ICSI Rm. Valcea

The XIVth Workshop of the European Society for Isotope Research
- ESIR 2017 -

Băile Govora, ROMANIA
25-29 June, 2017

Book of Abstracts

RAMNICU VALCEA
- 2017 -

ESIR Isotope Workshop XIV

European Society for Isotope Research – ESIR 2017
Băile Govora, Romania

June 25 – 29, 2017

Book of Abstracts

RÂMNICU VÂLCEA
2017

Book of Abstract: ESIR Isotope Workshop XIV
June 25-29, 2017, Băile Govora, Romania

ESIR Isotope Workshop XIV
Băile Govora, Romania, June 25-29, 2017

Publisher: National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI Rm. Vâlcea

Editor: Roxana Elena IONETE
Graphics: Camelia ASPRITA

Number copies: 100

ISBN: 978-973-0-24503-5

EUROPEAN SOCIETY FOR ISOTOPE RESEARCH

ESIR

The XIVth Workshop of the European Society for Isotope Research

- ESIR 2017 -

25-29 June 2017

Palace Hotel, **Băile Govora, ROMANIA**

Greetings of the organizers

Isotope Workshop of the European Society for Isotope Research (ESIR) has been organized successfully since its establishment in Lublin, Poland (1992), Książ, Poland (1994), Budapest, Hungary (1996), Portorož, Slovenia (1998), Kraków, Poland (2000), Tallinn, Estonia (2002), Seggauberg, Austria (2004), Leipzig, Germany (2005), Cluj-Napoca, Romania (2007), Złotniki Lubańskie, Poland (2009), Budapest, Hungary (2011) Freiberg, Germany (2013), and Zadar, Croatia (2015).

The XIVth Edition – ESIR 2017 is organized in Romania, at Băile Govora, and hosted by the National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI Rm. Vâlcea. It is a pleasure for the European Society for Isotope Research (ESIR) and for us, the organizers, to welcome you at ESIR 2017. We aim to bring together specialists in the different fields related to isotopes (radioisotopes, stable isotopes and non-traditional stable isotopes), to present state-of-the-art developments as well as key examples of application and to promote exchange of ideas between scientists.

This event its entended to serve as an exchange forum for scientists sharing the same passion for isotopes, from both academic and non-academic media, encouraging communication and collaboration across different areas of isotope applications, beyound the countries boundaries.

Based on your undertaking to present your new findings, data and methodologies, the scientific programme has grouped in six sections covering a broad range of topics, from "*Geology, earth science and paleoclimatology", "Environmental science, ecology and speleology", "Methodological and instrumental developments", "Hydrology and Geochemistry" with a special subsection for "Isotopes in precipitation across Europe",* to other *"General interest application: archeology, food safety, materials"*. Were received more than 91 contributions from 19 countries.

We are confident that each of us will contribute to make ESIR 2017 a successful workshop. Let's take advantage of these days of great scientific significance, aiming to gain new knowledge and colaborations, and enjoy the tranquility and beauty of nature that surrounds us here in Băile Govora.

We wish you a joyful time here in Băile Govora and an inspiring ESIR 2017!

On behalf of the organizing committee and ESIR Advisory Board,

Roxana Elena Ionete,
ESIR chairman, Head of the Department of Research-Development and Technology Transfer, National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI Rm. Vâlcea, Romania.

ESIR Isotope Workshop XIV

Băile Govora, Romania

June 25-29, 2017

Advisory Board

Roxana Elena Ionete – ESIR President (Romania)
Albrecht Leis – ESIR Vice President (Austria)
Stanisław Hałas - ESIR Vice President (Poland)
Diana Costinel – ESIR Secretary (Romania)
Nada Horvatinčić (Croatia)
Marion Tichomirowa (Germany)
István Fórizs (Hungary)
Adriana Trojanowska-Olichwer (Poland)
Bogdan Onac (USA)
Ana-Voica Bojar (Austria)
Mariusz-Orion Jędrysek (Poland)
Sonja Lojen (Slovenia)

Local Organising Committee:

Chair:	Roxana Elena Ionete - ICSI Rm. Vâlcea
Co-chairs:	Vasile Stanciu - ICSI Rm. Vâlcea
	Aurel Perşoiu - Ştefan cel Mare University, Suceava
	Forray Ferenc Lázár - Babeş-Bolyai University, Cluj-Napoca
Members:	Ioan Ştefănescu - ICSI Rm. Vâlcea
	Gheorghe Ioniţă - ICSI Rm. Vâlcea
	Carmen Varlam - ICSI Rm. Vâlcea
	Diana Costinel - ICSI Rm. Vâlcea
	Oana Romina Botoran - ICSI Rm. Vâlcea
	Raluca Popescu - ICSI Rm. Vâlcea
	Nicolae Şofîlcă - ICSI Rm. Vâlcea

SPEAKERS

Dr. Damian AXENTE

Senior research scientist at the National Institute for Research and Development of Isotopic and Molecular Technologies - ITIM Cluj-Napoca, Department of Physics and Technology of Isotopes (Romania)

Dr. Olivier F. X. DONARD

Director of the MARSS project "Center for Mass Spectrometry and Reactivity for Speciation Sciences", IPREM UMR 5254, Hélioparc, 64053 Pau (France)

Dr. Jaleh GHASHGHAIE

Professor at Université Paris-Sud, Paris-Saclay, Lab Ecologie, Systématique et Evolution, Orsay (France)

Dr. Pier A. de GROOT

Delta Isotopes Consultancy, Oostham (Belgium)

Dr. Christophe LÉCUYER

Professor of Geochemistry at Université Claude Bernard Lyon 1 and Institut Universitaire de France, Department of Earth Sciences, CNRS UMR 5276, Campus de la Doua, 69622 Villeurbanne (France)

Prof. Kazimierz ROZANSKI

Professor at **AGH University of Science and Technology,** Faculty of Physics and Applied Computer Science, Kraków (Poland)

Dr. Dariusz STRĄPOĆ

Senior Interpretation Development Geochemist at Schlumberger, Drilling & Measurements. Paris, (France)

Dr. Ashok VASEASHTA

Vice Provost for Research and Professor of Physics at the Molecular Science Research Center; Director of Research at the Institute for Advanced Sciences Convergence and International Clean Water Institute for Norwich University Applied Research Institutes, Herndon, VA (USA).

Information

Oral presentations

Keynote lectures are 30 minutes long (20-25 minutes presentation and 5-10 minutes discussion). Oral presentations are 15 minutes long (recommended: 10-12 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 space adjacent to the conference room and the material for setting the posters up is available at the Registration desk. Poster board dimensions are 70 cm (width) by 100 cm (length). There are two poster sessions, one on Monday, 26 June afternoon and the other on Wednesday, 28 June 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 Poster Presentation section in the Workshop Programme). Poster presenters should be available for discussion at their poster display during the scheduled time.

CONTENTS

HIDROLOGY AND GEOCHEMISTRY

ISOTOPES IN PRECIPITATION ACROSS EUROPE

GEOLOGY, EARTH SCIENCE AND PALEOCLIMATOLOGY

ENVIRONMENTAL SCIENCE, ECOLOGY AND SPELEOLOGY

HYDROCARBONS, PETROLEUM SYSTEMS, ENERGY INDUSTRY

METHODOLOGICAL AND INSTRUMENTAL DEVELOPMENTS

ISOTOPE GENERAL INTEREST APPLICATIONS: ARCHEOLOGY, FOOD SAFETY, MATERIALS

ISOTOPES IN THE ATMOSPHERE: WHAT CAN WE LEARN?

Kazimierz Rozanski

AGH University of Science and Technology, Faculty of Physics and Applied Computer Science,
Al. Mickiewicza 30, 30-059 Krakow, Poland
rozanski@agh.edu.pl

Earth's atmosphere is a dynamic reservoir containing both radioactive and stable isotopes of various elements. Radioactive isotopes present in the atmosphere have three major sources: (*i*) *in-situ* production via interactions of cosmic rays with atmospheric nuclei, (*ii*) releases of radioactive isotopes from the earth's surface and their subsequent transformations in the atmosphere, and (*iii*) anthropogenic emissions. Concentrations of radioactive isotopes in the atmosphere are controlled by spatio-temporal characteristic of sources and sinks, radioactive decay rates, and by atmospheric transport processes. Apart of radioactive labelling of some atmospheric constituents, also distinct differences in stable isotope composition of those constituents may occur, which can be further explored from the perspective of their potential applications. This is particularly true for atmospheric water vapour which belongs to the global water cycle and for atmospheric carbon dioxide which takes part in the global carbon cycle. While radioactive labelling of atmospheric constituents provides the opportunity to quantify time scales of diverse processes such as interhemispheric mixing of the atmosphere or exchange rates between the atmosphere and adjacent reservoirs (hydrosphere, lithosphere, biosphere), and provides the basis for various dating methods, phase changes and biogeochemical interactions associated with cycling of elements in nature produce specific stable isotope imprints which can be further explored as potential source indicators.

An overview on radioactive and stable isotopes of light elements occurring in the atmosphere will be presented. Emphasis will be given to isotopes of hydrogen, carbon and oxygen, from the perspective of their current and potential future applications. Examples of the usage of radioactive and stable isotope labelling associated with water and carbon cycle will be discussed in some detail.

Keywords: atmosphere, radioactive isotopes, stable isotopes, carbon cycle, water cycle.

AUTHIGENIC FORMATION OF NANOSTRUCTURED CALCITE IN A LACUSTRINE KARSTIC ENVIRONMENT (KUTI LAKE, CROATIA): STABLE ISOTOPE AND *FESEM* STUDY

Sonja Lojen[1,2], Srečo D. Škapin[1], Maja Ivanić[3], Tamara Troskot-Čorbić[4], Ivan Sondi[5]

[1]Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia;
[2]University of Nova Gorica, Vipavska cesta 13, 5000 Nova Gorica, Slovenia;
[3]Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia;
[4]INA-Industrija nafte d.d., Lovinčićeva 4, 10002 Zagreb, Croatia; [5]Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia
Corresponding author: *Sonja.Lojen@ijs.si*

The formation of authigenic calcite and isotopic composition of the sedimentary organic matter (SOM) and carbonate in a unique semi-enclosed lacustrine sedimentation system of a transitional deltaic land-sea environment of the Kuti Lake were investigated. The primary objective of this study was to determine the source of carbonaceous materials in recent sediments, particularly the relationship between the authigenically precipitated calcite and the allochtonous detrital carbonate.

The Kuti Lake is a karstic cryptodepression (altitude of the water table 0 m a.s.l.), situated in a karstic valley in the south-eastern part of the Neretva River delta plain in southern Dalmatia, Croatia. This semi-enclosed environment is part of a pristine wetland, subjected to riverine influence through porous karstic bedrock, deltaic deposits and occasional floods. The surrounding rocks are Triassic and Eocene carbonates (limestone, dolostone) and flysch. The lake is shallow (up to 4.5 m), non-stratified and predominantly freshwater, with occasional intrusions of seawater through the karstic bedrock (salinity up to 5 PSU). The trophic status of the lake is unclear, since it was characterised as eutrophic or oligotrophic by different authors within a period of few years.

Two sediment cores were analysed - one from the deepest part of the lake (sampling depth 4.5 m, length of the core 1 m) and another, from the secluded shallow area (sampling depth 1 m, length of the core 0.8 m). Redox potential and pH were measured on site in the sediment core immediately after retrieval. The sediments were cut into 2 cm segments and frozen until further analyses.

The particle size of sediments was analysed using laser diffraction (LD) while the mineral composition was examined by X-ray diffraction (XRD). The content of organic matter and carbonates were determined by the sedimentary organic carbon (Rock Eval pyrolysis) and nitrogen (EA-IRMS) analyses. The stable isotope compositions of C and N of sedimentary organic matter and carbonate mineral phase were analysed by EA-IRMS and ANCA-TG coupled to IRMS systems, respectively. The morphology of mineral particles was examined by field emission scanning electron microscope (FESEM).

The results showed that the river influence on the lake sediment is limited to occasional short-term flood events, which drain significant amount of organic and mineral detritus into the lake. Nevertheless, the authigenic formation of nanostructured calcite was found to be the most important source of sediments in the recent past. It can be produced by biomineralisation or abiotically by precipitation from supersaturated interstitial water, under prevailing physical and biogeochemical conditions. The FESEM analyses showed that calcite predominantly occurs in irregular and nanostructured forms typical for authigenically precipitated anhydrous carbonates, consisting of almost spherical nanosized subunits (Figure 1A).

Previous studies have shown that identical nanoscale morphological features of calcite can be formed in the presence of organic matter (Sondi *et al.*, 2008) and through the biological activities of bacteria that can govern initial formation and morphogenesis of carbonates on the nanoscale (Obst *et al.*, 2009). A compelling example of such precipitate is shown in Figure 1.

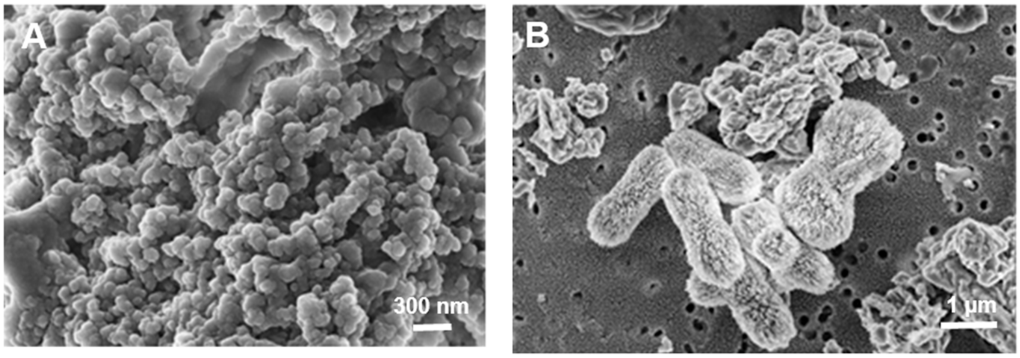


Figure 1. *The FESEM images of the authigenically precipitated calcite in the Kuti Lake sediments: the irregular shape of the early-formed nanostructured calcite precipitates (A) and calcite minerals precipitated on the bacteria cell walls (B).*

The stable isotope analysis of carbonates and sedimentary organic matter confirmed that calcites at both sampling stations were formed by active authigenic precipitation in the lake system, rather than by erosion of the surrounding carbonate rocks or terrigenous yields during the flood events. The δ^{13}C and δ^{18}O values of sedimentary carbonate (-6.2 to -0.7 and -9.5 to -2.7 ‰, respectively) were in most segments significantly lower than those determined in the surrounding carbonate rocks (in average +1.5 and -1.3 ‰, respectively), and indicate that the sedimentary carbonate is a mixture of meteogenic freshwater carbonate and detrital marine carbonates. The carbonates exhibiting high δ^{13}C values (around -1 ‰) and low δ^{18}O values are a result of calcite precipitation from interstitial water of meteogenic origin and ^{13}C-enriched dissolved inorganic carbon in methanogenic environment (Leng *et al.,* 2005; Rassmann *et al.*, 2016). This indicates intensive transfer of sedimentary carbon from the organic into the inorganic pool through the dissolution of biogenic CO_2 and its fixation in the authigenic mineral phase, resulting in predominantly authigenic origin of calcite in the investigated lake sediments.

Keywords: karst, lake, sediment, nanostructured calcite, stable isotopes

Acknowledgment: *The study was financed by the Croatian Science Foundation (NanoMin Project No. 2504), Slovenian Research Agency (research programmes P2-0091 and P1-0143) and the EU H2020 project MASSTWIN (contract No. 692241).*

References

Leng M.J., Lamb A.L., Marshall J.D., Wolfe B.B., Jones M.D., Holmes J.A., Arrowsmith C. (2005) Isotope in Lake Sediments. In: Leng M.J. (Ed.), Isotopes in Palaeoenvironmental Research. *Springer*, pp. 147-184.

Obst M., Dynes J.J., Lawrence J.R., Swerhone G.D.W., Benzerara K., Karunakaran C., Kaznatcheev K., Tyliszczak T., Hitchcock A.P. (2009) Precipitation of amorphous $CaCO_3$ (aragonite-like) by cyanobacteria: A STXM study of the influence of EPS on the nucleation process. *Geochimica et Cosmochimica Acta* 73:4180-4198.

Rassmann J., Lansard B., Pozzato L., Rabouille C. (2016) Carbonate chemistry in sediment porewaters of the Rhône River delta driven by early diagenesis (northwestern Mediterranean). *Biogeosciences* 13:5379–5394.

Sondi I., Škapin S.D., Salopek-Sondi B, *et al.* (2008) Biomimetic precipitation of nanostructured colloidal calcite particles by enzyme-catalyzed reaction in the presence of magnesium ions. *Crystal Growth & Design* 8:435-441.

CRITICAL ZONE IMPACT ON GROUNDWATER SALINIZATION DETERMINED FROM O, H, SR, AND ^{36}CL ISOTOPES IN THE BUFFELS RIVER, SOUTH AFRICA

Jani van Gend[1], **Jodie Miller**[1], **Catherine Clarke**[2], **Petrus Le Roux**[3],
Keith Fifield[4], **László Palcsu**[5]

[1] *Department of Earth Science, University of Stellenbosch, Stellenbosch, 7600, South Africa*
[2] *Department of Soil Science, University of Stellenbosch, Stellenbosch, 7600, South Africa*
[3] *Department of Geological Sciences, University of Cape Town, Rondebosch, 7701, South Africa*
[4] *Research School of Physics, Australian National University, Canberra, Australia*
[5] *Institute for Nuclear Research, Hungarian Academy of Sciences, H-4026 Debrecen, Hungary*
Corresponding author: *16455266@sun.ac.za (Jani van Gend)*

Agriculture is one of the main economic drivers in rural areas in Africa. However, agriculture uses large amounts of water which are often in short supply and the quality of the available water is often quite variable. The Buffels River valley in the Northern Cape of South Africa has no surface water resources and is wholly dependent on either potable water pumped from the perennial Orange River ~130 km to the north or local groundwater. Agriculture is the chief economic activity but groundwater in this catchment is mostly saline (salinity >1.4 psu or electrical conductivity (EC)> 2000µS/cm) and is therefore a major inhibitor to economic development. Because of the extremely high aridity in the region combined with high evaporation rates, salinity is thought to be a function of evaporation causing concentration of salts in the critical zone which are then flushed into the groundwater system when the winter rains fall. This project uses a variety of isotope systems to examine the groundwater system in this region and specifically to understand the processes of salt accumulation and transport within the critical zone and hence its impact on both the shallow and deep groundwater systems.

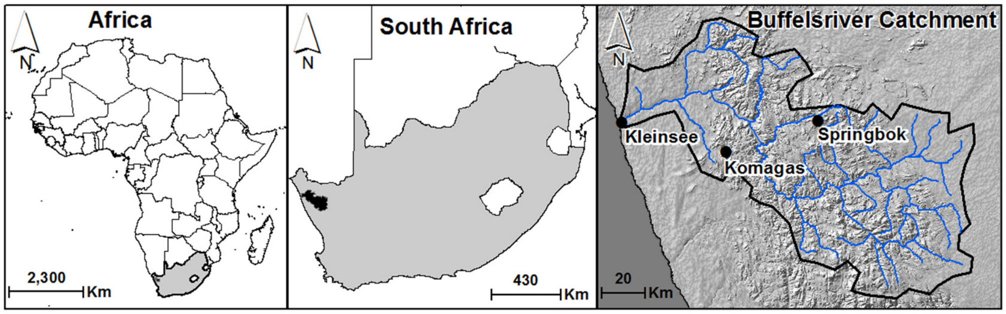


Figure 1. *The location of the Buffels River valley in South Africa*

The Buffels River catchment covers an area of approximately 9250 km^2 making it the largest ephemeral river in Namaqualand. The headwaters are located in the

Kamiesberg Mountains on the Bushmanland Plateau and the river subsequently cuts down through an escarpment before emerging onto the Tertiary coastal plain. Surface flow is rare and typically lasts only a few days after high rainfall events and is restricted to short sections of the river usually close to the point of emergence from the escarpment zone. Water within the catchment is almost exclusively hosted by shallow alluvial and perched aquifers (< 25 m) within the main river drainage although deeper basement aquifers are also present. The shallow alluvial aquifers result from alluvial fill discontinuities into the river valley which are further segmented into smaller aquifers by the irregular surface of the underlying basement gneisses (Benito *et al.*, 2011).

Within the river valley, the critical zone is dominated by sandy sediments largely derived from the surrounding Mesoproterozoic granitic gneisses. However, in places "Heuweltjies", evenly spaced circular mounds approximately 10 m in size consisting of soil and sediment with different geochemical characteristics, are prominent. Sections of the heuweltjies often contain highly saline sediment and is a possible source of the groundwater salts. The Heuweltjies are thought to be formed by the nesting and burrowing actions of the Southern Harvester Termite (Booi, 2011) and although undated, are considered to be "reasonably" old structures.

Sections within the Heuweltjies have elevated Na^+, K^+, Cl^- and SO_4^{2-} and EC levels over 2000µS/cm, similar to the local adjacent shallow groundwater. In other sections of the river, the groundwater EC drops to ~1200 µS/cm. Sr isotope analysis of groundwater shows very high $^{87}Sr/^{86}Sr$ ratios, in excess of 0.72225, with the highest value recorded being 0.78241. These values are derived directly from the local basement gneisses which also have distinctly radiogenic$^{87}Sr/^{86}Sr$ ratios in comparison to other local rock types. $^{36}Cl/Cl$ ratios were obtained on eight groundwater samples and record values between 189.9 x 10^{-15} and 22.0 x 10^{-15} $at.at^{-1}$. One sample of rainwater was also analysed and had a Cl^{36}/Cl ratio of 84.9 x 10^{-15} $at.at^{-1}$. In combination $^{87}Sr/^{86}Sr$ and $^{36}Cl/Cl$ isotope ratios indicate mixing of multiple groundwater components. $\delta^{18}O$ and δD ratios indicate that the groundwater is likely not derived from local rainfall since rainwater has a deuterium excess of ± 19, whilst the shallow groundwater has a deuterium excess of less than ± 10 and the shallow groundwater plots on an evaporation trend that intersects the local meteoric water line (LMWL) below the range of local rainwater $\delta^{18}O$ and δD ratios. This is consistent with the $^{36}Cl/Cl$ data where the coastal rainwater has $^{36}Cl/Cl$ ratios too low to be the source of the ^{36}Cl in the shallow groundwater system.

Currently, the working hypothesis is that the $^{36}Cl/Cl$ ratios are derived from leaching of salts in the Heuweltjies that formed under different climatic conditions in the past to account for the elevated $^{36}Cl/Cl$ ratios. The $\delta^{18}O$ and δD ratios may also have been derived from rainwater in the past when wetter colder conditions would have resulted in lower $\delta^{18}O$ and δD ratios than modern rainwater. However, in both cases it cannot be excluded that the $\delta^{18}O$, δD and $^{36}Cl/Cl$ ratios are derived from recharge further inland where the topographyis elevated. A further possibility is that the residence time of the chloride in the groundwater system is different to the residence time of the groundwater itself. This would be consistent with modern higher elevation recharge leaching old salt from the Heuweltjies as it passes down the catchment. Noble gas data currently being processed may shed further light on the age of the shallow groundwater and this may help clarify the groundwater interactions taking place. Understanding these interactions is critical to efforts to develop agriculture in the region because this would involve reworking of the Heuweltjies and might inadvertently release even higher salt loads into the groundwater system.

Keywords: Isotope Hydrology, Saline Groundwater, South Africa, Heuweltjies.

Acknowledgments: *This research is supported by the Water Research Council in South Africa. We acknowledge the logistical support provided by Emile Wegner and Danny de Wet as well the assistance from the NariesNamaqua Guest Lodge.*

References

Benito G., Botero B.A., Thorndycraft V.R., Rico M., Sánchez-Moya Y., Sopeña A., MacHado M.J., Dahan O. (2011) Rainfall-runoff modelling and palaeoflood hydrology applied to reconstruct centennial scale records of flooding and aquifer recharge in ungauged ephemeral rivers, *Hydrology and Earth System Sciences* 15: 1185-1196.

Booi N. (2011) *Structure and function of heuweltjies across a rainfall gradient in the South-Western Cape. Dissertation*, University of Stellenbosch.

APPLICATION OF STABLE ISOTOPES FOR INVESTIGATING THE DYNAMICS OF WATERS IN ROSIA MONTANA AND ZLATNA MINING AREAS

Calin Baciu[1], Delia Papp[2], Alexandra Cozma[1]

[1]Babes-Bolyai University, Faculty of Environmental Science and Engineering, 30, Fântînele Street, Cluj-Napoca, 400294, Romania
[2]Geological Institute of Romania, 1 Caransebeş Street, Bucharest, 012271, Romania
Corresponding author: *deliapapp@yahoo.com*

Problems related to water resources quality have become more and more critical, especially in areas that suffer a significant environmental impact. Mining activities are recognized as important polluters; however the contamination continues also after the the operation has ceased if proper measures of decommissioning and site remediation are not taken. We performed a comparative study based on isotopes in two representative mining areas, in order to assess the dynamics and water exchange between the underground and surface environment.

Rosia Montana and Zlatna gold mining areas are located in the Metaliferi Mountains of the South Apuseni mountain range (Romania). They belong to the "*Golden Quadrilateral*" mining district (900 km^2) which is well known for a long mining tradition that spans over the last 2000 years.

A systematic sampling campaign at these two mining sites has been conducted. All present types of water were included in the study: groundwaters, surface waters, mine waters and lakes. For Rosia Montana were chosen 28 sites (12 surface waters, 7 mine waters, 5 lakes and 4 drinking waters/ground waters). At Zlatna 25 sites were sampled (10 surface waters, 8 mine waters, 4 springs and 5 domestic wells). Samples were collected on a monthly basis from August 2013 to August 2015 at Rosia Montana, and from January 2015 to December 2015, at Zlatna.

A Picarro CRDS L2130-I analyser was used for the water isotopic analyses. The isotopic data are reported in the usual δ notation.

The results suggest that the water bodies from both Rosia Montana and Zlatna mining area have a meteoric origin (Figure 1). The range for all water types for both areas in case of δ^{18}O spans between –11.56‰ and –2.58‰, while for δD the values are in the range –80.54‰ to –32.11‰. Due to the different morphology of the area, at Rosia Montana the waters have a more pronounced shift to the right side of the LMWL than the waters from Zlatna. The deviation of the isotopic composition of lakes from the GMWL and LMWL are a consequence of evaporation processes. The slope of LEL is 5 at Rosia Montana, and 6 at Zlatna, and these are similar values to those defined by Clark and Fritz (1997) for moderate relative humidity. Precipitation is the main source of infiltration for both mining areas.

The complexity of the 140 km underground galleries in Rosia Montana increase the residence time of mine waters, modifying their initial isotopic composition. The mine waters from Rosia Montana are more affected by the seasonal variation than the mine waters from Zlatna (Figure 2 a, b). At Zlatna site, due to complete flooding of underground workings after mine closure, favourable conditions for mixing were created, and therefore seasonal variations in the isotopic composition of mine waters are more flattened.

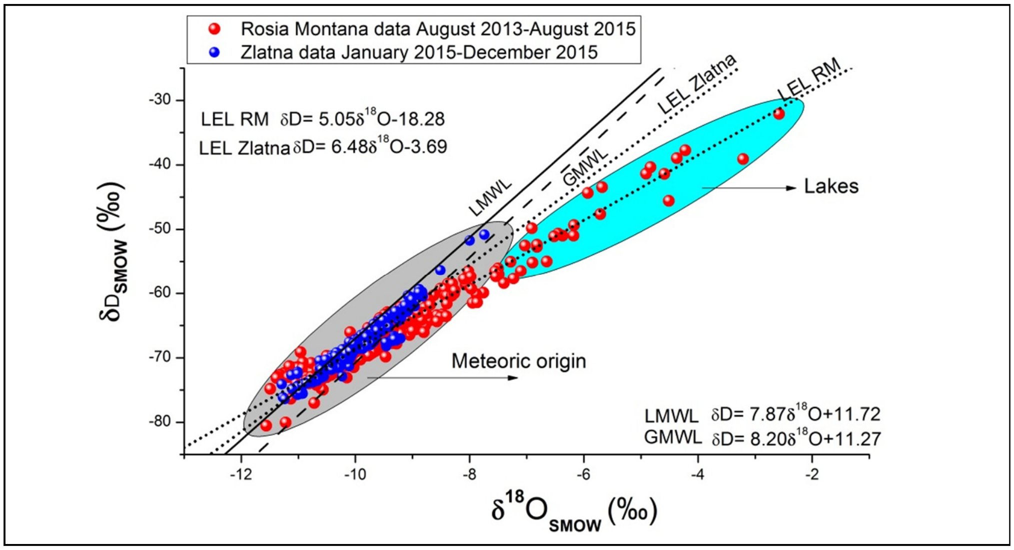


Figure 1. *Isotopic composition of all water types for both mining areas. Red dots represent the data from Rosia Montana, and blue dots represent data from Zlatna. The LMWL proposed for Rosia Montana (Cozma et al., 2017), and the GMWL established (Rozanski et al., 1993) were used.*

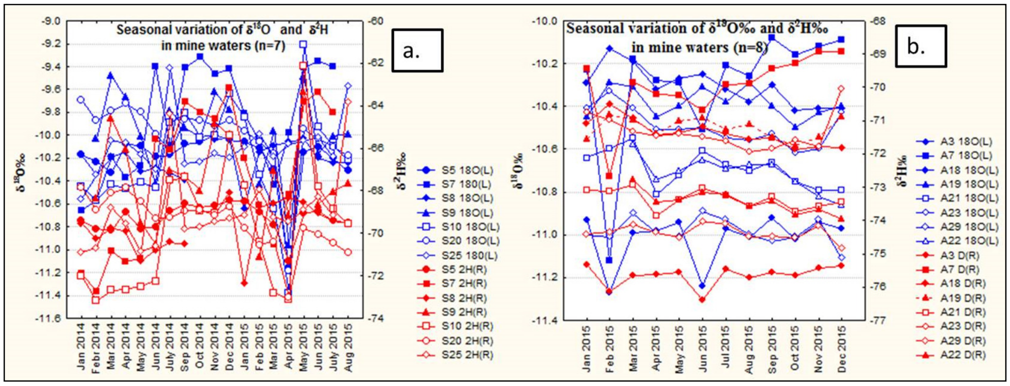


Figure 2. *Seasonal variation of $\delta^{18}O$ and δD values for both mining areas*
(a - Rosia Montana, b - Zlatna)

Keywords: water isotopes, mining areas, acid mine drainage, LMWL, recharge.

Acknowledgments: *This work was financially supported by a grant of the Romanian National Authority for Scientific Research, CCCDI – UEFISCDI, project 3-005 "Tools for sustainable gold mining in EU (SUSMIN)". The authors are grateful to Dr. Forray Ferenc (Babes-Bolyai University) for valuable help with the laboratory analysis.*

References

Clark I.D., Fritz P. (1997) Environmental isotopes in hydrogeology. CRC Press/Lewis Publishers, Boca Raton, 328 pp.

Cozma A., Baciu C., Papp D., Rosian G., Pop C. (2017) Isotopic composition of precipitation in Western Transylvania (Romania) reflected bt two local meteoric water lines. *Carpathian Journal of Earth and Environmental Sciences* 12(2):357-364.

Rozanski K., Araguas-Araguas L., Gonfiantini R. (1993) Isotope patterns in modern global precipitation. *Geophysical Monograph* 78: 1-35.

GAS GEOCHEMICAL SURVEY OF CIOMADUL VOLCANO (SOUTH HARGHITA MTS., ROMANIA): CONSTRAINTS ON THE ORIGIN OF FLUIDS

Boglárka-Mercedesz Kis[2], Artur Ionescu[1,2], Calin Baciu[1], Szabolcs Harangi[2], László Palcsu[3], István Futó[3]

[1]MTA-ELTE Volcanology Research Group, Department of Petrology and Geochemistry, Institute of Geography and Earth Sciences, Eotvos University Budapest (ELTE), Pazmany setany 1/C, Budapest, H-1117, Hungary
[2]Babes-Bolyai University, Faculty of Environmental Science and Engineering, Fântînele 30, Cluj-Napoca, 400294, Romania
[3]Institute for Nuclear Research, Hungarian Academy of Sciences, Bem tér 18/C, H-4026 Debrecen, Hungary
Corresponding author: *kisboglarka85@gmail.com*

Geochemical survey of quiescent volcanoes are important from the point of view of knowledge and understanding of some unexpected and highly hazardous events, volcanic eruptions, sudden degassing related to their presence (Carapezza *et al*., 2012; Sano *et al*., 2015). In our present work we give the results of the first comprehensive gas geochemical survey at Ciomadul dormant volcano, South Hargita Mts., Romania.

Ciomadul is the youngest volcano of the Carpathian-Pannonian region. Although no more volcanic eruptions are known since ca. 32 ka, collective evidences from geology, petrology and geophysics (Popa *et al*., 2012; Szakács and Seghedi, 2013; Harangi *et al*., 2015) indicate that future eruptions at Ciomadul cannot be excluded.

The chemical composition of gas samples indicates a dominant CO_2 content. Besides CO_2, other gases like CH_4, N_2, H_2S, Ne, and relatively important amounts of He (up to 0.05%) are present in the gas samples. The isotopic composition of He range between 0.14 to 3.25 Ra (air-normalized $^3He/^4He$ reported as R/Ra, where R= $^3He/^4He$ sample; Ra =atmospheric $^3He/^4He$ ratio = 1.4×10^{-6}), the $\delta^{13}C_{CO2}$ ranges between -1.40‰ and -4.61‰ vs. PDB.

Due to helium's chemical inertness, its isotopes are useful tracers of the origin of fluids. In the case of dormant volcanoes it has been demonstrated that active degassing of volatiles from cooling magmatic bodies/chambers occurs for a very long time after the last volcanic activity. It was proposed that the genesis of the gases vented over the area of Harghita Mts is mainly volcanic (Althaus *et al*. 2000; Vaselli *et al*. 2002), while moving westwards the Transylvanian Basin and eastward to the Carpathian Foredeep is characterized by crustal-type helium associated to hydrocarbon reservoirs (Etiope *et al*. 2004; Baciu *et al*. 2007). Our present data, with air-corrected helium isotopic ratios up to 3.25 R/Ra_c are fully consistent with their findings, suggesting a magmatic contribution for these volatiles.

Carbon isotopic composition $\delta^{13}C_{CO2}$ of the studied samples range between –1.40‰ and -4.61‰ vs. VPDB, consistent with previous measurements in the area: –4.4 to –4.7‰ (Vaselli *et al*., 2002). The isotopic compositions of the samples fall within the overlapping range of both the mantle degassing origin and provenance from thermal metamorphism of carbonate rocks in the basement.

The samples also show a wide range in $CO_2/^3He$ ratio, spanning between values lower than MORB, values similar to MORB, and values 1 to 2 orders of magnitude higher. On the basis of this wide range in the $CO_2/^3He$ ratio and relationship with the helium isotopic composition (R/Ra) the origin of CO_2 could be predominantly mantle-derived with significant component of crustal CO_2 for some samples.

Keywords: Ciomadul, dormant volcano, noble gases, origin of fluids.

Acknowledgments: *This research belongs to the scientific project supported by the OTKA (Hungarian National Research Fund) project number K116528, the Romanian National Research Council, CNCS – UEFISCDI, project number PN-II-ID-PCE-2011-3-0537.*

References

Althaus T., Niedermann S., Erzinger J. (2000) Noble gas studies of fluids and gas exhalations in the East Carpathians, Romania. *Chemie der Erde* 60:189-207.

Baciu C., Caracausi C., Etiope G., Italiano F. (2007) Mud volcanoes and methane seeps in Romania: main features and gas flux. *Annals of Geophysics* 50:501-512.

Etiope G., Baciu C., Caracausi A., Italiano F., Cosma C. (2004) Gas flux to the atmosphere from mud volcanoes in eastern Romania. *Terra Nova* 16:179-184.

Carapezza M.L., Barbieri F., Ranaldi M., Ricci T., Tarchini L., Barrancos J., Fischer C., Granieri D., Lucchetti C., Melian G., Perez N., Tuccimei .P, Vogel A., Weber K. (2012) Hazardous gas emissions from the flanks of the quiescent Colli Albani volcano (Rome, Italy), *Applied Geochemistry* 27:1767-1782.

Harangi Sz., Novák A., Kiss B., Seghedi I., Lukács R., Szarka L., Wesztergom V., Metwaly M., Gribovszki K. (2015) Combined magnetotelluric and petrologic constrains for the nature of the magma storage system beneath the Late Pleistocene Ciomadul volcano (SE Carpathians), *Journal of Volcanology and Geothermal Research*, 290:82-96.

Popa M., Radulian M., Szakács A., Seghedi I., Zaharia B. (2012) New seismic and tomography data in the southern part of the Harghita Mountains (Romania, Southeastern Carpathians): connection with recent volcanic activity, *Pure and Applied Geophysics* 169:1557-1573.

Sano Y., Kagoshima T., Takahata N., Nishio Y., Roulleau E., Pinti D., Fischer T.P. (2015) Ten-year helium anomaly prior to the 2014 Mt. Ontake eruption, *Scientific Reports* 5: 13069, doi:10.1038/srep13069.

Szakács A., Seghedi I. (2013) The relevance of volcanic hazard in Romania: is there any? *Environmental Engineering and Management Journal* 12:125-135.

Vaselli O., Minissale A., Tassi F., Magro G., Seghedi I., Ioane D., Szakács A. (2002) A geochemical traverse across the Eastern Carpathians (Romania): constraints on the origin and evolution of the mineral waters and gas discharge. *Chemical Geology* 182:637–654.

STABLE ISOTOPES SURVEY OF OLT RIVER – MIDDLE BASIN (ROMANIA). ATTEMPTS ON NITROGEN SOURCE IDENTIFICATION IN THE VICINITY OF THE RAMNICU VALCEA INDUSTRIAL AREA

Raluca Popescu, Diana Costinel, Oana-Romina Botoran, Roxana-Elena Ionete

National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI,
Uzinei Street no. 4, 240050, Râmnicu Vâlcea, Romania
Corresponding author: *raluca.popescu@icsi*

The stable isotopes survey covered the middle portion of the Olt River, located in Vâlcea County (Romania), crossing from north to south a distance of 135 km. The δ^2H and δ^{18}O were measured from water samples collected during six consecutive years, from 21 sampling points on the Olt River and its main tributaries. A multi-annual Local Meteoric Water Line (LMWL), $\delta^2H = 8.04 x \delta^{18}O + 9.79$, was obtained. The oxygen isotopic composition (δ^{18}O) for all water samples ranged from -12.30‰ to -7.73‰, with a mean value of -9.83 ± 0.67‰. Hydrogen isotopic composition (δ^2H) of the water samples ranged between a minimum of -90.3‰ and a maximum of -54.6‰, with a mean of -70.2 ± 6.5‰. The isotopic values for the middle Olt River basin (Olt River and its tributaries) were distributed along the LMWL and had a linear correlation of $\delta^2H = 7.11 x \delta^{18}O – 0.21$ (Figure 1). Olt River presented lower values and smaller variations for both isotopes, compared with its tributaries. The small isotopic variations in Olt River can be explained by the presence of dams (which control the flow, thereby reducing seasonal isotopic variations) and the addition of groundwater with depleted and constant isotopic composition (Popescu *et al.*, 2014).

