predominant methanogenic pathways in laboratory-scale fermentation of selected substrates.

The experiments were carried out on a continuous basis in bioreactors representing the industrial-scale system in a better way. Three laboratory continuous stirred tank reactors (5 L volume) were operated under various conditions (F1: T = 20 °C; F2: T = 30 °C; F3: T = 40 °C). Maize silage and manure were mixed, then put into bioreactors and fermented for 43 days. Anaerobic sludge from an anaerobic digester (Municipal Water and Sewage Company S.A. in Wrocław) was used as an inoculum. During experimental studies the biogas production was observed on a daily basis. Gas samples were collected by syringe from the bioreactors and injected into 20 mL vials filled with distilled water sealed by septa. Composition of biogas was measured by a gas chromatograph (AGILENT 7890A). The isotopic composition of methane and carbon dioxide were analyzed to estimate the predominant methanogenic pathways. The  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^{13}\text{C}(\text{CO}_2)$  values were determined using Finnigan MAT Delta E mass spectrometer. The H compositions were measured with Delta V Advantage mass spectrometer. The apparent fractionation factor ( $\alpha_c$ ) was calculated accordingly with the following equation:  $\alpha_c = (\delta^{13}\text{CO}_2 + 1000)/(\delta^{13}\text{CH}_4 + 1000)$ .

The obtained results show that: (1) the biogas production was the highest in the temperature of 30 °C with the maximum methane concentration above 75 %; (2)  $\delta^{13}\text{C}(\text{CH}_4)$  values were in a range from -43.7 to -19.9 ‰, (3)  $\delta\text{D}(\text{CH}_4)$  values ranged from -410.4 to -253.6 ‰ and (4)  $\delta^{13}\text{C}(\text{CO}_2)$  values varied from -10.0 to 13.7 ‰. The calculated apparent fractionation factor values ( $\alpha_c$ ) of F1, F2, F3 were lower than 1.055 and indicated the predominance of aceticlastic methanogenesis.

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## **Assessing the influence of ecosystems on stable isotopes and trace elements signature in plants**

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This work emphasizes the manner in which the stable isotopes and multi-element signature from different plants, collected from different ecosystems, are influenced by the geo-chemical morphology and by the bio-climate factors, with main application in food traceability. Discriminant analysis (DA) was used in our evaluation for the plant groups used as dependent variables (the same fruits and vegetables grown in different area from Romania) and stable isotopes ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) and mineral content (Cr, Mn, Co, Ni, Cu, Rb, Cd, Pb and U) as explanatory variables. The soil type (e.g. anthropogenic radioactive polluted soil, cernoziom, with small areas of sandy and salt soil, soil from mining area) and local climatic conditions affects the values of these parameters, in particular for oxygen  $^{18}\text{O}$ ,  $^2\text{H}$ , Rb and Ni. It was noted that the concentration of  $^2\text{H}$  and  $^{18}\text{O}$  increased in waters extracted from plants collected in areas with brown acid and brown ferilluvial soil (e.g. Rm. Valcea). The same pattern was also registered for the content of Rb and Ni, when comparing to the values for plants collected from the region with cernoziom and reddish brown soils (e.g. Bailesti and Bucovat – Dolj area). Near the Barzava uranium mine, with anthropogenic radioactive polluted soil, an insignificant increase of  $^2\text{H}$  and  $^{18}\text{O}$  values was observed in the water extracted from plants comparative with other water sources from the region. Instead, the mineral content (e.g. U, Mn, Rb and Ni) was high. This study highlights the strong correlation existing between plants geographic origin and multi-element and stable isotopes fingerprints, representing the principal approach in food provenance authenticity.

## Carbon and oxygen stable isotopes in paleo-environmental reconstructions

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Paleo-environmental reconstructions based on accurate isotopic investigations are important for environment science, archeology and geology equally. Such investigations occur in Department of geology and geoecology of Herzen University (Saint-Petersburg, Russia) using the NU Horizon IRMS (stable isotope ratio mass spectrometer, NU instruments). The measurements of carbon and nitrogen stable isotope ratios carry out with NU Horizon IRMS coupled to the elemental analyser EURO EA 3030 (EuroVector). The measurements of carbon and oxygen stable isotope ratios in carbonates have been carried out using the NU Horizon IRMS coupled to the Gas Prep system. Some examples of results and interpretations are shown.

The carbon stable isotope ratio in contemporary plants. Generally, it is known that contemporary plants extract light carbon isotopes from the atmosphere via photosynthesis, terrestrial plants get greater quantity of light isotopes than algae, average ratios are -25.5 ‰ and from -7 to -18 ‰, respectively [1]. Besides that, the ratio may depend on geographical location and environmental conditions. Our experiments show difference between  $^{13}\text{C}/^{12}\text{C}$  ratios in different parts of plants (Table 1, samples 1399 - 1401). It may be used for research the carbon isotopes fractionation by plants in details and for environment reconstruction.

Table 1.  $^{13}\text{C}/^{12}\text{C}$  ratios in contemporary samples

Sample number	Material	$^{13}\text{C}/^{12}\text{C}$ ratio (‰ VPDB)
Spb_1401	Cow lily ( <i>Nuphar lutea</i> ), leaf	-25.25 ± 0.05
Spb_1400	Cow lily ( <i>Nuphar lutea</i> ), stem	-25.85 ± 0.05
Spb_1399	Cow lily ( <i>Nuphar lutea</i> ), root	-25.45 ± 0.05
Spb_1402	Fish	-30.50 ± 0.07
Spb_1398	Grass	-26.23 ± 0.05

The same data are used to correct ages of archeological artefacts considering a freshwater reservoir effect [2]. In the Kulkova's multi-method research of the Neolithic site Serteya II [3] the ages of food-crust on pottery samples were determined by radiocarbon method. The radiocarbon quantity was adjusted based on measurement  $^{13}\text{C}/^{12}\text{C}$  ratios in contemporary plant and fish samples (Table 1, samples 1398, 1402). Thereby the pottery samples ages clarified, corrections were from 206 to 585 years. The carbon stable isotope ratio in food-crust on pottery shows a human diet. We determined the  $^{13}\text{C}/^{12}\text{C}$  ratios in the food-crust samples from the Neolithic site Serteya II, they are from -27.8 to 31.5 ‰. These values confirm plenty of freshwater products presence in the ancient local people diet.

Measurements of carbon and oxygen stable isotope ratios in carbonates aimed to determine the temperature of carbonate rocks formation and reconstruction of sediment conditions, the results are processed.

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## Carbon isotope fractionation during photosynthesis in submerged moss and aquatic plants

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Radiocarbon activity ( $a^{14}\text{C}$ ) and ratio of stable isotopes  $^{13}\text{C}/^{12}\text{C}$  ( $\delta^{13}\text{C}$  values) were measured in plant samples collected 2011-2012 in the natural habitat of the Plitvice Lakes, Croatia: terrestrial moss, water submerged moss, marsh and aquatic plants. All collected samples are C3 photosynthetic cycle plants. The  $a^{14}\text{C}$  and  $\delta^{13}\text{C}$  values of the plant tissue were compared with values of carbon reservoirs the plants use in photosynthesis: atmospheric  $\text{CO}_2$  and/or dissolved inorganic carbon (DIC) as well as with the carbon isotope composition of plants measured 30 years ago [1]. The fraction of each carbon reservoir in plants was determined and the  $^{13}\text{C}$  fractionation factor between DIC and organic tissue of a plant was calculated. Since there were no systematic paired measurements for  $a^{14}\text{C}_{\text{DIC}}$  and  $a^{14}\text{C}$  of plants at some locations in the old data set, we approximated the missing  $a^{14}\text{C}_{\text{DIC}}$  values by the values taken from [2]. There is a very good correlation between  $a^{14}\text{C}$  and  $\delta^{13}\text{C}$  of moss plant tissue in both periods which is a result of variation of the ratio of atmospheric and dissolved inorganic carbon in moss. The fraction of atmospheric carbon in submerged mosses ranges from 8 to 66 %. Calculated  $^{13}\text{C}$  fractionation factor between DIC and organic tissue of moss is  $-41 \pm 3 \text{ ‰}$ . Aquatic plants (algae, submersed species) sampled from ~30 cm depth show higher fraction of atmospheric carbon (~20 %) than a sample from 14 m depth (~0 %). Floating plants have 15 – 20 % of atmospheric carbon, while emerged plants have 90 – 100 % of atmospheric carbon (marsh plants, sedge, grasses). Calculated  $^{13}\text{C}$  fractionation factor between DIC and plant tissue for submersed and floating plants is  $-22 \pm 3 \text{ ‰}$ , which is the same as the  $^{13}\text{C}$  fractionation factor between the atmospheric  $\text{CO}_2$  and plant tissue for C3 plants. Emerged samples have higher dispersion in  $^{13}\text{C}$  fractionation factor values (from -9 ‰ to -147 ‰). The difference between the determined  $^{13}\text{C}$  fractionation factors for mosses and for aquatic plants (algae and floating plants) could be a result of different plant adjustment to photosynthesis of  $\text{HCO}_3^-(\text{aq})$  and  $\text{CO}_3^{2-}(\text{aq})$  molecules from DIC. Mosses are known to be adjusted to photosynthetic assimilation of  $\text{CO}_2$  there is probably an extra step of transformation of  $\text{HCO}_3^-(\text{aq})$  and  $\text{CO}_3^{2-}(\text{aq})$  to  $\text{CO}_2$  resulting in a larger  $^{13}\text{C}$  fractionation factor between DIC and plant tissue for mosses than for aquatic plants.

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## **Determination of the authenticity fruit spirits by isotope ratio mass spectrometry**

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In recent years, there is an increasing consumer interest for superior quality of food and alcoholic or non-alcoholic beverages. Originality, authenticity and the technological process are essential for top quality products. Modern, Serbian fruit spirit, with extremely rich variety of flavors is very attractive to consumers worldwide. Mass production and intensive marketing have caused many products to lose their authenticity, uniqueness, specificity and the distinctive feature of the region, therefore fruit spirits often becomes the subject of forgery due to its importance in the world market

The determination of  $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  isotope ratios is precise analytical method which can be used for checking the authenticity, botanical and geographical origin of fruit spirits. The instrument for stable isotope analysis consists the Elemental Analyzer (FlashEA 1112 HT) and Isotope Ratio Mass Spectrometer (Thermo Finnigan DELTA V Advantage).

In SP laboratory, we have made laboratory spirits from different kind of fruits, such as plum, pear, apple, white and red grape, quince, from different geographical origin (South and North part of Serbia) and spirits from sugarcane and corn. At the same time, we have prepared fruit spirits samples with different amount of added beet sugar (5 %, 10 %, 20 % and 50 % sugar was added on the weight of fruit).

For detection of adulteration, SP Laboratory analysed commercial spirits available in Serbian market. The results, some of them, are different regarding the values obtained for laboratory standard of fruit spirits. That indicates an addition of sugar from sugar beet or addition of C4 plants in order to increase the yield of ethanol and cheaper production. The different  $\delta^{18}\text{O}$  values are the result of different geographic locations where plant are grown.

The obtained results allow database establishment and classification of commercial fruit spirits based on botanical and geographical origin. Combined results of  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$  values gives important information about botanical origin of ethanol in alcoholic beverages and possibility of distinguishing between fruit spirits and spirits with non-fruit origin (made from beet sugar, maize, cane sugar). The value combination of the  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  ratios enabled us to designate the geographical origins of alcohol derived from the same kind of fruit.

## **Using stable isotopes from human bones to infer the diet of a Late Antiquity population from the Roman villae of Alpendre dos Lagares (Lusitania)**

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The reconstruction of ancient diets is possible given the well-established relationship between  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  signatures of the ingested food and of human body tissues. Long and short term diet of an individual can be gathered from bulk  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in collagen collected from the skeletal tissue. Furthermore, (bio)apatite, the mineral fraction of vertebral skeletons records, in carbonate ions, the consumption of vegetable and animal foods. Thus carbon-apatite and oxygen-apatite isotope ratios ( $\delta^{13}\text{C}_{\text{ap}}$  and  $\delta^{18}\text{O}_{\text{ap}}$ ) from bone apatite can, also, provide valuable information on the composition of the diet consumed by ancient humans.