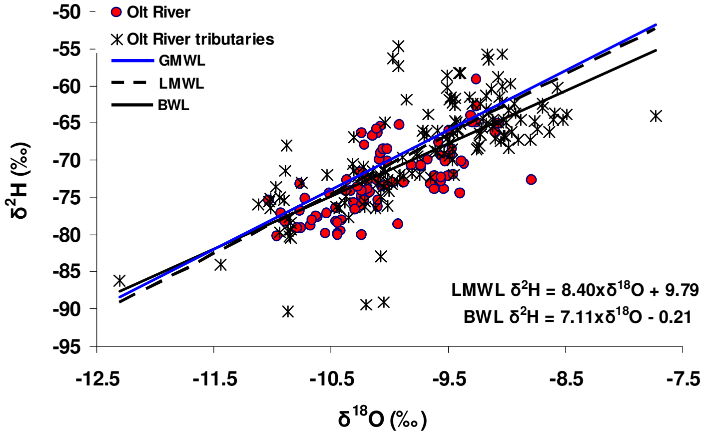


Figure 1. *δ-plot for the middle Olt River basin (LMWL - Local Meteoric Water Line, interrupted line; BWL – Basin Water Line, full line)*

Since tracing pollution sources and transformation of nitrogen compounds in surface- and groundwater is an issue of great significance worldwide due to the increased human activity, translated in high demand of water resources and pollution, in this work we also characterized, in terms of the physico-chemical and isotope composition - $\delta^{15}N$ of the inorganic nitrogen species, the hydrological basin of an important chemical industrial platform situated in the vicinity of Olt River (Ramnicu Valcea, industrial area). Throughout a period of one year, water samples from the Olt River and its more important tributaries were collected monthly in the industrial area, when the seasonal and spatial isotope patterns of the surface waters and the main sources of pollution were determined. Higher inorganic nitrogen concentrations (up to 10.2 mg NL^{-1}) were measured between November and April, which were designated as anthropogenic additions using mixing calculations. The main sources of pollution with inorganic nitrogen were agriculture and residential release. The inorganic nitrogen from the industrial waste water duct had a distinct $\delta^{15}N$ fingerprint (mean of −8.6‰). Also, one industrial release into the environment was identified for Olt River, at Ionesti site, in November. The mean precipitation samples had the lowest inorganic nitrogen concentrations (less than 5.5 mg NL^{-1}) with a distinct $\delta^{15}N$ fingerprint compared to the surface and industrial waters (Figure 2) (Popescu *et al.*, 2015).

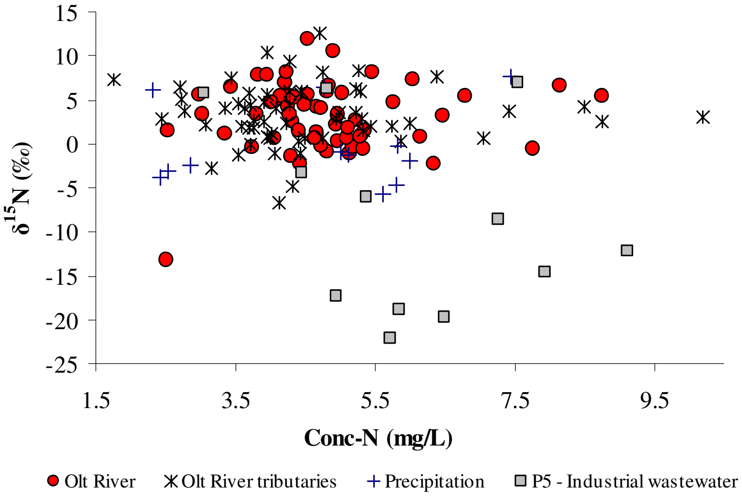


Figure 2. *$\delta^{15}N$ versus the total inorganic nitrogen concentration for all samples*

Keywords: stable isotopes, IRMS, Olt River, nitrogen-15.

References

Popescu R., Costinel D., Ionete R.E., Axente D. (2014) Isotopic fingerprint of the middle Olt River basin, Romania**,** *Isotopes in Environmental and Health Studies* 50(4):461-474.

Popescu R., Mimmo T., Dincă O., Capici C., Costinel D., Şandru C., Ştefănescu I., Ionete R., Axente D. (2015) Industrial area investigation using stable isotopes, *Science of the Total Environment* 353:17-23.

PALAEOCLIMATE RECONSTRUCTION BASED ON NOBLE GAS RECHARGE TEMPERATURES: TURONIAN AQUIFER, TADLA BASIN, MOROCCO

László Palcsu[1], Marianna Túri[1], Radouan Saadi[2], István Futó[1], Mihály Molnár[1], László Rinyu[1], Oum Keltoum Hakam[3], Hamid Marah[2]

[1]Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research, Hungarian Academy of Sciences, Bem tér 18/c, Debrecen, 4026 Hungary
[2]Centre National de l'Energie, des Sciences et Techniques Nucleaires (CNESTEN),
Rabat, Morocco, 65 rue Tansift, Agdal, Rabat, Maroc
[3]Department of Physics, Ibn Tofail University, Morocco 14 000, Kenitra, B.P 133.
Corresponding author: palcsu.laszlo@atomki.mta.hu

The present study is an environmental isotope investigation of groundwater samples from the Turonian Aquifer of Tadla Basin in Morocco for the purpose to reconstruct palaeotemperatures based on dissolved noble gas concentrations and radiocarbon dating. The collected groundwater samples were examined for $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$, water chemistry, noble gas concentrations, radiocarbon and tritium. Radiocarbon ages obtained from different isotope geochemical models indicates that the recharge of the unconfined and party the confined part of the aquifer occurred during the Holocene, while the most part of the confined aquifer contains water of the late Pleistocene.

The calculated noble gas solubility temperatures of the unconfined part of the aquifer are varying around the recent mean annual soil temperature of 22 °C. The noble gas temperatures of the confined part of the aquifer are a few degree C lower showing a colder recharge during the Last Glacial Maximum.

Keywords: groundwater, noble gas recharge temperature, palaeoclimate reconstruction, Tadla Basin, Morocco.

Acknowledgments: *The research was supported by the European Union and the State of Hungary, co-financed by the European Regional Development Fund in the project of GINOP-2.3.2.-15-2016-00009 'ICER'.*

THE STABLE ISOTOPIC COMPOSITION OF RIVERS IN ROMANIA

Aurel Perşoiu[1,2], **Bădăluţă Carmen-Andreea**[2,3], **Viorica Nagavciuc**[2,4], **Alexandru Onaca**[5], **Sandu Boengiu**[6], **George Murătoreanu**[7], **Florin Zainescu**[8]

[1]*Emil Racoviţă Institute of Speleology, Romanian Academy, Clinicilor 5, Cluj Napoca 400006, Romania*
[2]*Stable Isotope Laboratory, Ştefan cel Mare University, Universităţii 13, Suceava 720229, Romania*
[3]*Department of Geography, Ştefan cel Mare University, Universităţii 13, Suceava 720229, Romania*
[4]*Faculty of Forestry, Ştefan cel Mare University, Universităţii 13, Suceava 720229, Romania*
[5]*Department of Geography, West University, I.H. Pestalozzi 16, Timişoara 300115, Romania*
[6]*Department of Geography, University of Craiova, Al. Cuza 13, Craioca, Romania*
[7]*Faculty of Humanities, Valahia University, Târgovişte, Lt. Stancu Ion 35, Targoviste 130105, Romania*
[8]*Faculty of Geography, University of Bucharest, Bd. M. Kogălniceanu 36-46, Bucharest, Romania*
Corresponding author: *aurel.persoiu@gmail.com*

The aim of this study is to investigate the distribution of water isotopes in the Danube and its tributaries from the Southern Carpathian Mts. (in Romania), in order to determine the sources of precipitation feeding these rivers and their temporal dynamics in connection to climate.

Precipitation was collected monthly between March 2012 and June 2017 at 14 stations across Romania, and river water between August 2014 and June 2017, at 16 stations (Figure 1).

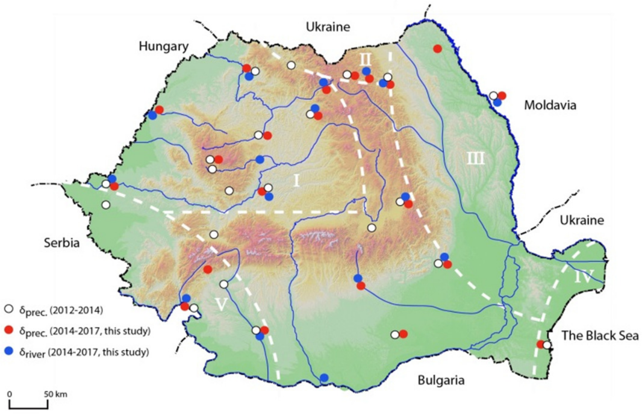


Figure 1. *Sampling sites for precipitation and river water*

Precipitations in the area have a dual (Atlantic and Mediterranean) source on the western and southern flanks of the Carpathians, while Atlantic air masses and re-evaporative sources are dominating on their eastern flanks. The time series of monthly $\delta^{18}O$ and δ^2H in precipitation in Romania (March 2012 May 2017) display a well-expressed seasonal variation, with maximum occurring usually in July, and minimum between November and January.

All river water samples show very small amplitude in their isotopic values, generally around the mean values in precipitation (Figure 1), but with reduced amplitude. Further, most river isotopic values in Western Romania plot above the Local Meteoric Water Line (LMWL, Figure 2), while rivers in NE Romania plot on or slightly below the LMWL.

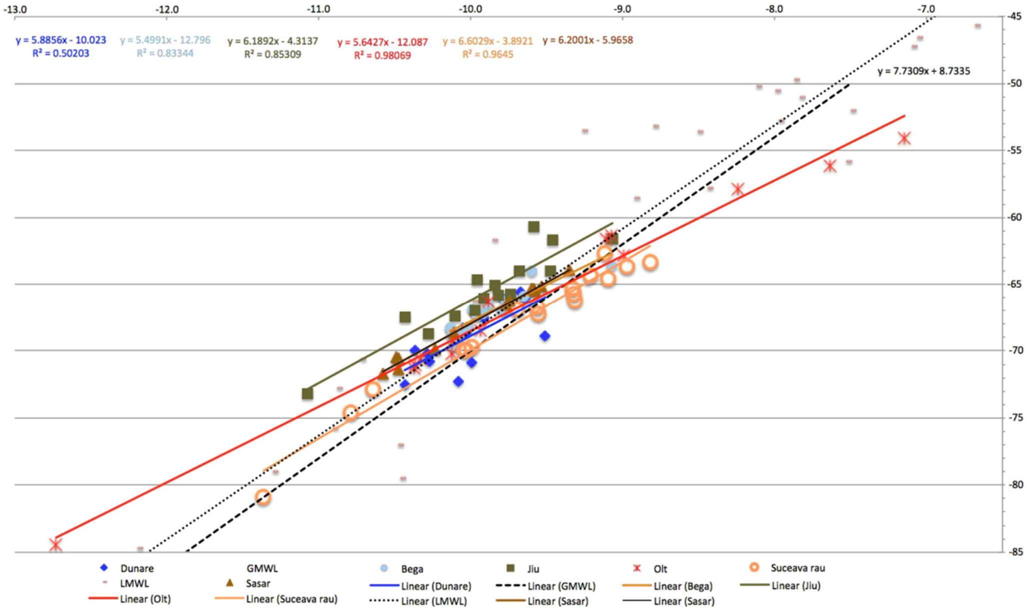


Figure 2. *Close-up view of river data plotted in figure 1.*

We hypothesize that a combination of Mediterranean-sourced moisture, increased prevalence of autumn precipitation, recycling of moisture in the arid Hungarian plains and possibly high input of strongly evaporated snowmelt to the rivers' discharge could account for these isotopic values in rivers in W Romania. Rivers in central Romania (Olt, red stars in figure 2) align along a strong evaporative line, with summer samples plotting well below the LMWL, while rivers in NE Romania (Suceava, orange circles in figure 2) are less affected by evaporation in summer, due to lower air temperatures, higher moisture content and cloudiness. All rivers show a clear shift in the minimum isotopic values towards late winter and spring, due to the influence of highly depleted isotopic waters originating from melting snow, while maximum values are recorded in late summer. The Danube, mixing waters from different European climatic zones has very constant values, clustered around the LMWL. The minimum values occur in late spring, under the influence of the snowmelt impulse from the Alps, while maxima occur in autumn, due to a combination of evaporation and Mediterranean moisture input.

Keywords: stable isotopes, rivers, precipitation, Romania.

Acknowledgments: *The work was supported by the International Atomic Energy Agency (18452) and UEFISCDI Romania (PNII-RU-TE-2014-4-1993).*

STABLE ISOTOPIC PERSPECTIVES ON HYDROCLIMATIC PROCESSES IN SUCEAVA RIVER BASIN

Carmen - Andreea Bădăluţă[1,2], **Viorica Nagavciuc**[2,3], **Aurel Perşoiu**[2,4]

[1]*Department of Geography, Ştefan cel Mare University of Suceava, Romania*
[2]*Stable Isotope Laboratory, Ştefan cel Mare University of Suceava, Romania*
[3]*Faculty of Forestry, Ştefan cel Mare University of Suceava, Romania*
[4]*Emil Racoviţă Institute of Speleology, Clinicilor 5, Cluj Napoca 400006, Romania*
Corresponding author: *carmenbadaluta@yahoo.com*

With few exceptions (*e.g.*, river capture) most of the water used in households in Romania is pumped from aquifers. In the NE part of Romania, ~1 million people are using water from the Suceava River Basin, bot from individual and community wells. These aquifers are recharged through precipitation falling on the eastern slopes of the Carpathian Mts. The moisture feeding precipitation is sourced from the Atlantic Ocean, Mediterranean and Black Seas. The amount of moisture arriving from each of these sources is modulated by the combined action of atmospheric pressure centers and the resulting wind patterns, and the ensuing precipitation patterns and amounts of moisture delivered to the region are highly variable. Further, climate models project changes in precipitation patterns in the area, with most of them agreeing on a general drying trend.

In this context, disentangling between the various moisture sources and a clear understanding of the recharge mechanisms of the local aquifers are required in order to adapt (or mitigate) to the projected climatic changes. In this study, we investigate the stable isotopic composition of precipitation, river and groundwater in the Suceava River Basin, in order to answer these problems.

Precipitation water was sampled monthly between December 2012 and December 2016 in Suceava, at 352 m above sea level. River water was sampled monthly from Suceava (172 km long, 16.5 m^3/s) and Soloneţ (38 km long, 1.2 m^3/s) rivers, between July 2014 and December 2016. Groundwater was sampled from 22 wells, between 269 and 940 m above sea level, from depths between 3 and 18 m, in October 2014, February, May and August 2015.

The isotopic composition of precipitation shows a good correlation with air temperature, with maxima in June-August and minima in December-February. Our results show high seasonally variation in the isotopic composition of rainfall (between -2.1 and -27.1‰ for $\delta^{18}O$, and between -10 and -205‰ for $\delta^{2}H$) and much lower in rivers (between -8.8 and -10.8‰ for $\delta^{18}O$, and between -62 and -75‰ for $\delta^{2}H$) and wells (between -8.5 and -10.6‰ for $\delta^{18}O$, and between -61 and -74‰ for $\delta^{2}H$). The average values of $\delta^{18}O$ and $\delta^{2}H$ were -10.9‰ and -76‰ in precipitation, -9.7‰ and -67 ‰ in rivers and -9.9‰ and -69‰ in wells.

The LMWL is defined by the equation $\delta^2H = 7.9*\delta^{18}O + 8.1$, while river and groundwater samples plot along two lines with lower slopes and intercept: $\delta^2H = 6,1*\delta^{18}O - 8,5$ (for river) and $\delta^2H = 7,4*\delta^{18}O +4,3$ (in groundwater).

HYSPLIT modeling of precipitation events suggest that most of the precipitation is derived from the North Atlantic, with continental sources contributing ~ of the moisture delivered to the site. An important finding is the high rate of precipitation events sourced from the Black Sea, as evident in the HYSPLIT trajectory modeling and the high (> 12 ‰) d-excess values of the associated meteoric water (indicative of highly evaporative conditions at the source, as is the case for the semi-closed Black Sea).

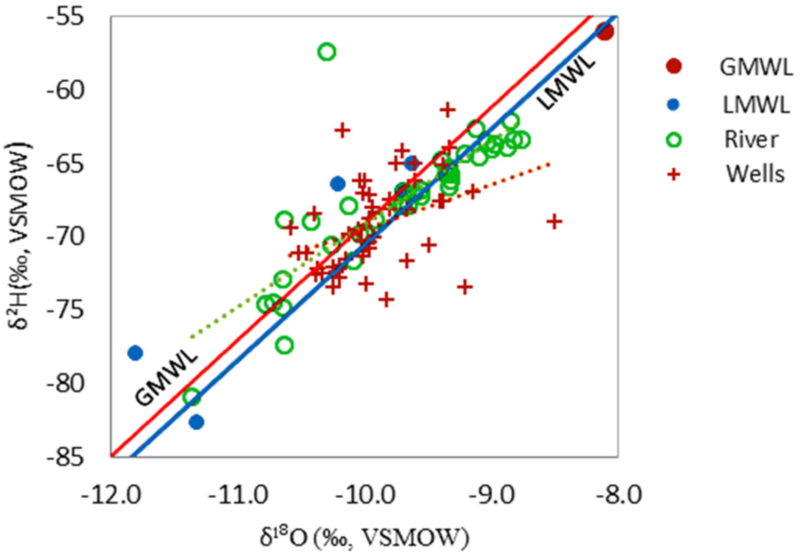


Figure 1. *Monthly mean values of $\delta^{18}O$ and δ^2H in precipitation at Suceava, surface streams and groundwater in Suceava River basin.*

The roughly similar mean values of precipitation and groundwater suggest local recharge of the aquifers and low residence times of the water in the underground. The water in the aquifers shows no clear altitude effect, possibly due the recharge at higher altitudes and mixing along the flowpaths. Evaporation in surface waters and from the topsoil leads to enriched values in summer in rivers, but this signal is not transmitted in the aquifers.

Keywords: stable isotopes, climate change, hydro-climatic processes, groundwater, NE Romania.

Acknowledgments: *The work was supported by UEFISCDI Romania (PNII-RU-TE-2014-4-1993) and the International Atomic Energy Agency (18452).*

NITRATES AND SULPHATES ISOTOPIC RESPONSE TO CHANGE OF ENVIRONMENTAL CONDITIONS IN THE SMALL DAM RESERVOIR

Beata Gebus-Czupyt[1], Stanisław Chmiel[2], Andrzej Trembaczowski[3], Stanisław Hałas[3]

[1]*Institute of Geological Sciences, Polish Academy of Science, ul. Twarda 51/55, 00-818 Warszawa, Poland*
[2]*Faculty of Earth Sciences and Spatial Management, Maria Curie-Skłodowska University,al. Kraśnicka 2cd, 20-718 Lublin, Poland*
[3]*Mass Spectrometry Laboratory, Institute of Physics, Maria Curie-Skłodowska University, pl. Marii Curie-Skłodowskiej 1, 20-031 Lublin, Poland*
Corresponding author: *b.gebus@twarda.pan.pl*

The stable isotopes studies of ions dissolved in water, such as NO_3^- and SO_4^{2-} are very usefull tool in hydrology and environmental sciences. With comparison with chemical data, they could provide information about the origin of these ions or processes occurring in the analyzed ecosystem (e.g. Mayer, 2005; Kendall *et al*. 2007, Kaown *et al*., 2009; Gebus & Hałas, 2015; Gebus, 2016). The studied area was theZemborzycki dam reservoir on the Bystrzyca River, located near Lublin (SE Poland). In this small reservoir designed for recreation purposeshave been developed recently a quickly progressing eutrophication process, caused mainly by excessive amounts of N and P compounds carried by the river. To effectively counteract the negative effects associated with this phenomenon, we should: (*1*) identify the main source of contaminants and (*2*) gain possible the broadest knowledge about processes occuring in N and P cycle and coupled with them other important elements, such as C and S, in analyzed aquatic system. Combined analyses of nitrate and sulphate isotopic composition were the first part of the studies, which have been used to demonstrate the usefulness of these methods.

Water samples have been collected three times in subsequent months from three points, between February and July in 2015, in different environmental conditions. The chemical parameters were determined in the Chemical Laboratory of Department of Hydrology UMCS, nitrates and sulphates isotopic composition ($\delta^{15}N$, $\delta^{18}O$ and $\delta^{34}S$, $\delta^{18}O$, respectively) were analyzed in Mass Spectrometry Laboratory, Institute of Physics UMCS using a dual-inlet and triple-collector mass spectrometer (Gebus, 2016; Gebus-Czupyt *et al*., *in progress*).

Both nitrate and sulphate concentration and their isotopic composition measurement results have shown considerable differences according to location and time of sampling. The highest concentrations of NO_3^- and SO_4^{2-} were observed at the inlet of the dam reservoir and they were decreasing along the reservoir in direction towards the dam. The highest concentrations of nitrates and sulphates (15.3 mg/dm^3 and 28.5 mg/dm^3, respectively) inflowing to the dam reservoir were noted in winter season, when the water was covered thin layer of ice. The results of nitrates isotopic composition ($\delta^{15}N = +5.13‰$ and $\delta^{18}O = +21.75‰$) in this time indicate their anthropogenic origin, probably nitrate fertilizers leaching from nearby agricultural areas, whilst isotopically light sulphates, with $\delta^{34}S = -2.22‰$ and $\delta^{18}O = +3.46‰$, were formed in the oxidation process of sulphides dispersed in the sub-soil carbonate rock. Generally lower concentrations of those compounds and higher values of both delta values, $\delta^{15}N$ and $\delta^{18}O$ in the case of nitrates and $\delta^{34}S$ and $\delta^{18}O$ of sulphates, for samples collected on April and July indicate the bacterial reduction processes occurring at the bottom part of the reservoir. The results indicated that intensive rains and strong winds (before 27.04) and partial draining of Zemborzycki dam reservoir water (June/July 2015) caused mixing of water masses with bottom sediments, in which typical are reduction conditions, favouring the occurrence of anaerobic organisms.

Keywords: nitrates, sulphates, isotopic composition, eutrophication.

References

Gebus B. (2016) In Polish: Badania skladu izotopowego azotanów ($\delta^{15}N$, $\delta^{18}O$), siarczanów ($\delta^{34}S$, $\delta^{18}O$) i fosforanów ($\delta^{18}O$) w zbiornikach wodnych – metody i zastosowania. Dissertation, Maria Curie-Skłodowska University.

Gebus B. and Halas S. (2015) Isotopic studies of nitrates – a short review. Annales UMCS Secti AAA, *Physica* 70: 83-112.

Kaown D., Koh D.C., Mayer B., Lee K.K. (2009) Identification of nitrate and sulfate sources in groundwater using dual stable isotope approaches for an agricultural area with different land use (Chuncheon, mid-eastern Korea). *Agriculture Ecosystems & Environment* 132(3-4):223-231.

Kendall C., Elliott E.M. and Wankel S.D. (2007) Tracing anthropogenic inputs of nitrogen to ecosystems. In: Michener R.H. & Lajtha K. (eds.), *Stable Isotopes in Ecology and Environmental Science*, 2nd edition, Blackwell Publishing, pp. 375- 449.

Mayer B. (2005) Assessing sources and transformations of sulphate and nitrate in the hydrosphere using isotope techniques. In: Aggarwal P. K. (ed.) Isotopes in the Water Cycle: Past, Present and Future of a Developing Science. Springer, Netherlands, pp. 67-89.

INTERACTION BETWEEN SPRING WATERS AND MINING LAKES IN THE UPPER HARZ MOUNTAINS (GERMANY) – AN ISOTOPE-HYDROCHEMICAL APPROACH

Elke Bozau[1], **Sonja Lojen**[2]

[1]*TU Clausthal, Hydrogeology, Leibnizstraße10, 38678 Clausthal-Zellerfeld, Germany*
[2]*Jožef Stefan Institute, Environmental Sciences, Jamova 39, 1000 Ljubljana, Slovenia*
Corresponding author: *elke.bozau@tu-clausthal.de*

The isotope ratios $^{18}O/^{16}O$ and $^{2}H/^{1}H$ of the surface waters in the Harz Mountains (Figure 1) - a mountain range up to 1100 m a.s.l. in North Germany - generally reflect the mean isotopic composition of the precipitation. According to the rising altitude of the mountain range combined with rising precipitation rates, a regional deviation of the global meteoric water line (GMWL) can be specified by the measured $\delta^{18}O$ and $\delta^{2}H$ data (Richter, 1987; Bozau et al., 2013).

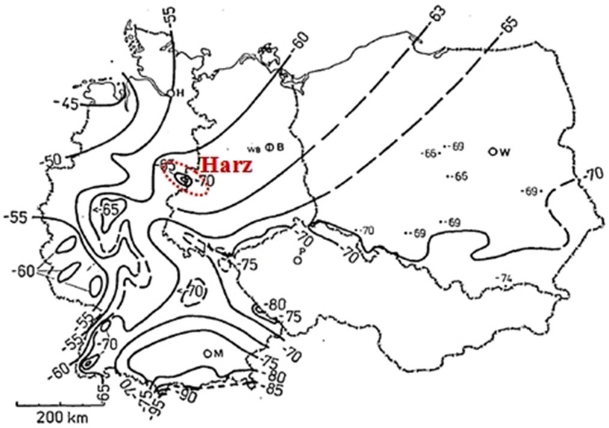


Figure 1. *The geographical situation of Harz Mountains at the former inner German border and the distribution of δ^{2}H-values [‰ SMOW] measured in modern groundwater in Central Europe (Contour map from Richter 1987)*

To investigate the relation between precipitation, surface water and lake water, major ions and trace metal concentrations, and the $\delta^{18}O$ and $\delta^{2}H$ values were analysed in springs and mining lakes of the Upper Harz Mountains. The surface waters of the Upper Harz Mountains are slightly mineralised and have specific electrical conductivities up to 300 µS/cm (Bozau *et al.*, 2015). Rising precipitation rates lead to lower elemental concentrations often combined with depleted ^{18}O and ^{2}H concentrations. Compared to the isotope values of the precipitation, catchment size and slight evaporation effects are seen in springs and lakes, respectively. One spring (Bielstein) with a relatively large and homogenous catchment area displays nearly constant $\delta^{18}O$ and $\delta^{2}H$ values, whereas most of the springs show seasonally variations of these values. High elemental concentrations and heavy isotope ratios are often correlated in spring waters such as measured in the water of the Innerste spring during the very dry autumn in 2010. Mining lakes mostly display the $\delta^{18}O$ and $\delta^{2}H$ values of the precipitation and surface runoff. These lakes are often characterised by slightly enriched isotopic values due to minor evaporation effects in the Upper Harz Mountains (Figure 2). Only during very dry seasons, evaporation effects are clearly indicated by the isotope ratios.

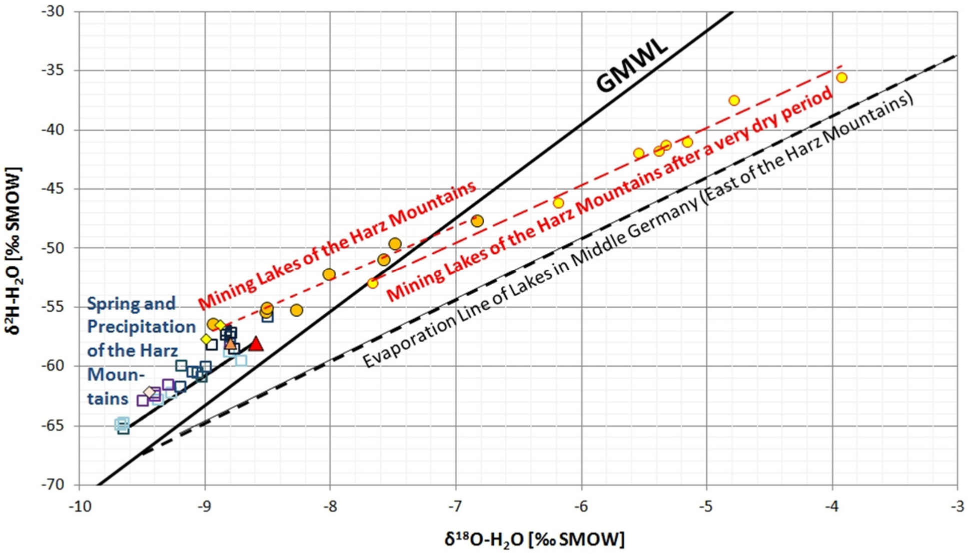


Figure 2. *Isotopic composition ($\delta^{18}O$ and $\delta^{2}H$) of the springs and mining lakes from the Harz Mountains compared to the Global meteoric water line (GMWL) and evaporation effects measured in lakes of Middle Germany*

The measured isotope ratios are very useful for a profound understanding of the hydrological cycle in the Upper Harz Mountains. Complete information (e.g., catchment size, evaporation potential) can only be provided by this isotope-hydrochemical approach. Therefore, $\delta^{18}O$ and $\delta^{2}H$ values of surface waters in the Upper Harz Mountains should be regularly investigated.

Keywords: $\delta^{18}O$, $\delta^{2}H$, Harz Mountains, hydrogeochemistry, surface water.

References

Bozau E., Stärk H.-J., Strauch G., Swanson C. (2013) Hydrogeochemical characteristics of spring water in the Harz Mountains, Germany. *Chemie der Erde - Geochemistry* 73(3): 283-292.

Bozau E., Stärk H.-J., Strauch G., Swanson C. (2015) Water quality and water-rock interaction in the Harz Mountains (Germany). *European Geologist* 40: 13-19.

Richter W. (1987) Deuterium and oxygen-18 in Central European groundwaters. *Isotopenpraxis. Isotopes in Environmental and Health Studies* 23(11): 385-390.

WATER ISOTOPIC VARIABILITY IN MALLORCA: A PATH TO UNDERSTANDING PAST CHANGES IN HYDROCLIMATE

Oana A. Dumitru[1,2], **Ferenc L. Forray**[2], **Joan J. Fornós**[3],
Vasile Ersek[4], **Bogdan P. Onac**[1,2,5]

[1]Karst Research Group, School of Geosciences, University of South Florida,
4202 E. Fowler Ave., NES 107, Tampa, 33620 USA
[2]Department of Geology, Babeş-BolyaiUniversity, Kogălniceanu 1, 400084 Cluj-Napoca, Romania
[3]Earth Sciences (Geology and Paleontology "Guillem Colom") Research Group, Department of Biology,
Universitat de les Illes Balears, Ctra. Valldemossa km 7.5, 07122 Palma de Mallorca, Spain
[4]Department of Geography, Northumbria University, Ellison Building, Newcastle upon Tyne, NE1 8ST, UK
[5]"Emil Racoviţă" Institute of Speleology, Clinicilor 5, 400006 Cluj-Napoca, Romania
Corresponding author: *odumitru@mail.usf.edu*

Understanding the isotopic variability and the sources of moisture in modern climate systems is required to develop speleothem isotope-based climate reconstructions. This is because oxygen isotopic values in speleothems are closely linked to temperature, rainfall amount, and large-scale atmospheric circulation. Here we present the first results on $\delta^{18}O$ and $\delta^{2}H$ composition of precipitations, cave drip waters, and groundwaters collected from different sites in Mallorca, (Balearic Islands, and Western Mediterranean), a key region for paleoclimate studies. Interpreting the isotopic variability of meteoric waters on this island is a challenging and complex task, considering the low amount of rainfall and its variable isotopic composition, which is influenced by both the cool North Atlantic Ocean and the much warmer Mediterranean Sea.

This study contains representative information to address three key problems:

(1) to what extent the $\delta^{18}O$ values of rainwater in Mallorca reflect different moisture sources;
(2) how similar is the isotopic composition of water in cave drips and rainfall; and
(3) what is the spatial variability of drip water $\delta^{18}O$ across the Island of Mallorca and within the investigated caves.

The stable isotopic composition of precipitation is in the range reported by GNIP Palma station. The calculated local meteoric water line $\delta^{2}H = 7.9\ (\pm 0.3)\ \delta^{18}O + 10.8\ (\pm 2.5)$ has a slightly lower slope than GMWL. Using the HYSPLIT atmospheric transport and dispersion model, we track two main sources of air masses affecting the study sites: rain events with the highest $\delta^{18}O$ values (> -5‰) originate over the Mediterranean Sea, whereas the more depleted samples (< -8 ‰) are sourced in the North Atlantic region. The deuterium excess values, ranging from 0.4 to 18.4‰, further support our findings.

To assess the isotopic variation across the island, water samples from eight caves (five of them are located within 0.5 km of the coastline) were collected. The $\delta^{18}O$ values range between -6.9 and -1.6‰. The spatial pattern of cave drip water $\delta^{18}O$ values can be primarily attributed to the source area of the water vapor. With one exception (Artà), the isotopic composition of waters in caves located along the coast (Drac, Vallgornera, Cala Varques, Tancada, and Son Sant Martí) indicates Mediterranean-sourced moisture masses. By contrast, the drip water $\delta^{18}O$ values for inland caves (Campanet, ses Rates Pinyades) or developed deep under the surface (>50 m) (Artà) exhibit more negative values. A well-homogenized aquifer supplied by rainwaters of both origins is clearly indicated by groundwater $\delta^{18}O$ values, which are within 2.4 ‰ of the unweighted arithmetic mean of -7.4 ‰. Although limited, the isotopic data presented here constitute the baseline for future studies using speleothem $\delta^{18}O$ records for western Mediterranean paleoclimate reconstructions.

Keywords: precipitation, cave drip water, groundwater, stable isotopes, Mallorca.

Acknowledgments: *This paper is a result of a research made possible by the financial support of the Sectoral Operational Programme for Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project POSDRU/159/1.5/S/132400 - "Young successful researchers-professional development in an international and interdisciplinary environment". The analyses were carried out on equipment founded by Integrated Network of Interdisciplinary Research-RICI grant no. 6/PM/I 2008 (MECS – ANCS) from Capacities Programme Module I – Investment in Research and Infrastructure Development at Babeş-Bolyai University. Part of this work was supported by MINECO, CGL2013-48441-P grant to J.J. Fornós.*

GEOCHEMISTRY AND ISOTOPIC COMPOSITION OF GROUNDWATERS IN MULTIAQUIFER SYSTEM OF THE DAIMISHCHE AREA, LENINGRAD ARTESIAN BASIN, RUSSIA

Anastasia Romanova

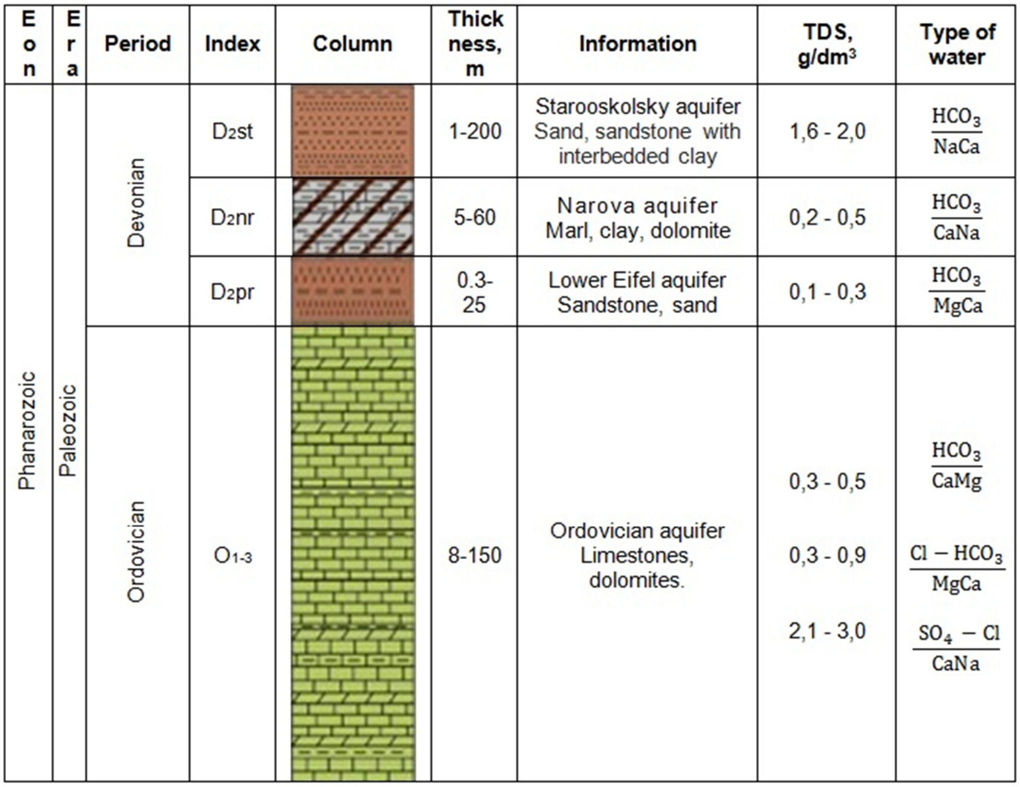
Institute of Geological Sciences, Polish Academy of Sciences (ING PAN),
Twarda 51/55, 00-818 Warsaw, Poland
a.romanova@twarda.pan.pl

Introduction

The study shows the results of 10-years (2007-2015) monitoring of groundwater chemical composition in 18 intakes (i.e. dug wells, drilled wells, natural springs) from four aquifers in Quaternary, Devonian and Ordovician sediments. Groundwater O and H isotopic composition have been studied to explain the water origin and potential mixing processes in the zones of hydraulic connections.

The study area is located in the central part of the Oredezh river valley, in the vicinity of Daymishche village, 80 km south of St.Petersburg, Russia. From hydrogeological point of view the study area belongs to the Leningrad artesian basin, where sedimentary formations of the Upper Proterozoic-Paleozoic and Quaternary sediments cover monoclinally the crystalline basement (Ignatovich, 1948). Several water-bearing horizons which are found in the basin are composed mainly of sandstones, dolomites, limestones and sands of various granulometric compositions, whereas impermeable formations are comprised mainly by clay, shale and siltstones. In Daymishche the groundwater monitoring station of the Russian State Hydrometeorological University (RSHU) is located. The station uses three wells of different depths to long term monitoring of chemical and isotopic composition of water in three aquifers, namely: the Middle Devonian Starooskolsky aquifer (D_2st), the Middle Devonian Narova aquifer (D_2nr), and the Ordovician aquifer ($O_{1\text{-}3}$). Other groundwater intakes are monitored for comparative studies (Figure 1).

The Quaternary sediments comprised by sands and clayey sands form the first, most shallow groundwater horizon. The thickness of quaternary sediments varies from 0.5 to 30 m. The aquifer is used for household water supply in Daymishche through numerous of dug wells. Middle Devonian Starooskolsky aquifer occurs in the hydraulic connection with the Quaternary water-bearing horizon and has outcrops in the river valley. The water-bearing rocks are red-colored sands and sandstones. Their thickness varies from 15 to 80 m. This aquifer is also used for household and drinking water supply in Daymishche. The so-called Narova formation constitutes the semi-permeable confining layer between the Starooskolsky and the Ordovician aquifers. It is composed mainly by marls, clays, shales, sometimes with lenses of water saturated sandstones. The thickness of the Narova formation varies from 20 to 55 m. This formation characterizes the lowest yield within the study area. The Ordovician aquifer is composed mainly of fissured karst limestones and dolomites. Its thickness varies from 5 to 130 m. The aquifer is main source of drinking water in this area. There are two wells in this aquifer, which supply water for Batovo village and for the monitoring station of the Hydrometeorological University.