In our investigation, eight human individuals excavated from seven individual graves (6<sup>th</sup> century to 8<sup>th</sup> century AD, confirmed by  $^{14}\text{C}$  data) of a Late Antiquity population from the Roman villae Alpendre dos Lagares (Serpa) in southern Portugal, were studied to infer about the inhabitants ancient diet. The analysis were performed on long compact bones and several analytical tools were used. Isotope Ratio Mass Spectrometry was used to obtain  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  ratios from bone collagen and  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  ratios from bone apatite. Fourier Transform Infrared Spectroscopy and X-Ray Diffraction were used to estimate the bone preservation status.

The preliminary results will be presented and discussed as a way to address the type of paleodiet (terrestrial versus marine resources) and, therefore, to evaluate the scale of food transportation influences in the diet of this Late Antiquity population from the Pax Julia in Lusitania region.

## **The climatic signal recorded by Swiss stone pine (*Pinus Cembra* L.) tree-ring oxygen and carbon isotopes in NE Romania**

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The isotopes composition of oxygen and carbon in the tree rings can provide paleoclimatic reconstructions with an annual resolution.

The aim of this study is to calibrate the paleoclimatic signal registered by stable isotope composition in tree rings to determine the relationship between the isotopic composition of the rainwater, the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in tree rings and the main climatic parameters.

For this study, we analyzed three wood series of Swiss stone pine (*Pinus cembra* L.) from living trees from Călimani Mts., NE Romania. The isotopic composition of O and C from the cellulose was analyzed at the Institute for Geological and Geochemical Research, Budapest, Hungary, using a high-temperature pyrolysis system (Thermo Quest TC-EA) coupled to an isotope ratio mass spectrometer (Thermo Finnigan Delta V) following a ring by ring (i.e., non-pooled) approach, and the isotopic composition of water was analyzed at the Stable Isotope Laboratory, Ștefan cel Mare University, Suceava, Romania, using a Picarro L2130i CRDS.

The average  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  level of cellulose for the period 2012 – 1893 is 29.4 ‰ and -23.8 ‰, respectively. Our record provides an updated calibration on earlier, more restricted, records [1]. The correlation between series is very good, the correlation coefficients being 0.82 for oxygen and 0.72 for carbon, except for the period from 1975 to 1995, when it drops to 0.4 for oxygen and 0.04 for carbon. This period corresponds to the opencast sulfur mining from Calimani Mts. which has been found already to disturb the climate signal also in tree ring radial growth [2].

Because this strongly positive correlation and the possibility to extend the tree ring chronology back in time for long periods; stable isotopes in tree ring could be an important tool for paleoclimatic reconstruction, providing precious information for a better understanding of climate variability in Romania and in Central Europe.

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## **Keynote lecture**

### **Time scales of groundwater flow: A contemporary perspective**

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The question how much time water spends underground before it emerges on the surface as a spring or is collected in the dug well, has always fascinated people. First tracer experiments aimed at identification of pathways of water movement underground are traced back to the ancient times. However, it was not until the Darcy's law was formulated in 1856, that the velocity of groundwater movement and in consequence its age, could be addressed in a quantitative manner. The presentation will provide an overview of concepts and tools developed over the past several decades allowing to quantify time scales of groundwater flow, from weeks to hundreds of thousands of years. Fundamental concepts such as Mean Residence Time (MRT) and Residence Time Distribution (RTD) function of groundwater in the given groundwater system will be presented. Emphasis will be given to environmental tracers (radioisotopes and trace substances). Quantifying timescales of groundwater flow plays an important role in groundwater hydrology, both in the development and management of groundwater resources. At the large temporal perspective extending to millions of years, the available tracer techniques help to identify groundwater recharged in climatic regimes which are different from the present climate, thus providing a key information needed to manage such groundwater resources. At shorter time scale environmental tracers provide a critical input to current groundwater vulnerability assessment schemes. Assessing vulnerability of groundwater resources to adverse effects of human activities is one of the most important problems in applied hydrogeology. Because of time lags inherent to the flow of water through geological media, changes in groundwater quality at the receptors may not be visible over the relatively short periods of time that are typically considered by policy makers, groundwater managers and the general public. Environmental tracer methods help to quantify those time lags. Finally, a new direction in applying environmental tracers in groundwater hydrology is their usage as independent tools for calibration of 3D numerical flow and transport models, particularly in situations when there is no other data on contaminant transport in the investigated system. The numerical flow models are typically calibrated with available hydraulic head fields. Good calibration of flow model does not guarantee proper transport in the framework of the migration model based on the calibrated flow model. Additional calibration of transport model based on independent data is required, followed by recalibration of the flow model. Environmental tracers play a key role here.

## Keynote lecture

### Groundwater dynamic in Southern Oman – A multi-isotope approach

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Arid areas are characterized by limited water resources with groundwater often being the only permanent fresh water available for drinking and as irrigation water. Current low precipitation and high temperatures greatly limit inputs to these subsurface reservoirs, suggesting they were higher during more humid periods in the distant past (>>1 ka BP). The climatic conditions of these areas have also long precluded settlement and farming. Anthropogenic water demand leading to abstraction was therefore negligibly low, and natural inflows were balanced by outflows, leading to a groundwater system depending only on variable recharge dynamic. Within the last 50 years the demand for agricultural production and human activities increased dramatically resulting in heavy groundwater abstraction at mostly lack of concern for sustainable water management. Consequently, an imbalance between input (groundwater recharge) and output (groundwater abstraction) is leading to large reductions in groundwater in storage. In face of sustainable water management and improving the knowledge about the important groundwater resource in the Najd, questions arising for research are: (i) Which water sources feed the aquifers currently? (ii) What do we know about recharge in previous “wet” periods? (iii) Do we have a groundwater age structuring in the Umm Er Radhuma (UER) aquifer system? These questions will be highlighted by application of stable water isotopes, noble gases and radioactive isotopes at the main groundwater aquifer system of the Najd in southern Oman. The monsoon affected Dhofar Mountains are the region of recent groundwater recharge into the outcropping UER aquifer D on the southern slope of the mountains and to north by subsurface flow. Stable water isotopes (2H, 18O) and hydrochemistry reflect this recharge process. Recently occurring major cyclones spend huge amounts of water to north of the mountains, the Najd region. They are a remarkable source of groundwater recently and significantly in the past under more humid conditions. This groundwater recharge process can be evidently shown by use of multi-isotope tracers, such as stable water isotopes, <sup>14</sup>C and <sup>36</sup>Cl concentrations, and He isotope ratios in connection with the hydrogeochemical character of the water types. <sup>36</sup>Cl decay and the accumulation of <sup>4</sup>He both provide the possibility to calculate groundwater residence times in a million year range. However, all of these tracers are subject to site-specific problems, such as how to determine the initial concentrations at recharge for <sup>14</sup>C and <sup>36</sup>Cl at best, or how to quantify the subsurface influx of helium. A well-recognized approach to overcome some of these problems is the combination of these dating tracers – not to say that is the complete truth.

## **Stable isotope analysis of Mt. Velebit karst hydrological system**

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Mt. Velebit is 145 km long mountain in the Croatian Dinaric Karst area, lying between the Adriatic Sea and the Ličko Polje and Gacko Polje fields. The massif is built of thick carbonate deposits of upper Triassic, Jurassic and Cretaceous age. In higher parts of the massif, mentioned rocks are covered with younger Oligocene to Lower Miocene carbonate breccias, probably deposited on the flanks of tectonically uplifted areas during older tectonic phase. Owing to its position between the Adriatic Sea and the continental Lika region and altitudes up to 1757 m, the mountain also serves as an important climatological border that results in high precipitation (>3500 mm/y). A more than 2000 meters thick karst rock succession caused very deep karstification was controlled by Adriatic Sea level during Pleistocene and tectonic structures of the massif. The discovery of many vertical and deep caves in last decades (including the deepest and longest caves in Dinaric karst: 1431 m deep Lukina jama, 1321 m deep Slovačka jama and 1026 m deep Cave system Velebit) gives us the opportunity of gathering new insights on karst hydrology. We use stable isotopes of oxygen ( $^{18}\text{O}/^{16}\text{O}$ ) and hydrogen ( $^2\text{H}/^1\text{H}$ ) in water as environmental tracers to get insight into the functioning of different karst subsystems of Mt. Velebit. The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values in water depend on various factors: precipitation origin, re-evaporation, re-condensation, season, terrain altitude etc. Therefore, the stable isotope composition of precipitation and karst groundwater can reveal information such as the mean recharge area elevation, the importance of winter and summer precipitation for recharge of a karst system and the average duration of water retention in a system. We compared stable isotope content of monthly precipitation samples with that of groundwater samples collected in caves and spring water samples collected at the main discharge points of a complex karst system that belongs to the massif. The stable isotope measurements were conducted using the water equilibration technique performed on Delta plus XP isotope ratio mass spectrometer (Thermo Finnigan) in conjunction with peripherals HDOeq42/24 (IsoCal) equilibration unit and Dual Inlet system (Thermo Finnigan).

## **Monthly variations of selected geochemical parameters and stable isotopes in thermal waters from deep wells in Slovenia**

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Aim of the study was to determine recharge characteristics of multi-layer wells and chemical indications of overexploitation. Geothermal aquifers in the north-east Slovenia which store thermal water of the Pleistocene age are monitored for groundwater level and temperature variations hourly, for water abstraction rate daily and for geochemical and isotopic composition of thermal water annually. Because their quantity state is deteriorating, additional monthly sampling of characteristic sodium and chloride concentrations and stable isotopes  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in thermal water was carried out between February 2014 and January 2015 beside the regular hydrodynamic observations of the system. Thermal water produced from four geothermal wells open between 720 and 1570 m below the ground was sampled: P-1 (Ptuj-Grad Formation) and P-3 (Mura Formation) in Ptuj, and Mt-4 (Špilje Formation) and Mt-6 (Mura Formation) in Moravske Toplice. Concentrations of sodium and chloride were analyzed by ICP-AES and IC at MFGI laboratory in Budapest, Hungary. Stable isotopes were determined by CRDS, Picarro 2130i at Hydroisotop GmbH laboratory in Schweitenkirchen, Germany and by MS Isoprime (GV Instruments) and MS Varian MAT 250 at Jožef Stefan Institute in Ljubljana, Slovenia. Results indicated no general seasonal trends of observed parameters despite strong seasonal variation of water abstraction from the Ptuj-Grad and Mura Formation, being the highest in winter. Duplicates showed that analytical errors were manageable; however, comparison between the laboratories did indicate shifts above the expected. Rather high variation of stable isotopes of thermomineral water from Mt-4 may be attributed to the preparation of samples for the isotope analyses due to very high TOC content. Differences between the measured minima and maxima of pH were below 7 %, of conductivity below 17 %, of sodium below 4 %, of chloride below 18 %, of oxygen-18 below 10 % and of deuterium below 4 %. This implies that chemical composition of thermal water is stable in a one-year period and monthly overexploitation of individual water-bearing layers cannot be observed by the use of the selected method according to gained datasets.

## **Hydrogeochemical and isotopic characteristics of the Žveplenica sulphide kartsic spring (Trebuša Valley, NW Slovenia)**

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Sulphide springs in Slovenia are very rare and they form a peculiar feature in a carbonate setting. The basic geological, hydrogeochemical and isotopic characteristics of the Žveplenica sulphide dolomite spring (Trebuša Valley, NW Slovenia) were investigated, along with the geochemical and mineralogical characteristics of the sediment deposited at the spring location. Geological mapping defined a small, structurally and lithologically isolated dolomitic aquifer. The major groundwater geochemical composition is  $\text{HCO}_3^- > \text{Mg}^{2+} > \text{Ca}^{2+}$ , indicating dissolution of dolomite. The concentration of  $\text{SO}_4^{2-}$  was very low. The groundwater was generally close to saturation with respect to calcite and dolomite. Geochemical modelling and other analyses indicated sulphur to originate not from gypsum and/or anhydrite, but from some other source. We suggest the origin of sulphur is dissolution of volcanogenic sulphidic enrichment in a highly variable, Ladinian clastic-limestone-volcanic rock association, forming the basis of early Carnian Cordevolian dolomite, from which the spring discharges. The measured  $\delta^{13}\text{C}_{\text{DIC}}$  value of -11.9 ‰ indicates groundwater with a contribution of degraded organic matter and dissolved inorganic carbon in the aquifer. The isotopic composition of oxygen ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ) and hydrogen ( $\delta\text{D}_{\text{H}_2\text{O}}$ ) was -8.1 ‰ and -51.4 ‰, respectively, and the tritium ( $^3\text{H}$ ) activity was 3.64 TU. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values indicated recharge from precipitation with  $\text{H}_2\text{S}$  exsolution, while the  $^3\text{H}$  activity shows groundwater older than 40 years. Mineralogical and geochemical analysis of sediment showed a typical carbonate (mostly dolomite) composition, which was in agreement with the geochemical and isotopic composition of the groundwater of the spring, indicating a deep sourced inorganic form of sulphur such as pyrite.

## **Altitudinal and seasonal isotope variation in meteoric and cave drip water in north Dalmatia (Croatia) – importance for the palaeoenvironmental studies**

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Palaeoenvironmental studies commonly rely on proxy records from different sources, one of which are speleothems – secondary carbonate deposits precipitated from the dripping groundwater within the cave environment. In order to ascribe isotopic signal in speleothems to particular past events, it is necessary to understand the hydrological behaviour and chemical variations of the water on its path from the vapour source, via precipitation, through the soil, towards the cave drip sites. Spatially and temporally dependent variations of water have been recently monitored in north Dalmatia (Croatia) at three locations with different climate settings and altitudes: Strašna peć Cave on Dugi otok Island (74 m a.s.l.), Manita peć Cave in Velika Paklenica canyon (Velebit Mt, 570 m a.s.l.) and Spilja u Zubu Buljme Cave (Velebit Mt, 1250 m a.s.l.). We conducted: i) 2-year monitoring of (micro)climate elements (air temperature T and relative humidity RH) inside and outside the caves; ii) 1-year collecting of the meteoric and cave drip water on monthly basis for the stable isotope ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) analyses, and iii) 1-year drip intensity monitoring to estimate the correlations to the rain events.

Isotopic composition of the precipitation showed expected altitude effect ( $\delta^{18}\text{O}$  decrease with increased altitude), which was substantially attenuated in the cave water. In spite of geographical position which suggests that the major atmospheric influence would be of the Mediterranean origin, overview of the isotopic imprint from the surrounding continental and coastal GNIP (Global Network for Isotopes in Precipitation) stations displays more complex situation, due to the Adriatic Sea deeply indented into European continent and near-coast orographic structures. Local meteoric water lines significantly differ from the global meteoric water line both by the intercept and the slope, showing mutual influence of the Atlantic and Mediterranean air masses, being similar in the low- and mid-altitudes, but quite different in the highest region.

Isotopically homogenized water that enters the cave is one of the prerequisites when planning speleothem-based palaeoenvironmental studies, and regardless of the drip intensity and response to the rain events, this condition was fulfilled at all drip sites. Along with typically stable cave environment (constant T and RH), it was rational to expect carbonate deposition in isotopic equilibrium with drip water, which would ensure that only cave temperature affected isotopic fractionation and the isotopic signal would be reliable in terms of palaeoclimate variations. Sadly, Spilja u Zubu Buljme had adversely high T variations ( $>5\text{ }^{\circ}\text{C}$ ), but Manita peć Cave and Strašna peć Cave apparently offer a good potential for further palaeoenvironmental studies.

## **Use of stable isotopes for tracing contamination in a groundwater protection area (Dravsko polje aquifer, NE Slovenia)**

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In Slovenia, groundwater from intergranular aquifers represents one of the major sources of drinking water. However, the country is also characterized with significant agricultural activities, which are most widespread on the shallow intergranular aquifers in the eastern and northeastern part of the country. The protection of groundwater is regulated with Groundwater Protection Areas act (GWPA), which limits certain activities in GW protection zones.

The Dravsko polje aquifer is a high-permeable intergranular aquifer, with numerous pumping stations intended for drinking water supply. The main contamination sources are municipal wastes from local urbanization and agriculture. Despite of implemented GWPA and accompanying regulations within the Water Management Plan (WMP), the groundwater quality of the Dravsko polje aquifer remains poor, mainly because of high nitrate and pesticide concentrations which exceed maximum concentrations determined in the Water Framework Directive (WFD, 2000/60/EC).

To get an insight into actual groundwater status of Dravsko polje area and to predict its future qualitative and quantitative status, an extensive research was carried out, where conceptual model of Dravsko polje aquifer was elaborated. One component of the conceptual model elaboration is represented by information concerning groundwater recharge and its dynamics, as well as groundwater chemical composition, transport of potential pollutants and determination of their sources. For that purpose, in the period between 2012 – 2013, samples of surface- and groundwater were collected for determinations of  $\delta^{18}\text{O}$ ,  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$ -DIC in groundwater on more than 100 locations evenly distributed across the Dravsko polje area. Analysis of  $\delta^{18}\text{O}$  in precipitation and groundwater provided an insight into groundwater dynamics and recharge mechanism of the aquifer, while determinations of  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$ -DIC along with available chemical analysis and field parameters provided information concerning sources, transport and fate of nutrients in groundwater. Results of the research, especially determination of natural status and identification of anthropogenic pollutants, represent a solid foundation for further groundwater protection activities oriented to main pollutants on micro level.

## **Groundwater mixing in the Gacka Area (Croatia), as revealed by stable water isotopes, tritium, CFCs and noble gases**

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Several karst springs in the Gacka area of Croatia were studied by using environmental tracers. The tracers used in this study included stable isotopes ( $^2\text{H}/^1\text{H}$ ,  $^{18}\text{O}/^{16}\text{O}$ ), tritium ( $^3\text{H}$ ), chlorofluorocarbons (CFCs) and noble gases ( $^3\text{He}$ ,  $^4\text{He}$ , Ne, Ar, Kr, Xe). They provide valuable information on the mean residence time and age distribution of the spring waters. In addition, the variation of precipitation's isotopic signal in spring discharges gives information on the mixing of waters with different transit time.  $^3\text{H}$  data themselves can only be used for estimation of the apparent mean residence time of the karst waters. CFCs, though useful in recognizing the co-existence of "young" (post-1993) water with "old" (CFC-free) water in other studies, could not be used in this study to resolve the mixing of waters of different ages. The unsuccessful application of tritium and CFCs in this study is attributed to the fact that both of the two water components in the binary mixing systems, i.e. the older and younger end-members, contain CFCs and tritium. It is shown in this study, however, that the combined use of tritium, CFCs and noble gases can provide a better assessment of models to account for groundwater mixing in this specific scenario. Furthermore, comparison of CFC and noble gas data reveal that during a dry weather period a significant space in the karst groundwater system is not filled with water. Particularly in such a situation tritium data alone can give erroneous results.

## Isotopic composition and geochemistry of mineral water springs and mofettes, a case study of Slovenia

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Mineral water and CO<sub>2</sub> gas springs (mofettes) in Slovenia are poorly investigated. The latter are characterized by diffuse and cold degassing of mainly CO<sub>2</sub>. The aim of the present study is to analyze fluids from the selected twelve springs located in north and northeast Slovenia in order to determine their origin and intensity of water-rock-gas interaction. Springs are situated in metamorphic and clastic rocks and have very low discharge of water. Few ten meters deep wells discharge water of Kotuljska, Lormanjska and Matjaževa slatina, captured springs are Ihovska, Komavarjeva, Polančeva and Radvenska slatina, spring at Slatinska graba and spring at Serdica, while springs at mofettes are Polička and Verjanska slatina and Žekš. Beside field parameters (pH, T, DO, conductivity) we analyzed main ions by ICP-OES and IC at MFGI laboratory in Budapest (Hungary) and total alkalinity by Gran titration at Jožef Stefan Institute in Ljubljana (Slovenia). Isotopic composition of oxygen ( $\delta^{18}\text{O}$ ) and deuterium ( $\delta\text{D}$ ) were determined by CRDS, Picarro 2130i at Hydroisotop GmbH laboratory in Schweitenkirchen (Germany) and  $\delta^{13}\text{C}_{\text{DIC}}$  (isotopic composition of dissolved inorganic carbon) and  $\delta^{13}\text{C}_{\text{CO}_2}$  (where possible) by IRMS ANCA-TG at Jožef Stefan Institute. Tritium was measured by ultra low level liquid scintillation analyser at the Hydrosys Labor in Budapest (Hungary). pH of investigated samples ranged from 4.52 to 6.56, conductivity from 70 to 2690  $\mu\text{S}/\text{cm}$ , T from 9.1 to 15.6 °C and DO from 0.02 to 8.75 mg/l. Low mineralized waters are Komavarjeva slatina, Polička slatina and the spring at Slatinska graba, moderately mineralized are Polančeva and Verjanska slatina while others can be named »true« mineral waters (having TDS of above 1 g/l). Most of them are of Ca-Mg-HCO<sub>3</sub> type but sodium can also be abundant. Geochemistry is controlled mainly by dissolution of carbonates. Total alkalinity ranges from close to 0 mM (recharge from precipitation) to 33 mM. pCO<sub>2</sub> (partial pressure) calculated by PHREEQC for Windows ranged from  $5 \times 10^5$  to  $7.4 \times 10^7$  ppm, which is up to  $2 \times 10^5$  (at location Lormanjska slatina) times higher compared to normal atmospheric pressure (316 ppm).  $\delta^{13}\text{C}_{\text{DIC}}$  ranged from -9.6 ‰ to +1.8 ‰ and indicated dissolution of carbonates. Degassed CO<sub>2</sub> had values of  $\delta^{13}\text{C}_{\text{CO}_2}$  around -2 ‰. Calculated saturation indexes ( $\text{SI}_{\text{calcite/dolomite}}$ ) were close to saturation.  $\delta^{18}\text{O}$  and  $\delta\text{D}$  highlighted their meteoric origin and CO<sub>2</sub> effects. The most recent rainwater was found in Komavarjeva, Polička and Verjanska slatina. The oldest waters flow from wells of Lormanjska and Matjaževa slatina (<0.5 TU). Others indicated mixing of older and recent rainwaters in different ratios with tritium values between 1.7 and 7 TU,  $\delta^{18}\text{O}$  between -9.9 and -10.7 ‰ and  $\delta\text{D}$  between -68.0 and -75.3 ‰. As expected, the investigation confirmed mixing of rainwaters with different residence time at natural springs while the composition of water in mofettes can be various; depending if some high mineralized water also discharges with gas.

## **Trans-boundary character of the several springs recharge area of the Middle Dalmatia, Croatia**

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Groundwater resources in karst areas are one of the most fragile environments of the world. Continuously increasing natural influences, caused by worldwide climate changes especially in Mediterranean region, and recent anthropogenic impact, obligate an intensive consideration of all influences connected with such a valuable water resource.

Recharge areas of these springs are composed of carbonate rocks, mainly well permeable Mesozoic, Eocene and Perms limestone, dolomites and impermeable Eocene flysch and lower Triassic and Neogene clastic sediments.

During the two years continuous monitoring of hydrogeochemical and environmental isotopes ( $^3\text{H}$ ,  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) was performed on Jadro and Žrnovnica springs as well as springs from surrounding catchments of the Krka and the Cetina rivers.

The use of obtained hydrogeochemical and environmental isotope data enabled new knowledge of groundwater origin and flow and recharge mechanism within the study catchment [1,2]. Obtained results confirmed some previous hypothesis about the origin of the Jadro and Žrnovnica spring water as well as the size of recharge area along the eastern hydrogeological border. There are quite serious indicators that few karst springs of the Cetina River catchment share the same recharge area of Jadro and Žrnovnica springs positioned in Bosnia and Herzegovina.

Consequently, for the future study recharge springs of the Cetina River and the Jadro and Žrnovnica springs should be considered as a trans-boundary aquifer. Future water resource management of all springs should include an intensive support of both countries for protection groundwater resources important for the most inhabitant part of the Middle Dalmatia.

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## Isotopic investigations of contemporary carbonate sedimentation in lakes from N Poland

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The study area of NE Poland is a region of most pronounced seasonal climatic contrasts and best preserved varved sediments in lakes. Within the project “Climate of northern Poland during the last 1000 years: Constraining the future with the past (CLIMPOL)” the isotopic investigations have been performed aiming to the creation of transfer functions for the reconstruction of temperature in the past.

The presented study will be focused on the results of isotopic measurements ( $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) for samples of water and contemporary carbonates collected from the lakes along the West-East transect in northern Poland, which have been chosen to form the CLIMPOL training set for calibration space-for-time. The measurements have been performed with use of continuous-flow IRMS Isoprime coupled with automated carbonate/water preparation device Multiflow.