Eon	Era	Period	Index	Column	Thickness, m	Information	TDS, g/dm^3	Type of water
Phanarozoic	Paleozoic	Devonian	D2st	▨	1-200	Starooskolsky aquifer Sand, sandstone with interbedded clay	1,6 - 2,0	$\frac{HCO_3}{NaCa}$
			D2nr	▨	5-60	Narova aquifer Marl, clay, dolomite	0,2 - 0,5	$\frac{HCO_3}{CaNa}$
			D2pr	▨	0.3-25	Lower Eifel aquifer Sandstone, sand	0,1 - 0,3	$\frac{HCO_3}{MgCa}$
		Ordovician	O1-3	▨	8-150	Ordovician aquifer Limestones, dolomites.	0,3 - 0,5 0,3 - 0,9 2,1 - 3,0	$\frac{HCO_3}{CaMg}$ $\frac{Cl - HCO_3}{MgCa}$ $\frac{SO_4 - Cl}{CaNa}$

Figure1. *Hydrogeological characteristic of the study* area

Results

In the study area three hydrogeochemical types of groundwater have been distinguished: (*i*) HCO_3-NO_3-Na-Ca-Mg type, in the Quaternary and Middle Devonian Starooskolsky aquifers, (*ii*) HCO_3-Ca-Na-Mg – in the Narova aquifer, and (*iii*) HCO_3-Ca-Mg-Na – in the Ordovician aquifer. The monitoring studies showed that over the past 10 years the chemical composition of groundwater in the studied area remained relatively stable: concentrations of HCO_3^-, Cl^-, SO_4^{2-}, Ca^{2+} were the most stable whereas the concentrations of Mg^{2+} and Na^+ revealed considerable variation. Such similarity in chemical compositions and ratios of major ions suggest the same groundwater origin, similar circulation system and potential extensive hydraulic connectivity between aquifers.

The values of total dissolved solids (TDS) in all groundwater during the entire monitoring period were in the range 111 - 837 mg/l. A characteristic feature of groundwater from Quaternary and Middle Devonian Starooskolsky aquifers is the elevated concentration of NO_3^-. The concentrations of NO_3^- exceeded the maximum admissible concentrations (MAC) for Russian and European norms, i.e. 45 mg/L and 50 mg/L, respectively (SanPiN 2.1.4.1074-01, Directive 98/83/EC). The highest concentration of NO_3^- was found in waters from the Quaternary aquifer. The trend of decreasing the NO_3^- contamination with depth has been observed. Another characteristic feature of water in Narova aquifer is the elevated concentration of Fe which varies from 0.1 to 0.7 mg/l and exceeds maximum admissible concentrations (MAC) for drinking water norms in Russia and European norms, i.e. 0.3 mg/L and 0.2 mg/L, respectively (SanPiN 2.1.4.1074-01, Directive 98/83/EC). Such Fe excess is caused by the nature of the aquifer rocks and presumably high concentration of iron compounds (e.g. iron sulfides) which undergo intensive dissolution by meteoric water.

Waters for isotopic analyses were sampled from 6 springs and wells at Middle Devonian Starooskolsky aquifers, Narova aquifer and Ordovician aquifer. All waters under consideration have $\delta^{18}O$ values in the range -13.5 to -10.1 ‰ and $\delta^{2}H$ values in the range -99 to -79 ‰ *vs* VSMOW and are located along the GMWL. The rainwater was monitored 3 times in 2012 (2 samples) and 2015; its isotopic composition was in the range of -14.05 to -6.26 ‰ for $\delta^{18}O$ and of -104.2 to -38.6 ‰ for $\delta^{2}H$. The isotopic composition of the Oredezh River has ranged from -12.62 to -12.1 ‰ and from 91 to -88.5 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively. The studied groundwater of Daimishche area belongs to the meteoric water of modern hydrological cycle (Clark and Fritz, 1997).

Keywords: groundwater, isotopic composition, pollution, chemical composition, Leningrad artesian basin.

References

Clark I. D., Fritz P. (1997) Environmental Isotopes in Hydrogeology. Lewis Publishers. New York, p. 342

Council Directive 98/83/EC on the quality of water intended for human consumption. (1998)

Ignatovich N. K. (1948) Hydrogeology of Russian platform. Moscow. (In Russian)

SanPiN 2.1.4.1074-01. Drinking water. Hygienic requirements for water quality of centralized drinking water supply systems. Quality control. (2002)

STABLE ISOTOPIC COMPOSITION OF PRECIPITATION IN ROMANIA

Aurel Perşoiu[1,2], Viorica Nagavciuc[2,3], Bădăluţă Carmen-Andreea[2,4], Alexandru Onaca[5], Sandu Boengiu[6], George Murătoreanu[7], Florin Zainescu[8]

[1]Emil Racoviţă Institute of Speleology, Romanian Academy, Clinicilor 5, Cluj Napoca 400006, Romania
[2]Stable Isotope Laboratory, Ştefan cel Mare University, Universităţii 13, Suceava 720229, Romania
[3]Faculty of Forestry, Ştefan cel Mare University, Universităţii 13, Suceava 720229, Romania
[4]Department of Geography, Ştefan cel Mare University, Universităţii 13, Suceava 720229, Romania
[5]Department of Geography, West University, V. Pârvan 4, Timişoara 300223, Romania
[6]Faculty of Science, University of Craiova, Al. Cuza 13, Craiova 200585, Romania
[7]Department of Geography, Valahia University of Târgovişte, Carol I no.2, Târgoviște 130024, România
[8]Faculty of Geography, University of Bucharest, Bd. M. Kogălniceanu 36-46, Bucharest, Romania
Corresponding author: aurel.persoiu@gmail.com

This study presents the results of a program aiming to monitors the isotopic composition of precipitation in Romania. Precipitation was collected monthly between March 2012 and June 2017 at 14 stations across Romania (Figure 1). Precipitation water was collected continuously using self-built collectors. A 5 l HDPE plastic canister was fitted with a funnel, prolonged with a plastic tube, channelling water to the bottom of the container. Excess air was allowed to escape the canister through to a narrow (4 mm), 2 m long plastic tube. Paraffin oil in the canister was used to minimize evaporation.

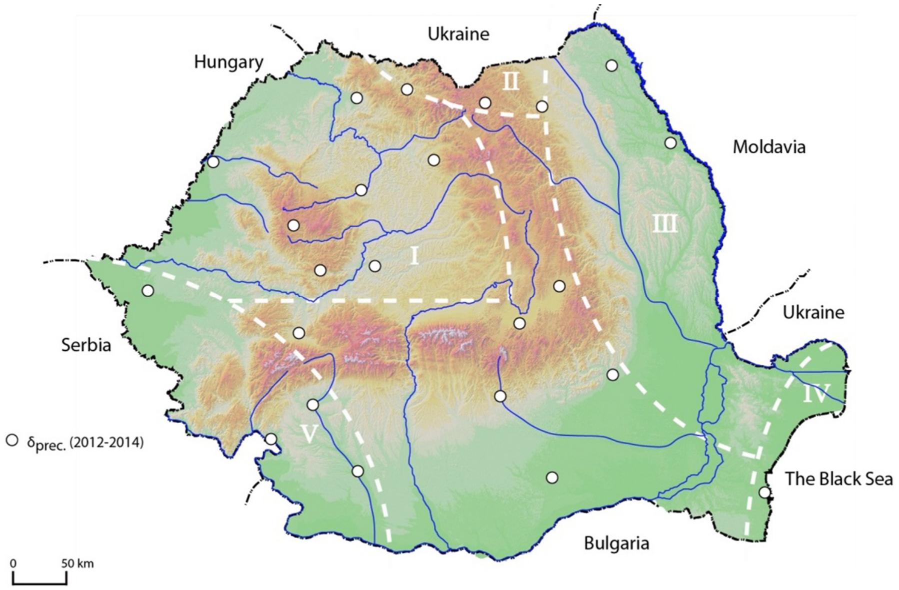


Figure 1. *Sampling sites for precipitation water*

Stable isotope analyses were performed using a Picarro L2130*i* CRDS analyzer coupled to a High Precision Vaporizer Module. Prior to analysis, samples were filtered using 0.45 µm nylon microfilters. Each sample was manually injected at least nine times, and the average of the last four injections was used, once the standard deviation was below 0.03 for $\delta^{18}O$ and 0.3 for $\delta^{2}H$. The results are normalized to the VSMOW-SLAP scale and reported in ‰ against VSMOW (Vienna Standard Mean Ocean Water), with precision better than ±0.03 ‰ and ±0.3 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively.

In this talk, we will discuss the general and local influences on the isotopic composition of precipitation, focussing on the role of large scale-circulation and the advection of moistures from various sources.

The main findings are summarized below. For all time series of monthly $\delta^{18}O$ and $\delta^{2}H$ in precipitation, the annual maximum values are registered almost exclusively in July (except for June 2012, discussed below and two instances in August), always in direct connections with maximum air temperatures; the minima are much more spread-out, occurring between November and February, with no clear connection to air temperature and/or precipitation amount extremes. The regression line between the $\delta^{18}O$ and $\delta^{2}H$ values gives a Romanian Meteoric Water Line defined by the equation $\delta^{2}H = 7.75*\delta^{18}O + 7.36$. LMWLs are much variable, indicating increased contribution of re-evaporated moisture and increase in the dominance of Mediterranean over Atlantic moisture sources with decreasing latitude. In Eastern Romania, the Black Sea is a major moisture contributor, mainly in autumn through spring, when NE circulation picks-up evaporatively enriched moisture from the sea surface and carries it westwards.

Keywords: stable isotopes, rivers, precipitation, Romania.

Acknowledgments: *Financial support was provided by UEFISCDI Romania through projects PN-II-RU-TE-2011-3-0235, PN-II-RU-TE-2014-4-1993, PN-II-CT-RO-FR-2014-2-0055; the IAEA and EEA Grants through project SEE 18.*

ISOTOPIC COMPOSITION OF PRECIPITATION IN CENTRAL EUROPE: COMPARISON OF TWO SITES WITH CONTRASTING CHARACTERISTICS

Michal Galkowski, Marek Dulinski, Anna Pierchala, Zbigniew Gorczyca, Kazimierz Rozanski

AGH University of Science and Technology, Faculty of Physics and Applied Computer Science,
Al. Mickiewicza 30, 30-059 Krakow, Poland
Corresponding author: *michal.galkowski@fis.agh.edu.pl*

Thorough understanding of factors controlling hydrogen and oxygen isotope composition of precipitation on various temporal and spatial scales is a prerequisite for successful applications of water isotopes as tracers in hydrology and is also a necessary step towards proper interpretation of ^{18}O and ^{2}H isotope records preserved in diverse climatic archives such as ice cores, lake sediments, soil organic matter, and many others. The IAEA/WMO Global Network of Isotopes in Precipitation (GNIP) played a central role in characterizing spatio-temporal variability of hydrogen and oxygen isotope composition of precipitation on the global scale during the past fifty years (Dansgaard, 1964; Rozanski *et. al*, 1991; Rozanski *et al*., 1993). Monitoring of tritium content in precipitation allowed recording the entire history of thermonuclear tritium in the atmosphere, thus providing excellent indicator of water age for groundwater hydrology. As samples analyzed in the framework of GNIP represent cumulative monthly precipitation, there is a need for better understanding of the link between the origin and rainout history of moist air masses and the isotopic signatures of precipitation recorded on the continents.

Here we present two types of data. First, a 40-year record ^{3}H, ^{2}H and ^{18}O concentration in monthly precipitation collected at Krakow-Balice GNIP station (50°04’N, 19°55’E, 220 m a.s.l.) is presented and discussed. The data are analysed on both monthly and annual time scale, including analysis of long-term trends. They are compared with selected meteorological parameters (precipitation amount, surface air temperature) and with other records available for European continent. Then, we discuss a 5-year record of ^{2}H and ^{18}O isotope composition of daily precipitation collected at high-altitude mountain station Kasprowy Wierch (49°14’N, 19°59’E, 1989 m a.s.l.), located in north-western High Tatra mountain ridge, southern Poland, approximately 100 km south of Krakow-Balice station. In total, 660 precipitation samples have been collected and analysed. Weighted monthly mean $\delta^{2}H$ and $\delta^{18}O$ values of daily precipitation collected at Kasprowy Wierch are compared with analogous data available for Krakow-Balice station.

Stable isotope composition of the analysed precipitation events varied in a wide range, from -2.9 ‰ to -26.6 ‰ for $\delta^{18}O$ and from -7 ‰ to -195 ‰ for $\delta^{2}H$. The local meteoric water line (LMWL) defined by daily precipitation data ($\delta^2H = (7.86 \pm 0.05)\delta^{18}O + (12.9 \pm 0.6)$) deviate significantly from the analogous line defined by monthly composite precipitation available for Krakow-Balice station ($\delta^2H = (7.82 \pm 0.11)\delta^{18}O + (6.9 \pm 1.1)$). While slopes of those LMWLs are statistically indistinguishable, the intercept of Kasprowy Wierch line is almost two times higher than that characterizing Krakow monthly precipitation. This is a well-documented effect associated with much higher elevation of Kasprowy Wierch sampling site. Single-event isotope data for Kasprowy Wierch precipitation correlate significantly with air temperature, with the slope of the regression line being equal 0.35 ± 0.02 ‰/°C for $\delta^{18}O$, and 2.90 ± 0.16 ‰/°C for δ^2H, whereas no significant correlation with precipitation amount could be established. The slope of monthly $\delta^{18}O$-temperature relationship is invariant with respect to the way how monthly temperature is evaluated (arithmetic or precipitation-weighted averaging of daily values).

The impact of moisture source regions and rainout history of the moist air masses on the isotopic composition of daily precipitation collected at Kasprowy Wierch site was analyzed using Hysplit back-trajectory modeling framework (Stein *et al*., 2015). Five-days backward trajectories were calculated for all analyzed precipitation events and the seasonal maps of trajectory distribution were produced. They illustrate the changes in the prevailing moisture transport patterns to the sampling site. In addition, the events yielding extreme isotopic composition of precipitation collected at Kasprowy Wierch (see above) were analyzed in some detail.

Keywords: precipitation, tritium, stable isotopes of water, moisture transport.

Acknowledgments: *The work was supported through statutory funds of the AGH University of Science and Technology (project No. 11.11.220.01).*

References

Dansgaard W. (1964) Stable isotopes in precipitation. *Tellus* 16: 436-468.

Rozanski K., Araguás-Araguás L., Gonfiantini R. (1993) Isotopic patterns in modern global precipitation. In: Swart P.K., Lohmann K.C., McKenzie J., Savin S. (eds) Climate Change in Continental Isotopic Records, Geophysical Monograph 78, *American Geophysical Union*, pp 1-36.

Rozanski K., Gonfiantini R., Araguás-Araguás L. (1991) Tritium in the global atmosphere: Distribution patterns and recent trends. *Journal of Physics G: Nuclear Physics and Particle Physics* 17:523-536.

Stein A.F., Draxler R.R., Rolf G.D., Stundler B.J.B., Cohen M.D., Ngan F. (2015) NOAA's HYSPLIT atmospheric transport and dispersion modelling system. *Bulletin of American Meteorological Society* 96:2059-2077.

ISOTOPE COMPOSITION OF PRECIPITATION AT LJUBLJANA AND PORTOROŽ (SLOVENIA) – PERIOD 2011-2015

Polona Vreča[1], Ines Krajcar Bronić[2], Albrecht Leis[3], Stefan Terzer[4]

[1]*Jožef Stefan Institute, Department of Environmental Sciences, 1000 Ljubljana, Slovenia*
[2]*Ruđer Bošković Institute, Department of Experimental Physics, 10000 Zagreb, Croatia*
[3]*JR-AquaConSol GmbH, Steyrergasse 21, 8010 Graz, Austria*
[4]*Isotope Hydrology Section, International Atomic Energy Agency,*
Vienna International Centre PO Box 100, A-1400 Vienna, Austria
Corresponding author: *polona.vreca@ijs.si*

The first monitoring of isotope composition of precipitation in Slovenia was performed in the period 1972-1975 in the frame of Ljubljanica River drainage basin investigations while regular and systematic monitoring began in 1981 in Ljubljana. The Slovenian Network of Isotopes in Precipitation (SLONIP) monitoring network has been extended during the last few decades to more than 30 different locations countrywide, mostly in the frame of short-term research projects performed by different institutions and the data were used in many hydrological, hydrogeological, climatological investigations and studies related to food authentication (Vreča and Malenšek, 2016 and references therein). SLONIP is still not a part of a national monitoring program such as that operating in European countries (e.g. Schürch *et al*., 2003) and a national isotope in precipitation database as well as a dedicated precipitation isoscape based on coherent periods are still not available for a region under the influence of mixing continental, Alpine and sub-Mediterranean climate.

Based on the review of the history of isotope in precipitation investigations performed in Slovenia in the period 1981–2015 we summarized information about sampling, analytical methods used and basic isotope data for a particular sampling location, identified the main gaps in the past research and presented general recommendations for future work in the frame of SLONIP (Vreča and Malenšek, 2016). Next step is to collect and evaluate available data before their compilation into a Slovenian 'ready-to-use' precipitation isotope database, which will be further used for geostatistical treatment to evaluate the distribution patterns useful for hydrological, climatological and food authentication applications.

The longest precipitation data sets (δ^2H, δ^{18}O, ^{3}H) exist for Ljubljana and Portorož (Vreča and Malenšek, 2016) and are also part of the Global Network of Isotopes in Precipitation (GNIP). The data were published and evaluated until the end of 2010 (Vreča *et al*., 2006, 2008, 2011, 2014, 2015). Therefore, the main purpose of this paper is to present results concerning the stable isotope composition of precipitation at Ljubljana and Portorož in relation to basic meteorological parameters (e.g. air temperature, precipitation amount) for the period 2011–2015 and to compare them with the past records.

Mean annual temperatures (T) and annual amounts of precipitation (P) varied considerably (i.e. 1°C difference in annual T and >700 mm in P) in the period 2011–2015 at both stations. The temperatures were on average higher than in the past, while the precipitation decreased considerably at Portorož but was similar as long-term mean at Ljubljana. The mean values for δ^2H and δ^{18}O, weighted by precipitation amount at Ljubljana (–56.9 ‰ and –8.45 ‰) and Portorož (–41.3 ‰ and –6.45 ‰) are similar to those observed for previous periods but indicate slightly more positive values in recent period. The change is more pronounced in the deuterium excess weighted mean values that amount to 10.7 ‰ and 10.3 ‰ for Ljubljana and Portorož, respectively, being 0.4 and 1.7 ‰ higher than those obtained for the period 2007–2010. The precipitation weighted least square regression local meteoric water lines result in $\delta^2H = (7.77\pm0.13)\times\delta^{18}O + (9.00\pm1.14)$ for Ljubljana and $\delta^2H = (7.56\pm0.18)\times\delta^{18}O + (7.25\pm1.21)$ for Portorož. Both lines indicate changes in slope and intercept that have to be inspected into more detail.

Key words: water stable isotopes, precipitation, hydrology, SLONIP, Slovenia.

Acknowledgments: *We acknowledge the financial support from the Slovenian Research Agency (research core funding No. P1-0143 and the bilateral Slovenian-Hungarian project N1-0054). The work of all colleagues who participated during long-term investigations is greatly acknowledged.*

References

Schürch M., Kozel R., Schotterer U., Tripet J.P. (2003) Observation of isotopes in the water cycle – the Swiss National Network (NISOT), *Environmental Geology* 45:1-11.

Vreča P., Krajcar Bronić I., Horvatinčić N., Barešić J. (2006) Isotopic characteristics of precipitation in Slovenia and Croatia: Comparison of continental and maritime stations, *Journal of Hydrology* 330(3-4):457-469.

Vreča P., Krajcar Bronić I., Leis A., Brenčič M. (2008) Isotopic composition of precipitation in Ljubljana (Slovenia). *Geologija* 51(2):169-180.

Vreča P., Krajcar Bronić I., Leis A. (2011) Isotopic composition of precipitation in Portorož (Slovenia), *Geologija* 54(1):129-138.

Vreča P., Krajcar Bronić I., Leis A., Demšar M. (2014) Isotopic composition of precipitation at the station Ljubljana (Reaktor), Slovenia – period 2007–2010, *Geologija* 57(2):217-230.

Vreča P., Krajcar Bronić I., Leis A. (2015) Isotopic composition of precipitation at the station Portorož, Slovenia – period 2017-2010, *Geologija* 58(2):233-246.

Vreča P., Malenšek N. (2016) Slovenian Network of Isotopes in Precipitation (SLONIP) - a review of activities in the period 1981-2015, *Geologija* 59(1):67-83.

TRITIUM IN PRECIPITATION IN GERMANY: FEATURES AND PATTERNS INDUCED BY LOCAL EVAPOURATION

Jürgen Sültenfuß

Institute of Environmental Physics, University of Bremen, Germany
suelten@uni-bremen.de

Tritium concentrations in precipitation have been monitored worldwide since decades. The Global Network of Isotopes in Precipitation was initiated in 1958 by IAEA and WMO, and became operational in 1961. But during last years the number of analysis diminished significantly. As in the Southern hemisphere and also in tropical and subtropical regions in the Northern hemisphere recent tritium concentration are declining towards limits of technical resolution the importance of recording these data in that regions might be unusable.

The German Federal Institute of Hydrology BfG still observes monthly mean concentration of tritium in precipitation. In these records some features are displayed and will be discussed along with tritium data in precipitation at the North Sea coast.

As there are: (*1*) differences between maximum concentrations in summer and minimum in winter give hints of the contribution of ocean surface water with low tritium admixed during the year; (*2*) identification of the variation of natural produced tritium in stratosphere by solar radiation; (*3*) contribution of local evaporated water to the 2-d pattern of tritium precipitation; (*4*) trend toward natural tritium. Does this confirm historical data?; (*5*) how stable/reliable are measured precipitation concentrations for the construction of an input for groundwater.

Figure 1 displays the monthly mean tritium concentration in precipitation for all locations in Germany (black dots). The precipitation data from the station Cuxhaven (deep blue line) are at the lower limit of the data range up to the 1990, and definitively at the upper limit after 2000.

Tritium concentration in the surface water in the German Bight increased significantly after the mid-1990ies (light blue line).

Tritium plus ^{3}He concentration from groundwater on East Frisian Islands in the southern North Sea (green dots) are higher than tritium in precipitation at inland locations.

Some recent rain samples from an East Frisian Island (Spiekeroog) and Bremen also show higher tritium concentrations (pink diamonds).

Obviously: In the southern North Sea tritium can serve as a tracer for the location of atmospheric water vapor production.

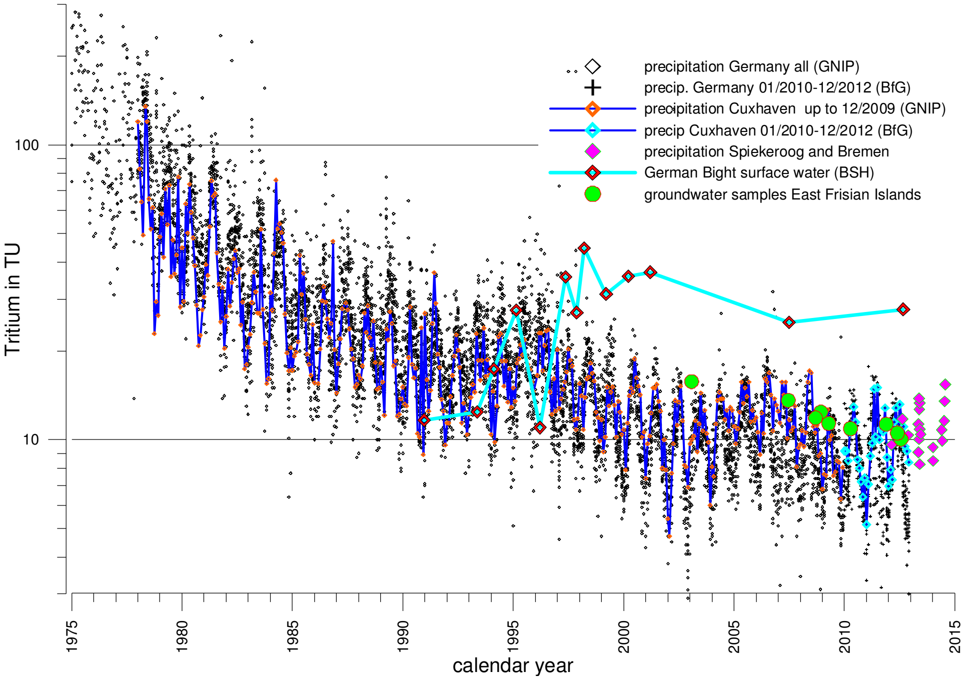


Figure 1. *The monthly mean tritium concentration in precipitation, in Germany*

Evidence from the long term tritium record: identification of the higher tritium load from the stratosphere during solar minimum in 1996 & 2006.

Keywords: tritium, precipitation, evaporation.

References

Hermann J., BSH (Bundesamt für Seeschiffahrt und Hydrographie), for tritium data North Sea
Schmidt A., BfG (Bundesanstalt für Gewässerkunde), Koblenz for tritium data in precipitation
Birner T. and Massmann G., University Oldenburg, for water samples from Spiekeroog
Houben G., BGR (Bundesanstalt für Geowissenschaften und Rohstoffe), Hannover, for water samples from Langeoog
IAEA/WMO (2014) Global Network of Isotopes in Precipitation. The GNIP Database. Accessible at: http://www.iaea.org/water

TRITIUM LEVEL IN INDIVIDUAL PRECIPITATION OF THE WARM MONTHS IN RAMNICU VALCEA IN 2008-2016 PERIOD

Carmen Varlam, Ionut Faurescu, Irina Vagner, Diana Bogdan, Denisa Faurescu

National Research and Development Institute for Cryogenics and Isotopic
Technologies – ICSI Rm. Valcea, 4 Uzinei Street, 240050 Rm. Valcea, Romania
Corresponding author: *carmen.varlam@icsi.ro*

Tritium is a radioactive isotope of hydrogen, with a half-life of 4500 ± 8 days, maximum beta energy of 18.6 keV and an average of 5.7 keV. It is present naturally from the interaction between cosmic rays and the upper atmosphere constituents. Large quantities of tritium were accumulated into the atmosphere from the past thermonuclear testing. Whether of natural or man-made origin, tritium is extremely mobile in the environment and in all biological systems. (IRSN, 2012)

Precipitation is the main mechanism for removing ^{3}H from the atmosphere. Moreover, it is the vehicle for the downward transport of ^{3}H within the troposphere.

Although the Global Network of Isotopes in Precipitation (GNIP) was established in the 60's by IAEA and WMO, many areas in the world lack long term monitoring tritium in precipitation, or due to a variety of reasons many of the data sets are not complete. Romania reports now by Rm. Valcea location isotopes in precipitation, but the records period start with 1999 for tritium and 2011, for stable isotopes. Regarding the tritium level in precipitation at Rm. Valcea location there was identified a particularity for the monthly tritium average and monthly precipitations average of long term period of observations: the months with maximum concentration are also months with maximum quantity of precipitations (Varlam *et. al*., 2013). In order to investigate this particularity there was collected and measured individual precipitation of the warm months during the period 2008-2016. Here we present the results of tritium concentration in individual precipitation with the aim of provide a relation between tritium concentration with the amount of the precipitation.

Atmospheric parameters, including the amount of precipitation, were recorded using a weather station Davis Vantage Pro2. Precipitation sampling at our Institute was performed with a typical rainwater collector (IAEA, 1989). It was decided to collect each individual precipitation in a month, the quantity corresponding to the collecting interval to be recorded, to be stored at low temperatures and at the end of the month to prepare both the individual precipitations and weighted mean of monthly precipitation for tritium concentration determination. They were measured in the same batch using the same conditions. The tritium concentration mean of the individual precipitation was calculated and compared with tritium concentration determined in the monthly composite precipitation. All the recorded values during the 2008-2016 periods were practically the same, taking into account the associated uncertainty of the tritium measurements.

The samples were measured by liquid scintillation method (ISO, 2010) with a Quantulus 1220 spectrometer for 500 min/samples. The liquid scintillation cocktail was Ultima Gold uLLT (PerkinElmer). The ratio sample: scintillate was 8:12 (g/ ml), in PerkinElmer polyethylene vials of 20 ml volume. The counting efficiency varied during the period reported here between 24.67% and 25.90% (at the best figure of merit). The background recorded for the tritium free water sample also varied, from 0.547 CPM (counts per minutes) to 0.684 CPM. The deuterium depleted water with a concentration below 15 ppm D/D+H was used as tritium free water. The limit of detection (ISO, 2010) was evaluated to be around 4 TU. The variation of tritium level presented below was calculated both for the annual arithmetic mean and for volume weighted annual mean according to WMO/IAEA recommendations (IAEA, 1992).

The monthly means of tritium concentration reported by our laboratory were essentially the same with those reported by IAEA, in 1999-2013 periods (considering associated uncertainty).

Important differences were recorded for the monthly amounts of precipitation, but no correlation were established between the amount of individual precipitation in warm months and measured tritium concentration. Peaks of tritium concentration were measured in individual precipitations demonstrating the influence of continental nuclear activity, but tritium concentration in our area is still low, an early average of 10 TU being registered.

Keywords: tritium, precipitation, warm period.

Acknowledgments: *This paper was prepared in connection with the work done for Experimental Cryogenic Pilot for Tritium and Deuterium Separation from ICSI Rm. Valcea.*

References

IAEA, International Atomic Energy Agency, Measurement of Radionuclide in food and the environment, Technical Reports Series no. 295, Vienna, (1989), 15pp.

IAEA, International Atomic Energy Agency, Statistical Treatment of Data on Environmental Isotopes in Precipitation, Technical Reports, Series no. 331, IAEA, Vienna,(1992), 781pp

IRSN - Institute for Radiological Protection and Nuclear Safety, Radionuclide sheet "Tritium and the environment", (2012), *http://www.irsn.fr* accesed on 16.03.2017

ISO 9698, International Standard Organization, Water Quality - Determination of tritium activity concentration - Liquid scintillation counting method, 2nd edn, ISO, Geneva, (2010).

Varlam C., Stefanescu I., Duliu O.G., Faurescu I., Bogdan D., Soare A. (2013) Tritium level in Romanian precipitation, Proc. Isotopes in Hydrology, Marine Ecosystem and Climate Change Studies, Monaco 2011, IAEA Vienna, pp. 139-146.

INFLUENCE OF ATMOSPHERIC CIRCULATION ON ISOTOPIC COMPOSITION OF PRECIPITATION IN FOOTHILL ALTAI MOUNTAINS (RUSSIA)

Natalia Malygina[1], **Alla Eirikh**[1], **Tatiana Barlyaeva**[2], **Tatiana Papina**[1]

[1]*Institute for Water and Environmental Problems, Siberian Branch of the Russian Academy of Sciences, 1, Molodezhnaya St., Barnaul, 656038, Russia*
[2]*Laboratoire d'Astrophysique de Marseille UMR 7326, CNRS-INSU, Marseille, 13388, France*
Corresponding author: *natmgn@gmail.com*

During the past three decades, several atmospheric and oceanic general circulation models (GCMs) have been enhanced by the capability to explicitly simulate the hydrological cycle of the two stable water isotopologues (water isotopes) HDO and $H_2{}^{18}O$ (Delavau *et al.*, 2016). The input parameters for GCM models that take into account the changes in isotopic composition of precipitation are the results obtained by the GNIP – Global Network of Isotopes in Precipitation (http://www-naweb.iaea.org/napc/ih/IHS_resources_gnip.html). In the wide area of Russia, at different times there were not more than 40 stations, which conducted the sampling of atmospheric precipitation at the same time.

This study presents the first results of isotopic composition of atmospheric precipitation and snow cover sampled in foothills of Altai during 2014-2016 (using GNIP recommendations). The isotopic composition of precipitation varied within a wide range with maximum 30, 204 and 51 ‰ for $\delta^{18}O$, δD and d_{exc} respectively. The comparison of results of the isotopic analysis of the snow cover integral samples with the corresponding in time interval the average weighted values of precipitation showed high consistency (Malygina *et al.*, 2016). We found that the isotope composition of precipitation is closely related to atmospheric circulation patterns – North Atlantic Oscillation through their effect on the sources and transport of atmospheric vapour (http://www.cpc.ncep.noaa.gov/data/teledoc/nao.shtml).

The backward trajectories of the motion of the air-masses responsible for Altai precipitation, calculated using HYSPLIT (http://ready.arl.noaa.gov/HYSPLIT_traj.php) model (>1200 trajectories), allowed to find the main regions-sources of precipitation (Figure 1).

The found relations can be used as the reliable transfer functions for the regional paleoreconstructions and climate modelling in Altai Mountains and/or to support robust interpretations of isotopic archive data.

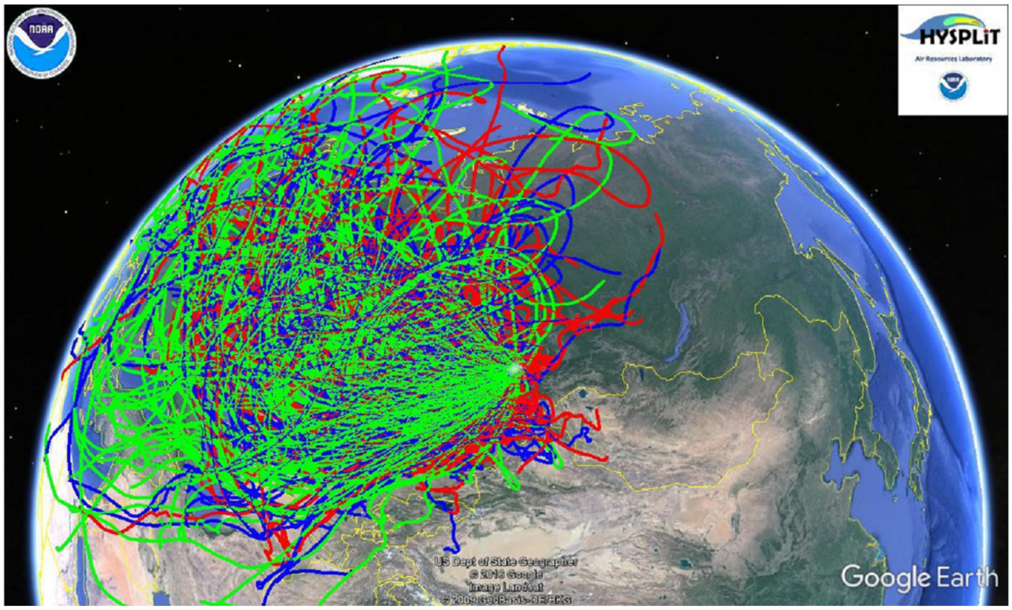


Figure 1. *Backward trajectories at 500 m (red lines), 1500 m (blue lines), and 3000 m (green lines) for air masses which determined precipitation in the Altai foothills*

Key words: isotopic composition, precipitation, foothills of Altai.

Acknowledgments: *This work was supported by the Russian Foundation for Basic Research (project no. 16-35-00188mol_a) and project № 0383-2016-005.*

References

Delavau C.J., Stadnyk T., and Holmes T. (2016) Examining the impacts of estimated precipitation isotope (δ^{18}O) inputs on distributed tracer-aided hydrological modelling, *Hydrology and Earth System Sciences*, doi:10.5194/hess-2016-539, in review.

Malygina N.S., Eirich A.N., Papina T.S. (2016) Isotopic composition of winter precipitation in Altai foothills, *IOP Conference Series: Earth and Environmental Science*, vol. 48:012011, doi:10.1088/1755-1315/48/1/012011.

http://www-naweb.iaea.org/napc/ih/IHS_resources_gnip. html

http://www.cpc.ncep.noaa.gov/data/teledoc/nao.shtml

http://ready.arl.noaa.gov/HYSPLIT_traj.php

DEUTERIUM EXCESS AS A RECHARGE AND FLOOD GENERATION TRACER IN THE VALESCURE CATCHMENT, FRANCE

Nicolas Patris, Jean-Denis Taupin, Christophe Bouvier

IRD, UMR HydroSciences, Montpellier, France
Corresponding author: *nicolas.patris@ird.fr*

The Valescure basin is a small headwater catchment of 3.9 km^2 located in the South of France (44.10°N, 3.83°E), at the southern boundary of the Cévennes mountains. It is delimited by steep hillslopes (altitudinal range 250 to 800 m a.s.l.) and is mainly covered by forest. The Cévennes area is prone to severe flash floods due to intense rainfalls (up to 500 mm in 24 hours) that can generate discharges exceeding 20 $m^3s^{-1}km^{-2}$ in small catchments of a few square kilometers. The Floodscale project (Braud *et al.*, 2014) was elaborated as part of the HYMEX framework (Ducrocq *et al*., 2014) and focused on the flood generating processes, combining multi-scale field studies and modelling.

The setup deployed in the Valescure basin allowed the geochemical (water stable isotopes, major ion chemistry, trace elements, dissolved organic matter) and physical monitoring of the hydrological system during three years (2012-2014), including a low-frequency year-round monitoring of spring and stream waters at base level, and a high-frequency (1 to 4h time step) monitoring of stream waters, soil water, and rain water during selected flood events (September to December each year). This was completed with the geochemical characterization of the underground water reservoir through two piezometers drilled in 2015.

This paper focuses on the year-round water isotopic composition from the main hydrological compartments: cumulative rain, stream, spring and underground waters. The rain was collected quasi bi-monthly at the center of the basin (410 m a.s.l.) in the vicinity of the main spring (Château spring). The deuterium excess (d_{exc}), defined as $d_{exc} = \delta^2H - 8\times\delta^{18}O$, is primarily sensitive to phase changes under non-equilibrium conditions. In the case of a watershed, the water retains the rainwater d_{exc} during transfer and storage processes. Evaporation is practically the only process through which d_{exc} may be altered, decreasing progressively in the remaining water as it gets isotopically enriched in both ^{18}O and ^2H.

From the results obtained we can draw a series of conclusions:

1. The local meteoric water line (LMWL) calculated over 3 years (rain samples with $d_{exc} > 7.0‰$) is close to the Global Meteoric Water Line (GMWL), representing the multiplicity of humidity origins (Mediterranean, Atlantic, continental Europe):

$$\text{LMWL: } \delta^2H = 7.7 \times \delta^{18}O + 10.7‰$$

2. Isotopic variability of the rain is high (δ^{18}O between -10.08‰ and +0.76‰). The mean rainwater deuterium excess over the 3 years (2012-2014) is d_{exc} = +12.7‰ (Figure 1).

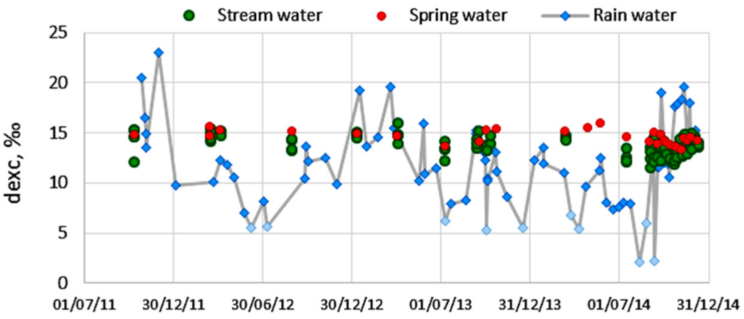


Figure 1. *Deuterium excess time series for Stream, Spring and Rain waters (light blue di-amonds indicate rain samples dexc < 7.0‰)*

3. Stream and spring waters have a much lower isotopic variability (e.g., spring δ^{18}O from -6.28‰ to -5.95‰ under base flow conditions, up to -5.47‰ at the peak of flood season) and a d_{exc} notably superior to the mean rain signal (d_{exc} = +14.5 to +15.0‰, Figure 1), which precludes a notable effect of evaporation for most rains, and indicates the unaltered transfer of the rainwater to the underground reservoir and streams. The underground water reservoir also shows a stable and high d_{exc} = +15.2‰.

4. Evaporation effect is limited but measurable on the stream waters d_{exc}, negatively correlated with δ^{18}O (Figure 2). Indeed, this signal is marked seasonally, consistently with the low velocity of the base-flow transfers in dry summer conditions.

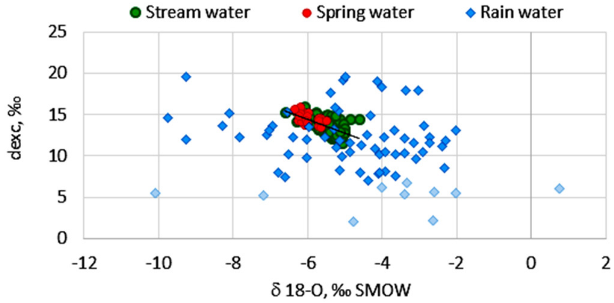


Figure 2. *Deuterium excess distribution as a function of δ^{18}O. Black line materializes the stream water (green dots) linear correlation*

5. Seasonal meteoric lines were calculated. They showed that rainwater d_{exc} was higher during fall (Oct-Dec) and winter (Jan-Mar) months than during spring (Apr-Jun) and summer (Jul-Sep) (Figure 3). This signal is largely disconnected from seasonal precipitation amounts. The mean d_{exc} of fall and winter rainwaters correspond closely to the spring water signature. This may reveal a seasonal pattern in the water recharge of the system, enhanced during autumn and winter when vegetation gets dormant.

6. The more depleted $\delta^{18}O$ of the spring compared to rainwater indicates that its recharge is not local and may occur a few hundred meters higher on the slopes (Figure 3), although the local altitudinal gradient is not known at the moment.

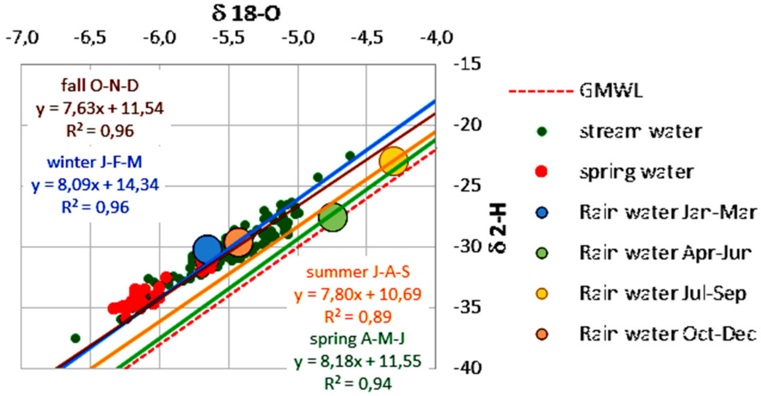


Figure 3. *Isotopic distribution in streams and spring waters. Large circles are rain water seasonal means (winter Jan-Mar to fall Oct-Dec). Colored lines are seasonal meteoric water lines*

Keywords: Water Isotopes, Deuterium Excess, Watershed Hydrology, Recharge, Seasonality

Acknowledgments: *Study funded by the Agence Nationale de la Recherche (ANR) FloodScale project under contract ANR- 2011- BS56- 027.*

References

Braud I., Ayral P.A., Bouvier C., *et al*. (2014) Multi-scale hydrometeorological observation and modelling for flash flood understanding. *Hydrology and Earth System Science* 18:3733-3761. doi:10.5194/hess-18-3733-2014

Ducrocq V., Braud I., *et al*. (2014) HyMeX-SOP1: The Field Campaign Dedicated to Heavy Precipitation and Flash Flooding in the Northwestern Mediterranean. *Bulletin of the American Meteorological Society* 95:1083-1100. doi:10.1175/BAMS-D-12-00244.1.

THE EFFECT OF THE SOLAR CYCLE TO THE COSMOGENIC TRITIUM IN METEORIC PRECIPITATION

László Palcsu[1], **Elemér László**[1], **Carmen Varlam**[2]

[1]Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research, Hungarian Academy of Sciences, Bem tér 18/c, Debrecen, 4026 Hungary
[2]National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI Râmnicu Vâlcea, 4 Uzinei Str., 240050 Rm. Valcea, Romania
Corresponding author: *palcsu.laszlo@atomki.mta.hu*

Production rates of cosmogenic nuclei are modulated by the variation of the magnetic strength of the Sun, while the atmospheric concentrations of theses isotopes are further controlled by many other factors. The atmospheric concentration of several isotopes and the change of solar activity and hence secondary neutron flux has already been proven. The temporal atmospheric variation of the most studied cosmogenic isotopes (^{14}C, ^{7}Be and ^{10}Be) shows a significant correlation with solar cycles. However, since the artificial tritium (radioactive hydrogen isotope, ^{3}H) input to the atmosphere due to nuclear weapon tests suppressed the expected variations of tritium production rate by three orders of magnitude, the natural variation of tritium in meteoric precipitation could not be detected so far. We have been analysing the tritium concentration of precipitation for more than 13 years. These results suggest a connection between the solar cycle and the tritium content of precipitation. Previous model calculations have shown that the tritium production rate has a periodic variability of 5% during a solar cycle. Due to the dilution effect of the atmospheric moisture, this effect is supposed to be further weakened in the surface precipitation. In the Danube-Carpathian region the natural tritium level in the precipitation is around 5−10 TU. These low concentrations can be accurately measured only since the last 2−3 decades. Moreover, since the 50’s the atmospheric thermonuclear bomb tests increased the tritium amount of precipitation by 2-3 orders of magnitude. After its maximum intensity in the early 60’s, the so-called bomb peak has already diminished to a stable level, and in the 2000’s years it is close to a natural level (~10 TU). In the period of 2001−2014, we have been continuously taking water samples from each precipitation events. Our study shows how the tritium concentration of monthly precipitations depends on the magnetic activity of the Sun. It can be observed that tritium concentration is varying by about 30% around mean value during the 11 years of the solar cycle. This is in accordance with the time series of other cosmogenic isotopes like ^{7}Be, ^{10}Be in the precipitation. We found trends in tritium time series for numerous locations worldwide being similar to the variation of secondary neutron flux and sun spot numbers. These variables seem to have similar

periodicities to that of solar cycle. Frequency analysis, cross correlation analysis, continuous and cross wavelet analysis provide mathematical evidence that the correlation between solar cycle and meteoric tritium does exist. Our results demonstrate that the response of tritium variation in precipitation to the solar cycle help us understand what solar-linked processes play a role in the water cycle. Nevertheless, continuous analysis has to be performed in the next decades so that we can reveal the behaviour of tritium of precipitation with respect of the Sun. Additionally, accurate tritium analyses of ice core depth profiles accumulated before the nuclear era will further strengthen the evidence of the link between solar cycle and tritium in precipitation.

Key words: cosmogenic tritium, solar cycle, precipitation.

Acknowledgments: *The research was supported by the European Union and the State of Hungary, co-financed by the European Regional Development Fund in the project of GINOP-2.3.2.-15-2016-00009 'ICER'.*

ROLE OF METEOROLOGICAL PROCESSES AND ISOTOPE EFFECTS ON THE STABLE ISOTOPE COMPOSITION OF PRECIPITATION ORIGINATED FROM THE MEDITERRANEAN REGION

György Czuppon[1*], Hajnalka Breuer[2], Emese Bottyán[2], Zoltán Kern[1], Gergő Simon[2], Tamás Mona[1], Júlia Göndöcs[2]

[1]*Institute for Geological and Geochemical Institute, Hungarian Academy of Sciences, Hungary,*
[2]*Department of Meteorology, Eötvös Loránd University, Hungary*
Corresponding author: *czuppon@geochem.hu*

Hungary is located in the transition zone which is influenced by meteorological (climatological) conditions of Atlantic, Mediterranean and North-eastern European regions. Previous investigation revealed that the majority of the moisture of the precipitation in this region derives from Mediterranean Basin (Bottyán *et al*., 2013; Czuppon *et al*., 2015). Moreover, this moisture originated in the Mediterranean region on the way to Hungary might be also influenced by evapotranspiration (continental moisture recycling).

A national monitoring network has been launched in 2012 in Hungary to collect and measure the stable isotope composition of daily precipitation at six stations. The network provides an opportunity to study and compare the stable isotope composition and the meteorological conditions related to same event. Clear systematics was observed in the stable isotope composition and WRF simulated total specific humidity (and the measured amount of precipitation) related to same Mediterranean events at different locations. It was found that the measured $\delta^{18}O$ (and δD) and total specific humidity show negative correlation. This observation can be explained by 1) different stage of the rainout process 2) distinct rate of equilibration of the raindrops with the vapor below the cloud 3) different heights of the melting layer and 4) different degree of evaporation of the raindrops on their way to the land surface.

In addition, we have also estimated the contribution of the evapotranspiration for the Mediterranean events and compared with the stable isotope composition.

Keywords: stable isotope, precipitation, Mediterranean moisture, WRF, Hungary.

Acknowledgments*: The research was financially supported by National Research, Development and Innovation Office (project NKFIH, OTKA 101664; PD 121387and SNN118205). György Czuppon also thanks for the support of the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.*

References

Bottyán E., Czuppon G., Weidinger T., Haszpra L., Kármán K. (2013) Determination of air moisture source region for precipitation in Hungary. – *Central European Geology*, 56, pp. 273.

Czuppon G., Bottyán E., Weidinger T., Kármán K., Haszpra L. (2015) Spatial and temporal variabilities in stable isotope compositions of precipitation and air moisture sources in Hungary. In: International Symposium on Isotope Hydrology: Revisiting Foundations and Exploring Frontiers (IAEA). p. 57.

VARIOGRAM ANALYSIS OF STABLE OXYGEN ISOTOPE COMPOSITION OF DAILY PRECIPITATION OVER THE BRITISH ISLES

Balázs Kohán[1], Jonathan J. Tyler[2,3], Matthew Jones[4,5], Zoltán Kern[6*]

[1]Deptartment of Environmental and Landscape Geography, Eötvös University, Budapest, Hungary
[2]Department. of Earth Sciences, The University of Adelaide, Adelaide, SA 5005, Australia
[3]Sprigg Geobiology Centre, The University of Adelaide, Adelaide, SA 5005, Australia
[4]School of Geography, The University of Nottingham, University Park, Nottingham NG7 2RD, UK
[5]Centre for Environmental Geochemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, UK
[6]Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences; Budapest, Hungary
Corresponding author: *kern@geochem.hu; zoltan.kern@gmail.com*

Water stable isotopes are important natural tracers in the hydrological cycle on global, regional and local scales. Daily precipitation water samples were collected from ~70 sites over the British Isles on the 23rd, 24th, and 25th January, 2012 (Tyler *et al*., 2016). Samples were collected as part of a pilot study for the British Isotopes in Rainfall Project, a community engagement initiative, in collaboration with volunteer weather observers and the UK Met Office.

Spatial correlation structure of daily precipitation stable oxygen isotope composition ($\delta^{18}O_P$) has been explored by variogram analysis (Webster and Oliver, 2007). Since the variograms from the raw data suggested a pronounced trend, very likely mirroring the spatial trend discussed in the original study (Tyler *et al*., 2016), a second order polynomial trend was removed from the raw $\delta^{18}O_P$ data and variograms were calculated on the residuals. Directional experimental semivariograms were calculated (steps: 10º, tolerance: 30º) and aggregated into variogram surface plots to explore the spatial dependence structure of daily $\delta^{18}O_P$.

Each daily data set produced distinct variogram plots.

- A well expressed anisotropic structure can be seen for Jan 23. The lowest and highest variance was observed in the SW-NE and NNE-SSW direction, respectively. Meteorological observations showed that the majority of the atmospheric flow was SW on this day, so the direction of low variance seems to reflect this flow direction, while the maximum variance might reflect the moisture variance near the elongation of the frontal system.
- A less characteristic but still expressed anisotropic structure was found for Jan 24 when a warm front passed the British Isles perpendicular to the east coast, leading to a characteristic east–west $\delta^{18}O_P$ gradient suggestive of progressive rainout. The low variance central zone has an ~100 km radius which correspond well to the width of warm frontal rainbands (Matejka *et al*., 1980). Although, the

axis of minimum variance was similarly SW-NE, the zone of maximum variance was broader and practically perpendicular to it. In this case, however, directions of the axes appear misaligned with the flow direction.

- We could not observe similar characteristic patterns in the last variogram calculated from the Jan 25 data set.

These preliminary results suggest that variogram analysis is a promising approach to link $\delta^{18}O_P$ patterns to atmospheric processes.

Keywords: isotope hydrometeorology, precipitation stable isotope, geostatistics, British Isles, spatial variance.

Acknowledgments: *Thanks to the Hungarian Academy of Sciences (Lendület program, No LP2012-27/2012 to Z.K.) and the National Research, Development and Innovation Office (SNN118205) the Slovenian Research Agency (ARRS:N1-0054).*

References

Matejka T. J., Houze R. A., Hobbs P. V. (1980) Microphysics and dynamics of clouds associated with mesoscale rainbands in extratropical cyclones. *Quarterly Journal of the Royal Meteorological Society* 106(447):29-56.

Tyler J. J., Jones M., Arrowsmith C., Allott T., Leng M. J. (2016) Spatial patterns in the oxygen isotope composition of daily rainfall in the British Isles. *Climate Dynamics* 47:1971-1987.

Webster R., Oliver M.A. (2007) *Geostatistics for Environmental Scientists*. John Wiley & Sons, Chichester, 330 pages, ISBN: 978-0-470-02858-2.

ANALYSIS OF THE SPATIAL CORRELATION STRUCTURE OF PRECIPITATION δ^{18}O OVER THE IBERIAN PENINSULA

Dániel Erdélyi[1,2], István Gábor Hatvani[1], Polona Vreča[3], Zoltán Kern[1*]

[1] *Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, H-1112 Budapest, Budaörsi út 45., Hungary*
[2] *Eötvös Loránd University, Department of Meteorology, H-1117 Budapest, Pázmány Péter stny. 1/A, Hungary*
[3] *Jožef Stefan Institute, Ljubljana, Slovenia*
Corresponding author: *kern@geochem.hu; zoltan.kern@gmail.com*

The aim of the study was to explore the spatial variance of precipitation δ^{18}O (δ^{18}Op) over the Iberian Peninsula on monthly-, seasonal- and annual scales. Monthly precipitation stable isotope data from 32 GNIP stations (IAEA, 2016) was acquired for the October 2002 -June 2006 period. In addition, data of 20 stations from a regional monitoring campaign for NW Iberia conducted between October 2004 - June 2006 (de Oliveira and da Lima, 2011) were also used. Using the coordinates of the stations (WGS84/World Mercator) and their elevation (m) best fit quadratic trend was removed from the data using multivariate regression analysis. Consequently 12 monthly (October 2002 - September 2003), 2 seasonal (winter: October 2002 - March 2003; Summer: April 2003 - September 2003) and an annual semivariogram was calculated on the obtained residuals. Moreover, an additional semivariogram was modelled using the 21-monthly mean (October 2004 - June 2006) of the additional 20 stations representing larger/extended dataset of the Iberian δ^{18}Op in time and space. In the case of the seasonal and annual semivariograms precipitation amount weighted δ^{18}O means were the input data. Remarkably gappy δ^{18}Op station records were omitted from the geostatistical analysis. Those were lacking stable isotope data for more than 20% of the total precipitation amount of the corresponding period of interest (seasonal, annual, or 21-month period).

Out of 16, 7 semivariograms (5 monthly and the two seasonal) were of nugget-type (Chilés and Delfinier, 2012). A common critical weakness that may be a major cause for the nugget-type of variograms is the underdeveloped sampling in space. Unfortunately, due to the lack of data from short distances, theoretical variograms were unsatisfactory. There is no month, in which more than two stations were sampling precipitation simultaneously within a ~100 km area, moreover within a ~50 km there was none. This was a significant obstacle, because knowing the short distance variance of δ^{18}Op could greatly help in e.g. evaluating the current monitoring network. The remaining 7 monthly and the annual semivariograms showed a rising section and stabilization around the mean variance. For the one extended dataset, the 16th semivariogram, with the 20 stations gave an exemplary empirical semivariogram with two sills, corresponding to ~100 km and ~500 km spatial range.

These information regarding the spatial variance of δ^{18}Op over the region, could serve as a stepping-stone for the improved geostatistical modelling of the precipitation isoscape for the Iberian Peninsula.

Keywords: geostatistics, Iberia, isotope hydrometeorology, precipitation stable isotope, spatial variance.

Acknowledgments: *Thanks to the Hungarian Academy of Sciences (Lendület program, No LP2012-27/2012 to Z.K.) and the National Research, Development and Innovation Office (SNN118205) the Slovenian Research Agency (ARRS:N1-0054).*

References

de Oliveira A. C. V., da Silva Lima A. (2011) Spatial variability in the stable isotopes of modern precipitation in the northwest of Iberia. *Isotopes in Environmental and Health Studies* 61(1):13-26.

IAEA (2016) Global Network of Isotopes in Precipitation. The GNIP Database, http://www.isohis.iaea.org, Accessed on 03 March 2016.

Chilés J. P., Delfinier P. (2012) Geostatistics. Wiley, Canada, 734 pages, ISBN: 978-0-470-18315-1.

LONG-TERM RECORD OF ^{2}H, ^{18}O AND ^{3}H VARIATIONS IN PRECIPITATION IN LEIPZIG

Gerhard Strauch[1], Peter Kowski[2], Stephan Weise[3], Kay Knöller[3]

[1]*Helmholtz Centre for Environmental Research UFZ, Leipzig, Permoserstraße 15, 04318 Leipzig*
[2]*Engelsdorf/Leipzig*
[3]*Helmholtz Centre for Environmental Research UFZ, Halle/Saale,*
Theodor-Lieser-Straße 6, 06120 Halle/Saale
Corresponding author: *gerhard.strauch@ufz.de*

The isotopic composition of hydrogen and oxygen in precipitation can draw a picture about the meteoric and, more interesting, the climate condition and development of a region. Under the focus of climatic changes, the variation of the water isotopes helps to greater understanding of air mass movements on a regional to continental scale.

The meteorological position of Leipzig in the middle East German lowland is characterized by a transitional influences between maritime (NW) and continental (NE, SE) air masses (Richter, 1987), and the seasonal effect of these air masses.

Over a period of 40 years, a long-term δ^{2}H record in precipitation from Leipzig was collected, expanded by δ^{18}O since 1986, and tritium values since 1978. Embedded in this Leipzig record, one additional temporally limited record from Bad Lauchstädt complete the precipitation character of this region.

A clear seasonality is observed in all records, but with different behaviour of the deuterium excess. Moreover, slightly enrichment is recognized in the ^{18}O of the Leipzig record. The results are compared to the long-term SI composition in German precipitation (Stumpp *et al.,* 2014). The tritium function of the Leipzig precipitation follows the trend of the Vienna record.

It is our aim, to discuss the Leipzig long-term record in the light of isotope variations in precipitation on the European scale.

Keywords: hydrogen-2, oxygen-18, precipitation, d-excess, tritium

References

Richter W. (1987) Deuterium and Oxygen-18 in Central European Groundwaters. *Isot. Environm. Health Stud.* 23(11):385-390. DOI: 10.1080/10256018708623855

Stumpp C., Klaus J., Stichler W. (2014) Analysis of long-term stable isotopic composition in German precipitation. *J. Hydrol.* 517:351-361

D/H FRACTIONATION DURING THE SUBLIMATION OF WATER ICE

Christophe Lécuyer[1,*], **François Fourel**[1], **and François Robert**[2]

[1]*Laboratoire de Géologie de Lyon, CNRS UMR 5276, University Claude Bernard Lyon 1, France*
[2]*Laboratoire de Minéralogie et Cosmochimie du Muséum, CNRS–MNHN UMR 7202, Paris, France*
**also at Institut Universitaire de France;*
Corresponding author: *clecuyer@univ-lyon1.fr*

Experiments of sublimation of pure water ice have been performed in the temperature range -105°C to -30°C and atmospheric partial pressures ranging from 10^{-6} to 10^{-1} mb. Sampling of both vapour and residual ice fractions has been performed with the use of a vacuum line designed for the extraction and purification of gases before the measurement of their D/H ratios. Sublimation was responsible for sizable isotopic fractionation factors in the range 0.969 to 1.123 for temperatures lying between -105°C and -30°C (Figure 1).

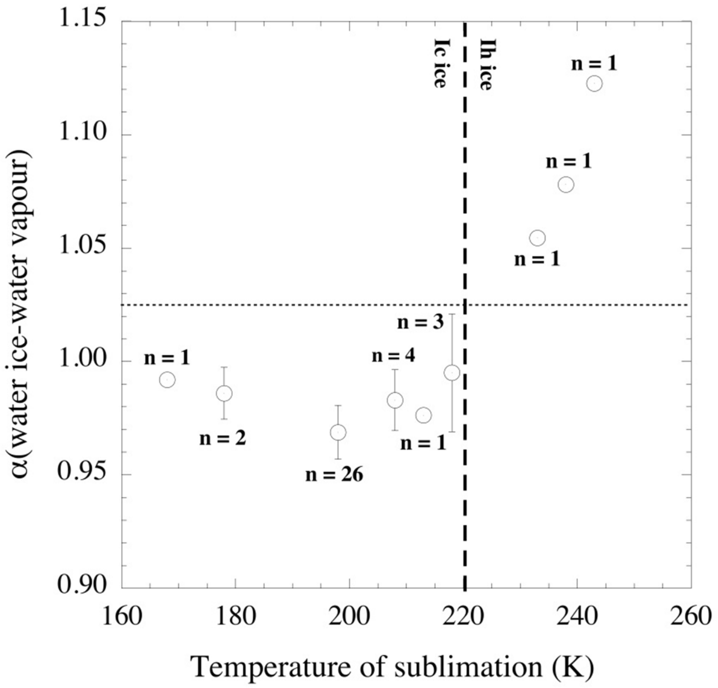


Figure 1. *D/H isotopic fractionation a between water ice and water vapour as a function of the temperature of sublimation (K).*

The fractionation factor exhibits a crossover at temperatures around -50°C with the water vapour fraction being D-depleted relative to the residual ice fraction at T lower than -50°C ($a_{ice\text{-}vapour}$ = 0.969 to 0.995). This crossover has implications for the understanding of the atmospheric water cycle of some terrestrial planets such as the Earth or Mars. For example, in the Earth's atmosphere, it concerns the mechanism involved in ice cloud formation. Cubic ice is dominant when droplets freeze at temperatures lower than -80 °C, these temperatures being relevant for clouds occurring in the polar stratosphere and those of the tropical tropopause. Sublimation of water ice also takes place in the most extreme cold regions of the Earth, such as the top of the highest mountains or in the central part of the Antarctic continent where sublimation of snow is a common phenomenon. In cosmochemistry, the D/H ratio is often used to trace the origin of extraterrestrial water (planets, asteroids, comets). The magnitude of deuterium enrichment or depletion between ice and water vapour cannot explain the differences in the D/H ratios amongst Jupiter comets and long–period comets families nor those that have been documented between Earth’s and cometary water.

Keywords: water cycle, water ice, sublimation, D/H, isotopic fractionation, comet.

BRINGING SPECIATION AND ISOTOPES TOGETHER TO IMPROVE OUR UNDERSTANDING OF THE FATE OF METALS IN THE ENVIRONMENT

Olivier F. X. Donard

Institut des Sciences Analytiques et de Physicochimie pour l'Environnement et les Matériaux
Centre of Mass Spectrometry for Reactivity and Speciation Sciences, Hélioparc 64000 Pau (France)
olivier.donard@univ-pau.fr

Scientific research during the last 20 years has shown that not only simple information on the metals, e.g. their total concentrations in a sample, but rather knowledge on chemical forms of metals and metalloids - their species - is an important issue in order to evaluate their reactivity, transport in the environment or their essentiality and toxicity in organisms. Hyphenated technics using separation techniques to ICP/MS have allowed to promote important knowledge in this domain. However, it is important now to open up further opportunities in this domains to improve our understanding of metals species at environmental traces levels but developing new concepts in sample preparation, detection and integration of detection opportunities by promoting new development in detection in instrumentation.

The hyphenation of chromatography techniques to ICP/MS have allowed to result in major advances in the global understanding of trace elements cycling. Tremendous progresses have been made over the last 20 years with the implementation of speciation analysis using hyphenated chromatography techniques to quadrupoles ICP/MS. This has led to the implementation of the use of isotopically labelled approaches in the analytical scheme and has brought tremendous progress to the field allowing to unravel major artifacts during the sample preparation and hence questioning global environmental results. The development of plasma based multicollector has allowed to use the flexibility of the instrument to evidence for the occurrence of different isotopic signature of Hg in the environment. Mass dependent and mass independent fractionation signatures of Hg have been related to sources and process and have then allow to shed new light on the global Hg cycling. Further progresses and questions appear now since we can look in greater detail at the isotopic fractionation of Hg species in the samples of fish samples for example. Their isotopic signatures are significantly different and this raises then fundamental questions with regards to the fate and transformation of Hg during its global cycling. In order to fully assess these questions, we need to fully control the full analytical chain to rely new global Hg cycling views on sound analytical progresses. The mass dependent fractionation and mass independent fractionation signatures are new tools to help tracing the origin and processes. This starts to be well established when dealing with total isotopic Hg fractionation budgets. In terms of information, we can now bring in both species specific isotopic signatures. This enhances the array of environmental descriptors. But then, there are important question related with precision and accuracy of these individual species isotopic determination during the whole analytical chain. We will review all of the critical steps of the analytical chain related to Hg determination in fish to evaluated the major advanced and areas of improvement so that we can lead to a better understanding of the global cycling of Hg highlighting again the need to reference materials in this new domain.

These developments have been realized in the MARSS project is to install a unique Mass Spectrometry Center for Reactivity and Speciation Sciences together. This center will be open to research groups. The scientific aims are advancing the frontiers of speciation analysis to: (i) understanding of the role of elements, esp. metals and metalloids, related to their chemical identity or isotopic signature, (ii) understanding of their primary reactivity associated with the chemical identity and transformation kinetics, (iii) identification of chemical species of interest in their surrounding matrices, on surfaces or interfaces leading to their localization by imaging and mapping in 2 or 3 dimensions. There will be five main activities developed on the platform which make it unique: (i) novel speciation research pathways, (ii) new instrumentation developments with the manufacturer's partners of the platform, (iii) academic access to national and international and (iv) an international teaching and training center. The MARSS center is to be opened to other research groups at the national and international level with the aim of being integrated to the national CNRS network and European Research Infrastructure of the ESFRI program.

CARBON AND OXYGEN ISOTOPES OF CARBONATES FROM FLYSCH ROCKS OF THE UKRAINIAN CARPATHIANS

Guliy V.[1], **Kril S.**[1], **Zagnitko V.**[2], **Kuzemko Ya.**[3], **Stepanov V.**[1],
Bilyk N.[1] , **Il'chenko T.**[4]

[1]*Ivan Franko National University of Lviv, Faculty of Geology, 4, Hryshevsky Str., Lviv, 79005, Ukraine*
[2]*Taras Shevchenko National University of Kyiv, Institute of Geology, Kyiv,*
90 Vasylkivska str., 03022, Ukraine
[3]*PAO "Interbudtunel", 1, Promyslova str., Kyiv, 01013, Ukraine*
[4]*Institute of Geochemistry, Mineralogy and Ore Formation, Kyiv, 34 Palladina str., 03680, Ukraine*
Corresponding author: vgul@ukr.net

Carbonates are wide spread developed in variable amounts in the flysch rocks of the Ukrainian Carpathians, which are composed mainly by interstratification of light gray massive sandstones, dark to black argillites and aleurolites, and sporadically limestones, dolostones and marles. Enumerated rocks are typical for all regional units of the studied territory (Guliy *et al*., 2016; Kril, 2014) and surrounding parts of the Carpathians (Bojanowski, 2007). There are orthogonal or (rarely) perpendicular fractures in the rocks which are often filled with late veins and druses of the newly formed minerals.

Two main ages, morphological and mineralogical generations of carbonates (Figure 1, 2) are distinguished within the flysch rocks. Early generation of the carbonates is represented by coarse grained detrital dolomite and finer calcite as cement (Figure 1). Late generation of big in size crystals of carbonates (mostly calcite, in some places aragonite (Kril, 2014) is main component of the carbonate (Figure 1, left), carbonate-quartz (Figure 2, left), and carbonate-sulphide (Figure 2, center) druses and veins (Guliy *et al*., 2016).

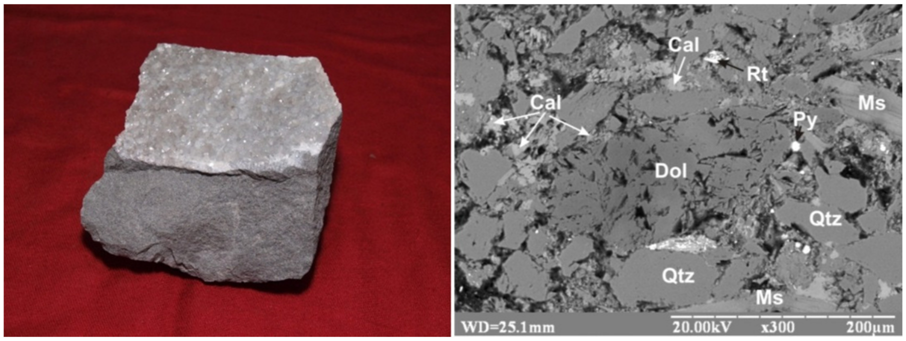


Figure 1. *Sandstones with druse of late calcites (left). Back-scattered image of the sandstone (right): detrital dolomite (Dol) and calcites (Cal) cement, Ms – muscovite, Py – pyrite, Rt – rutyl, Qtz – quartz*

Calcite druses and veins dominate; they contain everywhere at least small crystals of quartz, which has all the features of the Maramures "diamonds". Hydrocarbons seeps (yellow-green in color) on surfaces of the late druse in flysch rocks (see Figure 2, right) were found in the artificial outcrops of the new Beskyd tunnel. In these places quartz contains a large number of liquid and solid hydrocarbons inclusions.

Figure 2. *Shale with late calcite-quartz druse (left). Late quartz-calcite-sulphide druse on sandstone (in center). Hydrocarbons seep (yellow-green) on surface of the late druse in flysch rocks (right).*

Carbonates from the initial flysch rocks have δ^{13}C and δ^{18}O values similar to those of the typical marine limestone carbonates and are limited in a relatively narrow field (Figure 3).

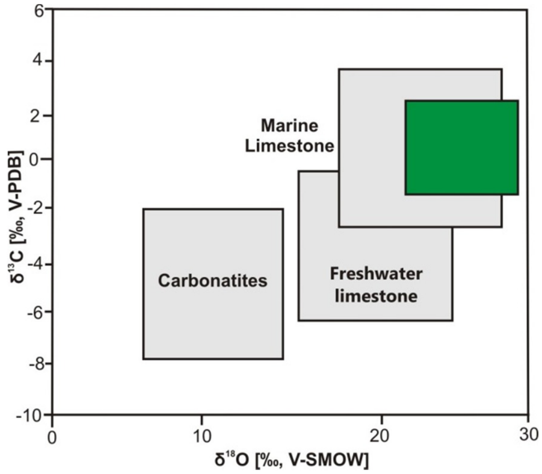


Figure 3. *δ^{13}C vs. δ^{18}O diagram shoving field of the stable isotopes values in the measured primary carbonates (green) concerning of the main nature carbon and oxygen reservoirs (after Hoefs, 2009).*

The spatial and composition relationship between carbonates of the first generation and druse mineralization indicates their commonness. Late carbonates were formed during faults development in lithified rocks: they have the characteristics of the open cavities. Carbon and oxygen data of the late carbonates commonly are close to δ^{13}C and δ^{18}O values determine for primary carbonates. It can be a good evidence for their inheritance, and formation of the late carbonates from solutions that actively interact with the host rocks. But some calcites enriched in heavy ^{13}C isotope ($\delta^{13}C$ up to +7.2 ‰) have been formed from mixing fluids. Late aragonite enriched with heavy carbon isotope ^{13}C ($\delta^{13}C$ up to +9.5 ‰) confirms possible connection between aragonite and neighboring ore mineralization (Kril, 2014).

Keywords: stable isotopes, carbonates, flysch, Ukrainian Carpathians.

References

Bojanowski M.J. (2007). The onset of orogenic activity recorded in the Krosno shales from the Grybow unit (Polish Outer Carpathians). *Acta Geologica Polonica* 57(4):509-522.

Guliy V., Kril S., Yemelyanov I., Kuzemko Ya., Stepanov V. (2016). Late sulphide-quartz-carbonate mineralization in the Krosno Zone rocks within the route of the New Beskydskyi Tunnel. *Mineralogical Review* 66(2):77-87.

Hoefs J. (2009). Stable Isotope Geochemistry. Verlag-Berlin-Heidelberg: Springer.

Kril S. Ya (2014). Isotopic composition of the carbonate veins in the Rakhiv-Tysa Fault Zone (Transcarpathians), *Mineralogicheskii Zhurnal* 36(3):30-39.

ISOTOPIC INVESTIGATION OF HYDRATED SULFATES OF PERMIAN-TRIASSIC AGE

Ana-Voica Bojar[1,2], **Stanislaw Hałas**[3], **Hans-Peter Bojar**[2],
Andrzej Trembaczowski[3]

[1]*Department of Geography and Geology, Salzburg University, Hellbrunnerstrasse 34, 5020 Salzburg, Austria*
[2]*Department of Geoscience, Studienzentrum Naturkunde, Universalmuseum Joanneum,*
Weinzöttlstraße 16, 8045, Graz, Austria
[3]*Mass Spectrometry Laboratory, Institute of Physics, Maria Curie-Skłodowska University,*
20-031 Lublin, Poland
Corresponding author: *ana-voica.bojar@sbg.ac.at*

The investigated hydrated sulfates (gypsum, polyhalite) occur in the evaporitic deposits of the Northern Calcareous Alps and in the so-called Central Alpine Mesozoic, Austria. Further samples investigated for this study are from New Mexico and Zechstein facies of Europe.

According to Gonfiantini and Fontes (1963) and Fontes and Gonfiantini (1967) for both oxygen and hydrogen isotopes the fractionation factor $\alpha = (1000 + \delta_{crystal.water}) / (1000 + \delta_{brine})$ between formation brine and water of crystallisation are not temperature dependent. Using the fractionation factors for oxygen and hydrogen, the calculated $\delta^{18}O$ and δD values of brines are: (*a*) for gypsum from -5.7 to -15‰ and -30.9 to -88.8‰, respectively; (*b*) for polyhalite from 14.4 to 3.4‰ and 42.5 to -6.1‰, respectively. Polyhalite loses crystallisation water at 285°C (Fisher *et al.*, 1996), its structure being more stable than that of gypsum, which loses water of crystallisation at 200°C (Kemp, 1999).

For the Northern Calcareous Alps, sulfur isotopic composition for both gypsum and polyhalite falls in a narrow range between 10 and 12‰. Triassic sulfates from the Central Alpine Mesozoic, consistently show a more enriched isotopic composition of sulfur, with delta values between 14 and 15‰ (Bojar *et al.*, 2016). The data suggest that sulfates largely preserve their initial marine sulfur isotopic signature. In contrast to sulfur, oxygen isotopic compositions of sulfate group in gypsum and polyhalite, shows a broader distribution between 6 and 20‰. For sulfates formed at low temperature in marine environment, the measured oxygen isotope composition is largely in disequilibrium with the oxygen isotope composition of water (Chiba and Sakai, 1985), between dissolved and precipitated sulfates fractionation being in order of 3.5‰ (Llyod, 1968). We interpret the measured trend and the shift of oxygen isotopic composition toward higher values than the marine ones, as reflecting partial equlibration of sulfates at higher temperatures.

Since polyhalites were not thermally overprinted over 275°C they have preserved their water of crystallisation and rather (re)crystallized at temperatures between 100°C to 200°C. On the other hand, secondary growth features were described for polyhalite of the Eastern Alps (Leitner *et al.*, 2013) showing recrystallization younger than Permian. We may assume that during this process reequilibration and /or incorporation of low amount of meteoric fluid took place.

Alpine overprint temperatures over 200°C were high enough in order to drive dehydration of gypsum to anhydrite. Rehydration to gypsum is possible if fluids are available and temperature decreases under the dehydration limit of the mineral. The calculated isotopic compositions of brine suggest that during rehydration/ recrystallization calcium sulfate (gypsum, anhydrite) incorporated meteoric water. Those meteoric waters were more depleted in the heavy isotope of oxygen and hydrogen than the present day meteoric water, indicating cooler conditions and/or higher altitudes. A few gypsum samples show their water of crystallisation close to the present global meteoric water line.

Acknowledgments: *We acknowledge CEEPUS mobility grant for Ana-Voica Bojar, mobility making possible cooperation with Mass Spectrometry Laboratory, Institute of Physics, Maria Curie-Skłodowska University*.

References

Bojar A.-V., Hałas S., Bojar H.-P., Trembaczowski A. (2017) Late Permian to Triassic isotope composition of sulfates in the Eastern Alps: palaeogeographic implications. *Geological Magazine*, DOI: 10.1017/S0016756816000996.

Chiba H. and Sakai H. (1985) Oxygen isotopic exchange rate between dissolved sulfate and water at hydrothermal temperatures. *Geochimica et Cosmochimica Acta* 48:993-1000.

Fisher S., Voigt W. and Köhnke K. (1996) The thermal decomposition of polyhalite K_2SO_4-$MgSO_4$-$2CaSO_4$-$2H_2O$. Crystal Research and Technology 31(1):87-92.

Fontes J.C. and Gonfiantini R. (1967) Fractionment isotopique de l´hydrogene dans l´eau de crystallization du gypse. *Comptes Rendue de l´Academie de Sciences*, *Paris*, 265:2-4.

Gonfianti R. and Fontes J.C. (1963) Oxygen isotopic fractionation in the water of crystallization of gypsum. *Nature* 2000:644-646.

Leitner C., Neubauer F., Genser J., Borojevic-Sostaric B. and Rantitsch G. (2013) $^{40}Ar/^{39}Ar$ ages of recrystallization of rock-forming polyhalite in Alpine rocksalt deposits. In Jordan F., Mark D.F., Verati C. (eds.) Advances in $^{40}Ar/^{39}Ar$ Dating: from Archaeology to Planetary Sciences. *Geological Society, London, Special Publications,* 378:207-244.

Lloyd R.M. (1968) Oxygen isotope behaviour in the sulfate-water system. *Journal of Geophysical Research* 73:6099-6110.

RECONSTRUCTION OF THE BLACK SEA LATE PLEISTOCENE TO HOLOCENE PALEOENVIRONMENTAL EVOLUTION BASED ON MICROFAUNAL AND STABLE OXYGEN ISOTOPE CHANGES

Andrei Briceag[1], **Anastasia Yanchilina**[2], **William B.F. Ryan**[2], **Marius Stoica**[3], **Mihaela C. Melinte-Dobrinescu**[1]

[1]*National Institute of Marine Geology and Geo-ecology, GeoEcoMar,*
23-25 Dimitrie Onciul Street, RO-024053 Bucharest, Romania
[2]*Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA*
[3]*University of Bucharest, Faculty of Geology and Geophysics, Bucharest, Romania*
Corresponding author: *andrei.briceag@geoecomar.ro*

The Black Sea is a semi-enclosed marginal basin, which connects with the Mediterranean Sea through the Bosphorus Strait, Marmara Sea and Dardanelles Strait. Beside the connection with the Mediterranean Sea, in the Late Pliocene-Pleistocene times the Black Sea experienced a period of connection with the Caspian Sea through the Manych Corridor due to the melt waters from the Scandinavian ice sheets (Fedorov, 1977; Chepalyga *et al*., 2004; Bahr *et al*., 2006; Major *et al*., 2006).

In the deeper parts of the Black Sea basin, i.e. below 200 m water depth, Ross and Degens (1974) identified three litho-stratigraphic units (from young to old): Unit 1 (the microlaminated coccolith ooze, deposited under marine conditions), Unit 2 (the sapropel mud, corresponding to an anoxic phase), and Unit 3 (the lacustrine lutite deposited during the freshwater or oligohaline stage).