The measurements of  $\delta^{18}\text{O}$  for lake water (47 samples) demonstrate variability of values from -7.7 to -1.9‰ (VSMOW) and show a general W to E gradient. The  $\delta^2\text{H}$  measurements have been performed so far for 22 samples and the results vary from -71 to -19‰ (VSMOW). The plot of  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  reveals linear correlation with the equation:  $\delta^2\text{H} = 7.9\delta^{18}\text{O} - 4.6$  ( $R^2 = 0.80$ ), which slope is identical to GMWL, while intercept is ca. 15‰ lower.

The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of carbonates from sediment traps have been determined for 35 samples, and the results range from -13.1 to -6.1‰ ( $\delta^{18}\text{O}$ , VPDB) and from -10.6 to +0.15‰ ( $\delta^{13}\text{C}$ , VPDB).

The obtained results have been used to calculate temperatures from  $\delta^{18}\text{O}$  according to the “temperature equation” [1], which produced exotic results of 35 °C on the average. These results demonstrated that during the  $\text{CaCO}_3$  precipitation the isotopic equilibrium was not present. On the other hand, the correlation between  $\delta^{18}\text{O}$  in water and  $\delta^{18}\text{O}$  in carbonates ( $R^2 = 0.76$ ) suggested that carbonates recorded the isotope composition of water in which they were formed.

It seems that temperature signal can be recovered from the isotope dataset, as the values of  $\delta^{18}\text{O}$  in sediment trap carbonate and summer temperature (June, July, August) correlated ( $R^2 = 0.38$ ). This simple linear equation was tested as a transfer function to reconstruct the temperature for CLIMPOL master site record from Lake Zabinskie. The comparison of calculated temperatures and instrumental record for the last 120 years showed that generally the average temperature can be reconstructed, but the inter-annual variability was poorly reflected in the reconstructions.

The presented study is a part of the project “Climate of northern Poland during the last 1000 years: Constraining the future with the past (CLIMPOL)”, funded within Polish-Swiss Research Programme, <http://www.climpol.ug.edu.pl>.

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## Deuterium as a tracer in experimental hydrogeology

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The unsaturated zone represents an important buffer between the water table of an aquifer and surface where contamination may occur. The vulnerability of an aquifer to pollution is directly related to hydraulic characteristics of the unsaturated zone. Understanding the mechanisms and rates of movement of pollutants in aquifers is an important issue in the process of groundwater protection. Experimental work like tracing experiments in Lysimeter studies is one of the most valuable tools to investigate characteristics, groundwater flow and solute transport in the unsaturated zone. Transport behaviors of different contaminants have been studied with tracer experiments using a Lysimeter facility in the Selniška Dobrava aquifer. The lysimeter site is designed as a field laboratory. Dimensions are 2 x 2 m, 5 m deep, with walls 0.2 m thick. There are 10 sampling and measuring points at different depths (from JV-1 to JV-10) with approximately equal distances by depth. For sampling groundwater in the unsaturated zone drainage samplers connected to a water sampling system were installed [1].

Three different combined tracing experiments were performed over period of six years. In all three cases deuterated water was used as conservative tracer. Deuterated water is known as an very useful tracer for this purpose [e.g. 2,3] due to its conservative behavior. Moreover, deuterated water is easy to handle sample for analysis, non-toxic and has a reasonable price. Compared to other groundwater tracers, deuterium shows the highest degree of conservativeness [4]. For this reason deuterium was chosen to study water movement. In the first experiment also uranine was used as second tracer. However, our data have shown that uranine has a relatively high degree of adsorption in the soil zone. Therefore it can be used as indicator for preferential flow paths. As the transport properties of uranine may be comparable to other polar contaminates it can be used to trace movement of such pollutants. In the second case study nitrate transport was studied [5]. The movement of selected pharmaceutical substances was investigated in the third tracing experiment. Each experiment took place over a time period of approximately two years. In first period samples were collected at intervals of 14 days, and after this the sampling period was extended to one month. For evaluation of breakthrough curves from a tracing test the computer program TRACI'95 was used. With TRACI'95 the mean flow velocity and vertical dispersion were estimated.

A review of all three tracing experiments will be presented. The flow regimes of water movement in the unsaturated zone determined by deuterium tracer tests in all three experiments have been compared. The mean flow velocity of water through unsaturated zone has been estimated in the range 0.010 – 0.014 m/d in all three cases. Also movement

characteristics of investigated pollutants and uranium have been defined. Results showed that deuterium is very suitable conservative tracer in the experimental hydro(geol)ogy.

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## **Distribution of stable isotope composition in river waters from Romania – preliminary investigations**

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Stable isotopes in river waters represent a good proxy indicator for the behavior of the hydrological cycle and can also be used to understand its relation with climate. In order to understand these relations, long term monitoring of climate, hydrology and isotopic characteristics of various water types involved in the hydrologic cycle are needed. The aim of this study is to investigate the relations between river and meteoric waters and to investigate the source of precipitation feeding these rivers. Stable isotopes in rivers were monitored at 17 sites in Romania, between August 2014 and April 2015; a network paralleling the one in precipitations. Stable isotope analyses were performed using a Picarro L2130i analyzer at the Suceava Stable Isotope Laboratory. The results show that the isotopic composition of river water varies between -9 ‰ and -11.4 ‰ for  $\delta^{18}\text{O}$  and between -64‰ and -81‰ for  $\delta^2\text{H}$ . The lowest values are in rivers from NE Romania (Suceava and Soloneț River) and the highest in W Romania (Tarnava, Crișul Repede and Bega River). All river water samples show very small amplitude in their isotopic values, generally around the mean values in precipitation. However, the amplitude in variations is extremely reduced in river waters (between 0.1 and 2.3 ‰ for  $\delta^{18}\text{O}$ ), as compared to precipitation waters (up to 7 ‰ for  $\delta^{18}\text{O}$ ). There is a general tendency of reduced amplitude in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  with increasing discharge, however, more data is needed to support this conclusion. We hypothesize that the reduced amplitude could be a result of our sampling during the autumn through spring months, with snow melting in the catchment area dampens the precipitation (and climate) related isotopic signal. This hypothesis is further supported by the discharge-isotopic composition relation, the smallest (in terms of discharge) river showing the largest (2.3 ‰ for  $\delta^{18}\text{O}$ ) isotopic variability (Suceava and Solonet rivers).

We see a clear differentiation between rivers in NW and NE Romania, with d-excess values around 10 or slightly above 10, and rivers in SW Romania, with d-excess values between 12 and 14, possibly indicating contribution from Mediterranean-derived precipitation.

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## Keynote lecture

### Carbon cycling in karstic areas: application of traditional and potential of non-traditional stable isotopes

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Karst features are a result of rock weathering, e.g. the reaction of carbonate rock with the CO<sub>2</sub> and water. The magnitudes, variations, locations and mechanisms governing the global CO<sub>2</sub> cycling are still uncertain and under continuing debate, so karstification processes are increasingly gaining attention as a potential “missing sink” of CO<sub>2</sub>. Because of the rapid kinetics of carbonate dissolution and precipitation, the CO<sub>2</sub> consumption by carbonate weathering can – on short time scale in terms of geological time – by far exceed that of the silicate weathering, which is considered as a main geological sink of atmospheric CO<sub>2</sub> throughout Earth’s history. In the ecosystem-scale C cycle research, the geochemical terrestrial processes have long been neglected. Although biogenic CO<sub>2</sub> fluxes in vegetated karst regions are prevailing, they can occasionally be surpassed by the CO<sub>2</sub> exchange patterns dominated by carbonate weathering and cave ventilation. To partition the C fluxes between biogenic and geogenic processes in karstic areas, a carbon mass- and isotope balance is needed. Here the C isotope analysis is the primary tool, including both stable isotopes (<sup>13</sup>C/<sup>12</sup>C), as well as radiocarbon. The partitioning of geological fluxes between those related to carbonate and silicate weathering, however, can be facilitated by the use of non-traditional isotopes, such as Ca and Mg, which can differentiate between igneous sources and sedimentary processes. The CO<sub>2</sub> flux partitioning using stable isotopes of carbon in mixing equations and multisource models with known C isotopic compositions of endmembers may be subject to large uncertainties, if the biogeochemical processes which govern or participate in the carbon cycle are not taken into account appropriately. Therefore, attention will be paid to the quantification of processes which cause considerable isotope fractionation, such as dissolution in open vs. closed system, repeated cycles of carbonate dissolution, CO<sub>2</sub> degassing and carbonate precipitation, isotopically selective microbial C cycling and forced CO<sub>2</sub> degassing because of ventilation. By taking these fractionations into consideration, the uncertainties of the model calculation because of uncertain or wrongful  $\delta^{13}\text{C}$  values of the end members can be reduced. In the lecture, some examples of quantification of C fluxes and partition between biogenic and geogenic sources and processes in carbonate systems from the karstic Alpine and Dinaric areas from Slovenia and Croatia will be presented. The focus will be on river systems, karst aquifers, cavities and soil fluxes in vegetated areas. Quantification of C fixation in carbonate (tufa, flowstone) and fluxes across the water – atmosphere interface will be discussed, as well as estimation of contribution of geogenic processes to the ecosystem carbon fluxes in karst forests and grasslands.

## Study of Dinaric karst using isotope methods: project REQUENCRIM

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In the frame of the project Reconstruction of the Quaternary environment in Croatia using isotope methods (REQUENCRIM) the investigation of palaeoenvironment and palaeoclimate in the Dinaric karst in Croatia has been performed. Dinaric karst covers half of the Croatian territory having the wide range of karstic forms already proven as good palaeoenvironmental archives, such as terrestrial and submerged speleothems, tufa deposits, karst lake sediments, and marine algal rims. Within this research various carbonate sediments from different climate zones are studied: speleothems from 3 locations in littoral Croatia, mountainous Gorski Kotar region and central Croatia, lake sediments from Plitvice Lakes, tufa deposits from Zrmanja River, and marine algal rims from different locations along the eastern Adriatic coast. Research is based on isotope methods that include analysis of stable isotopes  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  in carbonate deposits,  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  in water, and radioactive isotopes  $^{14}\text{C}$  and U-Th series for dating. Additionally, mineralogical composition and CHN analyses of lake sediments and physico-chemical analyses of water are performed. The expected outcome of the research is the following: climate and/or environment records in stable isotope composition of speleothems and tufa, differences in palaeoclimate/ palaeoenvironment conditions in various regions, how various carbonate deposits record conditions in time of deposition, comparison of tufa from Zrmanja River area with the tufa deposits from other areas of Dinaric karst, relative sea level changes during the late Holocene, how recent sea level change impact living algae (*Lithophyllum byssoides*), changes in the environment/climate during last ~200 years by studies of lake sediment depth profiles.

The project is financed by the Croatian Science Foundation for the period 2014 – 2018. In the first year of the project we started with: sampling of rainwater, dripwater and speleothems in 3 caves and monitoring of conditions inside and above the caves; sampling and some isotope measurements of the lake sediments from different locations in two lakes of the Plitvice Lakes system; sampling and some isotope measurements of tufa deposits from the Zrmanja River, as well as water chemistry analysis of the Zrmanja River; prospecting of marine algal rims along eastern Adriatic coast, collecting of samples and some isotope measurements. The Project team of the interdisciplinary research consists of chemists, geologists, geographers, a physicist and a biologist.

The work was performed within the project 1623 "Reconstruction of the Quaternary environment in Croatia using isotope methods" financed by the Croatian Science Foundation.