In the early Holocene, water composition in the Black Sea evolved from fresh to marine; biotical turnover mirrors this change. The transition of the Black Sea from an inland lake to a marine basin during the last glacial/deglacial episode is still generating discussion in the scientific community. In this study, high resolution microfaunal analyses coupled with isotopic and calcium carbonate performed on an AMS ^{14}C dated core, 09 SG 13, revealed changes that occur in the Black Sea from the Last Glacial Maximum through the transition to the present day semi-enclosed marine basin. In the sedimentary record this deglaciation accumulated allochthonous continentally derived red sediments, simultaneous with the global Heinrich Event 1, 18 to 15 kyr BP. This sediments are characterized by depleted δ^{18}O and Mn, increased Ti/Ca ratio as well as higher values of kaolinite and illite, probably indicating that their origin is from a more northern location (i.e., the Alps and the Fennoscandinavian Ice Sheet) (Yanchilina *et al*., in prep.).

In the studied core, situated at 200 m water depth, two lithological units, respectively the youngest Unit 1 (Coccolith Mud) and the oldest Unit 3 (Lacustrine lutite), were identified, with the base dated 24.5 kyr BP (into the latter part of

Marine Isotope Stage 2, MIS 2, glacial period). Since Unit 2 is missing, either the water depth was not enough to develop the sapropel facies or it was naturally eroded. This gap extends between the Younger Dryas and the mid-Holocene when the freshwater Neoeuxinian Lake transformed into a saltwater sea. From the ostracods point of view this transformation is represented by the disappearance of the fresh-brackish ostracod taxa (Caspian in origin) and by the appearance of brackish-marine ones (Mediterranean in origin). The core contains a red-clay and silt interval belonging to the post-glacial melt-water pulse of the Heinrich Event 1. In this sequence, the sedimentation rate increases by a factor of four. The oxygen isotopes are very light (< -6 ‰) in the glacial period, reach < -7 in the melt water pulse and then gradually become heavier and stabilize on a plateau of -4 in the Younger Dryas. The Oxygen isotopes shows the development of a strong vertical stratification of the Neoeuxine lake in the post-glacial Bølling/Allerød warming period, stratification that is not present in the glacial period or red-clay interval. The glacial cold period is marked by the presence of the cold-water ostracod species *Candona fabaeformis* while the post-glacial warming by the warm-water ostracod *Erpetocypris* sp. In the upper part of the core, in Unit 1, a brackish ostracod assemblage, with low diversity and abundance was identified. This interval is characterised by the presence of polyhaline ostracods (Boomer *et al*., 2010; Ivanova *et al*., 2012) with Mediterranean origin (i.e., *Hiltermannicythere rubra*, *Cytheroma variabilis* and *Palmoconcha granulata*). The ostracods from this assemblage tolerate salinities comprised between 17-21 ‰ and characterise a sub-littoral environment.

The aim of this study is to refine the last 25,000 years Black Sea stratigraphy and to decipher the paleoenvironmental and paleoecological conditions by the integration of the fossil record (i.e. micro and macrofauna) with the oxygen isotope fluctuations, $CaCO_3$ values and AMS ^{14}C dating. Detailed micropaleontological studies, based on ostracod and foraminifera analyses, are also presented herein.

Keywords: ostracods and foraminifers; sea level fluctuation; Black Sea; red clay.

Acknowledgments: *The authors thank to the whole crew of the research vessel Mare Nigrum (owner GeoEcoMar), for the support gave during the scientific cruises on the Black Sea. We are indebt to Prof. Dr. Werner Piller, who kindly help us to perform micropaleontological studies to SEM, in Graz University. We are indept to the late General Director of GeoEcoMar, Dr. Gheorghe Oaie, who provided the studied cores, to Dr. Irina Catianis for her assistance with measurements of organic matter and carbonate content and to the late geologist Constantin Ungureanu, who helped us with the sedimentological studies. This research was financially supported by the National Project Nucleu PN 16 45 02 01.*

References

Bahr A., Arz H.W., Lamy F., Wefer G. (2006) Late glacial to Holocene palaeoenvironmental evolution of the Black Sea, reconstructed with stable oxygen isotope records obtained on ostracod shells. *Earth and Planetary Science Letters* 241:863-875.

Boomer I., Guichard F., Lericolais G. (2010) Late Pleistocene to Recent ostracod assemblages from the western Black Sea. *The Journal of Micropaleontology* 29:119-133.

Chepalyga A.L., Sadchicova T.A., Leonova N.B., Nesmeianov S.A., Pirogov A.N. (2004) Caspian-Black Sea water exchange along Manyche-Kerch Watergate in the Late Pleistocene. *Papers from the Int. Conf*. (24-27 September 2004, Volgograd-Astrakhan), Humanistica. In: Ekologiia antropogena i sovremennosti: priroda i chelovek" Sbornik statey Mezhdunarodnoi Konferentsii (Ecology of the Anthropogene and Contemporaneity: Nature and Man), pp. 50-53 (In Russian).

Fedorov P.V. (1977) Late Quaternary history of the Black Sea and southern seas of Europe. In: Kaplinand P.A., Shcherbakov F.A. (Eds.), Paleogeografiia i otlozheniia pleistotsena iuzhnykh morei SSSR [Paleogeography and Deposits of the Pleistocene of the Southern Seas of the USSR]. *Nauka*, Moscow, pp. 25-32 (in Russian).

Ivanova E.V., Murdmaa I.O., Karpuk M.S., Schornikov E.I., Maret F., Cronin T.M., Buynevich I.V., Platonova E.A. (2012) Paleoenvironmental changes on the northeastern and southwestern Black Sea shelves during the Holocene. *Quaternary International* 261:91-104.

Major C.O., Goldstein S.L., Ryan W.B.F., Lericolais G., Piotrowski A.M., Hajdas I., 2006. The co-evolution of Black Sea level and composition through the last Deglaciation and its paleoclimatic significance. *Quaternary Science Reviews* 25:2031-2047.

Ross D.A., Degens E.T. (1974) *Recent sediments of the Black Sea*. In: Degens E.T. and Ross D.A. (Eds.) The Black Sea: Geology, Chemistry, and Biology. American Association of Petroleum Geologists, Tulsa, USA: 183-199.

APPLICATIONS OF STABLE ISOTOPE STUDIES ON CAVE DEPOSITS

Bogdan P. Onac

School of Geosciences, University of South Florida, USA & Emil Racovita Institute of Speleology, Cluj-Napoca, Romania
bonac@usf.edu

Caves are natural openings in Earth, large enough to provide access to humans. Since caves are void spaces, they tend to fill over time with a variety of autochthonous and allochthonous materials, such as clastic sediments, speleothems, ice, bones, etc. These deposits may be preserved for long periods of time (up to millions of years) since cave environments are protected from surficial weathering and underground temperature and relative humidity remain constant year around in the inner parts of caves.

Cave deposits encompass three main categories: clastic, organic, and chemical, all yielding a wealth of paleoclimate and paleoenvironmental information. Recent developments in a suite of analytical facilities, including stable isotope techniques, opened unprecedented opportunities to karst scientists to advance the understanding of caves as physical, chemical, and biological environments. This translates into more challenges and also, exciting new discoveries.

Presently, there is a resurgence of studies using stable isotope analysis on different cave deposits aiming to answer questions, ranging from the origin of caves and their mineral accumulations, to complex climatic and environmental reconstructions.

By far, most of the cave-related stable isotopic applications are directed towards speleothems (e.g., stalagmites and flowstones), which are secondary mineral deposits precipitated from cave seepage water. They are sensitive to climate and environmental changes as their growth mechanism is linked to Earth's atmosphere, hydrosphere, and biosphere in a number of ways. For example, $\delta^{2}H$ (in fluid inclusions) and $\delta^{18}O$ values provide critical information on air temperature, source, amount, and composition of meteoric precipitation. No one needs to be reminded that speleothem records are the terrestrial geographic complement to marine records and the warm-climate complement to ice core. Thus, following the strategy of the ice core community, cave scientists have adopted a long-term vision that allowed them to establish long (up to 640,000 years) speleothem-based oxygen isotopic composition of precipitation in key locations and correlate them to others around the world. Carbon isotopic variations in speleothems may reflect a variety of potential processes (photosynthetic pathway of plants, degassing, etc.), although in some specific cases, one of these processes may dominate the others, and a primary environmental signal can be extracted.

A novel approach in speleothem research is the carbonate clumped isotope analysis (reported as Ä^{47}), which can be used to determine the formation temperature of carbonate minerals. This technique is based on the temperature-dependent over abundance of ^{13}C-^{18}O bonds in the crystal lattice compared to a stochastic distribution. The proxy is still new, thus calibrations, corrections, and other technical challenges are yet to be further refined.

Oxygen and hydrogen isotopic composition of ice are extremely valuable paleoclimatological proxies. The perennial ice deposits accumulated in caves and lava tubes, with few notable exceptions, received inadequate attention for two main reasons: *1*) rarely, are older than 500 years and *2*) a host of factors (freezing, sublimation, etc.) can potentially affect the δ^2H and $\delta^{18}O$ values of cave ice. Nevertheless, the isotopic studies conducted on ice accumulated in caves from Canada, Switzerland, and Romania revived a research direction that is clearly under investigated. For example, a recent study on the 10,500-year old ice preserved in Scarisoara Ice Cave (Romania) allowed reconstructing the Holocene winter climate variability in Central and Eastern Europe.

A relatively untapped paleo-archive is apparently locked in cave guano deposits accumulated under long-term bat maternity roosts. Bats are feeding on insects whose dietary preferences reflect the local vegetation of which distribution is controlled by the local/regional climate and human impact (deforestation, fire). Thus, stable isotope analyses of bulk guano or insect chitin potentially provide useful information on changes in the regional vegetation assemblage (via $\delta^{13}C$), human impact and local N-cycle ($\delta^{15}N$), as well as source (δ^2H) and amount ($\delta^{13}C$) of precipitation.

Mineralogy, mineral processes, and speleogenesis are other fields that benefit from stable isotope investigations. $\delta^{18}O$ and $\delta^{13}C$ values of cave carbonates allow deciphering whether certain minerals assemblages were precipitated from low-temperature solutions or thermal fluids. Certain cryogenically-precipitated carbonate minerals are known to be accompanied by large carbon and oxygen stable isotope fractionation. Very high $\delta^{13}C$ values (up to +17‰) measured in cave calcite are indicative of rapid freezing of water accompanied by a quick kinetic CO_2 degassing. Such process typically occurs either in relation to permafrost conditions or presence of perennial ice accumulation in caves.

Until recently it was thought that sulfuric acid speleogenesis (SAS) produces cave sulfate deposits with ^{34}S-depleted isotopic signatures compared to those of the original source of S in sulfate rocks. However, such values alone do not provide enough information to clearly distinguish SAS from other speleogenetic pathways driven by carbonic acid, ascending thermal waters, or other processes. Thus, the combined use of $\delta^{18}O$ and $\delta^{34}S$ systematics of cave sulfate minerals (mainly gypsum) appears to be a better approach in recognizing various processes involved in speleogenesis, especially when dealing with complex cave systems.

Keywords: cave deposits, stable isotopes, paleoclimate, paleoenvironment.

Acknowledgment: *This presentation was developed based on results from numerous research project funded over the years by the Romanian National Authority for Scientific Research (CNCS) and the National Science Foundation (USA).*

OXYGEN AND CARBON STABLE ISOTOPE VARIABILITY IN *Pinus cembra* L. A 400-YEAR PERSPECTIVE OF SUMMER CLIMATIC CONDITIONS IN THE NORTHERN CARPATHIAN MTS. (EASTERN EUROPE)

Viorica Nagavciuc[1,2,3], Zoltán Kern[2], Aurel Perşoiu[3,4], Ionel Popa[5]

[1]Faculty of Forestry, Ştefan cel Mare University, Suceava, Romania
[2]Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences MTA, Budapest, Hungary
[3]Stable Isotope Laboratory, Ştefan cel Mare University, Suceava, Romania
[4]Emil Racoviţă Institute of Speleology, Cluj Napoca, Romania
[5]National Research and Development Institute for Silviculture Marin Dracea, Câmpulung Moldovenesc, Romania
Corresponding author: *nagavciuc.viorica@gmail.com*

The climate is continuously changing, with major impacts on both natural environment and human society. In order to better understand the responses to these changes, as well plan for future adaptation and mitigation scenarios, it is necessary to place the present-day climatic changes into a longer context.

The aim of this study is to (*i*) calibrate the relationship between the stable isotopic (oxygen and carbon) composition of Swiss stone pine (*Pinus cembra*) tree rings and the main climatic parameters in the Northern Carpathian Mts. (Romania, Eastern Europe), (*ii*) provide the first palaeoclimatic reconstitution in Romania based on the isotopic composition of tree-ring cellulose, and (*iii*) to test the hypothesis that sulphur mining in the vicinity of tree sampling sites have not altered the climatic signal recorded by the stable isotopic composition of tree rings, contrary to the similar signals recorded by tree-ring width.

For this study, we have analysed wood samples of Swiss stone pine from living and subfossil trees from Călimani Mts., N Romania, aged between 1600 and 2012 AD. The isotopic composition of oxygen and carbon from the cellulose was analysed using a high-temperature pyrolysis system (Thermo Quest TC-EA) coupled to an isotope ratio mass spectrometer (Thermo Finningan Delta V) (Saurer *et al.*, 1998) following a ring-by-ring (*i.e.*, non-pooled) approach at the Institute for Geological and Geochemical Research, Budapest, Hungary.

The relationships between the isotopic composition of tree rings and climatic parameters were evaluated using the nearest grid point data from 0.1°x0.1° ROCADA gridded data (Dumitrescu and Birsan, 2015), using CLIMTREG software, what using a moving time window that varied from 21 days to 121 days. (Beck *et al.*, 2013).

The tree ring cellulose $\delta^{18}O$ and $\delta^{13}C$ values showed a strong positive correlation with maximum air temperature (r = 0.6 for $\delta^{18}O$ and r = 0.5 for $\delta^{13}C$, respectively), mean temperature (r = 0.6 for $\delta^{18}O$ and r = 0.45 for $\delta^{13}C$, respectively), and sunshine duration (r = 0.69 for $\delta^{18}O$) and negatively correlated with precipitation amount (r = -0.5 for $\delta^{18}O$ and r = 0.3 for $\delta^{13}C$) and nebulosity (r = 0.6 for $\delta^{18}O$) during the summer months (June, July and August), while correlations with tree-ring widths were lower ($r^2 < 0.3$), thus implying a superior potential of the stable isotopic composition of tree rings as climatic proxies. Sulphur exploitation was active at the location of our sampling sites between 1972 and 1992, and the release of sulphur lead to the breakdown of the growth-climate relationship (based on TRW measurements). However, the relationships between tree-ring cellulose $\delta^{18}O$ and $\delta^{13}C$ values and climate highlighted above were maintained over the period of sulphur exploitation, thus implying that the related environmental impact disturbed the cambial activity however, did not influenced remarkably the biochemical cycles of cellulose synthesis and the accompanying isotope effects.

Next, we have used these correlations to characterise the climatic variability in N Romania, since AD 1600. The coldest summers occurred between 1650-1690, 1730-1850, and 1960-1980, while the warmest ones between 1690-1725, 1850-1875, and since 1980 until present, with the maximum values in the 21st century (Figures 1 and 2).

By Romania's position in East - Central Europe, where Atlantic, Mediterranean and Scandinavian climate influences converge, and strong correlation between dendroisotopic signal and climate could be an important tool for paleoclimatic reconstruction and has a great potential to contribute to our understanding of climate variability of the entire continent.

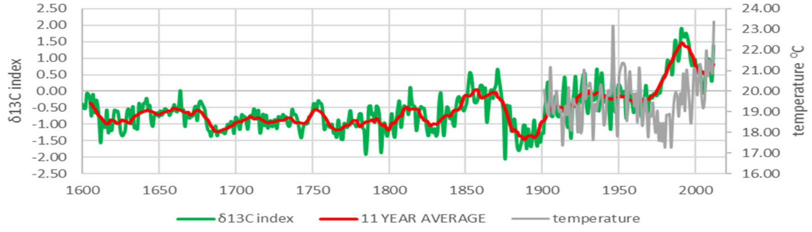


Figure 1. *Carbon stable isotope variability in Pinus cembra L. in the Northern Carpathian*

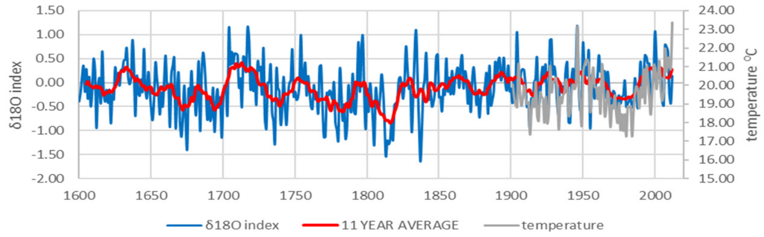


Figure 2. *Oxygen stable isotope variability in Pinus cembra L. in the Northern Carpathian*

Keywords: tree rings, $\delta^{13}C$, $\delta^{18}O$, palaeoclimate.

Acknowledgments: *LP2012-27/2012, CLIMFOR 18SEE, PN-II-RU-TE-2014-4-1993.*

A NOVEL APPROACH TO RAPID ELEMENTAL AND ISOTOPIC IMAGING OF CARBONATES

Ciprian Stremțan[1], Virgil Drăgușin[2], Olga Borovinskaya[3], Dominique Blamart[4]

[1]Teledyne CETAC Technologies, Omaha, NE 68144, USA
[2]Institute of Speleology "Emil Racoviță", Bucharest, 050711, Romania
[3]TOFWERK AG, Thun, CH-3600, Switzerland
[4]Laboratoire des Sciences du Climat et de l'Environment LSCE-IPSL CEA-CNRS-UVSQ,
Gif-Sur-Yvette CEDEX, France
Corresponding author: Ciprian.stremtan@teledyne.com

Accurate dating of paleoclimate archives is essential for all paleoclimate reconstructions. In this respect, speleothems are widely acknowledged as outstanding archives of past climate information, as well as robust candidates for U-series geochronology. However, sampling uncertainty is a major concern and often the investigator faces the difficult task of having to compromise between spatial resolution and data quality.

In this contribution we present a new rapid screening technique for fast identification of sampling regions within speleothems that are less suitable for U-series chronology.

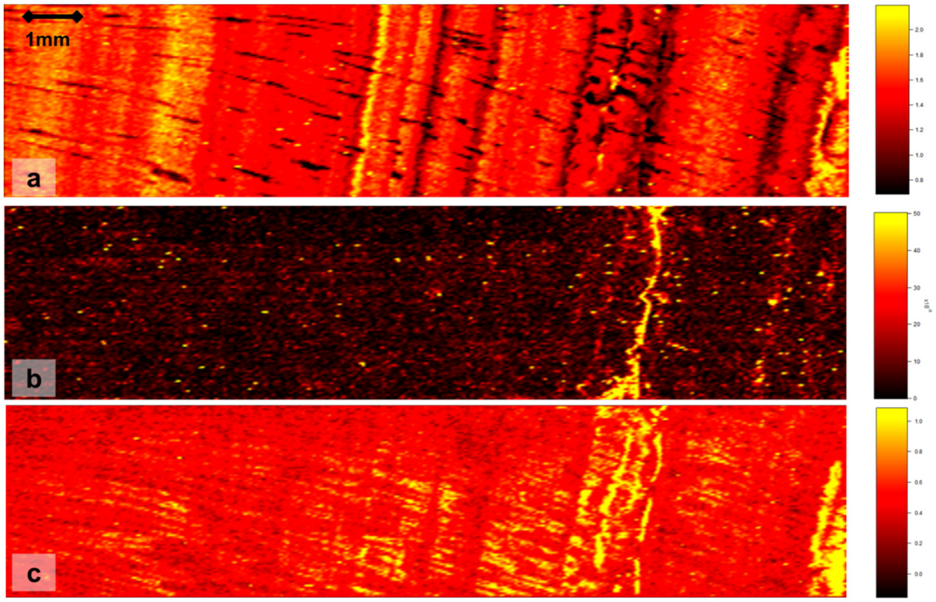


Figure 1. *High-resolution images for selected elements. All scales are in ppm (a) Spatial distribution of U; (b) Spatial distribution of Th; (c) Spatial distribution of Y.*

High-resolution, rapid elemental imaging by means of laser ablation (LA) - time of flight mass spectrometry (TOF) (Figure 1) is implemented for the first time to resolve growth increments smaller than 40µm that show chemical fingerprints of detrital input (*e.g.*, high ^{232}Th and selected REE, low ^{238}U/^{232}Th ratio). In addition, coupling of the highly sensitive, simultaneous, and fast TOFWERK's icpTOF with the Teledyne CETAC's Aerosol Rapid Introduction System (ARIS) allows for much faster acquisition of data that can be subsequently used in paleoclimate reconstructions. We compared key trace element concentrations of the ablated areas on a stalagmite collected from Izvorul Tăușoarelor Cave (Romania) with stable isotope data (δ^{18}O and δ^{13}C) previously acquired on the same growth bands and found concurrent geochemical trends.

Rapid imaging of stalagmites by means of LA icpTOF proves to be a powerful tool for dramatically decreasing sampling uncertainty and increasing the accuracy and precision of the data used in paleoclimate reconstructions. Furthermore, the screening procedure is very fast, thus saving valuable analytical time and resources. The robustness of this method makes it easily adaptable to other types of samples that are relevant to paleoclimate studies (e.g., corals, ice cores, etc.).

Keywords: laser ablation, icpTOF, imaging, paleoclimate.

ISOTOPE GEOCHEMISTRY OF CARBONATES OF LOESS-RELATED SOILS IN WESTERN HUNGARY

**István Fórizs, Bernadett Bajnóczi, Viktória Mozgai, Máté Szabó,
István Hegyi, Mária Tóth**

Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, H-1112 Budapest, Budaörsi út 45., Hungary
Corresponding author: *forizs.istvan@csfk.mta.hu*

Although the low-temperature formation of dolomite has been accepted after a several decades long dispute, and even a book was dedicated to this topic (Deelman, 2011), very few papers report on stable isotope geochemistry of dolomite in modern soils (e.g. Capo *et al*. 2000; Kohut *et al*. 1995).

Loess and loess-derived soils in the Carpathian Basin are characterised by the presence of carbonate phases, both calcite and dolomite. The genesis of calcite and isotope geochemistry of bulk carbonate have already been studied (e.g. Koeniger et al. 2014), but the isotope geochemistry of dolomite in loess-derived soils received little attention.

The aim of our study is to describe the stable isotopic characteristics of carbonate phases (calcite, dolomite) in loess-derived soils in two sites having the same annual amount of precipitation, but different topological positions in Western Hungary. The study site Szár Hill is situated about 17 km north-east of Lake Balaton, where the soil is loess-derived, whereas the study site Komárom-Szőny is at the right bank of the River Danube north of Szár Hill, where the soil formed on calcareous alluvial sediments mixed with loess. On the latter site the soil is obviously wetter.

Figure 1 shows the stable carbon and oxygen isotopic composition of calcite and dolomite phases at both study sites. The $\delta^{13}C_{dolomite}$ varies from -4.3‰ to +2.3‰, and the $\delta^{18}O_{dolomite}$ from -7.8‰ to -2.2‰ approximately along a line, and the overlap between the two sites is remarkable. It indicates that the origin of dolomite at the two sites is the same, and there are at least two generations at both sites. Most of the points are situated at the upper right end of the mixing line, and probably that is the loess-inherited dolomite (detrital dolomite), because its isotopic compositional range touches that of dolomite rocks in the nearby Transdanubian Range, Hungary (Haas *et al*. 2017). The other generation of dolomite is possibly pedogenic.

The $\delta^{13}C_{calcite}$ varies from -15.8‰ to -4.2‰, while the $\delta^{18}O_{calcite}$ from -12.3‰ to -6.6‰ again approximately along a line, but in this case the data scatter is higher. Data of the two sites are rather separated, although there are few overlapping data. The soil on the site Komárom-Szőny is wetter, which may explain the more negative $\delta^{13}C$ values, but not the more negative $\delta^{18}O$ values, because the $\delta^{18}O$ of precipitation is approximately the same. If we consider the effect of the River

Danube, it may explain the δ^{18}O shift, because the multi-annual δ^{18}O value of the Danube is lower than the local precipitation by about 2‰ (Fórizs *et al*. 2005). The variations in the δ values are wide, which again may indicate that soil calcite consist at least two generations, similar to the dolomite.

Investigations of soil texture, morphology of carbonate phases and in situ ion probe measurements of stable isotopic composition of individual carbonate grains (both calcite and dolomite) are planned in the near future to check the hypotheses described above.

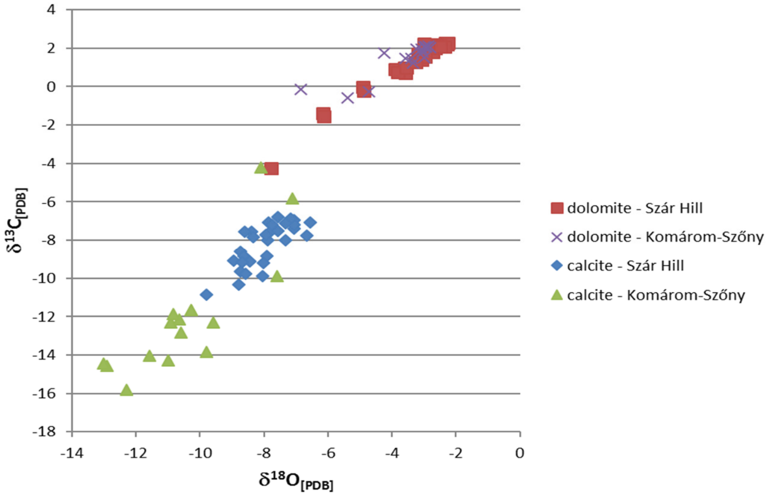


Figure 1. *The stable C and O isotopic composition of calcite and dolomite in bulk loess-related soils in Hungary*.

Keywords: soil, calcite, dolomite, stable isotopes, loess, Hungary.

References

Capo R. C., Whipkey C. E., Blachère J. R., Chadwick O. A. (2000) Pedogenic origin of dolomite in a basaltic weathering profile, Kohala peninsula, Hawaii. *Geology* 28:271-274

Deelman J. C. (2011) Low-Temperature Nucleation of Magnesite and Dolomite. A comprehensive version. Compact Disc Publications, Eindhoven, The Netherlands. http://www.jcdeelman.demon.nl/dolomite/bookprospectus.html

Fórizs I., Berecz T., Molnár Z., Süveges M. (2005) Origin of shallow groundwater of Csepel Island (south of Budapest, Hungary, Danube River): isotopic and chemical approach. *Hydrological Processes* 19(17):3299-3312

Haas J., Hips K., Budai T., Győri O., Lukoczki G., Kele S., Demény A., Poros Zs. (2017) Processes and controlling factors of polygenetic dolomite formation in the Transdanubian Range, Hungary: a synopsis. *International Journal of Earth Sciences (Geol Rundsch)* 106:991-1021

Koeniger P., Barta G., Thiel Ch., Bajnóczi B., Novothny Á., Horváth E., Techmer A., Frechen M. (2014) Stable isotope composition of bulk and secondary carbonates from the Quaternary loess-paleosol sequence in Süttő, Hungary. *Quaternary International* 319:38-49

Kohut K., Muehlenbacks K., Dudas M. J. (1995) Authigenic dolomite in a saline soil in Alberta, Canada. *Soil Science Society of America Journal* 59:1499-154

CLIMATIC SIGNALS RECORDED IN ROMANIAN CARPATHIANS ICE CAVES

Carmen-Andreea Bădăluţă[1,2], **Aurel Perşoiu**[1,3], **Natalia Piotrowska**[4]

[1] *Stable Isotope Laboratory, Ştefan cel Mare University of Suceava, Romania*
[2] *Department of Geography, Ştefan cel Mare University of Suceava, Romania*
[3] *Emil Racoviţă Institute of Speleology, Cluj Napoca, Romania*
[4] *Institute of Physics-CSE, Silesian University of Technology, Gliwice, Poland*
Corresponding authors: *carmenbadaluta@yahoo.com; aurel.persoiu@gmail.com*

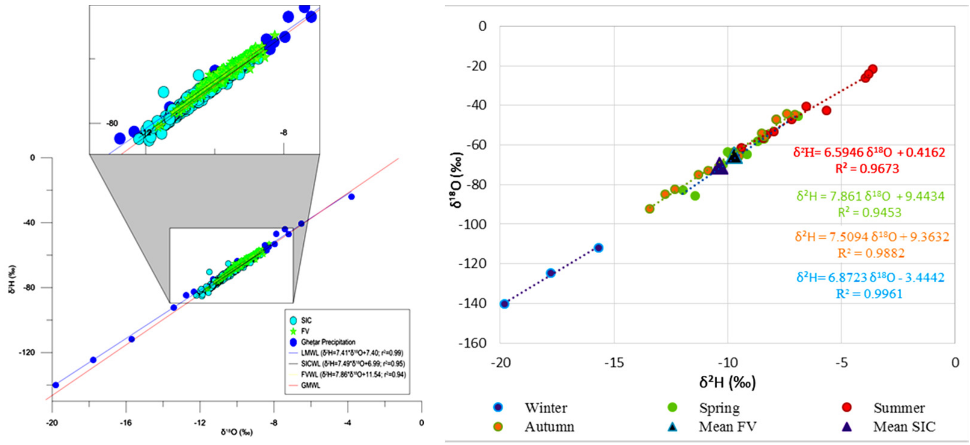
One of the best archives to reconstruct past climatic variability in the Romanian Carpathians are ice caves, rock-hosted caves containing perennial accumulations of ice. Ice in such caves forms through the freezing of shallow (5-15 cm deep) lakes accumulated from percolating water, preserving the climatic signal recorded by the isotopic composition of precipitation outside the cave. While freezing takes places in winter only, the water can accumulate during specific periods of the year, depending on the morphology of the cave, so that the climate of different seasons can be reconstructed by analyzing the isotopic composition of ice.

In the Apuseni Mountains (western Romania), two ice caves host perennial ice blocks that formed through the successive accumulation of annual layers of ice over the past millennium: Scărişoara ice cave (SIC) and Focul Viu ice cave (FV). In these caves, ice has formed by the freezing of water accumulated in summer (FV) and autumn through winter (SIC), respectively. In this paper, we present a reconstruction of climate variability in the Apuseni Mountains during the past ~900 years, based on the analyses of ice from two cores drilled in FV and SIC ice caves. The age of the ice was established based on radiocarbon analyses of organic matter trapped in the ice, and climate was reconstructed using the isotopic composition of the ice as proxy for summer (FV) and winter (SIC) air temperature.

The two caves are located at ~1150 m above sea level, 25 km apart, in similar climatic conditions. The mean annual temperature in the region is ~6 °C and precipitation amount reaches 1200 mm/year. The isotopic composition of precipitation varies between -3.6 ‰ for $\delta^{18}O$ and -22 ‰ for δ^2H in summer, and -19.8 ‰ for $\delta^{18}O$ and -140 ‰ for δ^2H in winter, with mean values of -9.5 ‰ for $\delta^{18}O$ and -64 ‰ for δ^2H. Monthly isotopic values plot along a Local Meteoric Water Line, defined by the equation $\delta^2H = 7.9*\delta^{18}O+8.14$. The d-excess is close to 10, being higher (between 12 and 15) in autumn, when moisture from the evaporatively enriched Mediterranean Sea surface waters reaches the study site.

Radiocarbon analyses of the two cores (~5 m long each) shows that the ice has accumulated during the past ~900 years. While no major hiatuses were observed, ice level monitoring in SIC and sporadic observations in FV demonstrated that 1) the annual layering is not preserved in neither of the two caves and 2) melting could lead to the loss of ice spanning 0-20 years, below the resolution (<40 years) of the radiocarbon dating. Thus, the two ice bodies could be used to reconstruct the climatic variability on a multidecadal scale.

The isotopic composition of ice in the two cores plots along the LMWL (Figure 1), being higher for FV ($\delta^{18}O$ = -9,7‰) than for SIC ($\delta^{18}O$ = -10,3‰). In both caves, the isotopic profile indicates higher values prior to AD 1200, and lower and highly variable, between AD1200 and 1800, corresponding to the Medieval Warm Period (MWP) and Little Ice Age (LIA), respectively. Further, both summer and winter temperatures during the MWP show less variability than during the subsequent LIA. The coldest decades occurred in the 16th and 17th centuries. The d-excessparameter, interpreted as indicating the moisture source, has lower values during the MWP and higher during the LIA, suggesting a predominance of isotopically enriched moisture sources during the coldest periods of the past 1000 years.



a) b)

Figure 1. *Stable isotopes data: a) $\delta^{18}O$ and $\delta^{2}H$ in ice core (FV and SIC) and precipitation to Ghețar; b) seasonal distribution of $\delta^{18}O$ and $\delta^{2}H$ in precipitation to Ghețar and mean of $\delta^{18}O$ and $\delta^{2}H$ in ice core from FV and SIC*

By their position in western Romania, the two caves receive moisture from both the Mediterranean and the Atlantic, the former isotopically enriched. Previous studies (Hurell, 1995; Trouet *et al.*, 2009) suggested that during the MWP, NAO+ (where NAO stands for North Atlantic Oscillation, the leading mode of variability in the Northern Hemisphere, defined as the difference of atmospheric pressure between the Icelandic Low and Azores High) conditions prevailed in Europe. During periods dominated by NAO+ conditions, the storm tracks carrying moisture from the Atlantic towards Europe are shifted northwards leaving SE Europe rather dry. However, our results contradict these findings, suggesting than during the warm MWP SE Europe received more Atlantic precipitation, than during the cold LIA, when it was receiving increased amounts of Mediterranean precipitation. These results suggest that the study region "behaves" in a manner similar to Western Europe, receiving increased amounts of Atlantic moisture during periods characterized by

NAO+ conditions (*e.g.*, during the MWP), and more from the Mediterranean during prevailing NAO_ conditions. While tempting, we didn't correlate the short-term variability of summer and winter temperatures with existing records of annual past climate changes and/or possible forcings (*e.g.,* volcanic eruptions, known years of extreme temperatures etc). We did find, nevertheless, that colder winter periods correlate surprisingly well with periods of reduced solar activity, suggesting that the later could have played an important role in shaping the climate of the NH.

Key words: Focul Viu, Scărişoara, stable isotopes, ice cave, Western Carpathians.

Acknowledgments: *The research leading to these results has received funding from EEA Financial Mecanism 2009 - 2014 under the project contract no 18SEE, and from UEFISCDI Romania, project number PNII-RU-TE-2014-4-1993.*

References

Hurrell J. W. (1995) Decadal trends in the North-Atlantic Oscillation – regional temperatures and precipitation. *Science* 269(5224):676-679.

Trouet V., Esper J., Graham N. E., Baker A., Scourse J. D., Frank D. C. (2009) Persistent Positive North Atlantic Oscillation Mode Dominated the Medieval Climate Anomaly, *Science* 324(5923):78-80.

VARIATIONS IN COLLAGEN $\delta^{13}C$ AND $\delta^{15}N$ VALUES OF RED DEER SINCE THE LATE PLEISTOCENE UNTIL TODAY

Sławomira Pawełczyk[1], Maciej Sykut[2], Natalia Piotrowska[1], Magdalena Niedziałkowska[2], Krzysztof Stefaniak[3], Bogumiła Jędrzejewska[2], Anna Stankovic[4]

[1]*Silesian University of Technology, Institute of Physics - Centre for Science and Education, Konarskiego 22B, 44-100 Gliwice, Poland*
[2]*Mammal Research Institute PAS, Białowieża, Poland*
[3]*Department of Palaeozoology, University of Wrocław, Wrocław, Poland*
[4]*Institute of Genetics and Biotechnology, University of Warsaw, Warsaw, Poland*
Corresponding author: *Slawomira.Pawelczyk@polsl.pl*

Red deer (*Cervus elaphus*) is herbivore species that is numerous in both open and forested habitats in Europe both today and through prehistory (Stevens *et al.*, 2006). Our ongoing project is targeted at habitat selectivity by red deer since Late Pleistocene based on the analyses of stable isotope composition of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) in connection with mtDNA analysis. Plants within forested environments are typically depleted in $\delta^{13}C$ by 2 - 5‰ in comparison to plants and trees in open environments, a phenomenon known as the “canopy effect” as herbivores incorporate the isotopic signatures of the plants they eat into their body tissues (Stevens *et al.*, 2006), values of $\delta^{13}C$ can indicate their habitats. Faunal bone collagen $\delta^{13}C$ and $\delta^{15}N$ values are increasingly used as palaeodietary indicators. Additionally, mammal $\delta^{13}C$ and $\delta^{15}N$ values can also indirectly indicate past climatic changes, as the $\delta^{13}C$ and $\delta^{15}N$ values in the environment, particularly in plants, fluctuate depending on local environmental conditions such as temperature and aridity (Richard and Hedges, 2003). The results of the stable isotope analyses will be compared to the history of red deer populations, phylogeography of the species (based on ancient and contemporary mtDNA analysis), and data on climate and environmental changes in Europe from Late Pleistocene until today.

The project is still in progress. Collagen was extracted from bone samples and in frame of this project 95 red deer collagen samples have been radiocarbon dated by AMS in the Gliwice Radiocarbon Laboratory. Sample locations stretched from Tyrrhenian islands (Corsica and Sardinia), through the Central Europe and Ural to Siberia. The calibrated ages of majority of the samples (n=73), mostly from European sites, fall into the period of the last 10 kaBP. Only one sample, coming from Apennine Peninsula, was found in the time period between 10 and 27 kaBP, while the oldest bones have been discovered in Siberia and Ural, reaching the ages from 27 to 48 kaBP. The time scale will be used for study of temporal distributions of $\delta^{13}C$ and $\delta^{15}N$.

Samples of red deer bone collagen were isotopically analysed in Gliwice Mass Spectrometry Laboratory using an EuroVector elemental analyser coupled to a continuous flow IsoPrime mass spectrometer. $\delta^{13}C$ and $\delta^{15}N$ results are reported in per mil (‰) relative to VPDB and AIR standards, respectively. Each sample was run in triplicate, with analytical errors of 0.1‰ and for $\delta^{13}C$ and 0.2‰ for $\delta^{15}N$.

All isotope measurements presented here were made on well-preserved collagen, as determined by collagen C/N ratios. The atomic C/N ratios calculated for almost all of the samples in this study were between 2.9 and 3.6 which is within the range expected for pure collagen.

For the set of 106 measurements of the red deer samples (prehistorical and modern) analysed the $\delta^{13}C_{VPDB}$ ranged from -26.05‰ to -18.84 and the $\delta^{15}N_{AIR}$ ranged from 0.06‰ to 10.56‰.

Keywords: stable isotopes, carbon, nitrogen, red deer, collagen.

***Acknowledgments**: The research was a part of project: “Genetic diversity and habitat selectivity of red deer (Cervus elaphus) in Europe and Asia’ in the Late Pleistocene and Holocenefunded by the National Science Centre (grant no. UMO-376 2013/11/B/NZ8/00888) and the budget of the Mammal Research Institute PAS in Białowieża.*

References

Richards M.P., Hedges R.E.M. (2003) Variations in bone collagen $\delta^{13}C$ and $\delta^{15}N$ values of fauna from Northwest Europe over the last 40 000 years, *Palaeogeography, Palaeoclimatology, Palaeoecology* 193:261-267.

Stevens R.E., Lister A.M., Hedges R.E.M. (2006) Predicting diet, trophic level and palaeoecology from bone stable isotope analysis: a comparative study of five red deer populations, *Oecologia* 149:12-21.

ANOMALOUS ISOTOPE ^{33}S IN ROCKS SHARYZHALGAI UPLIFT OF THE SIBERIAN CRATON AND SO_2 IN ELECTRICAL DISCHARGE

Alexander Ignatiev[1], **Tatiana Velivetskaya**[1], **Sergey Vysotskiy**[1], **V. Levitskiy**[2], **S. Budnickiy**[1], **Victoria Yakovenko**[1]

[1]*Far East Geological Institute FEB RAS, Vladivostok, Russia*
[2] *Institute of Geochemistry. AP Vinogradov, Irkutsk, Russia*
Corresponding author: *ignatiev@fegi.ru*

The thermodynamic, kinetic and biogenic fractionation processes of sulfur isotopes ^{32}S, ^{33}S and ^{34}S depends on mass-dependent isotope fractionation (MDF), and lead to characteristic fractionation arrays with a slope that is proportional to the relative difference between the isotopes (Urey 1947; Matsuhisa *et al*. 1978). It is described by the simple equation $\delta^{33}S = 0.515 \times \delta^{34}S$ (Hulston & Thode, 1965). In the study of the isotopic composition of minerals and rocks of the Earth believed that strictly observed the MDF of sulfur isotopes. The first violation of MDF of sulfur isotopes was found in the Archean rocks (Farquhar *et al.*, 2000) Sulfur isotope anomalous in rocks older than 2.45 Ga was similar to signatures observed in the products of photochemical experiments, and speculated that an atmospheric influence on Earth's early sulfur cycle was preserved in the sulfur isotope record (Pavlov and Kasting, 2002).

The growing dataset and hypotheses related to mass-independent sulfur fractionation (MIF) are evaluated, emphasizing that which remains to be learned about the evolution of the record, the compositions of key reservoirs. Given that Δ^{33}S anomalies have only recently been discovered in a number of regions of the world, we can assume that in Russia may be present rocks that also have MIF of sulfur isotopes. Here we present evidence that the Archean and Paleoproterozoic rocks of the Siberian craton contains Δ^{33}S anomalies.

We carried out research sulphide samples Sharyzhalgay granulite complex, which is one of the main structural elements of margin salient of the Siberian craton. We have studied samples of rocks his major complexes: Cheremshanskaya suite, Kitoi granulite complex and Onot greenstone belt. To study the isotopic composition of sulfur we used a new in situ technique with femtosecond laser sampling that takes advantage of continuous He flow isotope-ratio-monitoring gas chromatography–mass spectrometry to achieve precise analysis of stable sulfur isotopes – ^{32}S, ^{33}S and ^{34}S. Samples, as small as several nanomole, can be analyzed.

Using this method it was discovered the anomalous mass independent fractionation of sulfur isotopes Δ^{33}S ($\Delta^{33}S = \delta^{33}S - 0.515 \times \delta^{34}S$) with values ranged from -1.17‰ to +2.75‰. Given that investigations have consistently demonstrated large magnitude $\Delta^{33}S$ signals stemming from SO_2 photolysis, this process is probably the most important in explaining the Archean record.

In the study of multi-isotopic composition of sulfur in the subaerial volcanic ashes (Mapepe Formation of South Africa) was discovered a unique combination of a negative value $\delta^{34}S$ and with a positive value $\Delta^{33}S$ (Philippot *et al*., 2012; Muller *et al*., 2016). These sulfur isotope composition values obtained under subaerial volcanic activity cannot be explained by any of the photochemical experiments and theoretical calculations known to date.

However, mass-independent effect of sulfur isotopes in this case, can be explained by the results obtained in our experiments. Experimental studies fractionation of sulfur isotopes in electric discharges allowed establishing MIF in SO_2. Reaction of SO_2 dissociation was carried out in high-voltage pulsed discharge with a frequency of 50 Hz in a quartz reactor. The reaction products were condensed on the walls of the reactor in the form of S^8 and SO_3. Elemental sulfur was collected by washing the reactor with hexane. Sulfur precipitated as fine crystals by evaporation of hexane. Sulfur crystals are melted, thus forming a droplet suitable for the measurement of sulfur isotopic composition. Value $\delta^{34}S$ elemental sulfur was equal to -10.0 +/- 0.4‰ at atmospheric pressure of SO_2 and increased to -8.4 +/- 0.7‰ while reducing the pressure to 0.1 mbar. At the same time, the effect of the independent mass fractionation increasing with decreasing pressure and changes from $\Delta^{33}S$ + 0.24‰ atmospheric pressure to + 1.57‰ a pressure of 0.1 mbar. Unlike SO_2 fotodissociation reactions in which $\delta^{34}S$ and $\Delta^{33}S$ have positive values in the dissociation reactions in electrical discharges $\delta^{34}S$ takes negative values, but the value remains positive for $\Delta^{33}S$, what can serve as a basis for an explanation for the unique combination of a negative value $\delta^{34}S$ and with a positive value $\Delta^{33}S$ for subaerial volcanic activity in Archean.

Keywords: Sulfur isotopes; Mass-independent fractionation; Laser ablation; IRMS; Archean.

Acknowledgments: *This study was supported by the Russian Foundation for Basic Research, grant #15-05- 00740.*

References

Farquhar J., Bao H., Thiemens M.H. (2000) Atmospheric influence of Earth's earliest sulfur cycle. *Science* 289:756-758.

Hulston J.R., Thode H.G. (1965) Variations in the S33, S34, and S36 contents of meteorites and their relation to chemical and nuclear effects. *Journal of Geophysical Research* 70:3475-3484.

Matsuhisa Y., Goldsmith J.R., Clayton R.N. (1978) Mechanisms of hydrothermal crystallization of quartz at 250°C and 15 kbar. *Geochimica et Cosmochimica Acta* 42:173-182.

Pavlov A.A., Kasting J.F. (2002) Mass-independent fractionation of sulfur isotopes in Archean sediments: Strong evidence for an anoxic Archean atmosphere. *Astrobiology* 2(1):27-41.

Urey H.C. (1947) The thermodynamic properties of isotopic substances. *Journal of Chemical Society*, 562-581.

DETRITAL ZIRCON U-PB DATING FROM THE CARBONIFEROUS ROCKS OF THE FORE-SUDETIC MONOCLINE, POLAND

Urszula Zagórska[1], Sylwia Kowalska[1], Jiří Sláma[2], Krzysztof Wolański[3]

[1] *Oil and Gas Institute – National Research Institute, Kraków, Poland*
[2] *The Czech Academy of Sciences, Prague, Czech Republic,*
[3] *PGNiG SA, Geology and Hydrocarbon Production Branch, Poland*
Corresponding author: *kowalska@inig.pl*

The growing availability of isotopic study eg. detrital zircon U-Pb dating, allows for its more common application in paleogeography or sedimentary basins history reconstruction, performed during hydrocarbons exploration. Zircon grains found in sedimentary rocks bear information about the crystallization age of the source rock due to its resistance to transport and weathering. Analysis of about 100 detrital grains per sample allows to gain statistically meaningful age populations, identifying the source regions and constraining the maximum depositional ages. The last is very useful in strata lacking of biostratigraphic data, like studied Carboniferous rocks of the Fore-Sudetic Monocline.

The Fore-Sudetic Monocline is part of the Variscan foreland basin stretching from the area of Germany to Poland. Carboniferous basin is assumed to be tectonostratigraphic equivalent of the Rheno-Hercynian zone in Germany (Mazur *et al*., 2010). There is a need to broaden knowledge of the Carboniferous strata in Poland as they are the reservoir and source rocks of hydrocarbons. The aim of the study was to determine whether the analysis of detrital zircon ages allows to distinguish the stratigraphic age of Carboniferous sandstones.

Zircon grains separation was conducted at the Oil and Gas Institute – NRI by the standard method of heavy liquid and magnetic separation. Samples were crushed to fraction <320um and separated with neodymium magnet and subsequently by SPT heavy liquid (~2,8 g/cm^3). Separation was followed by determination of U-Pb ages using a laser ablation Mass Spectrometry (LA-ICP-MS). Dating was performed by dr Jiří Sláma at Czech Academy of Sciences, Prague according to procedure described by Košler *et al*., (2002) and Košler & Sylvester, (2003). Hand-picked grains were mounted in epoxy resin and polished to half-thickness of the grains for further analysis. Prior to lasing internal structure of the zircon grains was analyzed under SEM-CL in order to choose analytical spots.

Analyses were performed for eight samples from four wells: Września IG-1, Siciny IG-1, Paproć 29 and Kobylin 1. The Września IG-1 well was selected for test because of the best documented Upper Carboniferous age by biostratigraphic methods. Previous study reported presence of zircons as young as 312 Ma (Mazur *at al*., 2010) in the sample from this well. The current study confirmed the Upper

Carboniferous age of the strata but in the absence of younger than 320 Ma age populations. Probability density plots obtained for the Września IG-1 borehole show similarities to published by Mazur *at al.*, (2010) for 30 analytical spots, but for the larger statistical probe, the dominating age population was 330-350 Ma.

Samples from Siciny IG1 well show strong Carboniferous zircon ages domination, similar to the Września IG-1. In contrast to the other wells, data from the Siciny IG-1 do not contain age populations older than 620 Ma. The Presence of both Westphalian (Pennsylvanian) and Namurian A-B ages (Upper Mississippian – Lower Pennsylvanian boundary) was noted in the Siciny IG-1 borehole according to biostratigraphy (Górecka-Nowak, 2007; 2008). The presented data do not contradict the palynological data, but rather help to constrain the stratigraphic position to Namurian A-B boundary belonging to the lower Pennsylvanian.

Samples from boreholes Paproć 29 and Kobylin 1 are characterised by the presence of much older zircon grains mainly of the Proterozoic age, from which the youngest are 420 Ma. Taking into account the results of the palynological dating in the Paproć 29 (Górecka-Nowak, 2007; 2008) and the position of samples in the profile, the stratigraphic position of the Carboniferous rocks from that boreholes is interpreted as Mississippian (Lower Carboniferous). Age population of about 503 Ma years could originate from the Cambrian volcanic rocks like the one that constitute Kaczawa Mts. (Kryza & Zalasiewicz, 2008).

The results of U-Pb zircon dating allow for unambiguous distinction of Upper Carboniferous strata, mainly sourced from already elevated Variscides, from older rocks, which the source area were strata not younger than Silurian (with a predominance of Proterozoic). Obtained zircon age populations show a drastic change in provenance regions between the time of sedimentation of Września IG-1 and Siciny IG-1 rocks, comparing to Paproć 29 and Kobylin 1. The difference in detritus provenance could be used to distinguish between the Lower and Upper Carboniferous strata in the region. Taking into account chronostratigraphic position of analysed samples and given uncertainty of palynospore zone determination, it can be stated that this significant change in detritus source areas occurred probably at the turn of Mississippian and Pennsylvanian. The data obtained for the Upper Carboniferous rocks indicate a very fast exhumation of the Variscan massif, because of short lag time between detrital age and assumed sedimentation age of Upper Carboniferous sandstones.

Keywords: Fore-Sudetic Monocline, Carboniferous, U-Pb dating, zircons, provenance analysis.

References

Górecka-Nowak A. (2007) Palynological con straints on the age of the Carboniferous clastic succession of SW Poland (Fore-Sudetic area) based on miospore data. *Geo log ical Quar terly* 51: 39-56.

Górecka-Nowak A. (2008) New interpretations of the Carboniferous stratigraphy of SW Poland based on miospore data. *Bulletin of Geosciences* 83: 101-116.

Košler J., Fonneland H., Sylvester P., Tubrett M., Pedersen R.B., (2002) U–Pb dating of detrital zircons for sediment provenance studies: A comparison of laser ablation ICPMS and SIMS techniques. *Chemical Geology*, 182: 605-618.

Košler J., Sylvester P.J., (2003) Present trends and the future of zircon in geochronology: Laser ablation ICPMS. *Reviews in Mineralogy and Geochemistry*, 53: 243-275.

Kryza R., Zalasiewicz J., (2008) Records of Precambrian–Early Palaeozoic volcanic and sedimentary processes in the Central European Variscides: A review of SHRIMP zircon data from the Kaczawa succession (Sudetes, SW Poland), *Tectonophysics,* 461: 60-71.

Mazur S., Aleksandrowski P., Turniak K., Krzemiński L., Mastalerz K., Górecka-Nowak A., Kurowski L., Krzywiec P., Żelaźniewicz A., Fanning M. C., (2010) Uplift and late orogenic deformation of the Central European Variscan belt as revealed by sediment provenance and structural record in the Carboniferous foreland basin of western Poland. *International Journal of Earth Sciences (Geol Rundsch)*, 99: 47-64.

EXPERIMENTAL STUDY OF MASS-INDEPENDENT OXYGEN ISOTOPE EFFECTS IN HYDROGEN PEROXIDE FORMATION

Tatiana Velivetskaya, Alexander Ignatiev, Victoria Yakovenko, Sergey Vysotskiy

Far East Geological Institute, Prospect 100-letya Vladivostoku 159, Vladivostok, 690022, Russia
Corresponding author: *velivetskaya@mail.ru*

Hydrogen peroxide is an important atmospheric component involved in various gas-phase and aqueous-phase transformation processes in the modern Earth's atmosphere. Hydrogen peroxide has also been hypothesized to play significant role in the chemistry of the ancient Earth's atmosphere. It is critical to understand this transformation process and the budgets of atmospheric species.

Stable oxygen isotopes (^{16}O, ^{17}O and ^{18}O) can provide insight into the source, sink and transformation processes of H_2O_2 in the atmosphere. Some gas-phase reactions in the atmosphere lead to mass-independent fractionation (MIF) of isotopes. (Savarino and Thiemens, 1999) have revealed unusual enrichment in the isotopes ^{17}O and ^{18}O in dissolved atmospheric H_2O_2. They found that the relationship between $\delta^{17}O$ and $\delta^{18}O$ for H_2O_2 rainwater showed an offset from the experimentally determined mass-dependent fractionation line. This offset, $\Delta^{17}O$, defined as $\Delta^{17}O = \delta^{17}O - 0.511\ \delta^{18}O$, was gauged to be 1.2 – 2.4‰. (Savarino and Thiemens, 1999a) suggest that MIF may derive from the $H + O_2$ reaction (for the modern atmosphere). However, in the ancient atmosphere, before ~2.4 Ga, O_2 was present in low concentrations, less than 10^{-5} times compared to the present atmospheric level (PAL) of O_2. Under those conditions, other mechanisms would play an especially important role in generating atmospheric H_2O_2.

Therefore, we have undertaken some laboratory experiments to investigate MIF of oxygen isotopes in the process of H_2O_2 formation from direct dissociation of H_2O using an electrical discharge to initiate dissociation of water vapour in the absence of any additional O_2. We are also interested in how the isotopic effect in hydrogen peroxide can be affected by an additional component presented in the reaction at various concentrations. We found a positive MIF signal (~1.4 ‰) in the no-O_2 added experiments, and this signal increased to ~2.5 ‰ once O_2 was added (Velivetskaya *et al.*, 2016). We suggest that if O_2 concentrations are very low, the hydroxyl radical recombination reaction is the dominant pathway for H_2O_2 formation and is the source of MIF in H_2O_2. The experimental results presented here can be considered in the context of H_2O_2 formation by direct photon dissociation of water vapour in the Earth's initial oxygen-free atmosphere, as our laboratory experiments show that H_2O_2 can be generated in an anoxic atmosphere.

Keywords: mass-independent fractionation; oxygen isotopes.

Acknowledgments: *We greatly appreciate the financial support for this research provided by the Russian Foundation for Basic Research (grant # 15-05-00794).*

References

Savarino J. and Thiemens M.H. (1999) Analytical procedure to determine both $\delta^{18}O$ and $\delta^{17}O$ of H_2O_2 in natural water and first measurements, *Atmospheric Environment* 33:3683-3690.

Savarino J. and Thiemens M.H. (1999a) Mass-Independent Oxygen Isotope (^{16}O, ^{17}O, ^{18}O) Fractionation Found in Hx, Ox Reactions, *Journal of Physical Chemistry A.* 103:9221-9229.

Velivetskaya T.A., Ignatiev A.V., Budnitskiy S.Y., Yakovenko V.V., Vysotskiy S.V. (2016) Mass-independent fractionation of oxygen isotopes during H_2O_2 formation by gas-phase discharge from water vapour, *Geochimica et Cosmochimica Acta* 193:54-65.

PRELIMINARY RESULTS OF A STALAGMITE PALAEOCLIMATE RECORD COVERING THE TRANSITION OF THE LAST INTERGLACIAL/GLACIAL PERIOD

László Palcsu[1], László Elemér[1], Gabriella Kiss[1], István Futó[1], Marianna Túri[1], Marjan Temovski[1], Hai Cheng[2]

[1]Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research, Hungarian Academy of Sciences, Bemtér 18/c, Debrecen, 4026 Hungary
[2]Institute of Global Environmental Change, Xi'an Jiaotong University, 28 Xianning West Road, Xi'an 710049, Shaanxi, China
Corresponding author: *palcsu.laszlo@atomki.mta.hu*

Here we show the preliminary results of a stalagmite palaeoclimate record. The stalagmite grew in Baradla Cave, Hungary, between 98 and 129 kyr before present, covering MIS5e and MIS5d and partly MIS5c. Since the stalagmite is found broken, the upper, and maybe the lower part can be also found in the cave, hence a wider time period can be studied. The first results show that oxygen isotope ratio is hardly changing during the interglacial/glacial transition.

The cave is known for stalagmites from MIS5e. Demény *et al*. (2017) has just published a palaeoclimate study from another part of the cave, which is about 4 km from our site. Although, the climatic signal is expected to be the same, there are significant differences in the stable oxygen signature. Further studies have to be performed to reveal these effects.

Key words: stalagmite, oxygen isotope ratio, U-Th dating, past climate.

Acknowledgments: *The research was supported by the European Union and the State of Hungary, co-financed by the European Regional Development Fund in the project of GINOP-2.3.2.-15-2016-00009 'ICER'.*

References

Demény A., Kern Z., Czuppon G., Németh A., Leél-Őssy S., Siklósy Z. , Lin K., Hu H.-M, Shen C.-C., Vennemann T.W., Haszpra L. (2017) Stable isotope compositions of speleothems from the last interglacial - Spatial patterns of climate fluctuations in Europe, *Quaternary Science Reviews*, 161: 68-80.

CARBON ISOTOPE FRACTIONATION DURING DARK RESPIRATION IN C3 *vs* C4 PLANTS

Jaleh Ghashghaie[1], Camille Bathellier[2], Franz-W. Badeck[3]

[1]*Ecologie, Systématique et Evolution, Université Paris-Sud, CNRS, AgroParisTech,*
Université Paris-Saclay, 91400, Orsay, France,
[2]*Research School of Biology, ANU College of Medicine, Biology and Environment,*
Australian National University, Canberra 2601 ACT, Australia
[3]*Council for Agricultural Research and Economics, Genomics Research Centre,*
via San Protaso 302, Fiorenzuola d'Arda, 29017, Italy
Corresponding author: *Jaleh.ghashghaie@u-psud.fr*

The photosynthetic discrimination against ^{13}C leads to a ^{13}C-depletion of plant organic matter while the CO_2 left behind in the atmosphere becomes ^{13}C-enriched. Thus, records of the variation of the isotopic composition of CO_2 above ecosystems can be used to distinguish between photosynthetic and respiratory fluxes. However, the generally accepted hypothesis in such studies that no discrimination occurs downstream photosynthetic fixation is now questioned (Ghashghaie *et al.,* 2003; Badeck *et al.,* 2005; Cernusak *et al.,* 2009).

Several studies have shown that the CO_2 respired by leaves in the dark is ^{13}C-enriched compared to organic matter, while it is ^{13}C-depleted in the case of roots mainly in C_3 herbaceous species, suggesting opposite "apparent respiratory fractionation" in leaves *versus* roots (for a recent review see Ghashghaie & Badeck, 2014, and references therein). Apparent respiratory carbon isotope discrimination (ΔR) is calculated as difference between carbon isotope composition of respiratory substrates ($\delta^{13}C_S$) and of respired CO_2 ($\delta^{13}C_R$). This respiratory discrimination is shown to be highly variable, changing among species, with environmental conditions (Tcherkez *et al.,* 2003), and at diurnal time-scales (Werner & Gessler, 2011).

We have already shown that the intramolecular ^{13}C-distribution in hexoses (Rossmann *et al.,* 1991) together with the relative activities of decarboxylating pathways (PDH *vs.* Krebs cycle) is one of the causes at the origin of the ^{13}C-signal in leaf-respired CO_2 and its variability (Tcherkez *et al.,* 2003). For roots, we have shown that the prevalence of pentose phosphate pathway (PPP) and Krebs Cycle could explain the ^{13}C-depletion in respired CO_2 (Bathellier *et al.*, 2009), but the impact of anaplerotic pathway i.e. CO_2 (re)fixation *via* phospho*enol*pyruvate carboxylase (PEPc), which similarly to PPP is more active in roots, on the $\delta^{13}C$ of root-respired CO_2 is not elucidated yet.

C_4 leaves discriminate only slightly during respiration (contrarily to C_3 leaves). It would be interesting to examine if this is related to the high PEPc activity in C_4 leaves (analogous to roots having higher PEPc activity and lower respiratory fractionation). We thus measured the carbon isotope composition ($\delta^{13}C$) of both CO_2 respired and bulk organic matter (OM) in leaves and roots of C_3 (bean and peanut) and C_4 (maize) plants during early ontogeny. PEPc activity and malate concentrations were also determined in maize leaves.

C_3 leaf-ΔR (Figure 1b) becomes more and more negative after leaf autotrophy onset (i.e. respired CO_2 becomes ^{13}C-enriched). C_3 root ΔR (Figure 1b) remains almost unchanged and around zero in both C3 species, increasing slightly in bean roots at adult stage. C_4 leaf and root ΔR (Figure 1a) change in parallel after leaf emergence (stage 10). Maize respired-CO_2, which is initially ^{13}C-enriched (negative ΔR), then becomes ^{13}C-depleted in roots (positive ΔR), while mature leaves show no apparent fractionation ($\Delta R \approx 0$).

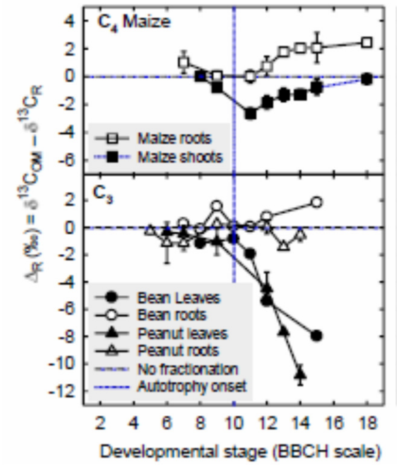


Figure 1. *Changes in apparent respiratory carbon isotope fractionation (ΔR) in leaves (black symbols) and roots (red symbols) of C_4 (a) and C_3 (b) plants during ontogeny. Stage 10 corresponds to the beginning of the first leaf autotrophy (indicated by the vertical dotted line). The horizontal dashed lines correspond to no respiratory fractionation ($\Delta R \approx 0$). Data are means ± SE of 3-10 measurements on different plants. Positive ΔR values indicate ^{13}C-depletin in respired CO_2 and negative ΔR values to ^{13}C-enrichment in respired CO_2 compared to OM. Maize data are from Ghashghaie et al. (2016), bean data from Bathellier et al. (2008), and peanut data from Ghashghaie et al. (2015).*

As expected, similarly to C_3 roots, almost no apparent respiratory discrimination (ΔR) is observed in C_4 (mature) leaves. C_4 leaves show an opposite trend for ΔR compared to C_3 leaves. ΔR of C_4 roots changes similarly to that of C_3 roots but with higher variations. These results could be attributed to a higher PEPc activity in roots of C_3 plants (compared with C_3 leaves) analogous to C_4 leaves. Indeed, contrarily to Rubisco, PEPc discriminates in favour of ^{13}C, leaving behind ^{13}C-depleted CO_2 thus leading to a lower overall respiratory discrimination. Interestingly, similarly to C_3 leaves, a light-enhanced-dark-respiration (LEDR) effect was also observed in maize leaves at the beginning of the dark period, with highly ^{13}C-enriched leaf-respired CO_2 ($\delta^{13}CR \approx -3.5‰$), due to the decarboxylation of malate accumulated in the light. PEPc activity and malate concentration measured on maize leaves confirm the above conclusions.

Keywords: Carbon isotope discrimination, metabolic pathways, respiratory metabolism, leaves *vs* roots, C_3 herbaceous *vs* woody species, ontogeny.

Acknowledgments: *JG and CB are grateful to Laboratoire d'Ecologie, Systématique et Evolution (ESE) for financial support of the experiments and analyses, and the platform Métabolisme-Métabolome and BIOEMCO (INRA, Grignon) for performing isotopic analyses on organic matter and respired CO2, respectively*.

References

Badeck F.W., Tcherkez G., Nogués Piel C., Ghashghaie J. (2005) Post-photosynthetic fractionation of stable carbon isotopes between plant organs - a widespread phenomenon, *Rapid Communications in Mass Spectrometry* 19(11): 1381-1391.

Bathellier C., Badeck F.W., Couzi P., Harscoët S., Mauve C., Ghashghaie J. (2008) Divergence in $\delta^{13}C$ of dark respired CO_2 and bulk organic matter occurs during the transition between heterotrophy and autotrophy in Phaseolus vulgaris plants, *New Phytologist* 177(2): 406-418.

Bathellier C., Tcherkez G., Bligny R., Gout E., Cornic G., Ghashghaie J. (2009) Metabolic origin of the $\delta^{13}C$ of respired CO_2 in roots of *Phaseolus vulgaris*, *New Phytologist* 181(2): 387-399.

Cernusak L.A., Tcherkez G., Keitel C., Cornwell W.K., Santiago L.S., Knohl A., Barbour M.M., Williams D.G., Reich P.B., Ellsworth D.S., Dawson T.E., Griffiths H.G., Farquhar G.D. and Wright I.J. (2009) Why are non-photosynthetic tissues generally ^{13}C enriched compared to leaves in C_3 plants? Review and synthesis of current hypotheses, *Functional Plant Biology* 36(3):199-213.

Ghashghaie J., Badeck F.W., Lanigan G., Nogués S., Tcherkez G., Deléens E., Cornic G., Griffiths H. (2003) Carbon isotope fractionation during dark respiration and photorespiration in C_3 plants, *Phytochemistry Reviews* 2(1): 145-161.

Ghashghaie J., Badeck F.W., (2014) Opposite carbon isotope discrimination during dark respiration in leaves versus roots – a review, *New Phytologist* 201(3): 751-769.

Ghashghaie J., Badeck F.W., Girardin C., Sketriené D., Lamothe-Sibold M., Werner R.A., (2015) Changes in $\delta^{13}C$ of dark respired CO_2 and organic matter of different organs during early ontogeny in peanut plants, *Isotopes in Environmental and Health Studies* 51(1): 93-108.

Ghashghaie J., Badeck F.W., Girardin C., Huiqnard C., Aydinlis Z., Fonteny C., Priault P., Fresneau C., Lamothe-Sibold M., Streb P., Terwilliger V.J. (2016) Changes and their possible causes in $\delta^{13}C$ of dark-respired CO_2 and its putative bulk and soluble sources during maize ontogeny, *Journal of Experimental Botany* 67(9): 2603-2615.

Rossmann A., Butzenlechner M., Schmidt H.L. (1991) Evidence for a non-statistical carbon isotope distribution in natural glucose, *Plant Physiology* 96(2): 609-614.

Tcherkez G., Nogués S., Bleton J., Cornic G., Badeck F., Ghashghaie J. (2003) Metabolic Origin of Carbon Isotope Composition of Leaf Dark-Respired CO_2 in French Bean, *Plant Physiology* 131: 237-244.

Werner C., Gessler A. (2011) Diel variations in the carbon isotope composition of respired CO_2 and associated carbon sources: a review of dynamics and mechanisms, *Biogeosciences* 8: 2437-2459.

THE $\delta^{13}C$ AND $\delta^{15}N$ IN GUANO FROM ROMANIAN CAVES

Ferenc L. Forray[1], **Daniel M. Cleary**[2], **Jonathan G. Wynn**[2], **Bogdan P. Onac**[1,2,3]

[1]Department of Geology, Babeş-Bolyai University, Kogălniceanu 1, 400084 Cluj-Napoca, Romania,
[2]Karst Research Group, School of Geosciences, University of South Florida, 4202 E. Fowler Ave., NES 107, Tampa, 33620 USA
[3]"Emil Racoviță" Institute of Speleology, Clinicilor 5, 400006 Cluj-Napoca, Romania
Corresponding author: *ferenc.forray@ubbcluj.ro*

Understanding the complex drivers behind Earth's past climate changes may help predict the likelihood, extent, and patterns of future changes. Cave deposits are of special interest because caves provide somewhat isolated environments that are physically and chemically more stable on short time scales, allowing for a better preservation of deposits that archive environmental conditions (speleothems, guano, sediments, etc). Geochemical studies of cave guano, including studies using stable isotopes in particular, can provide paleoecological (relative abundance of C3-, C4- or CAM-type plants, vegetation changes, feeding behavior of bats) and paleoclimate (precipitation) records. Cave guano $\delta^{13}C$ values reflect the dietary preferences of bats that are controlled by local vegetation dynamics, which in turn depend on local climatic conditions.

The aim of the present study is to demonstrate the usefulness of stable carbon and nitrogen isotopes in bat guano as proxies for paleoclimate changes. We show multiple records of environmental changes in Romania for the past 2500 years using $\delta^{13}C$ and $\delta^{15}N$, derived from precisely ^{14}C - dated bat guano cores recovered from Gaura cu Muscă (GM), Zidită (ZC), and Măgurici (MC) caves (Onac *et al*., 2014; 2015; Forray *et al*., 2015; Cleary *et al*., 2016).

The correlation between $\delta^{15}N$ and $\delta^{13}C$ values is significant ($p < 0.01$), but not strong, suggesting that both variables are influenced by water availability. Drier periods indicated by higher $\delta^{13}C$ values correspond with lower $\delta^{15}N$ values and vice-versa for wetter conditions. The instrumental climate record (precipitation amount) for the past 50 years nearby the cave supports this relationship.

$\delta^{13}C$ values in guano at the Medieval Warm Period (MWP) - Little Ice Age (LIA) transition changed markedly only in the GM record. In the other two caves the carbon isotopic values indicate a steady onset of LIA at around AD 1200 but without significant climatic changes before ~AD 1450 and rapidly ending between ca. AD 1870 and 1900. The beginning of the 20th century is characterized by an average $\delta^{13}C$ value of –25.2‰ up to ca. AD 1965 (which indicate a moderate change toward warmer period). This moderate change is reflected in the $\delta^{15}N$ values as well. More rapid changes in $\delta^{13}C$ values are recorded after AD 1970. These rapid changes by 0.5 to 1.5‰ were recorded within a few years indicate swings between several cold and warm events. A relatively consistent diet-guano fractionation factor may suggest that long term variation in δ^{15}N values of guano can be used as an integrator of the local terrestrial N-cycle.

We also present some new data on δ^{13}C values in recent guano monitored for more than one year and data from a nearby meteorological station.

Keywords: climate, guano, cave, carbon stable isotopes, Romania.

Acknowledgments: *This research was supported through Romanian CNCS grant PN–II–ID–PCE 2011–3–0588 to BPO.*

References

Cleary D.M., Onac B.P., Forray F.L., Wynn J.G. (2016) Controls on δ^{15}N values of cave bat guano: an assessment for reconstructing paleoclimate and environmental changes. *Palaeogeography, Palaeoclimatology, Palaeoecology* 461:87–97. doi: 10.1016/j.palaeo.2016.08.012.

Forray F.L., Onac B.P., Tanţău I., Wynn J.G., Tămaş T., Coroiu I., Giurgiu A. (2015) A Late Holocene environmental history of a bat guano deposit from Romania: an isotopic, pollen and microcharcoal study. *Quaternary Science Reviews* 127:141-154. doi: 10.1016/j.quascirev.2015.05.022.

Onac B.P., Forray F.L., Wynn J.G., Giurgiu A.M. (2014) Guano-derived δ^{13}C-based paleo-hydroclimate record from Gaura cu Muscă Cave, SW Romania. *Environmental Earth Sciences* 71: 4061-4069. doi: 10.1007/s12665-013-2789-x.

Onac B.P., Hutchinson S.M., Geantă A., Forray F.L., Wynn J.G., Giurgiu A.M., Coroiu I. (2015) A 2500-year Late Holocene multi-proxy record of vegetation and hydrologic changes from a cave guano-clay sequence in SW Romania. *Quaternary Research* 83: 437-448. doi: 10.1016/j.yqres.2015.1001.1007.

CLIMATIC SIGNALS IN TREE-RING WIDTH AND STABLE ISOTOPES COMPOSITION OF *Pinus Sylvestris* L. GROWING IN THE INDUSTRIALIZED AREA NEARBY KĘDZIERZYN-KOŹLE

Barbara Sensuła[1] **and Sławomir Wilczyński**[2]

[1]*Silesian University of Technology, Institute of Physics — Center for Science and Education,*
Konarskiego 22B, 44-100 Gliwice, Poland
[2]*Department of Forest Protection, Entomology and Forest Climatology,*
University of Agriculture in Krakow, Al. 29Listopada 46, 31-425 Kraków, Poland
Corresponding author: *barbara.sensula@polsl.pl*

The main aims of these studies were dendrochronological and mass spectrometric analysis of the impact of climate on tree rings width and stable isotopes composition in pine (*Pinus sylvestris* L.). Scots pine has been used in bio-monitoring studies in Silesia Region (Sensuła, 2016a,b; Sensuła, 2015; Sensuła *et al.,* 2015a,b; Sensuła *et al*., 2016), because this species is sensitive to climate and the anthropogenic effect. The conifers were growing in the vicinity of chemical factories in Kędzierzyn-Koźle (Poland) in the period of time from 1920s to 2012 AD. The combined usage of tree ring width and isotopic composition data provides historic records of the environment changes. These data allows identifying the behavior adaptation of pine growing under pollution stress to climate changes. The incremental rhythm of the studied pine populations was not identical (Figure 1), probably due to their different sensitivities to some climatic factors.

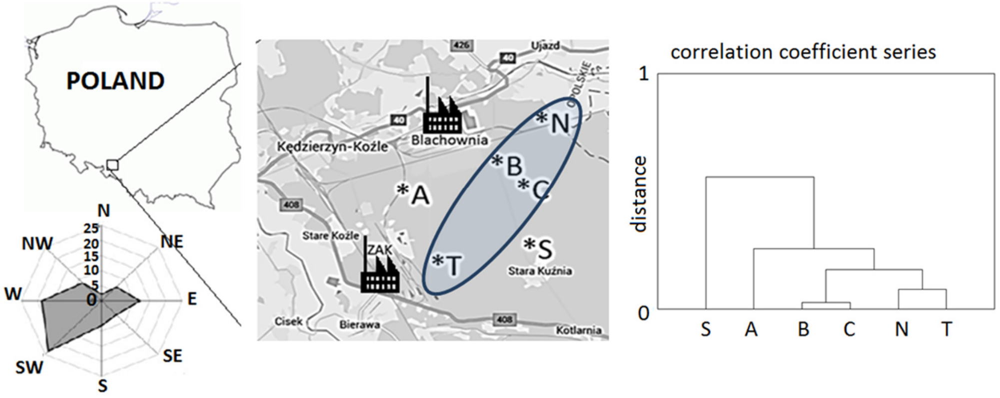


Figure 1. *Sampling sites (A, B, C, N, S, T) in the vicinity of the chemical factories in the southern part of Poland; Localization of the pine population with similar response; dominant wind direction, and the dendrogram of clusters of pine population based on the similarity of their response to climatic conditions.*

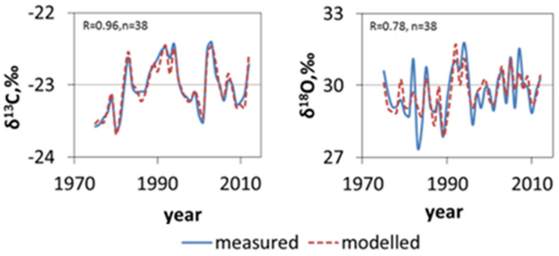


Figure 2. *$\delta^{13}C$ and $\delta^{18}O$ chronologies of Scots pine growing in the industrial area (raw and modelled data)*

This study evidences also, that the isotopic records in tree-rings α-cellulose can be a sensitive bio-indicators of the way that the components of air and water may be changed by the trees in response to the climate changes and anthropogenic effects. To describe the variation of the carbon and oxygen isotope composition of cellulose in annual tree-rings of pine caused b y climate changes and human activities we used a model based on multiple regressions (Figure 2).

Diffuse air pollution (carbon dioxide) caused the variation in the ratio of water used in plant metabolism to water lost by the plant through transpiration (WUE). In the period of time from 1975 and 2012, according to NASA the global concentration of mid-tropospheric carbon dioxide ranged from ~330 ppm to ~393 ppm whereas the global surface temperature, relative to 1951-1980 average temperatures, ranged from -0.01°C to 0.76°C. During this period time with increase of CO_2 emission also WUE increases (from 94 to 122µmol/mol), and it has been observed that Water use efficiency might been strongly correlated with variability of the surface temperature (r=0.81)

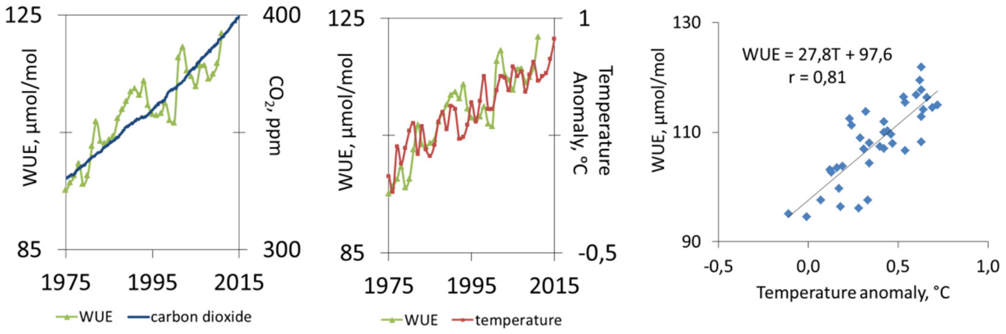


Figure 3. *Changes in water use efficiency due to global distribution and variation of the concentration of mid-tropospheric carbon dioxide in parts per million (ppm) and global surface temperature relative to 1951-1980 average temperature*

Keywords: pine, climate, tree rings width, stable isotopes, water use efficiency

Acknowledgments: *The research and publication were a part of - "Trees as bioindicators of industrial air pollution during the implementation of the pro-environmental policy in the Silesia region (BIOPOL)" funded by the National Science Centre allocated on the basis of decision number DEC-2011/03/*

D/ST10/05251 (PI: B. Sensuła). Publication was supported under the rector's grant in the area of research and development, Silesian University of Technology, grant no RGJ-45/RIF/2017 (PI: B. Sensuła).

References

Sensuła B. (2016a) $\delta^{13}C$ and water use efficiency in the glucose of annual pine tree rings as ecological indicators of the forests in the most industrialized part of Poland. *Water, Air, and Soil Pollution* 227:68.

Sensuła B. (2016b) The impact of climate, sulfur dioxide, and industrial dust on $\delta^{18}O$ and $\delta^{13}C$ in glucose from pine tree rings growing in an industrialized area in the southern part of Poland. *Water, Air, and Soil Pollution* 227:106.

Sensuła B. (2015) Spatial and short-temporal variability of $\delta^{13}C$ and $\delta^{15}N$ and water-use efficiency in pine needles of the three forests along the most industrialized part of Poland. *Water, Air, and Soil Pollution* 226(11):362.

Sensuła B., Opała M., Wilczyński S., Pawełczyk S. (2015a) Long and short-term incremental response of *Pinus sylvestris* L. from industrial area nearby steelworks in Silesian Upland, Poland. *Dendrochronologia* 36:1-12.

Sensuła B., Wilczyński S., Opała M. (2015b) Tree growth and climate relationship: dynamics of scots pine (Pinus sylvestris L.) growing in the near-source region of the combined heat and power plant during the development of the pro-ecological strategy in Poland. *Water, Air, and Soil Pollution* 226:220.