## **Cave-based palaeoenvironmental research within the REQUENCRIM project**

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Apart from coastal, lacustrine and riverine environments, Project "Reconstruction of the Quaternary environment in Croatia using isotope methods" (REQUENCRIM) includes caves, i.e. speleothem-based researches. Within the crystal lattice, spelean carbonate comprises series of stable and radioactive isotopes routinely used for the reconstruction of the palaeoenvironmental conditions. As the isotope composition of the speleothem depends on the cave drip water content, which itself reflects soil and atmospheric settings, thorough sampling and monitoring of the three caves and their surrounding have been conducted. Each cave is located in different environmental and climate zone: Nova Grgosova Cave (239 m a.s.l.) in NW Croatia with continental climate - Cfb, Lokvarka Cave (760 m a.s.l.) in W Croatia also having continental climate - Cfb, and coastal Modrič Cave (32 m a.s.l.) in S Croatia with submediterranean climate - Cfa. Two speleothems were collected from the deep interior of each cave. In order to record drip intensity, drip-loggers were mounted on the sites of collected stalagmites, coupled with water containers. Concurrently with drip water, rain/snow has been collected on monthly basis above each cave, and microclimate elements (air temperature and relative humidity) have been monitored during the 1-year period. Stable isotopes ratios ( $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$ ) of radiometric dated (U-Th,  $^{14}\text{C}$ ) speleothems will be analysed in order to determine isotopic variations in the past, which reflects temperature fluctuations and vegetation changes above the caves, both governed by the air mass distribution and climate changes. Contemporary air masses' dominance in studied regions and their isotopic signature in meteoric and cave water will be determined by the water samples analyses.

Our results overlapped with accomplishments of the other REQUENCRIM teams will provide further insight into regional Quaternary environmental variations, which will surely contribute to the existing knowledge in broader European context.

The work was performed within the project 1623 "Reconstruction of the Quaternary environment in Croatia using isotope methods" financed by the Croatian Science Foundation.

## **Isotope and chemical analyses of the surface lake sediments in two karstic lakes, Plitvice Lakes, Croatia**

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In the frame of the Croatian Science Foundation Project "Reconstruction of the Quaternary environment in Croatia using isotope methods" part of investigation refers to the study of recent lake sediments in two karstic lakes from the Plitvice Lakes system. Lake sediments may provide a continuous, high-resolution record of environmental changes within the lakes' ecosystem and regional catchment and have been used widely to study natural environmental changes or human-induced impact. For this study we selected two lakes where surface lake sediments (top 40 cm) were taken by gravity corer at several locations. Sediment cores were taken in a big lake, Prošće (area 6.8 km<sup>2</sup>, max. depth 42 m), at 6 locations and in a small lake, Kaluđerovac (area 0.2 km<sup>2</sup>, max. depth 14.5 m), at 3 locations. The sediment cores were taken at different water depth and at different distances from the coast. In the sediment profiles (~40 cm long) analyses of  $\delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  of carbonate and organic fraction and CHN analyses have been performed, and mineralogical composition will be determined. The preliminary results of the first year of the Project presented in this study included 3 sediment cores from Lake Prošće: at the mouth of the Matica River on 1 m depth, at the Liman bay, 5 m depth, and at the deepest point of the lake, 42 m, and 3 cores from Lake Kaluđerovac: on 1.7 m depth, on 4.5 m depth, both near the shore on the SE of the lake and at the deepest point of the lake, 14.5 m depth.  $\delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values indicated different ratio of authigenic and allochthonous fractions at different sampling points at Lake Prošće, as well as an implication of the stronger influence of the water current at the mouth of the Matica River. Strong influence of photosynthesis and calcite precipitation from dissolved inorganic carbon was observed at the deepest points of both lakes. The CHN analyses also showed stronger influence of allochthonous organic material in Lake Prošće, increasing near to the mouth of the Matica River. The composition of Lake Prošće sediment varied for different locations, e.g. carbonate fraction from 20 to 80 %, organic fraction from 16 to 20 % and C/N ratio from 16 to 19. The composition of sediment from Lake Kaluđerovac was similar at all three locations; carbonate fraction was ~95 %, organic fraction ~1 % and C/N ~11, implying that here autochthonous material prevails. The preliminary data showed that isotope and CHN analyses in several sediment cores taken from different micro locations in two lakes can provide important information on paleoenvironmental changes, and also help in predicting future trends in environmental evolution following the global and local/regional influence of these changes.

The work was performed within the project 1623 "Reconstruction of the Quaternary environment in Croatia using isotope methods" financed by the Croatian Science Foundation.

## Isotope and chemical analyses of water and tufa in the Zrmanja River, Croatia

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In this study we present preliminary results of isotope analyses of tufa deposits and chemical analyses of water in the Zrmanja River. The Zrmanja River is 69 km long, located in the Dinaric karst, the NW Dalmatian plateau, and flows into the Adriatic Sea (Novigradsko more Bay). The area is influenced by Mediterranean and continental climate. The Zrmanja River and its tributary the Krupa River are characterized by tufa precipitation in water stream forming tufa barriers. The aim of this study is reconstruction of palaeoenvironment / paleoclimate settings from fresh-water carbonates/tufa and comparison with the similar areas in the Dinaric Karst (Plitvice Lakes, the Krka River).

The activities include sampling of water in the Zrmanja River at several locations in all seasons, in situ measurements of water (T, pH, conductivity), separation of dissolved inorganic carbon (DIC) from water, sampling of recent tufa at several locations along the river course and sampling of fossil tufa deposits. The analyses of  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  age /  $a^{14}\text{C}$  will be performed for tufa deposits and DIC, and water analyses will include determination of Ca, Mg, bicarbonate and dissolved organic carbon (DOC) concentrations.

For the investigation we have chosen 6 points for water sampling along the water course from spring to town Obrovac, 50 km downstream. Calculated saturation index of  $\text{CaCO}_3$  based on measured parameters showed good conditions for tufa precipitation in the most part of Zrmanja River. Radiocarbon activity of DIC ( $a^{14}\text{C}_{\text{DIC}}$ ) measured from the Zrmanja River spring downstream showed slight increase from 80 to 90 pMC.  $^{14}\text{C}$  age of old tufa barrier Gazin Kuk showed the age from 2600 to 5600 yr BP (age not corrected for hard water effect).

The results of tufa and water analyses will be used for determination of the conditions for tufa precipitation in the Zrmanja River; determination of time period of tufa precipitation; comparison of  $^{14}\text{C}$  and U-Th ages of tufa; determination of initial  $^{14}\text{C}$  activity of tufa in the Zrmanja River area.

The work was performed within the project 1623 "Reconstruction of the Quaternary environment in Croatia using isotope methods" financed by the Croatian Science Foundation for period 2014 – 2018.

## Monitoring of algal rims within the scope of the project REQUENCRIM

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Algal rims, primarily formed by red coralline alga *Lithophyllum byssoides*, are considered to be precise sea level indicators. We have recently started with the study of algal rims along the eastern Adriatic coast using isotope methods and our first results in the Central Adriatic on the islands of Vis, Ravnik and Biševo showed that algal rims morphology could be related to the distinguished periods of climate changes during last two millennia. In the framework of the project Reconstruction of the Quaternary environment in Croatia using isotope methods (REQUENCRIM) we focus on palaeoenvironment and palaeoclimate research of algal rims in order to establish the chronology of relative sea level changes along the Croatian coast and the link between the morphological structure, climate change and sea level change for the late Holocene. Our research showed that although the alga grows today, it does not form rims any more. Within the project we started to monitor existing rims on the island of Vis with the aim to determine how recent sea level change impact living algae (*Lithophyllum byssoides*). In the contribution methodology and results of the first year monitoring of algal rims will be presented. The status of the prospected living *thalli* of *Lithophyllum byssoides* (living, partly eroded, completely eroded/non-existing) was determined twice (in September 2014 and July 2015). Understanding the potential effects of climate change, raising temperature and sea level on *Lithophyllum byssoides* will help us to explain the relationship between the increased sea level rise and the changes of algal rim morphology.

The monitoring of algal rims has been funded within the Croatian Science Foundation project no. 1623 "Reconstruction of the Quaternary environment in Croatia using isotope methods".

## Relative sea-level change and climate change in the Eastern Adriatic based on the isotopic study of algal rims

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The two millennia sea-level curves along the Eastern Adriatic coast are primarily based on archaeological coastal remains as well as geomorphological and sedimentological markers. Today, the approach to the study of sea level variations is multidisciplinary and includes the use of a variety of different markers and their combinations where possible. However, most of the methods used till now do not provide enough precision. In order to obtain more precision and better accuracy of sea-level curves our latest research along the eastern Adriatic has been centred on algal rims as sea-level markers. Their fossil bio-constructions have proven to be precise sea-level indicators ( $\pm 10$  cm) in microtidal environments. Algal rims formed by algae *Lithophyllum byssoides* allow us to study the relative sea level change and climate change during the last two millennia with much more consistency and accuracy. Under favourable conditions *Lithophyllum byssoides* build up reef like bioconstructions just above the biological mean sea-level which can be  $^{14}\text{C}$  dated. Within the project *Reconstruction of the Quaternary environment in Croatia using isotope methods* we study algal rims on several locations along the eastern Adriatic coast. As *Lithophyllum* and mollusc shells found inside the rims are dated using  $^{14}\text{C}$  analyses (LSC and AMS) marine radiocarbon reservoir effect should be considered. Previous research has assumed that *Lithophyllum* does not appear to be subject to any kind of marine radiocarbon reservoir effect. Those assumptions were based on the dating of living *thalli*. Our results showed that this is not the case and before further investigations and interpretations it is necessary to resolve this issue. Consequently, we started the study of the MRE along the eastern Adriatic as the  $^{14}\text{C}$  reservoir effect may have a significant influence to the final  $^{14}\text{C}$  results and it is very important for chronological accuracy in temporally short studies like the study of 2 ka relative sea level variation. In research of MRE we engaged the analyses of pre-bomb samples from museum collections and the analysis of paired samples from the algal rims.

The work was performed within the project 1623 "Reconstruction of the Quaternary environment in Croatia using isotope methods" financed by the Croatian Science Foundation.

## Stable isotope composition of surface and deep waters from Plitvice Lakes

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Within the project "The influence of climatic changes and environmental conditions on biologically induced precipitation of tufa and sedimentation process in the Plitvice Lakes", contracted between the Ruđer Bošković Institute and the National Park Plitvice Lakes, various isotopic data for water, tufa, lake sediments and atmosphere were collected in the period from April 2011 to April 2014. Here we present isotopic composition ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) of surface and deep waters. The study area was the Plitvice Lakes system of 16 lakes separated by tuffa barriers and interconnected by waterfalls. Surface water was collected at 8 locations along the water course in length of ~10 km from Matica (the main stream feeding the lakes) to the Korana River (the outflow from the lake system), while the deep water was collected at 4 sediment traps in different lakes (IRB1 and IRB2 in Lake Kozjak at water depth 6 m and 8 – 10 m, respectively, IRB3 in Lake Prošće at 6 m, IRB4 in Gradinsko Lake at 2 m).

Both  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  of water show seasonal variations with higher values during summer, but the seasonal variations ( $<1.4\text{‰}$  in  $\delta^{18}\text{O}$ ,  $<9\text{‰}$  in  $\delta^2\text{H}$ ) are much smaller than in precipitation of the area ( $\delta^{18}\text{O}$  values in precipitation varied from  $-16\text{‰}$  to  $-2\text{‰}$ , and  $\delta^2\text{H}$  from  $-120\text{‰}$  to  $-10\text{‰}$  [1] confirming that the waters of the system are well mixed. No difference between deep and surface waters is observed if the mean values are concerned. A slight increase in both mean  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values and their seasonal variations is observed for locations along the water course, from  $-10.7 \pm 0.1\text{‰}$  at Matica to  $-10.3 \pm 0.3\text{‰}$  at the Korana River. Influence of heavy summer rains and snow melting was observed by slight increase and decrease, respectively, in  $\delta^{18}\text{O}$  values compared to the average/"normal" values in both surface and deep waters.

The LMWL for the Plitvice Lakes precipitation is  $\delta^2\text{H} = 7.8 \delta^{18}\text{O} + 11.7$  [1]. All surface waters in this study lie on the line  $\delta^2\text{H} = (6.5 \pm 0.3) \delta^{18}\text{O} - (2.8 \pm 3.0)$ ,  $R^2 = 0.88$ , and the deep water on the line  $\delta^2\text{H} = (5.8 \pm 0.3) \delta^{18}\text{O} - (9.5 \pm 3.0)$ ,  $R^2 = 0.91$ . Lower slopes and intercepts of both relations compared to the LMWL indicate influence of evaporation of surface waters that is more pronounced in big lakes, and also more pronounced in deep than in surface waters.