Sensuła B., Wilczyński S., Piotrowska N. (2016) Zastosowanie metod dendrochronologicznych oraz spektrometrycznych w monitorowaniu drzewostanów sosnowych na obszarach przemysłowych. *Sylwan* R. CLX (9):730-740.

iWUE AS A FINGERPRINT OF POLLUTIONS FOR SOUTHERN POLAND

Sławomira Pawełczyk and Barbara Sensuła

Silesian University of Technology, Institute of Physics - Centre for Science and Education,
Konarskiego 22B, 44-100 Gliwice, Poland
Corresponding author: *Slawomira.Pawelczyk@polsl.pl*

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. Human activities have altered atmospheric composition and climate. It has implications for plants physiology and physical response. Since the beginning of industrial revolution, the $\delta^{13}C$ of the atmospheric CO_2 has decreased due to emission of ^{13}C-depleted CO_2 from human activities such as fossil fuels burning and land clearing. The so called Suess effect is reflected in tree rings $\delta^{13}C$. Emissions of SO_2, 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 SO_2 can cause the closure of stomata and reduce negative carbon isotope composition. Carbon isotopic composition ($\delta^{13}C$) in tree rings has been widely used to estimate temporal and spatial variations in intrinsic water use efficiency (iWUE), which is defined as the ratio of photosynthetic carbon assimilation (A) to stomatal conductance (g). The $^{13}C/^{12}C$ ratio in trees is controlled at the leaf level by the ratio of intercellular (C_i) to ambient (C_a) CO_2 concentrations. If C_i is high relative to C_a, strong discrimination against ^{13}C yields isotopically light biomass. Conversely, if C_i is low - discrimination against ^{13}C results in higher $\delta^{13}C$ values. Therefore, any change in carboxylation and/or stomatal conductance that altered ratio C_i/C_a is recorded as a change in $\delta^{13}C$. Variations in atmospheric $\delta^{13}C$ should be taken into consideration and $\delta^{13}C$ in tree rings must be analysed in relation to atmospheric $\delta^{13}C$ at the moment of its assimilation (Silva and Horwath, 2013).

Presented results concern measurements of $\delta^{13}C$ on α-cellulose extracted from trees annual growth rings (from spruce and pine for mountain and Silesia region respectively) for Polish mountain regions as well as Silesia region - the most industrialised area in Poland. The selected research areas: Sudeten, Tatras and Silesia region represent regions with various intensification of anthropopression. The forest of the Sudeten Mountains located on the east of “black triangle” and outside coal mining and industrial regions experienced massive tree death in the 1970s and 1980s. The Tatra Mountains as a huge mountain barrier intercept a wide spectrum of air pollutants coming from various directions. A time span for investigations mountain region is rather long and covers years 1850-2010 AD. The conifers grew in Silesia region are exposed to anthropogenic stress typical for heavily urbanized areas. Sampled areas were in close proximity to the heat and power plant in Łaziska (LA) and the nitrogen factory in Kędzierzyn-Kozle (KK). The annual rings of pine covered a time span from 1975 to 2012 AD.

Samples of α-cellulose were isotopically analysed in Gliwice Mass Spectrometry Laboratory using an EuroVector elemental analyser coupled to a continuous flow IsoPrime mass spectrometer. $\delta^{13}C$ results are reported in per mil (‰) relative to VPDB standards. Each sample was run in triplicate, with analytical errors of 0.1‰ and for $\delta^{13}C$.Values of $\delta^{13}C$ in tree rings were used for assessing changes in iWUE.

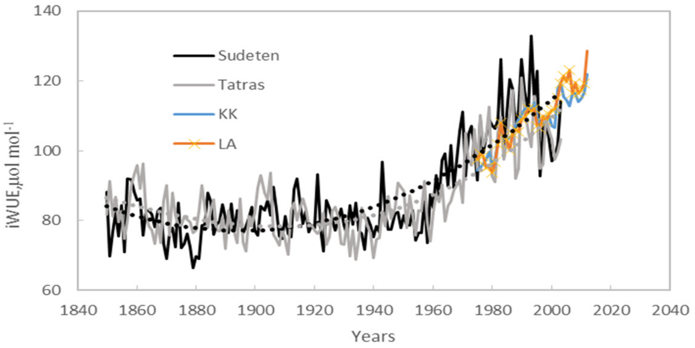


Figure 1. *Comparison of iWUE for: Sudeten, Tatras, Łaziska (LA) and Kędzierzyn-Kozle (KK).*

Numerous studies have reported widespread increases in iWUE coinciding with rising atmospheric CO_2 concentration over the past century. Investigations for mountain and Silesia regions confirm that the intrinsic water use efficiency of trees (the ratio between carbon uptake and water loss through transpiration) increases as stomatal conductance decreases in response to elevated CO_2 (Figure 1). In the case of $\delta^{13}C$ increasing trend is observed in the years 1960 -1990 and 1970 -1990 for Sudeten and Tatras respectively due to SO_2 emission. Differences in iWUE, calculated from data sets include not only trend of CO_2 concentration changes but also trend of SO_2 concentration changes.

Key words: carbon isotope, tree ring, iWUE, pollutions.

Acknowledgments: *The research was a part of: projects: "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 number1557B/P01/2009/37 and BIOPOL project "Trees as bioindicators of industrial air pollution during implementation of pro-environmental policy in the Silesia region" - funded by the National Science Centre allocated on the basis of the decision number DEC-2011/03/D/ST10/05251*

References

Silva L.C.R., Horwath W.R. (2013) Explaining Global Increases in Water Use Efficiency: Why Have We Overestimated Responses to Rising Atmospheric CO_2 in Natural Forest Ecosystems? *PLoS ONE* 8(1):e53089, doi:10.1371/journal.pone.0053089.

K40 AND TRITIUM FROM THE ROMANIAN SECTOR OF BLACK SEA WATER

Romul Mircea Margineanu, **Corina Anca Simion, Claudia Mariana Gomoiu,**
Ana-Maria Blebea-Apostu

Horia Hulubei National Institute for RD in Physics and Nuclear Engineering - IFIN-HH
Bucharest-Magurele, Romania
Corresponding author: *romulus@ifin.nipne.ro*

The Black Sea is a continental sea with an area of 423 000 km2, a volume of 547000 km3 and the catchment area is 1864000 km^2, (Murray, 1989). The Romanian coastline has 256 km long from Musura arm in North, to Vama Veche in South (Stanchev, 2011).

The artificial radionuclides in this environment could represent a threat for life in all its forms. Thus, in this paper we report the specific activity of two radionuclides in sea water, namely K40 and Tritium. The sea water was sampled from 21 to 23 July 2015, from Periboina Canal to Vama Veche (see Figure 1).

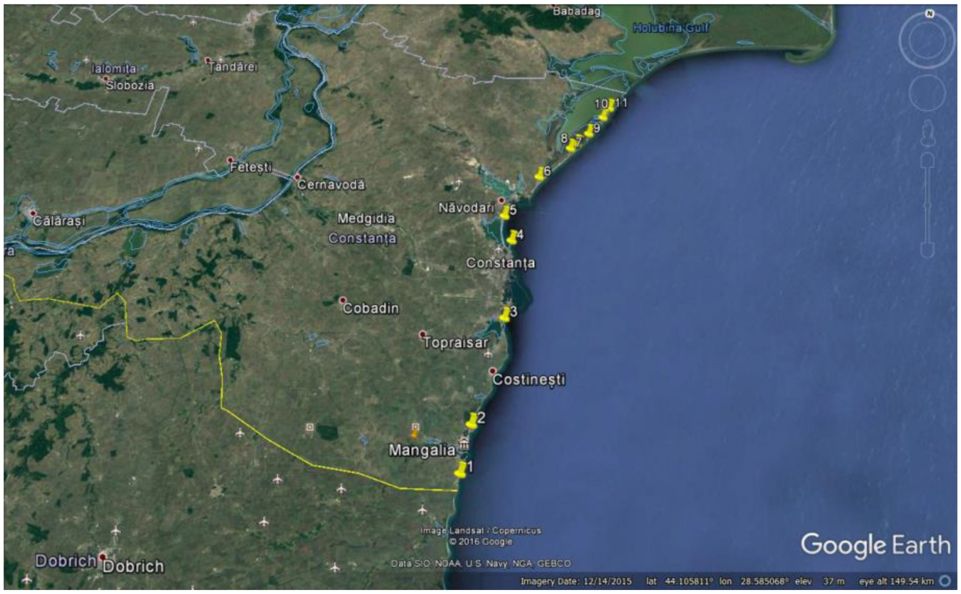


Figure 1. *Sample sites of sea water along the Romanian coast, image from Google Earth®*

All sample measurements were performed by using high resolution gamma spectrometry in underground laboratory in ultralow radiation background from Unirea salt mine in Slanic-Prahova. The measurements were performed using a CANBERRA system with a 120% relative efficiency HPGe detector. Tritium in water samples was analyzed by an ultra-low level liquid scintillation spectrometer QUANTULUS 1220^{TM}.

The environmental radioactivity and dose rate along the Romanian coast was reported in previous papers (Margineanu, 2013 and 2014). The data show that the seashore is characterized by very low levels of natural and artificial radionuclides. Tritium in sea water was measured on samples collected in 2012 and the results are reported in (Varlam, 2013).

The specific activity of K40 in sea water ranges from 0.9 to 5.9 Bq/L and for tritium for 2.8 to 8.4 Bq/L. The spatial distribution of these values is shown in Figure 2. The surface water samples were taken near seashore, in the first layers of 10÷30 cm from a total 50 cm depth. Cernavoda NPP being the source of tritium in sea water, the values found in July 2015 suggest a possible routine emission. This supposition is strengthened by the specific activity of tritium found in Seimeni discharge Canal equal to 2.9 Bq/L and in the swamp near Canal equal to 13.60 Bq/L, sampled in the same interval.

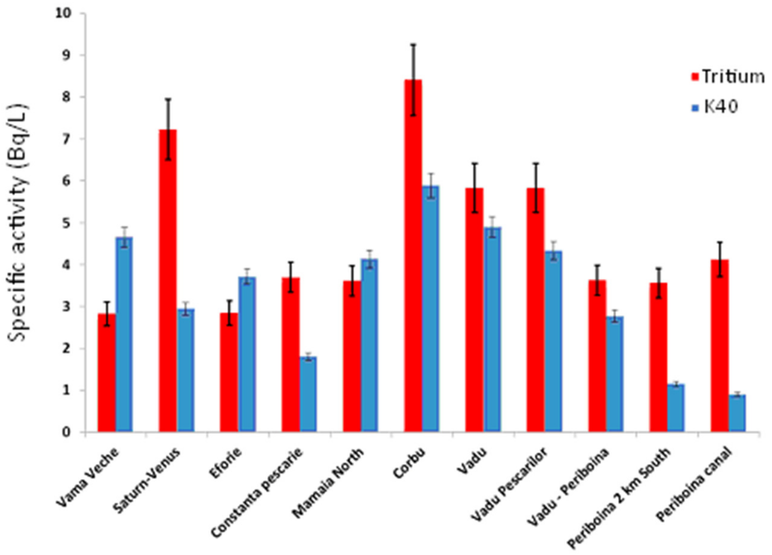


Figure 2. *K40 and Tritium in Black Sea water*

Concluding remarks - All results indicate no risk of exposure for humans, and, at the same time, could contribute to a better understanding of marine processes and anthropogenic environmental impact.

Keywords: K40, Tritium, Cernavoda NPP, underground lab, Black Sea.

Acknowledgments: *This work has been done within the BS ERA NET 041 project in the frame of BS-ERA.NET Pilot Joint CAll 2010/2011 and by the Romanian National Authority for Scientific Research Project No. PN-16 42 02 03.*

References

Margineanu R.M., Duliu O.G., Blebea-Apostu A.M., Gomoiu C.M., Bercea S. (2013) Environmental dose rate distribution along the Romanian Black Sea Shore, *Journal of Radioanalytical and Nuclear Chemistry* 298: 1191-1196, DOI 10.1007/s10967-013-2545-4.

Margineanu R.M., Blebea-Apostu A.M., Gomoiu C.M., Costea C., Dumitras D., Ion A., Duliu O.G. (2014) Radiometric, SEM and XRD investigation of the Chituc black sands, southern Danube Delta, Romania, *Journal of Environmental Radioactivity* 138:72-79.

Murray J.W., Jannasch H.W., Hon Jo S., Anderson R.F., Reeburgh W.S., Top Z., Friederich G.E., Codispoti L.A., Izdar E. (1989) Unexpected changes in the oxic/anoxic interface in the Black Sea, *Nature* 338:411-413, doi:10.1038/338411a0.

Varlam C., Patrascu V., Margineanu R.M., Faurescu I., Vagner I., Faurescu D., Duliu O.G. (2013) Tritium activity concentration along the Western shore of the Black Sea, *Journal of Radioanalytical and Nuclear Chemistry* 298(3):1679-1683.

Stanchev H., Palazov A., Stancheva M., Apostolov A. (2011) Determination of the Black Sea area and coastline length using GIS methods and Landsat 7 satellite images, *Geo-Eco-Marina* 17:27-31.

REFLECTION OF STABLE ISOTOPES WITH INUNDATION PATTERN AT MATANG MANGROVE FOREST RESERVE(MMFR) MALAYSIA

Waseem Razzaq Khan[1*] , **M. Nazre**[1], **Syaizwan Zahmir Zulkifli**[2], **Umer Rashid**[3], **Kamziah Abd Kudus**[1], **Martin Zimmer**[4]

[1]*Department of Forest Management Faculty of Forestry University Universiti Putra Malaysia, 43400 UPM Serdang Selangor*
[2]*Department of Biology Faculty of science Universiti Putra Malaysia, 43400 UPM Serdang Selangor*
[3]*Institute of Advance Technology Universiti Putra Malaysia, 43400 UPM Serdang Selangor*
[4]*Leibniz-Center for Tropical Marine Ecology (ZMT) Fahrenheitstrasse 628359 Bremen Germany*
Corresponding author: *waseemjatoi4@gmail.com*

Matang mangrove forest reserve (MMFR) is referred as world best mangrove forest. Mangrove forest is the inundated forest. In the inundation pattern of mangrove forests, the nutrient profile for the growth of mangrove species also changes. This study was performed to analyze the elemental profile *of Avicenniaalba, Sonneratia ovata, Rhizophoramucronata, Burgueriaparviflora* with different inundation pattern with the help of isotopic tool (IRMS) and atomic absorption spectrometer (AAS). Stable isotopes are the fingerprints or key indicators of the healthy ecosystem. The C, N ratio and δ^{13}C, δ^{15}N ratio fluctuate with inundation, highlighting that biotic and abiotic factors are affecting the values in the form of salinity, pollution, anoxic soil condition and microbial decomposition. In MMFR mangrove species elemental profile of macro nutrients (i.e. C, N, P); trace elements (B, Mn, Fe, Cu, Zn) and cations (Na, Mg, K, Ca) showed the distribution of elements with inundation, which also affect the growth. The results also revealed that the δ^{13}C and δ^{15}N ratios from the collected samples were ranged between -33.8 to -28.41‰ and 8.66 to 3.84‰, respectively. The results depicted that beside other factors, the salinity and pollution also affect stable isotopic ratio in ecosystem of MMFR which declined the growth or productivity of sampled species by disturbing rich nutrient profile.

Keywords: Matang Mangrove, inundation, isotopic tool, anoxic soil, nutrients profile.

ADVANCES IN RADIOCARBON DATING AT RoAMS LABORATORY

Gabriela Odilia Sava, Iuliana Stanciu, Oana Gaza, Tiberiu Bogdan Sava, Corina Anca Simion, Doru Pacesila, Bianca Stefan, Alexandru Vasiliu, Vasile Mosu

Horia Hulubei - National Institute for Physics and Nuclear Engineering,
30th Reactorului Str., Magurele Ilfov 077125, Romania
Corresponding author: *gabriela.sava@nipne.ro*

Since its foundation in 2013 the RoAMS laboratory started to explore its possibilities to measure the radiocarbon content (^{14}C) in various types of sample materials for scientific and non-scientific purposes. To the already classic materials, like wood, bone, charcoal, in the last half of year the laboratory received an increasing request for new material types like painting canvas, leather, papyrus and paper, in the field of cultural heritage and art work authentication and peat, foraminifera and humic acid for the environmental studies. In this regard, the laboratory activity has been extended and started to make use of new instruments and methods for the sample physicochemical pre-treatment. This procedures were required to eliminate the possible intruder materials which would lead to a distortion of the proper age determination. The adopted techniques for the elimination of the contaminants and the radiocarbon dating results are presented in the following.

CARBON ISOTOPE COMPOSITION AND SOURCES OF AEROSOL PARTICLES IN URBAN SITE

Andrius Garbaras, Agne Masalaite, Justina Sapolaite, Ruta Bariseviciute, Zilvinas Ezerinskis and Vidmantas Remeikis

State Research Institute Center for Physical Sciences and Technology, Vilnius, Lithuania
Corresponding author: *andrius.garbaras@ftmc.lt*

Carbonaceous particles are one of the most important components of the atmospheric aerosol. These particles have crucial effects on atmosphere, climate, and human health thus the studies of their sources, composition and chemical processing are highly desirable. Different approaches can be used to identify carbonaceous aerosol sources. The stable carbon isotopes can be used to get information about sources and processing of carbonaceous aerosol (Ceburnis *et al.*, 2016; Garbaras *et al.*, 2015; Garbarienė *et al.*, 2016; Masalaite *et al.,* 2017; Masalaite *et al.*, 2015). The main objective of this study is to explain the observed variation of $\delta^{13}C_{TC}$ values of aerosol particles from urban site during change of the seasons (from winter to summer).

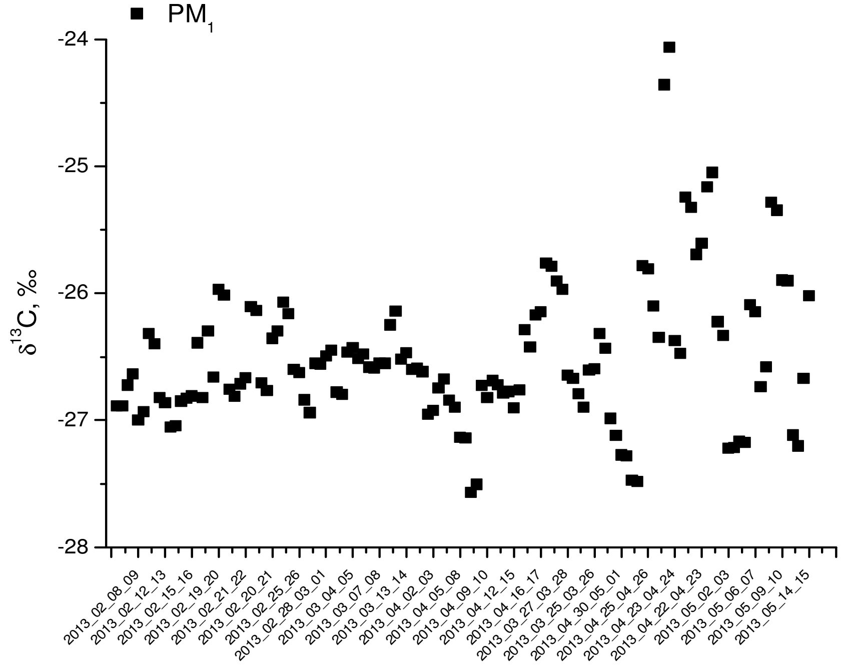


Figure 1. *Variation of $\delta^{13}C_{TC}$ values of aerosol particles during change of the seasons (from winter to summer).*

The aerosol samples were collected at an urban site (54º38′ N, 25º18′ E) in Lithuania from 05 02 2013 to 15 05 2013. PM_1 size fraction samples were collected on 150 mm diameter quartz microfiber filters (Whatman QM-A) using a high–volume (500 L/min) sampler "Digitel DH–77". The $\delta^{13}C$ values of bulk total carbon ($\delta^{13}C_{TC}$) were measured using an elemental analyser (Flash EA 1112) coupled to an isotope ratio mass spectrometer (Thermo Finnigan Delta Plus Advantage) (EA – IRMS).

The results revealed that ^{13}C depleted aerosol particles were dominant during winter. Meanwhile the aerosol most enriched in ^{13}C was observed during a late spring reaching maximum ($\delta^{13}C_{TC}$ = -27.6±0.2 ‰) on 8 April. This variation was related to a few main sources dominating during separate seasons. The source mixing equation allowed us to distinguish the impact of the biomass burning and fossil fuel combustion during a cold season and the input of the biogenic source during a warm season.

Keywords: aerosol particles, carbon isotopic ratio, IRMS.

References

Ceburnis D., Masalaite A., Ovadnevaite J., Garbaras A., Remeikis V., Maenhaut W., Claeys M., Sciare J., Baisnée D., O'Dowd C.D. (2016) Stable isotopes measurements reveal dual carbon pools contributing to organic matter enrichment in marine aerosol. *Scientific reports,* 6:36675, doi: 10.1038/srep36675.

Garbaras A., Masalaite A., Garbariene I., Ceburnis D., Krugly E., Remeikis V., Puida E., Kvietkus K., Martuzevicius D. (2015) Stable carbon fractionation in size-segregated aerosol particles produced by controlled biomass burning. *Journal of Aerosol Science,* 79(0):86-96, doi:http://dx.doi.org/10.1016/j.jaerosci.2014.10.005.

Garbarienė I., Šapolaitė J., Garbaras A., Ežerinskis Ž., Pocevičius M., Krikščikas L., Plukis A., Remeikis V. (2016) Origin Identification of Carbonaceous Aerosol Particles by Carbon Isotope Ratio Analysis. *Aerosol and Air Quality Research* 16:1356-1365.

Masalaite A., Holzinger R., Remeikis V., Röckmann T., Dusek U. (2017) Characteristics, sources and evolution of fine aerosol (PM 1) at urban, coastal and forest background sites in Lithuania. *Atmospheric Environment* 148: 62-76.

Masalaite A., Remeikis V., Garbaras A., Dudoitis V., Ulevicius V., Ceburnis D. (2015) Elucidating carbonaceous aerosol sources by the stable carbon $\delta^{13}C$ TC ratio in size-segregated particles. *Atmospheric Research* 158:1-12.

EVALUATION OF APPARENT KINETIC ISOTOPE EFFECT (AKIE) AS TOOL TO DETERMINE THE DEGRADATION PATHWAYS OF CHIRAL ORGANIC POLLUTANTS

Silviu-Laurentiu Badea

Earth and Life Institute, Université Catholique de Louvain, 1348 Louvain-la-Neuve, Belgium
silviu-laurentiu.badea@uclouvain.be

Stable isotope analytical techniques represent a promising, breakthrough methodology that may be used to evaluate the environmental fate of chlorinated organic compounds and determine the risk posed by them. Currently, stable isotope mass spectrometric techniques are a key technology helping to improve understanding of the biogeochemistry of organic compounds since they have been increasingly used for the *in situ* characterisation of biodegradation processes (Meckenstock *et al*., 2004). Compound specific stable isotope analysis (CSIA) exploits the preferential transformation of lighter isotopomers during a degradation reaction (due to the preferential cleavage of the ^{12}C-Cl or ^{12}C-Br bonds compared with the ^{13}C-Cl or ^{13}C-Br bonds), thus leading to an enrichment of heavier isotopes in the residual phase of the biodegradation process (Elsner & Imfeld, 2016). The subject of compound specific isotope analysis (CSIA) using gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) for environmental investigations represents an important step forward in contemporary environmental science. Concepts and applications are currently available for carbon and hydrogen based CSIA of the more simple organic contaminants such as BTEX, chlorinated ethenes that are already integrated into common monitoring strategies for polluted sites, while for pesticides and emerging contaminants it needs further developments. In this respect, the Rayleigh concept has been widely used in environmental studies (Meckenstock *et al*., 2004) to relate the change of bulk isotope ratios of a compound to the extent of their degradation. Nevertheless, alone, the bulk isotope ratios (expressed as enrichment factors ε_{bulk}) cannot give a complete knowledge about the mechanisms and pathways of organic pollutants degradation at contaminated sites. Since 2005, a new concept linking observable stable isotope fractionation to transformation pathways of organic pollutants (Elsner *et al.*, 2005) has been used to elucidate the reaction mechanisms. This concept takes into account (*a*) non reacting positions within a compound as well as (*b*) effects of intramolecular isotopic competition so that enrichment factors ε_{bulk} can be converted into estimates of apparent kinetic isotope effects. Since many organic pollutants have a chiral skeleton, the enantioselective stable carbon isotope analysis (Badea & Danet, 2015) (ESIA) has emerged as an innovative technique to assess the environmental fate of chiral emerging compounds by

combining in one experimental technique both compound specific isotope analysis (CSIA) and enantioselective analysis. In the current study, a factorial design model (Lundstedt *et al.,* 1998) was build using MODDE 9.0 software (Umetrics, Umea, Sweden) in order to predict the enrichment factors and the AKIEs for some chiral pesticides (α-hexachlorocylohexane (Badea *et al*., 2011) (Bashir et al., 2013)) and chiral polychlorinated biphenyls (PCBs). Furthermore, the apparent kinetic isotope effect (AKIE) was calculated for the above mentioned compounds and based on these values, different reaction mechanisms were discussed. The calculated AKIE values are in good agreement with previously published data in the literature and are typical of certain degradation reactions, being within the *maximum* kinetic isotope effects (KIE) (Elsner *et al*., 2005) (expressed by so called semiclassical Streitwieser limits) for the breakage of typical chemical bonds. These calculations and the deduced degradation pathways might improve the knowledge about the fate and natural attenuation of organic pollutants at contaminated sites.

Keywords: AKIE, CSIA, chiral analysis, ESIA.

References

Badea S.L., Danet A.F. (2015) Enantioselective stable isotope analysis (ESIA) – A new concept to evaluate the environmental fate of chiral organic contaminants. *Science of The Total Environment*, 514: 459-466.

Badea S.L., Vogt C., Gehre M., Fischer A., Danet A.F., Richnow H.H. (2011) Development of an enantiomer-specific stable carbon isotope analysis (ESIA) method for assessing the fate of α-hexachlorocyclohexane in the environment. *Rapid Communications in Mass Spectrometry*, 25(10): 1363-1372.

Bashir S., Fischer A., Nijenhuis I., Richnow H.H., (2013) Enantioselective Carbon Stable Isotope Fractionation of Hexachlorocyclohexane during Aerobic Biodegradation by Sphingobium spp. *Environmental Science & Technology*, 47(20): 11432-11439.

Elsner M., Imfeld G. (2016) Compound-specific isotope analysis (CSIA) of micropollutants in the environment – current developments and future challenges. *Current Opinion in Biotechnology*, 41: 60-72.

Elsner M., Zwank L., Hunkeler D., Schwarzenbach R.P. (2005) A new concept linking observable stable isotope fractionation to transformation pathways of organic pollutants. *Environmental Science & Technology*, 39(18): 6896-6916.

Lundstedt T., Seifert E., Abramo L., Thelin B., Nyström Å., Pettersen J., Bergman R. (1998) Experimental design and optimization. *Chemometrics and Intelligent Laboratory Systems*, 42(1-2): 3-40.

Meckenstock R.U., Morasch B., Griebler C., Richnow H.H. (2004) Stable isotope fractionation analysis as a tool to monitor biodegradation in contaminated acquifers. *Journal of Contaminant Hydrology*, 75(3-4): 215-255.

ESTIMATION OF UPTAKE RATE OF CARBON DIOXIDE THROUGH THE SKIN BY MEASUREMENT OF CARBON ISOTOPE RATIO OF EXHALED AIR

István Csige, István Futó, Róbert Janovics, Mihály Molnár, László Rinyu, László Palcsu, István Major, Marianna Túri, Erzsébet Sóki, József Molnár

MTA Atomki, Isotope Climatology and Environmental Research Centre,
4026 Debrecen Bem ter 18/c, Hungary
Corresponding author: *csige.istvan@atomki.mta.hu*

The final product of post-volcanic activity is the exhalation of deep origin mofette gas, which contains mostly carbon dioxide. Dry carbon dioxide spas, established on mofettes, are often used for therapeutic treatments of patients suffering from vasoconstriction. These are dry ’saunas’ where patients sit or stand in empty ’pools’, and deep origin gases swirl around their bodies healing several medical complaints (Figure 1. left side). In this work we have studied the rate of uptake of carbon dioxide through the skin when the lower part of the body is immersed into high (> 50 %) concentration of carbon dioxide. The setup of our experiment is shown on the right side of Figure 1.

Figure 1. *Dry carbon dioxide spa established on natural gas exhalation in Mátraderecske, Hungary (left side); and the experimental setup to study the uptake rate of carbon dioxide through the skin (right side).*

In the experiment we have used bottled carbon dioxide, the $\delta^{13}C$ for which was lower than the $\delta^{13}C$ in exhaled air of the subject person during normal metabolism. During the carbon dioxide treatment, however, the human body absorbed low $\delta^{13}C$ carbon dioxide through the skin, which entered the blood circulation and reduced the $\delta^{13}C$ in the exhaled air. We have developed a bio-kinetic mathematical model to describe the transport of carbon dioxide in the human body including the uptake of carbon dioxide through the skin. Comparing the results of model calculations and experimental measurements of $\delta^{13}C$ in the exhaled air before, during and after

the treatment of the subject person, we were able to estimate the uptake rate of carbon dioxide through the skin which we have found to be 4-10 cm^3/minute.

Keywords: Carbon dioxide, skin, mofette, uptake rate.

Acknowledgments: *The research was supported by the European Union and the State of Hungary, co-financed by the European Regional Development Fund in the project of GINOP-2.3.2.-15-2016-00009 'ICER' and of TÁMOP-4.2.6-15/1-2015-000.*

RADIATION DECONTAMINATION OF SOILS INTEGRATED IN AN ECONOMICALLY PROFITABLE RENEWABLE ENERGY PROJECT

Elena Agarwal[1] and Iurie Bosneaga[2]

[1]*University of Academy of Sciences, Chisinau, Republic of Moldova*
[2]*Institute of Applied Physics of Academy of Sciences, Chisinau, Republic of Moldova*
Corresponding author: *iubosneaga@gmail.com*

Radio-contaminated territories (Chernobyl, Mayak, Fukushima, and many others - of minor, local importance) represent a sound scientific, techno-economical, social problem and inevitably provoke radiophobia, compromising applied nuclear science and technologies. We demonstrate that, in conditions of the proper management, these problematical contaminated areas should not be abandoned technologically and, on the contrary, could be transformed - in an economically profitable way - into renewable energy oases. Additionally, an output of the advanced adsorbent (radio-activated carbon) could be obtained.

The technology consists of the cultivation of special quick-growing plants which intensely absorb radionuclides (mainly Cs^{137} and Sr^{90}). The proposed integrated technology uses solar energy twice: firstly - for the ordinary photosynthetic accumulation of the potential (chemical) energy in wood, and secondly - for the pyrolysis of the obtained wood due to the concentrated thermal solar energy. The resultant products - activated carbon (enriched with the distributed radionuclides), plus collateral qualitative gas and liquid fuels - ensure high economic indices of the total process.

Decontamination of soils is based on the natural characteristic (feature) of plants and animals - to concentrate (absorb) in their tissues radioactive caesium (*Cs*) and strontium (*Sr*) from the soil. Such a selective concentration in plant tissue of *Cs* and *Sr* (inclusively, of radionuclides Cs^{134}, Cs^{137}, Sr^{90}) can be “amplified” - by proper choosing of the convenient plant species and some other conditions. The chemical and physical properties of *Cs* and *Sr* are similar to the properties of, respectively, potassium (*K*) and calcium (*Ca*) - both being key elements for living cells (that is why caesium and strontium - along with potassium and calcium - are selectively absorbed by the living organisms). So, reduction of potassium and calcium in the contaminated soils - is one of the efficient procedures for the intensification of radionuclides (Cs^{134}, Cs^{137}, Sr^{90}) absorption. (It means that potassium and calcium fertilizers should not be used for the proposed decontamination technology).

Radio-activated carbon - in the contrast to the “traditional” activated carbon (which is widely used in water treatment, food, chemical and many other applications, inclusively for the measurement of radon concentration in air) - ensures more efficient adsorption, and it is due to the ionization of the polluted medium.

Accompanying to the proposed technology - is the eternal problem of the radioactivity influence upon plants and animals. With reference to the numerous world-wide known observations (already done and in progress, inclusively in the radio-contaminated zones), we prepare the revealing experiment, which could appear to be the decisive in the challenging dispute between “accumulation” and “threshold” theories. The only remaining obstacle for such an experiment implementation is the exclusion of the radioactive isotope K^{40} action upon the plants’ metabolism, and it is bound up with the expensive task of removing radioactive K^{40} from the soil.

Keywords: decontamination, radio-activated carbon, K^{40} removing.

MONITORING OF RADIONUCLIDES CONCENTRATION IN MOSS SAMPLES IN ROMANIA

E. Simion, A. Gherasim, D. David

National Environmental Protection Agency, Radioactivity Laboratory,
Splaiul Independentei 294, RO-060031, Bucuresti, Romania
Corresponding author: *elena.simion@anmp.ro*

Natural bio-indicators of environment contamination, mosses are very good indicators of the environmental radioactive contamination. This study was carried out over a period of 7 years, between 2009 - 2016, in order to identify, analyze and interpret the presence of the natural and artificial (Cs-137, mainly due to NPP Chernobyl nuclear accident in 1986) radionuclides in soil and moss, as well as to study the migration of Cs-137 from soil to moss in different regions of Romania.

Radionuclide activity levels in moss samples were measured using a gamma spectrometer equipped with germanium detector (HPGe) of high purity and resolution.

We analyzed the spatial and temporal distribution of the samples analyzed, correlated with the average monthly amount of precipitation recorded during sampling and specific activity obtained as a result of gamma spectrometric analyzes. Also studied the dependence of the Cs-137 transfer factor from soil and the altitude moss that grows muscles.

The results obtained indicated that spatial distribution of the Cs-137 activities is highly non-uniform, mostly due to geographical characteristics of each sampling location.

Keywords: mosses, activity levels, cesium-137, contamination, natural radionuclides, gamma spectrometry, radionuclide migration.

Acknowledgements. *The authors acknowledge the great assistance and support in sample sampling provided by our colleagues from National Environmental Radioactivity Surveillance Network – Romania.*

DISTRIBUTION OF ORGANICALLY BOUND TRITIUM IN SOIL AROUND NUCLEAR POWER PLANT

Lin Du[1], Shao-zhong Gu[2], Zheng-hai Xia[2], Yu-hua Ma[1,3], Qin Zhang[1,4], Ke Deng[1,4], Jia-yu Liu[1,4], Lai-lai Qin[1,4], Guang-hua Wang[1], Wei Liu[1,*]

[1]*Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China*
[2]*CNNC Nuclear Power Operations Management Co.Ltd, Haiyan, China, 314300*
[3]*Shanghai Tech University, Shanghai, China, 201210*
[4]*University of Chinese Academy of Science, Beijing, China, 100049*
Corresponding author: Liuwei_0918@126.com

In the last years there has been increasing interest in the behavior of tritium in environment, especially the formation of organically bound tritium (OBT)(Boyer *et al.*, 2009; Kim *et al.*, 2013). As one of the most important environmental mediums, soil plays a significant role in tritium migration and conversion. In order to explore the distribution and formation mechanism of OBT in soil, the distribution characteristic of OBT in soil around Qinshan Nuclear Power Plant in China were investigated and the source of OBT in the soil was also preliminarily analyzed in this study.

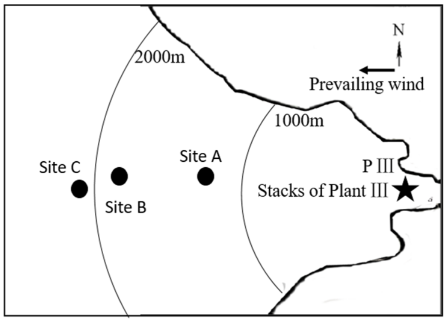


Figure 1. *Sites of collection of soil samples from the Qinshan NPP*

As shown in Figure 1, 3 soil sampling locations (Site A, B and C) were chosen considering wind direction, distance to the stacks of Plant β (two HWRs). Soil cores in depth of 0-25cm were sampled. Each soil sample was freeze-dried to extract the HTO and then the dried sample was divided into different groups according to their particle sizes using sieve shaker, including 2000-250µm, 250-53µm, 53-20µm and <20µm. The OBT in soils was converted to HTO using combustion technique. The HTO concentration, as well as the HTO concentration extracted by freeze-drying method, was determined by LSC (OBT in <20µm soil particles was not measured because of the little sample size).

The results showed that the OBT activities in soil ranged from 6.554±4.407Bq/L to 119.403±26.194Bq/L and the OBT in soil showed particle size, depth and space distribution characteristic. In most of the cases, the OBT concentrations in 53-250µm were the highest in deep soil (5-25cm), and the OBT concentrations in surface soil (0-5cm) were significantly lower than that in other soil layers. By comparing the OBT concentrations in soil samples collected from different sites, we found that the operation of NPP could affect the space distribution of OBT in some degree.

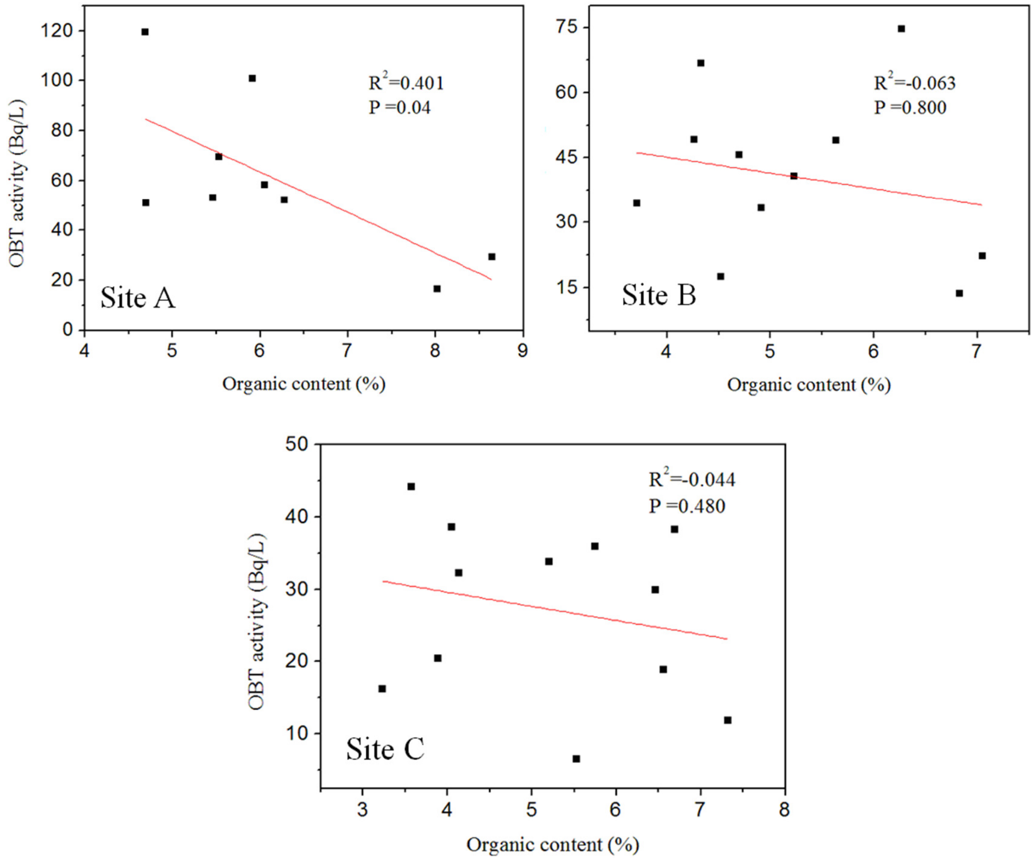


Figure 2. *The correlation analysis between the OBT activity and organic content*

Based on the correlation analysis between the OBT activity and organic content and the OBT/HTO ratios, present research preliminarily analyzed the source of OBT in soil. As shown in Figure 2, the results demonstrated that there was no direct relationship between OBT and total organic content. According to Table 1, the OBT/HTO ratios were similar in the soil with particle size of >53-250µm and 20-53µm, with values of 1.36 ± 0.19 and 1.40 ± 0.14, respectively, which were significantly higher than the ratio in >250µm soil, with a value of 1.17 ± 0.18. OBT/HTO could imply the ability of organism to convert HTO to OBT in some degree, so the results suggested that more living organisms being related to the conversion of OBT exist in the soil with particle size of 53-250µm and 20-53µm. Since various microorganisms mostly exist in the soil with particle size of 53-250µm and 20-53µm (Kim *et al.*, 2014; Wang *et al.*, 2011; Zhang *et al.*, 2009), it can be preliminarily deduced that the difference of OBT/HTO ratio in different particle size soils may be correlated with the distribution of microorganisms.