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## **Carbon isotopic investigations of Zolushka Cave**

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Zolushka cave situated on the Ukrainian/Moldovian border is one of the largest gypsum caves in the world. It was excavated for the first time in the middle of the last century. Excavation was possible due to the water level change caused by quarry works undergoing in the close vicinity of the cave. Phreatic hypogene caves are usually huge (tens and hundreds of kilometres long) underground labyrinths of poor air exchange with the outside atmosphere (low pressure climate type of cave). Due to the dimensions and of the weak link with surface, they become, inter alia, the giant "traps" for different gases, which are "produced" by both the biosphere (soil, micro-organisms, plants, decomposition of organic material, etc.), and the processes taking place in the cave (gases dissipated from water) and in the deeper parts of rock massifs (chemicals oxidation, fumes, radon migration etc.). The chemical composition of air of hypogene caves atmosphere forms under the influence of various factors and has both the common and specific features in each case. One of its most distinctive features of Zolushka cave is high (1 – 3 % or more) content of CO<sub>2</sub>. The other important feature of the cave is organic-rich sediment of till now not known origin. Here we present some pilot carbon isotopic study of the organic sediment as well as atmospheric CO<sub>2</sub> sampled in the cave. We hope that using stable and radioactive carbon isotopes we will be able to resolve processes undergoing in the still active cave.

## **Applications of Cavity Ring-Down Spectroscopy (CRDS) to isotopologues of water, as well as nitrogen and oxygen isotopes in N<sub>2</sub>O for soil studies**

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Over the past five years, advances in cavity-enhanced absorption spectroscopy have fundamentally changed the way scientists study carbon, nitrogen and water cycling between the subsurface, surface, plants and the atmosphere. With the continuous evolution of performance, including high precision, low drift and part-per-billion resolution, along with compact, field-deployable and easy-to-use instruments, scientists are increasingly able to leave their labs and make measurements directly in the field. Here we describe how Picarro's Cavity Ring-Down Spectroscopy technology can be applied to (i) spatial and temporal changes in hydrological systems and (ii) N<sub>2</sub>O emissions and nitrogen cycling between the soil, plants and atmosphere. The Picarro Continuous Water Sampler, when coupled to a L2130-i CRDS analyzer, now enables real-time, continuous measurements of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in liquid water for the construction of high resolution water isotopologue data sets through time and space.

The CWS was deployed on the Sacramento River Delta to understand local evaporation and residence time of water in the delta system. We will also discuss recent enhancements to Picarro's mid-infrared platform for measuring nitrogen and oxygen isotopes in N<sub>2</sub>O, including site-specific  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ . This system can be used to identify N<sub>2</sub>O sources and sinks, and improve predictive models of N<sub>2</sub>O emissions from the soil.

## **Carbon isotope ratios of dissolved inorganic carbon (DIC) and carbonates measured with a field deployable isotope ratio infrared spectrometer**

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Laser-based Isotope Ratio Infrared Spectrometers (IRIS) offer the potential to perform precise, *in-situ* analysis of isotopologues of gases such as CO<sub>2</sub>. We are presenting a middle-infrared laser-based sensor platform that is capable of simultaneously determining both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  isotope ratios of carbon dioxide. We will show results using this analyzer to probe CO<sub>2</sub> from head space processes, specifically for the analysis of dissolved inorganic carbon (DIC), and carbonates.

$\delta^{13}\text{C}$  values of pore water with a DIC of 2.3 mmol/l was analyzed by acidifying about 1 ml of water with H<sub>3</sub>PO<sub>4</sub> in a labco borosilicate vial. Before running the gas through the Delta Ray, the sample was settling for 5 h. We achieved an internal precision for  $\delta^{13}\text{C}$  of ~0.07 ‰, and an external reproducibility of  $\delta^{13}\text{C}$  of ~0.15 ‰. We will also present a depth profile of pore water from a sediment core collected at the floor of Eckernförde Bay, Baltic sea.

Measurements of three reference materials (NBS 18, NBS 19 and LSVEC) were performed, and NBS 18 treated as an unknown. Five samples of NBS-18 of approximately 1 mg each were acidified using a few droplets of 100 % H<sub>3</sub>PO<sub>4</sub> and left for equilibration overnight at 25 °C. NBS-19 and LSVEC samples were treated identically and used for linearity calibration and scale contraction of the measured  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. The obtained values for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  were  $-5.0 \pm 0.1$  ‰ and  $-23.3 \pm 0.1$  ‰, respectively, in agreement with the values certified by IAEA of  $-5.01 \pm 0.04$  ‰ and  $-23.2 \pm 0.1$  ‰, within the analytical uncertainty.

## Towards the study of isotopic anomalies, $\Delta^{17}\text{O}$ and $\Delta^{33}\text{S}$ , in terrestrial samples

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The **isotope anomalies** (IA) received recently a great attention by a number of investigators [eg. 1,2,3 and references therein], therefore we propose here a novel approach in their study as described below. By IA we understand the deviations of  $\delta^{17}\text{O}$  and  $\delta^{33}\text{S}$  from respective values of 0.52  $\delta^{18}\text{O}$  and 0.52  $\delta^{34}\text{S}$  predicted by the mass-dependent theory [4,5]. These anomalies, denoted as  $\Delta^{17}\text{O}$  and  $\Delta^{33}\text{S}$ , are encountered to be large in meteorites and stratospheric trace gases ( $\text{O}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{SO}_4$ ,  $\text{CO}$ ), but very small at Earth surface level. The major source of the anomaly of oxygen isotope ratios ( $\Delta^{17}\text{O}$ ) is atmospheric ozone and  $\text{CO}_2$ , whilst that of  $\Delta^{33}\text{S}$  recorded in Precambrian sulphides and sulphates result most likely due to ionization phenomena of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  in ancient Earth atmosphere. The distinct anomaly of stratospheric  $\text{CO}_2$  is diluted with isotopically normal  $\text{CO}_2$  when it enters the troposphere, hence at the ground level  $\text{CO}_2$  shows a little anomaly. Hoag et al. (2005) [6] predicted  $\Delta^{17}\text{O} = +0.15\text{‰}$  only for the tropospheric  $\text{CO}_2$ . Hence the IA were not well recognized at Earth surface level by far, due to severe analytical difficulties of isotope analysis of  $\delta^{17}\text{O}$  and  $\delta^{33}\text{S}$  by mass spectrometry.

The goal of this research is to overcome the most crucial difficulty by applying negative ion mass spectrometry. With the proposed idea we will attack the problem of the analysis of minor variations of  $\delta^{17}\text{O}$  and  $\delta^{33}\text{S}$ , because no interfering peaks occur in the mass spectra of  $\text{O}^-$  and  $\text{S}^-$ . Necessary precision of  $\delta^{17}\text{O}$  determination should be enhanced several times in comparison to that attained nowadays by using of positive ion mass spectrometry.

We will try to enhance maximally the precision of isotope ratios determination by isotope ratio mass spectrometer (IRMS) on one hand, and on the other hand, we will increase the efficiency of isotope determinations by simplification of the sample preparation procedures. To achieve these goals we have constructed a triple collector and dual inlet mass spectrometer, in which we used the alignment and electromagnet manufactured by Nuclide, Pennsylvania, in 70's of the 20<sup>th</sup> century. The collector assembly of this IRMS has been designed for the measurements of negative ions  $\text{O}^-$  and  $\text{S}^-$  produced from being easily prepared gases like  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{SO}_2$ . Particularly such measurements yield highly promising results regarding the intensity of the negative ion beam of oxygen ( $\text{O}^-$ ) generated from  $\text{CO}$  gas at the resonance electron energy of 11 eV.

In dependence of the achievement degree of the outlined goals, we would be able to investigate smaller or larger IA recorded in various type of terrestrial carbonates, sulphates and sulphides and perhaps some components dissolved in waters. This will be rather exploring study of rock samples of different geological age. We will put major attention to study IA in times of global crisis like those encountered in Permian/Triassic and K/T boundaries. In those

boundaries great variations of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  have been already recorded in sedimentary carbonates [7] and  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  in marine sulphates [8,9].

In this lecture we will present our up-to-date aspiration towards studies the IA anomalies in terrestrial samples.

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## High-precision measurements of $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ stable isotopes ratios in groundwater

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Measurements of the  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  stable isotope ratios in water are commonly used to identify the groundwater catchment area, mean residence time, geochemical processes in hydrogeology. Measuring mass differences of molecular compounds (ratios) can be done by a variety of mass spectrometer designs. Cavity ring down spectrometry (CRDS) is one of the techniques used by Picarro L2130-i spectrometer. The spectrometer was purchased thanks to the DRINKADRIA project financed by IPA Adriatic Cross Border Cooperation Programme. Measurement methodology is based on fact that every small gas-phase molecule has a unique near-infrared absorption spectrum. At sub-atmospheric pressure, a series of narrow, well-resolved, sharp lines, each at a characteristic wavelength exists and these lines are well-spaced and their wavelength is well-known, so the concentration of any species can be determined by measuring the strength of this line, i.e. absorption. The instrument consists of autosampler, vaporizer, two vacuum pumps and measurement unit (CRDS) with computer. The instrument simultaneously measures  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  stable isotope ratios in water samples. The measurement accuracy guaranteed by manufacture for  $\delta^{18}\text{O}$  is 0.03 ‰ and achieved is 0.01 to 0.03 ‰ depending upon water chemistry. The measurement accuracy guaranteed by manufacture for  $\delta^2\text{H}$  is 0.2 ‰ and achieved is 0.03 to 0.07 ‰ depending upon water chemistry. In the period from August 2013 till May 2014 groundwater duplicate samples were collected from Lobar water sources. One group of samples were analyzed by Isotopic Ratio Mass Spectrometry (IRMS) in Laboratory for measurement of stable isotopes, Department of Physics, Faculty of Medicine in Rijeka, Croatia, and another in Joanneum Research Resources Forschungsgesellschaft, Institute of Water, Energy and Sustainability, Department of Isotope Hydrology and Environmental Analytics, Graz, Austria. The duplicate samples that left at Croatian Geological Survey were measured using Picarro L2130-i. Values measured by cavity ring down spectrometry were compared with the values obtained with the isotopic ratio mass spectrometry and negligible difference was observed.

## Deuterium and Hydrogen Ratios Determine Proton Spin-Lattice T1-Weighted Magnetic Resonance Images: Clinical Applications in Cancer

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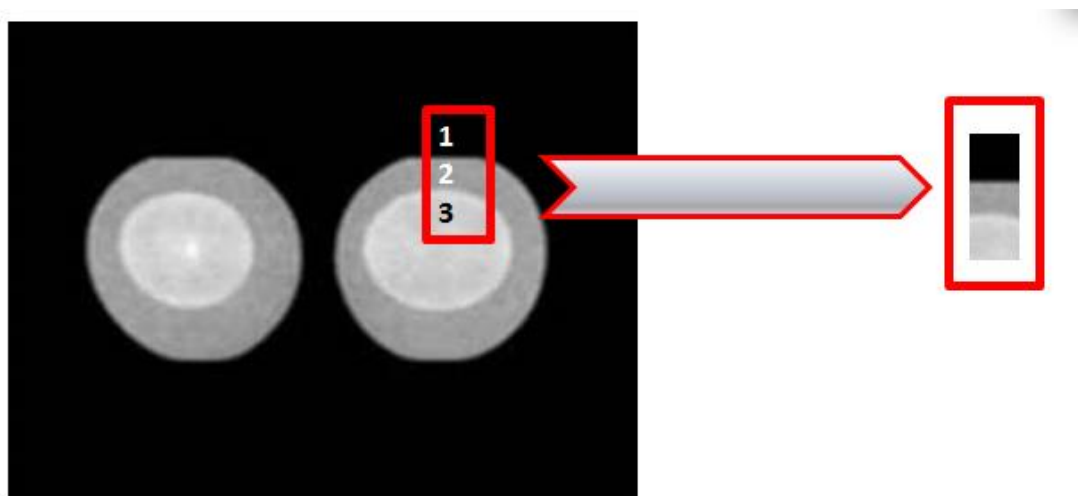
Decreased  $^1\text{H}$  spectra spin-lattice relaxation-based 3D images of tissue water and fat using whole-body  $T_1$ -weighted magnetic resonance imaging (MRI) outperform all other radiological diagnostic tools to detect cancer. A relative loss in proton signal can also be seen in egg white when compared to egg yolk using clinically applied axial MRI (Figure 1,  $^1\text{H}$  detection in water and fat, 1.5 T). We herein report close correlations ( $R^2 = 1$ ; Correlation = -1) between measured deuterium and hydrogen ratios in egg white and yolk (Table 1) via isotope ratio mass spectrometry ( $^2\text{H}$  Content (D; ppm) IRMS) as well as that of MRI Red-Green-Blue (RGB) intensities and luminescence, respectively, using color code analysis by Microsoft Windows Paint HyperText Markup Language (HTML) image analysis (Figure 1; version 6.3, Build 9600).

Table 1. Comparison of measured deuterium and hydrogen ratios in egg white and yolk via isotope ratio mass spectrometry and MRI Red-Green-Blue (RGB) intensities and luminescence via HTML image analysis.

	Background (1)	Egg White (2)	Egg Yolk (3)	yolk/white	white/yolk
RGB (MRI)	0	159	201	126.4 %	79.1 %
Luminescence (MRI)	0	152	188	123.7 %	89.9 %
2H content (D; ppm)	0	152	122	80.3 %	124.6 %

Our results demonstrate that MRI is an excellent  $^2\text{H}/^1\text{H}$  biomarker imaging tool of compartmentalized tissue water and fat composition. When mitochondria are failing cytoplasmic water and saturated fatty acid pools can potentially decrease MRI proton signals by their increased  $^2\text{H}_2\text{O}/^2\text{H}^1\text{HO}/^1\text{H}_2\text{O}$  ratio resulting in a deuterium enriched lattice. Such lattice yields a relative decrease in  $^1\text{H}$ -NMR signals and luminescence of primary and metastatic tumor tissues, residing in abdominal and pelvic organs. The brain, on the other hand, is a predilection site for deuterium accumulation due to the blood brain barrier's exclusion of low deuterium-carrying circulating triglycerides as a prelude to myelination and synaptic vesicle turnover. In neurocytes the entire saturated and monounsaturated lipid pool is produced

locally by *de novo* biosynthesis from deuterium rich dietary glucose. Therefore the mechanisms of brain tumors gaining proton signals and luminescence on non-contrast spin-lattice-based fluid-attenuated inversion recovery (FLAIR) images involve the breakdown of the blood brain barrier's fatty acid discriminating function and its resulting effect on gaining access to deuterium depleting fatty acids from circulation. Thus mitochondrial low deuterium fatty oxidation provides the deuterium-depleted signal-yield during water production in brain tumors. Biochemical mechanisms detailed above should help radiologists to metabolically characterize tumors that contrast out by severely altered deuterium depleting mechanisms in comparison with those found in host tissue water and fat pools.



**Figure 1.** Color code analysis by MS Paint (version 6.3, Build 9600) using sections of MRI images of egg white and yolk for comparison with IRMS deuterium content provided in Table 1. (1: background, 2: egg white, 3: egg yolk)

## SHRIMP IIe/MC an isotope multitool

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SHRIMP IIe/MC (Sensitive High Resolution Ion MicroProbe) is a Secondary Ion Mass Spectrometer (SIMS) that is capable to *in situ* isotopic and chemical surface analyses of solid targets [1-7]. A high-energy beam of primary ions is focused onto a small area (from 5 to 30  $\mu\text{m}$  diameter) on the surface of the target. The ion bombardment sputters atoms and molecules from the sample. These secondary ions are gathered using electrostatic lenses and transferred to a mass spectrometer, in which they are separated according to their relative masses. SHRIMP IIe has high mass resolution which is achieved by the use of a double-focusing mass spectrometer, simultaneous energy and mass refocusing, with a very large turning radius, magnet radius is 1000 mm and electrostatic analyser radius is 1272 mm. That is why instrument has a beam line over 7 m long and weighs more than 14 tons [8].

The SHRIMP has the high secondary ion transmission necessary to detect trace elements [9,10] while maintaining the high mass resolution required to resolve the many molecular interferences that result from chemically complex minerals. The operation at high transmission with a mass resolution sufficient to distinguish MREE (medium rare-earth elements) from LREE (light rare-earth elements) oxides, and Pb from Hf dioxides makes the SHRIMP ideal for low level trace element analyses of geologic materials and U-Th-Pb geochronology [11]. It can be used for routine measurement of the isotopic composition of, for example, Pb, U, Th, O, S, C, Mg, Ca, Ti, B, Li, Si and Cr, and the abundances of most elements in the periodic table in geological, cosmochemical, experimental, or industrial samples.

The SHRIMP IIe/MC has a multicollector which allows subpermil ( $>0.2\text{‰}$ ) resolution for isotopic ratios of C, O, S, and other geologically interesting elements [8]. The use of charge mode electrometers allows the minor isotopes of  $^{36}\text{S}$ ,  $^{17}\text{O}$ , and  $^{13}\text{C}$  in carbonate to be measured using a faraday cup instead of an electron multiplier, even though the countrate is only a few hundred thousand cps in most cases. The use of high-sensitivity hall probes instead of NMR allows for multiple isotopic systems (O, S in sulphates, O, C in carbonates) to be analysed in a single analytical spot via field switching. Stable isotope geochemistry examines the change of the isotopic composition of an element (H, Li, B, C, N, O, S) produced by chemical or physical processes. SHRIMP measurement of S isotopes has been used to understand mineral growth mechanisms and genesis, follow changes in fluid compositions and to constrain the conditions under which rocks and ore deposits form [12].

For isotopically uniform electrical insulators such as zircon, SHRIMP IIe/MC has demonstrated a capability to produce replicate oxygen isotopic analyses over a period of several hours that have a standard deviation of better than 0.2 ‰. SHRIMP IIe/MC main use is U-Pb geochronology. It provides rapid, reliable dating of micron-scale domains in U-bearing

trace minerals at the 1-2 % level. The current technique comprises a measurement of Pb isotopes, U, Th, and uranium oxide species which are used to calibrate the relative ionization efficiency of U and Pb. SHRIMP analyses are advantageous in that the fine spatial resolution (in range 20  $\mu\text{m}$ ) allows targeting of subgrain domains in mineral grains with complex growth histories, avoiding inclusions or metamict domains [8]. When temporal precision higher than 1 % is required, the SHRIMP IIe/MC can be used to screen zircon grains for lead loss, inherited cores, or other problems that may inhibit or complicate TIMS analysis.

The small analytical volume ( $\sim 1000$  cubic microns) allows minimal sample consumption [13]. This allows for later whole-grain dissolution, combined U-Pb-Th dating, or the use of multiple *in situ* techniques on the same sample, such as SHRIMP IIe U-Pb geochronology, SHRIMP IIe/MC oxygen isotope analysis, and then laser ICPMS Hf isotopic analysis. SHRIMP IIe has been used for the U-Pb geochronology of minerals such as zircon, titanite, perovskite, allanite, rutile, baddeleyite, monazite, and xenotime [3,8,10,14-18].

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## The high precision oxygen isotope analysis of phosphates

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Since two decades silver orthophosphate ( $\text{Ag}_3\text{PO}_4$ ) has successfully been used in oxygen isotope analysis of natural phosphates. Natural phosphates, both biogenic and abiogenic, can be relatively simply converted to  $\text{Ag}_3\text{PO}_4$  by digestion in HF and subsequent precipitation with  $\text{AgNO}_3$  solution. There are three methods of converting  $\text{Ag}_3\text{PO}_4$  into a permanent gas amenable for  $^{18}\text{O}$  isotope analysis by IRMS [1]: (1) The fluorination method, although oxygen extraction is quantitative in reaction with  $\text{BrF}_5$ ,  $\text{ClF}_3$ , or  $\text{F}_2$  and it requires at least 15 hours for completion [2]. (2) A rapid oxygen extraction method by graphite reduction was developed by O'Neil et al. [3] in which  $\text{Ag}_3\text{PO}_4$ -graphite mixtures sealed in silica tubes were heated in a resistance oven to 1200 °C. (3) High temperature conversion of  $\text{Ag}_3\text{PO}_4$  to CO in a glassy carbon reactor held at 1450 °C [1].

In this study we investigated the graphite reduction of  $\text{Ag}_3\text{PO}_4$  in detail. We applied resistance heating of Pt-Ir boat in vacuum. The following observations at final reaction temperatures varying from 430 to 915 °C were made: (i)  $\text{CO}_2$  extraction yield, (ii) oxygen isotopic composition of  $\text{CO}_2$  (iii) mass loss of the reactants. Our study lead us to further improvements of the oxygen isotope analysis of phosphates. The  $\text{CO}_2$  yield and oxygen isotopic composition were determined on a calibrated dual inlet and triple collector isotope ratio mass spectrometer. We noticed the following three stages of the reduction process: (1) At temperatures below 590 °C only  $\text{CO}_2$  is formed, whilst silver orthophosphate decays to pyrophosphate. (2) At higher temperatures 590-830 °C predominantly CO is formed from silver pyrophosphate which decays to metaphosphate. (3) At temperatures above 830 °C the meaningful sublimation of silver orthophosphate appears. These observations were accompanied by the oxygen isotope analysis of the obtained  $\text{CO}_2$ . The measured  $\delta^{18}\text{O}$  value varied from -11.93‰ (at the lowest temperature) to -20.32‰ (at the highest temperature). The optimum reduction temperature range was found to be 780 to 830 °C. At this temperature range the oxygen isotopic composition of  $\text{CO}_2$  is nearly constant whereas reaction efficiency is nearly complete. The determined difference between  $\delta^{18}\text{O}$  value of oxygen in silver phosphate and that in  $\text{CO}_2$  extracted from this phosphate is +0.72 [4]. Using this method  $\delta^{18}\text{O}$  values in two commercial and one synthesised silver orthophosphate reagents have been determined on the VSMOW scale [5].

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## Extraction chromatography separation of lead and determination of $^{210}\text{Pb}$

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Ratios of isotopes, and ratios of isotopes members of natural decay chains, are used as radioactive clock for timing natural geological materials like sediments and rocks, locating samples at the moment in earth history and correlating them with other events and incidents. Ratio of  $^{238}\text{U}$  to  $^{210}\text{Pb}$  is commonly used.  $^{210}\text{Pb}$  emits low-energy beta particles ( $E_{\beta\text{max}} = 20 \text{ keV}$  (81 %), 61 keV (19 %)), and gamma rays ( $E_{\gamma} = 46.5 \text{ keV}$ ). Hence,  $^{210}\text{Pb}$  could be detected by gamma spectrometry, liquid scintillation counting (LSC) and other techniques. Indirect techniques for  $^{210}\text{Pb}$  determination have been more usual because  $^{210}\text{Pb}$  directly determined by gamma spectrometry can be disturbed by poor counting efficiency, self-absorption in the source and adsorption in the detector measurements. Lead separation from sample is required for indirect techniques of determination. Using extraction resins (Sr resin, Pb resin) and variations of acids concentration in mixture, lead could be separated from other cations, isolated and preconcentrated with contented recovery. After separation,  $^{210}\text{Pb}$  could be detected on LSC through its daughter nuclei  $^{210}\text{Bi}$  and  $^{210}\text{Po}$  with classical LSC detection using scintillator after radiochemical equilibrium was achieved. Detection by LSC has lack of self-absorption but waiting for equilibrium with daughter nuclei  $^{210}\text{Bi}$  and  $^{210}\text{Po}$  is disadvantage of the method. Consequently, separation of lead on extraction chromatography resins and determination of  $^{210}\text{Pb}$  by LSC will be presented here.

## **Application of a solid electrolyte reduction reactor in CF-IRMS for $\delta^{15}\text{N}$ determination of organic substances**

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Compound-specific isotope analysis of individual organic substances is a powerful tool for tracing nitrogen (N) source and transformation in biogeochemical cycles. Reduction of  $\text{NO}_x$  is of great importance and interest in air pollution control especially in the high temperature combustion processes. A high temperature electrochemical solid electrolyte reactor (SER) based on stabilized zirconium dioxide ( $0.9 \text{ ZrO}_2 \cdot 0.1 \text{ Y}_2\text{O}_3$ ) has been designed for reduction  $\text{NO}_x$  in a continuous-flow isotope-ratio mass spectrometry (CF-IRMS) system. A solid electrolyte possesses the oxygen ions related conductivity at high temperatures (800 – 1000 °C). The SER is made of tubular, thin-walled zirconia ceramics with inner diameter of 1 mm and of 10 cm total length. The working temperature of micro-reactor is ~950 °C. Our constructed device is coupled to a Delta Plus isotope ratio mass spectrometer via a cryogenic trap and Combustion III. To assess the performance of the new reduction reactor the samples of IAEA 600 (caffeine), acetonitrile ( $\text{CH}_3\text{CN}$ ), and  $\text{N}_2\text{O}$  gas were analyzed.  $\delta^{15}\text{N}$  values obtained using conventional Cu wires reduction reactor and SER were considered.  $\delta^{15}\text{N}$  values of caffeine, acetonitrile and  $\text{N}_2\text{O}$  obtained using commercial reduction reactor were  $2.16 \pm 0.69 \text{ ‰}$  ( $n = 6$ ),  $1.52 \pm 0.27 \text{ ‰}$  ( $n = 7$ ),  $-0.82 \pm 0.11 \text{ ‰}$  ( $n = 3$ ), respectively. Those when using SER were  $1.60 \pm 0.11 \text{ ‰}$  ( $n=4$ ),  $1.58 \pm 0.39 \text{ ‰}$  ( $n = 8$ ),  $-1.78 \pm 0.26 \text{ ‰}$  ( $n = 5$ ), respectively. Only for acetonitrile the  $\delta^{15}\text{N}$  values were close when using two kind of reduction reactors but standard deviations were worse in case of using the SER. For IAEA 600 and  $\text{N}_2\text{O}$  the  $\delta^{15}\text{N}$  values were different. Unexpected was that the signal amplitudes ( $m/z$  28) using SER were 1.5 – 2 times higher than those with using commercial reduction reactor. The performance of SER can be improved by means of using a new working electrode made of Pt and Rh like in a 3-way catalytic converter in the exhaust system of many modern petrol engine vehicles. The main advantages of our solid electrolyte reduction reactor are the reliability, the greater active surface prolonging the lifetime of the reactor, particularly for nitrogen isotope analysis. Most importantly, the new reactor design supplies a much greater degree of high-temperature conversion.

## Different potential uncertainties in the $^{210}\text{Pb}$ dating method

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The  $^{210}\text{Pb}$  dating method is widely used for determining the ages of young sediments (0 – 200 y). In order to apply this method, measurements have to be made to determine the activity levels of  $^{210}\text{Pb}$  consisting of two components: the supported  $^{210}\text{Pb}$  (generated *in situ* from  $^{226}\text{Ra}$ ) and the unsupported  $^{210}\text{Pb}$  (deposited via airborne fallout).

The aim of this study is to analyze two potential uncertainties associated with the  $^{210}\text{Pb}$  measurements, namely the effect of the silicates found in the sediments and the variation of the mass attenuation in concordance with an used reference. In order to achieve this, sediment cores were collected from three lakes situated in the Rodnei Mountains National Park (Buhaiescu, Stiol and Muced Lake), one from the Ciomadu Mountains (St. Anna Lake) and one from the Danube Delta (Iacob Lake).

The total  $^{210}\text{Pb}$  content of the sediments was determined via  $^{210}\text{Po}$ , which is the alpha particle emitting progeny of the  $^{210}\text{Pb}$ . The method implies chemical separation using  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{H}_2\text{O}_2$  and  $\text{HF}$ .  $^{209}\text{Po}$  tracer was used for determining the chemical yield and spontaneous deposition was made onto stainless steel discs. Measurements were then carried out using PIPS detectors.

Results show, that if the acidic digestion is carried out without the use of  $\text{HF}$ , the ages of the sediment layers tend to appear 1 – 19 % younger because of the  $^{210}\text{Po}$  restrained in the silicate crystals. The leaching processes can cause contaminates the Teflon dishes with 20 – 30 % of the present activities. The highest values (30 %) measured in silicates is attributed to the Iacob Lake, causing changes of 19% in the sediment ages, explainable by the great variability of silicates. After the leaching of Muced lake sediments no silicates were retained, because of the early peat bog state of the lake. 16 % of the total activity of  $^{210}\text{Pb}$  in the Stiol lake sediment is given by the silicates, producing a rejuvenation of 2 %. The silicates of the Buhaiescu Lake are responsible for 9 % of the total  $^{210}\text{Pb}$  content, causing a decrease of 1 % in the ages of the sediments. The overall uncertainty of the  $^{210}\text{Pb}$  method is of 5 – 19 %, the silicates influencing the  $^{210}\text{Pb}$  activity concentrations with up to 30 %.

The other difficulty regarding the  $^{210}\text{Pb}$  dating method is the compositional difference between the layers of each sediment column. The linear and mass attenuation coefficients of two sediment cores were determined, proving different absorption potentials. Samples underwent drying and homogenization, after which they were put into aluminum boxes having specific geometry. Measurements were carried out using an multichannel HPGe semiconducting detector. Each layer was measured separately for 300 s having a  $^{210}\text{Pb}$  point source on top. The attenuation coefficients of each sediment layers were compared to that of the IAEA 385 Irish Sea Sediment ( $0.366 \text{ g/cm}^2$ ), which is used in the relative activity determination methods. The samples showed variations from  $0.348 \text{ g/cm}^2$  to  $0.699 \text{ g/cm}^2$ . The presumed  $\gamma$  activities of each sediment layer were calculated by taking into account the absorption capacity of each layer. Global errors for each layer can be made in the 1 – 83 % range by comparing the those obtained by the  $^{210}\text{Po}$  method; the IA3 sediment core had an average error of 24 %, while IA4 of 20 %, both values being 2.5 times higher than the errors generated by the  $^{210}\text{Pb}$  dating method.

## Precise determination of isotopic composition of lithium and potassium with use of improved three-filament thermal ionization ion source for TIMS

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Lithium has two naturally occurring stable isotopes  $^6\text{Li}$  and  $^7\text{Li}$  with abundances of 7.52 % and 92.48 %, respectively, and it belongs to the elements with the lowest abundance among light elements. In Li the lighter isotope is less abundant than the heavier one. Lithium have the largest relative mass difference (about 16 %) of any stable isotope pair except from hydrogen and helium, which is a favorable circumstance for their high fractionation in nature. The concentrations and isotope ratio ( $^7\text{Li}/^6\text{Li}$ ) of Lithium dissolved in groundwater and surface waters provide important geochemical information on their origin [1].

The ratio of potassium isotopes is used in potassium-argon method to determine the age of rocks, in which the potassium concentration is measured by the isotope dilution method. The accuracy of the obtained age determination strongly depends on the accuracy of the isotope ratio determination. Thermal ionization mass spectrometry (TIMS) is one of the methods of precise analysis of Li and K isotope ratios [2-5].

Lithium and potassium belong to the first group of the Periodic Table, so their ionization energy is relatively low. The thermal ionization ion source is therefore especially convenient for lithium and potassium as well. Our improved triple filament ion source is equipped with two evaporator filaments and one ionizer filament installed between them in front of the extraction slit, perpendicularly to the plane of that slit. The ionizer filament is wide enough to prevent cross-contamination processes, so different samples can be loaded on the evaporator filaments and their isotope ratios can be measured one after another without venting the spectrometer chamber. To avoid any cross-contamination, the measuring time should be kept relatively short.

The ion source should enable independent control of the temperature at which the sample evaporates and of the temperature at which ionization occurs to get stable ion current beam. Additionally, appropriate ion optics systems are needed to effectively drive the majority of generated ions into the mass analyzer. Therefore in our triple filament ion source we also successfully modified the overall ion optics in order to improve its efficiency.

The values of  $\delta^7\text{Li}$  for the samples of natural waters by TIMS method is achieved with reproducibility of about a few permil or better. This method of lithium isotope determination requires neither complicated chemical preparation of the investigated samples, nor large quantities of material, thus being one of the simplest methods.

In the full presentation during the conference it will be presented: (1) the method of sample preparation, (2) the schematic diagrams and photos of our modified triple filament ion source, (3) numerical simulations of the ion beam forming in the ion source, (4) mass spectra of K and Li obtained by using our ion source, (5) some results of Li isotope analysis in lithium-abundant mineral waters from three geological regions of Poland: Carpathians Mts., Carpathian Foredeep and Holy Cross Mts.

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## **Isoprime100 instrument and gas geochemical application, determination of thermal maturity**

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Isoprime100 GC-IRMS instrument is capable to measure low concentration of natural gas. We measure carbon isotope ratio of mud gas (isotube) and cutting gas beside test gas. The gas may be biogenic, thermogenic or mixed and carbon isotope ratio depends on its origin. Thermal maturity determination is important in hydrocarbon industry. We use C1-C4 component carbon isotope ratio for thermal maturity determination.

## **Investigation and development of generator of technetium-99m based on activation and wasteless technology**

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Technetium-99m is generated by beta-decay of parent radioisotope of molybdenum-99 (<sup>99</sup>Mo). In medical laboratories for its separation from <sup>99</sup>Mo the generators of technetium are used. Chromatographic generators are characterized by their compactness and simplicity of usage, they are the most widespread in the world. In chromatographic generators <sup>99</sup>Mo is used, which is received from the reaction of the fission of <sup>235</sup>U that results in the great amount of radioactive waste. The real alternative to the uranium technology is organization of almost waste free processing of <sup>99</sup>Mo based on the use of reaction of radiological capture (n,γ) in research reactors.

The process of washout of technetium-99m by sodium chloride solution from the column sorbent is the most critical in the operation of the generator. This process is the ion exchange, but ionic displacement also takes place. Various researchers have considered the problems associated with the elution of technetium-99m from the generators. In order to eliminate undesirable effects it is optimal to keep the generator of technetium-99m free of saline (dry) in between "daily elutions". It helps to reduce the radiolysis of water and accordingly – of the recovery pertechnetate.

Also it is necessary to evaluate the influence of stabile molybdenum on the yield of technetium-99m. There was established the dependence of the yield of technetium-99m out of the generator from the adsorbed mass of molybdenum. This dependence allows determination of the mass of molybdenum which is required for the desired production of the generator with a given activity of technetium-99m [1]. There was established the coefficient of proportionality for the sorbent which enables to determine the maximum weight of molybdenum adsorbed on the column of the generator, at which 100 % yield of <sup>99m</sup>Tc is achieved. This coefficient depends on the dispersion and the characteristics of the pore structure of the sorbent.

On the basis of this research carried out at the Tomsk Polytechnic University in cooperation with Sibnuclon Ltd. there takes place the development of the unique construction of a new-generation generator of technetium-99m. This is a one-needle generator of technetium-99m with the systems of column purge and prepackaging of the eluate with a given activity.

This work was supported by the Russian Federation represented by the Ministry of Education and Science of Russia (project № RFMEFI57514X0034).

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## **Application of $^{14}\text{C}$ method for biogenic component determination in waste and liquid fuels**

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Increase of  $\text{CO}_2$  concentration in the atmosphere during 20<sup>th</sup> century is a consequence of intensive use of fossil fuels. The increase of  $\text{CO}_2$  concentration can be slowed down by the use of biogenic materials for energy production and/or transport.

One of the method for determination of the fraction of the biogenic component in any type of fuel or waste is the  $^{14}\text{C}$  method, which is based on different content of  $^{14}\text{C}$  in biogenic (reflects the modern atmospheric  $^{14}\text{C}$  activity) and in fossil component (no  $^{14}\text{C}$  present). The method can be applied to various types of fuels used in waste-to-energy plants (such as solid communal waste, used car tyres), to liquid fuels, even to the  $\text{CO}_2$  produced by combustion of various fuels. Any measuring technique used in  $^{14}\text{C}$  dating laboratories could be used. Here we present comparison of characteristics (precision, complexity, price) of various techniques (sample preparation and measurement) for biogenic fraction determination by the  $^{14}\text{C}$  method.

A case of liquid fuels will be specially discussed. According to the EU Directive 2009/28/EC all (liquid) fuels have to contain at least 10 % of bio-fuel, i.e., blend of biogenic origin, by 2020. A technique of direct measurement in liquid scintillation counters of the  $^{14}\text{C}$  content in liquid fuel is simple and fast but has a main disadvantage: different liquid colours cause different quenching and thus changes in the measurement efficiency. We propose a new data evaluation technique that uses liquids of different colours to construct calibration curves for modern and background samples [1]. The technique depends neither on the fossil matrix or the biogenic additive type. Lowest detectable biogenic fraction is 0.5 %.

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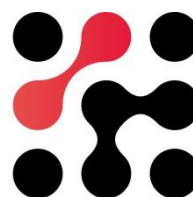


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