Table 1. *The mean value of OBT/HTO ratio in different particle size soil.*

Particle size/µm	OBT/HTO ratio
>250	1.17 ± 0.18
53-250	1.36 ± 0.19
20-53	1.40 ± 0.14

Keywords: Soil sample, OBT, distribution characteristic, OBT/HTO ratio, microorganisms

References

Boyer C., Vichot L., Fromm M., Losset Y., Tatin-Froux F., Guetat P., Batot P.M. (2009) Tritium in plants: a review of current knowledge. *Environmental and Experimental Botany* 67: 34-51.

Kim S.B., Baglan N., Davis P.A. (2013) Current understanding of organically bound tritium (OBT) in the environment. *Journal of Environmental Radioactivity* 126: 83-91.

Kim S.B., Stuart M., Bredlaw M., Festarini A., Beaton D. (2014) HT to HTO conversion and field experiments near Darlington Nuclear Power Generating Station (DNPGS) site [J]. *Journal of Environmental Radioactivity* 132: 73-80.

Wang F., Liu W., Tang J.C. (2011) Progresses in microbial oxidation of hydrogen and its isotopes in soil. *Nuclear Techniques* 34 (2): 143-146.

Zhang W., Jiang X.J., Hu Y. (2009) Distribution Patterns of Microbial Community in Soil Water –Stable Aggregates and the Effects of Tillage on Them in a Paddy Soil. *Journal of Southwest University* (Natural Science Edition) 31(3): 131-135.

ATMOSPHERIC C-14 OBSERVATION DURING 2013-2016 IN RAMNICU VALCEA, ROMANIA

Ionut Faurescu, **Carmen Varlam, Irina Vagner, Denisa Faurescu,
Diana Bogdan, Diana Costinel**

*National Research and Development Institute for Cryogenics and Isotopic Technologies –
ICSI Rm. Valcea, 4 Uzinei Street, 240050 Rm. Valcea, Romania*
Corresponding author: *ionut.faurescu@icsi.ro*

The paper presents radiocarbon variation in the atmosphere of Ramnicu-Valcea, Romania. Natural ^{14}C results from cosmic neutrons acting on nitrogen atoms in the stratosphere and in the upper troposphere. The annual production level is around 1.40×10^{15} Bq and the atmospheric stock of radiocarbon at equilibrium is around 140×10^{15}Bq (UNSCEAR, 2008). In the environment, ^{14}C exists in two main forms: as $^{14}CO_2$, it acts as stable carbon dioxide, which means it can remain in gas form in the air, becoming bicarbonate and carbonate in water; during photosynthesis, $^{14}CO_2$ is incorporated in the organic material, forming its carbon skeleton. Equilibrium between the specific activity of atmospheric carbon and that of organic material is then finally reached and maintained by carbon recycling.

The samples were collected in the vicinity of the Experimental Pilot Plant for Tritium and Deuterium Separation (PESTD) from the Institute of the Cryogenics and Isotopic Technologies (ICSI) placed about 10 km south from the Ramnicu Valcea city (Romania), in the Govora industrial area. This facility is an experimental project in the national nuclear energy research program, which has the aim of developing technologies for tritium and deuterium separation. Until now, PESTD normal operation was with heavy water and tritiated water below exemption level approved by Romanian legislation. Foreseen experiments will be done with tritiated heavy water moderator from Cernavoda NPP (two CANDU-6 reactors), known to contain about half of the C-14 production of a Heavy Water Reactor. The largest contributor (>95%) to the production of ^{14}C in CANDU reactors is neutron activation of ^{17}O in the heavy-water moderator (IAEA, 2004). Considering the fact that one of the important releases of PESTD is gaseous radioactive effluents, the baseline of atmospheric C-14 was a must for environmental program. It should be noted that in the Govora industrial area operates a 315 MW Coal-Fired Thermoelectric Power Plant and two chemical plants.

From literature, in the terrestrial environment the ^{14}C specific activity, expressed in Bq/kgC, is constant in the environmental components and at equilibrium with the specific activity of atmospheric CO_2 (Roussel-Debet *et al*., 2006; Roussel-Debet, 2007, 2009). Uninfluenced by nuclear facilities, the ^{14}C specific activities for the biological compartments of the terrestrial environment reached their maximum values (more than 400Bq/kgC) in the mid-1960s, due to fallout from atmospheric nuclear arms testing. These activities have slowly decreased since then (by less than 0.5% per year) with the end of testing and the continuous increase in CO_2 from fossil fuels (gasoline, coal, gas). A radiocarbon background level (250Bq/kgC) was established by international regulatory bodies (IAEA, 2004). Above this background level, other than the normal production of ^{14}C by cosmic radiation, will be considered pollution.

In order to determine radiocarbon activity in the atmosphere, samples were collected monthly by absorption of CO_2 into sodium hydroxide (NaOH) at Ramnicu Valcea. In addition, control materials (tree leaves and wild vegetation), primary standards (Carbonate, IAEA-C2), and process blanks (marble) were analyzed. Radiocarbon measurements were performed using the direct absorption method. This consists in measuring ^{14}C contained in a known quantity of carbon, as carbon dioxide, obtained from a sample, standard or background material, counted in an ultra-low level liquid scintillation counter Quantulus 1220. ^{14}C results were normalized for deviation of the measured $\delta^{13}C$. The $^{13}C/^{12}C$ ratio was measured by isotope ratio mass spectrometry on a Delta V IRMS on small aliquots of sodium carbonate resulted from absorption of CO_2 into sodium hydroxide. Values are given relative to the VPDB standard, with overall precision typically ±0.1 ‰. $\delta^{13}C$-corrected $\Delta^{14}C$ data are given relative to NBS oxalic acid activity, corrected for decay (Stuiver and Polach, 1977).

The results have a clear decreasing trend, but due to local influence caused by continuously production of fossil CO_2 we cannot observe $\Delta^{14}C$ seasonal variations.

Keywords: radiocarbon, atmosphere, direct absorption method, liquid scintillation spectrometry.

Acknowledgments: *This work was performed within the framework of the Experimental Pilot Plant for Tritium and Deuterium Separation (PESTD) from National R&D Institute for Cryogenics and Isotopic Technologies - ICSI Rm. Valcea.*

References

International Atomic Energy Agency - IAEA (2004) Management of waste containing tritium and carbon-14. Technical reports, nr 421. Vienna: IAEA. p. 5-37. Available online at *http://www-pub.iaea.org/MTCD/ publications/PDF/TRS421_web.pdf, accessed on 23.03.2017*

Roussel-Debet S. (2007) Evaluation of 14C doses since the end of the 1950s in metropolitan France. *Radioprotection*, 42 (3): 297-313.

Roussel-Debet S. (2009) Bilan des mesures OPERA terrestre 2007-2008. IRSN, rapport DEI/SESURE 2009-19.

Roussel-Debet S., Gontier G., Siclet F., Fournier M. (2006) Distribution of carbon 14 in the terrestrial environment close to French nuclear power plants. *J Environ Radioact*., 87(3): 246-259.

Stuiver M., Polach H., (1977) Discussion: reporting of ^{14}C data. *Radiocarbon*, 19(3):355–63.

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (2008) Sources and effects of ionizing radiation. Report Vol. I: sources. United Nations publications, New York.

SULPHUR ISOTOPES IN SOIL AROUND THE THERMOELECTRIC POWER PLANT PLOMIN (CROATIA)

Neža Malenšek[1], Gordana Medunić[2], Sonja Lojen[3,4], Nina Zupančič[1]

[1]*Department of Geology, Faculty of Natural Science and Engineering, University of Ljubljana, Aškerčeva 12, Ljubljana, Slovenia*
[2]*Deparment of Geology, Faculty of Sciences, University of Zagreb, Horvatovac 95, Zagreb, Croatia;*
[3]*Department of Environmental Sciences, Jožef Stefan Institute, Jamova 30, Ljubljana, Slovenia;*
[4]*Faculty of Environmental Sciences, University of Nova Gorica, Vipavska 13, Nova Gorica, Slovenia*
Corresponding author: *sonja.lojen@ijs.si*

This study reports for the first time thesulphur isotopes and S forms measured in soil polluted with sulphur derived from the thermoelectric power plant Plomin (TPPP). The TPPP is located on the eastern coast of the Istrian peninsula (North Adriatic, Croatia), and is considered as the prime air polluter in Istria (Božičević Vrhovčak *et al.*, 2005). During the period 1970-2000, the TPPP was powered by the domestic Raša coal. It is characterised by high natural radioactivity, and uniquely high sulphur content up to 14 wt. % (Medunić *et al.*, 2016a), and is known as super high-organic-sulphur (SHOS) coal (Chou, 2012). Since 2000, imported low-S coal has been in use, but the presumable airborne ash particles from a nearby waste could be considered as a source of the environmental pollution.

Chemical analysis of soil in the vicinity of the TPPP showed that the soil is severely polluted with sulphur and polycyclic aromatic hydrocarbons, while moderately with Se, and Cd (Medunić et al., 2016b). Sulphate aerosols were considered as a major pollution source, however, little has been known about the fate of sulphur in soil following the switch in fuel to low-S coal.

In this study, newly collected soil samples (n=11), 3 samples of ash, and 6 SHOS Raša coal samples were analysed for the sulphur content and its stable isotopic composition ($\delta^{34}S$). The aim of the study was to estimate the source and fate of S in the investigated topsoil.

The soil samples were taken at different distances downwind (SW) from the TPPP, while the control soil was sampledupwind (NE) 10 km away from the TPPP. Analytical work included the following measurements: total S in coal, sulphate in ash, and sulphate and the organic (humic and fulvic) sulphur in soil. The extraction of total sulphur from coal, ash, and humic extracts was made by the combustion with Eschka mixture. Following the wet chemical process, sulphate was recovered in the form of $BaSO_4$ (Brüchert and Pratt, 1996). Sulphur concentrations in bulk samples, together with the isotopic composition of S were determined by EA-IRMS (IsoPrime 100 with PyroCube).

The bulk S concentration in the SW soil sample at 100 m distance from the TPPP (close to 4 wt. %) is significantly higher compared to that at the control site(0.04 wt. %), and decreases rapidly to less than 0.6 wt.% in a distance of 0.5 km (Figure 1A). The speciation analysis showed that the majority of S (>95 %) is present in organic form, mostly bound to humic acids (Figure 1B). The δ^{34}S values of bulk Raša coal samples were between -5 and -10 ‰. In most soil samples within 1 km from the TPPP, bulk δ^{34}S were slightly positive. The δ^{34}S values of sulphate in soil samples were between +1 and +5.5 ‰. The δ^{34}S values of humic acids ranged from -3.5 to 3 ‰, while fulvic S showed positive values for all soil samples, namely between 1.5 and 6 ‰. These results are indicative of the atmospheric deposition of ^{34}S-depleted fly ash and sulphate, which had derived from the SHOS Raša coal combustion as the main sources of S in analysed soils close to the TPPP. At distances exceeding 1 km, δ^{34}S values of soil S gradually increase to values more than 20 ‰, which indicates on a fading influence of airborne contamination from the TPPP.

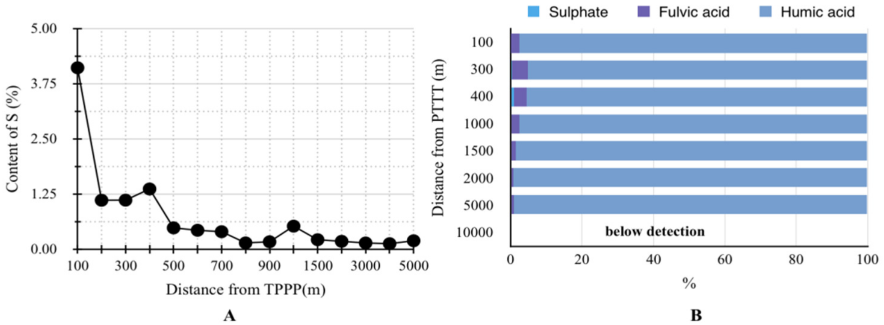


Figure 1. *A. Relation between soil S values and their distance from the TPPP. B. Shares of sulphur bound in sulphate, humic, and fulvic acids.*

Keywords: sulphur isotopes, SHOS Raša coal, soil, thermoelectric power plant.

Acknowledgments: *This study was funded by the Research Agency of Slovenia, program P1-0143, and the EU H2020 project MASSTWIN (grant agreement no. 692241).*

References

Božièeviæ Vrhovèak M., Tomšiæ Ž., Debrecin N. (2005) External costs of electricity production: Case study Croatia. *Energy Policy* 33:1385-1395.

Brüchert V., Pratt L.M. (1996) Contemporaneous early diagenetic formation of organic and inorganic sulfur in estuarine sediments from St. Andrew Bay, Florida, USA. *Geochimica et Cosmochimica Acta* 60:2325-2332.

Chou C.L. (2012) Sulfur in coals: A review of geochemistry and origins. *International Journal of Coal Geology* 100:1-13, DOI: 10.1016/j.coal.2012.05.009.

Medunić G., Rađenović A., Bajramović M., Švec M., Tomac M. (2016a) Once grand, now forgotten: what do we know about the superhigh-organic-sulphur Raša coal?. *Mining-geological-petroleum engineering bulletin (Rudarsko-geološko-naftni zbornik)* 34:27-45.

Medunić G., Ahel M., Božičević Mihalić I., Gaurina Srček V., Kopjar N., Fiket Ž., Bituh T., Mikac I. (2016b) Toxic airborne S, PAH, and trace element legacy of the superhighorganic - sulphur Raša coal combustion: cytotoxicity and genotoxicity assessment of soil and ash. *Science of the Total Environment* 566–567:306-319, DOI: 10.1016/j.scitotenv.2016.05.096.

STABLE ISOTOPES IN PINE TREE RINGS: GLUCOSE, α-CELLULOSE, WOOD

Barbara Sensuła and **Sławomira Pawełczyk**

Silesian University of Technology, Institute of Physics — Center for Science and Education,
Konarskiego 22B, 44-100 Gliwice, Poland
Corresponding author: *barbara.sensula@polsl.pl*

The stable isotope ratios of light elements in plants are valuable tools in the investigation of past climate change, because of the isotopic fractionation which occurs during basic physiological processes responsible for plant growth. Since the beginning of the 20th century there has been much discussion about how the external environmental factors affect the physiological processes that control tree growth. It has been reported that such effects can be manifest also in the stable carbon and oxygen isotope composition of wood and its components.

Early studies of the stable isotope ratios in tree rings used whole wood to reconstruct climate change and to analyze the impact of human activity on the environment. Since the 1970s most palaeoclimate studies have concentrated on the analysis of α-cellulose, as the dominant and the most easily isolated component of wood. Experiments have shown that the stable isotopes of α-cellulose provide a more reliable proxy of past climate and that whole wood does not reflect the climate in the same way as α-cellulose. The immediate background to these analyses was dendrochronological research involving isotope ratio measurements on trees (glucose and α-cellulose) from Niepołomice Forest (Sensuła and Pazdur, 2013).

This study reports the results of isotopic analysis of pine (*Pinus Sylvestris* L.). The conifers grew in Silesia (Poland) in the area exposed to anthropogenic stress typical for heavily urbanized areas and areas in close proximity to the heat and power plant in Łaziska (LA), the nitrogen factory in Kędzierzyn-Kozle (KK) and the steelworks in Dabrowa Gornicza (HK) and in one comparative site in Olesno (OL) ca 100 km from industrial area (Sensuła, 2016a,b; Sensuła *et al.*, 2016). The annual rings covered a time span from 1975 to 2012 AD.

The α-cellulose extraction was by applying Green's (1963) method, whereas the acid hydrolysis of α-cellulose to glucose was by applying Chambat's *et al.*, (1997) method.

Measurement of carbon and oxygen isotope ratios were carried out at the Mass Spectrometry Laboratory (Department of Radioisotopes, Institute of Physics, Gliwice, Poland), using the isotope ratio mass spectrometer IsoPrime coupled to the Eurovector GV Instruments (Manchester, UK) elemental analyzer at a combustion temperature of 1020°C (for carbon and nitrogen) and at higher temperature (1350°C) in a pyrolysis reactor (for oxygen). To displace moisture-containing air in the α-cellulose and glucose samples, the samples were heated and put into the special home-made box filled with argon.

We reported the isotope values in the delta notation:

$$\delta = (R_{sample}/R_{standard} - 1, \text{‰})$$

for carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$), respectively, relative to the international standard, which is V-PDB (Vienna Pee Dee Belemnite) for carbon and V-SMOW (Vienna Standard Mean Ocean Water) for oxygen. R_{sample} and $R_{standard}$ are the molar fractions of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ for the sample and the standard, respectively.

Whereas the isotope fractionation factors $\alpha_{A\text{-}B}$ values were reported in the following notation:

$$\alpha_{A\text{-}B}=(1000+\delta_A)/(1000+\delta_B)$$

We present the first results of:
(*1*) isotopic composition of wood, α-cellulose and glucose (Figure 1) and
(*2*) carbon isotopes fractionation factors between wood and its components (Figure 2): wood (A) and α-cellulose (B), α-cellulose (A) and glucose (B), wood (A) and glucose (B); and oxygen isotopes fractionation factors between α-cellulose (A) and glucose (B).

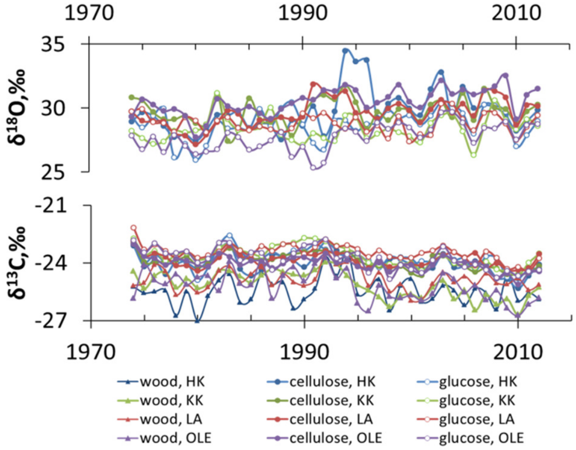


Figure 1. *$\delta^{13}C$ and $\delta^{18}O$ chronologies from Silesia*

The mean value of carbon isotope fractionation factors between cellulose and glucose is equal ~1: whereas lower value is observed between wood and cellulose, and the lowest value of carbon fractionation factor is observed between wood and glucose. The mean value of oxygen isotopes fractionation factor between cellulose and glucose is higher than 1.

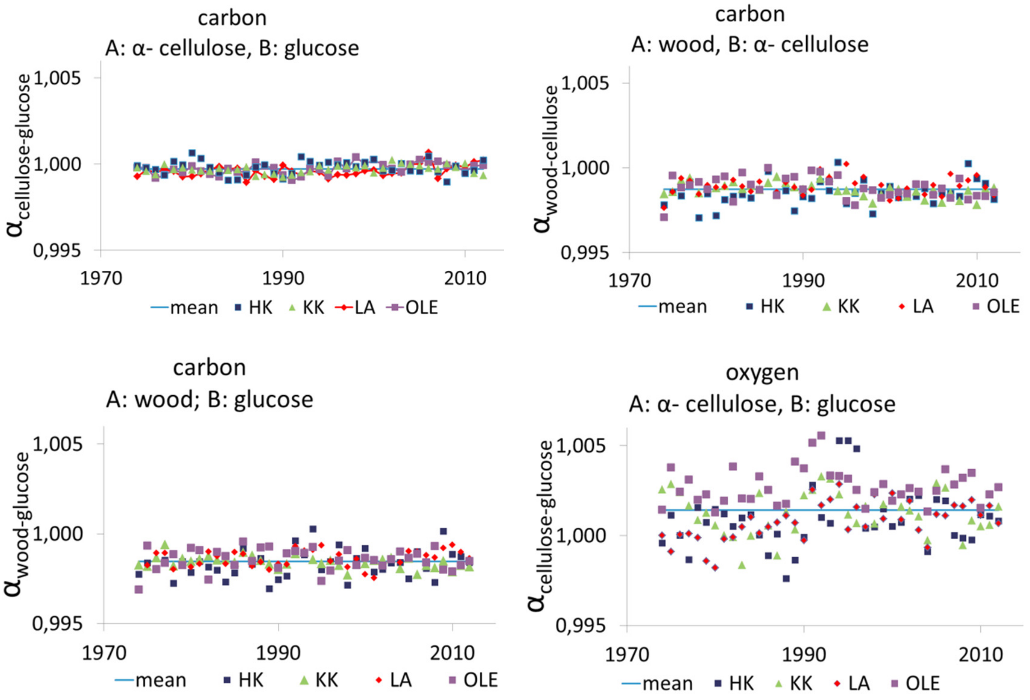


Figure 2. *Carbon and oxygen isotopes fractionation factors between wood and its components.*

Keywords: carbon, oxygen, pine, isotope fractionation

Acknowledgments: *The research was a part of: BIOPOL project "Trees as bioindicators of industrial air pollution during implementation of pro-environmental policy in the Silesia region" - funded by the National Science Centre allocated on the basis of the decision number DEC-2011/03/D/ST10/05251*

References

Sensuła B. (2016a) δ^{13}C and water use efficiency in the glucose of annual pine tree rings as ecological indicators of the forests in the most industrialized part of Poland. *Water, Air, and Soil Pollution* 227:68.

Sensuła B. (2016b) The impact of climate, sulfur dioxide, and industrial dust on δ^{18}O and δ^{13}C in glucose from pine tree rings growing in an industrialized area in the southern part of Poland. *Water, Air, and Soil Pollution* 227:106.

Sensuła B., Pazdur A. (2013) Influence of climate change on carbon and oxygen isotope fractionation factors between glucose and α-cellulose of pine wood. *Geochronometria* 40(2):145–152.

Sensuła B., Wilczyński S., Piotrowska N. (2016) Zastosowanie metod dendrochronologicz-nych oraz spektrometrycznych w monitorowaniu drzewostanów sosnowych na obszarach przemysłowych. *Sylwan* R. CLX (9):730-740.

BIVALVE *Glycymeris pilosa* AS DATA ARCHIVE OF THE GLOBAL ATMOSPHERIC ^{14}C CHANGE AND THE SUESS EFFECT

Melita Peharda[1], Andreja Sironić[2], Damir Borković[2], Krešimir Markulin[1]

[1] *Institute of Oceanography and Fisheries Šetalište Ivana Meštrovića 63, 21 000 Split, Croatia*
[2] *Institut Ruđer Bošković, Bijenička cesta 54, 10 000 Zagreb, Croatia*
Corresponding author: asironic@irb.hr

Investigation of geochemical composition of bivalve shells can provide information on the changes in marine environment occurring during the organism's life span. *Glycymeris pilosa* is a relatively large (>8 cm) and a long-lived bivalve (>60 years) that is locally abundant in the Adriatic Sea. Its growth increments are annual and clearly visible in shell cross sections, which enable correct temporal positioning of geochemical data obtained from different shell parts.

In this study we present results of ^{14}C and ^{13}C analyses in carbonates of five individual shells that grew in period 1948-2015 in the north Adriatic Sea. Samples were collected by SCUBA diving from ~10 m depth near Barbariga, Istria. In laboratory, shells were measured, area of the hinge of one shell valve was cut, acetate peel replicas of shell cross section were prepared following procedure from Peharda et al. (2016) and longevity of shells was estimated. Carbonate samples were drilled from the external surface of the second valve, each sample covering between one and five growth increments depending on the width of the increment. Four live collected and one fossil individual were analyzed. ^{14}C analyses of shell carbonates from all individual shells revealed ^{14}C increase characteristic for a reflection of atmospheric ^{14}C bomb peak. Calendar years corresponding to growth increments of the fossil shell from which carbonate samples were collected were determined by using the trend of ^{14}C increase along its growth line compared to a temporal ^{14}C curve obtained from live samples. The comparison was made by means of finding the best fit between two curves by implementing the least square method. This was also verified by the schlerochronological fit.

The intensity of the ^{14}C peak observed in the shells is damped and delayed compared to the atmospheric bomb peak in the northern hemisphere. Suess effect is indicated in a temporal decrease of δ^{13}C values in the umbo of the shells. Results of this study clearly illustrate the potential of *G. pilosa* as geochemical data archive.

Keywords: *Glycymeris pilosa,* ^{14}C bomb peak, Suess effect, north Adriatic.

Acknowledgments: *Research has been supported by the Croatian Science Foundation under the project SCOOL (IP-2014-09-5747).*

References

Peharda M., Black B.A., Purroy A., Mihanović H. (2016) The bivalve *Glycymeris pilosa* as a multidecadal environmental archive for the Adriatic and Mediterranean Seas. *Marine Environmental Research* 119:79-87.

CARBON BASED PROXIES OF PALAEOENVIRONMENTAL RECORDS IN THE SEDIMENTS OF TWO LAKES, THE PLITVICE LAKES, CROATIA

Nada Horvatinčić[1], Andreja Sironić[1], Jadranka Barešić[1], Ivan Sondi[2], Ines Krajcar Bronić[1], Damir Borković[1]

[1]*Laboratory for low-level radioactivities, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia*
[2]*Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6,*
University of Zagreb, Zagreb, Croatia
Corresponding author: *asironic@irb.hr*

Six sediment cores, top 30-40 cm, from two lakes of different sizes, Lake Prošće and Lake Kaluđerovac, situated in the karst region of the Plitvice Lakes system, Croatia, were studied by mineralogical and structural, C/N and total organic carbon (TOC) and isotopic analyses (a^{14}C and δ^{13}C of carbonate and organic fractions). Morphological and structural properties of the calcite particles at micron and submicron-sized level indicate that calcite mineral phase is formed by active authigenic precipitation in investigated lake systems. The sediment is composed mainly of calcite, however, this study showed that the OM fraction has an important role and that analyses of both fractions and the relation between them give good overview of the processes in the lake. In the small Lake Kaluđerovac measured distributions of carbonate and OM fractions, C/N, TOC, and a^{14}C and δ^{13}C values of both fractions along the sediment depth showed similar values for all three cores with small variations in each core indicated very homogenous precipitation of autochthonous calcite. In the bigger Lake Prošće, the large differences in sediment composition of the three cores indicated different conditions of sediment precipitation inside the lake: in the coastal area the sediment was found to be a mixture of allochthonous and autochthonous fractions, while the deep-water sediment indicated in-situ calcite precipitation and aquatic OM produced in the lake.

The response of the lake sediment to the environmental conditions does not depend particularly on the size of the lake, but the surrounding environmental conditions could have great influence on the sediment composition. Extreme hydrological events in 1981 and 2010 were identified by disturbances in carbon isotopes distributions. Local anthropogenic influence was not evident, but the response to the global contaminations was observed by the occurrence of a ^{14}C peak in both carbonate and organic fractions. Increased bioproductivity in Lake Prošće in the last decades can be correlated with the slight increase of the lake water temperature in last three decades.

The detailed work has been described in the accepted paper: Horvatinčić N., Sironić A., Barešić J., Sondi I., Krajcar Bronić I., Borković D., Quarternary International, 2017. doi: 10.1016/j.quaint.2017.01.022.

Keywords: lake sediments, carbon isotope analyses, C/N analyses, mineral composition, Plitvice Lakes, Croatia.

Acknowledgments: *The work was funded by the project HRZZ-IP-11-2013-1623 Reconstruction of the Quaternary environment in Croatia using isotope methods (REQUENCRIM), the Croatian Science Foundation.*

CH_4 – SIMPLE MOLECULE, MANY MYSTERIES

Dariusz Strąpoć[1], Shahnawaz R.M. Khan[2]

[1]*Schlumberger, Paris, France*
[2]*Schlumberger, Houston, Texas, USA*
Corresponding author: *dstrapoc@slb.com*

Methane is the simplest hydrocarbon and hence one would expect its fate in nature to be the most straightforward. However, methane in the subsurface can come from variety of origins (biogenic from methanogenesis in organic-matter-rich sediments and hydrocarbon reservoirs; thermogenic from thermal cracking of organics or from specific inorganic reactions of minerals and fluids, e.g. serpentinization) and can be altered and/or transported by many different processes. Methane's small molecular size permits its high mobility, even in low-permeable shales (e.g. cap-rocks of petroleum reservoirs). On the other hand, methane is characterized by very high adsorption affinity in organics-rich rocks (coals or organic shales) and in hydrates. Small molecular weight of methane, however, causes large relative differences between its isotopologues, enabling sensitivity of $\delta^{13}C$ and $\delta^{2}H$ to all the processes listed above.

Hereby, we present such susceptibility of $\delta^{13}C$ and $\delta^{2}H$ of methane in a perspective of sedimentary basin evolution, petroleum systems and petroleum exploration. In this paper we will show methane isotope continuous log records on examples of *i*) worldwide occurrences of deep primary biogenic methane persisting much deeper than pasteurization depths; *ii*) large-scale commercial accumulations of biogenic methane worldwide (conventional and unconventional); *iii*) mixing of thermogenic and biogenic gases via leakage (including diffusion), migration and dissolution seen globally in petroleum exploration wells and their resulting impact on overall hydrocarbon fluid properties; *iv*) generation of artificial methane at drill bit and its impact on interpretation of mud gas data obtained while drilling; *v*) isotopic fractionation of methane degassing from drilling mud at the surface prior to mud's reinjection, which can misleadingly shift the signature of methane observed during drilling of geological formations.

Isotopic composition of methane integrated with best quality and most complete molecular composition of properly sampled accompanying gases, can fingerprint contributions of methane origin and assess the magnitude of alteration processes in the subsurface. Therefore, as such, the deceptive vulnerability of methane isotopic signatures to natural and human-induced processes (e.g. drilling operations), on the contrary, enables tremendous interpretative power of $\delta^{13}C$ and $\delta^{2}H$.

Keywords: methane, carbon, hydrogen, isotopes, biogenic, thermogenic, mixing, diffusion, drill bit metamorphism, mud gas, logging, isotope fractionation.

Acknowledgments: *We thank Shell International for allowing to present data and for active participation in this research. We also thank any Schlumberger colleagues that contributed to the collection of the data during the commercial jobs.*

ORIGIN OF HYDROCARBON GASES, CARBON DIOXIDE AND HYDROGEN SULPHIDE FROM SELECTED PETROLEUM FIELDS OF THE ZECHSTEIN MAIN DOLOMITE CARBONATES OF THE SOUTHERN PERMIAN BASIN (POLAND): ISOTOPIC AND GEOLOGICAL APPROACH

Maciej J. Kotarba[1], **Elżbieta Bilkiewicz**[1], **Stanisław Hałas**[2]

[1]AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Al. Mickiewicza 30, 30-059 Kraków, Poland
[2]Maria Curie Skłodowska University, Faculty of Mathematics, Physics and Computer Science, Pl. Marii Curie-Skłodowskiej 5, 20-031 Lublin, Poland
Corresponding author: *ebil@agh.edu.pl*

The objective of this study was to determine the origin of natural gases (hydrocarbons, CO_2 and H_2S) accumulated in the Ca_2 carbonate reservoir. Gas generation, migration and mixing processes ware established based on molecular and isotopic compositions of nine gas samples from seven petroleum fields, i.e. hydrocarbon (C_1 to C_7) and non-hydrocarbon (H_2S, CO_2, N_2, H_2, Ar, He) components, $^{13}C/^{12}C$ in CH_4, C_2H_6, C_3H_8 and CO_2, $^2H/^1H$ in CH_4, and $^{34}S/^{32}S$ in H_2S in relation to geological setting. Moreover, stable sulphur isotope composition of sulphates of Basal Anhydrite (A2d) of PZ2 (Stassfurt) and Upper Anhydrite (A1g) of PZ1 (Werra) cycles of over- and underlying the Ca2 carbonates, respectively and organic compounds of oils accumulated in Ca2 carbonate reservoirs was used for explaining the origin of H_2S. Previous studies (Kotarba *et al*., 2000) revealed that the hydrocarbon gases in the Ca2 carbonate reservoir were mainly thermogenic in origin and sourced from dispersed organic matter in the Ca2 carbonates. The occurrence and preliminary studies on the origin of hydrogen sulphide and carbon dioxide suggest that these natural gas components have common origin related to MSR and/or TSR processes (Kotarba and Hałas, 1986).

Totally nine natural gas samples from producing wells were analysed (Table 1). Molecular composition was determined chromatographically in a set of columns on Hewlett Packard 5890 Series II, Hewlett Packard 6890 Series and Chrom 5 gas chromatographs. Stable carbon and hydrogen isotope analyses were performed using Finnigan Delta Plus and Micromass VG Optima mass spectrometers. The stable carbon isotope data are expressed in the δ notation ($\delta^{13}C$, ‰) relative to VPDB on a scale such that NBS-22 (an oil) is -30.03‰. The stable hydrogen isotope data are reported in δ notation (δ^2H, ‰) relative to the VSMOW.

Fourteen anhydrite core samples for analyses of their stable sulphur isotope composition from Basal Anhydrite and Upper Anhydrite cycles were collected. Nine oil samples from carbonate reservoirs of the Ca2 strata were analysed for stable sulphur isotope composition of their organic compounds. Isotope analysis of SO_2 gases obtained from both anhydrite and oil samples was performed off-line on a dual inlet and triple collector isotope ratio mass spectrometer with precision of ±0.05‰, whilst overall reproducibility of $\delta^{34}S$ referred to the VCDT standard was better than 0.2‰. For normalization of delta values the NBS-127 standard (BaSO4) with $\delta^{34}S$ = +21.17‰ (Halas and Szaran, 2001) was analysed in every series of samples.

Table 1. *Gas indices, stable carbon, hydrogen and nitrogen isotope composition and analysed natural gases and present-day temperature of the Main Dolomite reservoir*

Sample code	Gas indices						Stable isotopes (‰)							Present-day temperature (°C)
	C_{HC}	C_2H_6/ C_3H_8	C_2H_6/ iC_4H_{10}	CDMI	EPR	GSI	$\delta^{13}C$ (CH_4)	δ^2H (CH_4)	$\delta^{13}C$ (C_2H_6)	$\delta^{13}C$ (C_3H_8)	$\Delta^{13}C$ (C_2H_6 – C_3H_8)	$\delta^{13}C$ (CO_2)	$\delta^{34}S$ (H_2S)	
Ba-1	3.27	2.16	14.6	4.06	0.03	3.423	-53.4	-262	-37.8	-27.6	-10.2	-0.6	-9.8	91
Bl-1	4.65	1.32	4.75	4.51	0.03	13.3	-57.8	-249	-33.2	-28.5	-4.7	-2.1	-4.4	80
Bu-1	5.93	3.32	32.6	1.80	0.02	3.11	-52.9	-249	-37.2	-29.2	-8.0	-5.1	-5.5	80
Ga-1	4.23	1.59	5.50	2.67	0.02	22.8	-50.4	n.a.	-33.8	n.a.	n.a.	n.a.	-0.9	110
KP-5	2.66	1.18	5.17	4.14	0.03	14.2	-54.6	-242	-39.0	-29.5	-9.5	n.a.	-3.9	65
KP-9	1.61	1.11	1.66	0.69	0.00	14.2	-54.8	n.a.	n.a.	n.a.	n.a.	n.a.	-3.2	66
KP-11	2.03	1.38	1.44	1.33	0.01	15.4	-54.5	n.a.	n.a.	n.a.	n.a.	n.a.	-5.5	67
Re-1	5.33	1.71	9.3	3.68	0.03	7.21	-57.2	-268	-39.7	-29.6	-10.1	-10.0	-7.8	71
Zb-1	3.42	1.83	10.9	5.41	0.04	1.79	-50.8	-257	-37.5	-29.0	-8.5	-10.1	-9.6	86

$C_{HC} = CH_4/(C_2H_6+C_3H_8)$; CDMI = $(CO_2/[CO_2+CH_4])$ 100 (%); $H_2S\text{-}HC = 1\text{-}H_2S/(\Sigma C_1\text{-}C_7 + H_2S)$,
$C_1/\sum(C_1\text{-}C_5)$ (Hydrocarbon ratio) = $CH_4/(CH_4+C_2H_6+C_3H_8+C_4H_{10}+C_5H_{12})$, EPR = $CO_2/[CO_2 +\sum(C_1\text{-}C_7)]$,
GSI = $H_2S /[H_2S +\sum(C_1\text{-}C_5)]$*100 (%)
n.a. - not analysed

Molecular and isotopic (Table 1) compositions of natural gas and stable sulphur isotope composition of organic compounds of oils from the Zechstein Main Dolomite (Ca2) carbonate reservoirs of PZ2 cycle and sulphur isotope composition of sulphates of Basal Anhydrite (A2d) of PZ2 and Upper Anhydrite (A1g) of PZ1 cycles of over- and underlying the Ca2 carbonates of the Polish Permian Basin. These in relation with geological conditions reveal that in analysed natural gases: (*i*) the hydrocarbon components were generated by both microbial and thermogenic processes. The microbial methane was generated by fermentation and also during carbon dioxide reduction. Thermogenic hydrocarbons were generated during a single generation process of early low-temperature stage of "oil window" from type II kerogen; (*ii*) CO_2 was generated during microbial and thermal transformations of organic matter, MSR and/or TSR processes and during carbonate dissolution by fluid migration; (*iii*) H_2S could be generated during TSR and/or MSR processes and thermal decomposition of sulphur-containing compounds of dispersed organic matter and oil.

Keywords: hydrocarbon gases, carbon dioxide, hydrogen sulphide, MSR, TSR.

Acknowledgments: *The study was undertaken as the statutory research of the Faculty of Geology, Geophysics and Environmental Protection at the AGH University of Science and Technology in Kraków, project No. 11.11.140.626.*

References

Halas S., Szaran J. (2001) Improved thermal decomposition of sulfates to SO_2 and mass spectrometric determination of $\delta^{34}S$ of IAEA SO-5, IAEA SO-6 and NBS-127 sulfate standards, *Rapid Communication Mass Spectrometry* 15: 1618-1620.

Kotarba M.J., Hałas S. (1986) Sulfur isotope ratios and the origin of hydrogen sulfide from Zechstein sediments of Polish part of Permian basin. 6th International Conference on Geochronology, *Cosmochronology and Isotope Geology*, Cambridge. Terra Cognita 6, p. 207.

Kotarba M.J., Więcław W., Stecko Z. (2000) Composition, origin and habitat of natural gases within Zechstein Main Dolomite strata of the western part of the Fore-Sudetic area, SW Poland. *Przegląd Geologiczny* 48: 429-435 (in Polish with English abstract).

ORIGIN OF METHANE FROM GEOLOGIC SOURCES CONSTRAINED BY ISOTOPIC AND MOLECULAR COMPOSITION – APPLICATION TO ROMANIA

Artur Ionescu[1,2], Calin Baciu[1], Giuseppe Etiope[3,1], Boglarka-Mercedesz Kis[2], Antonio Caracausi[4], Franco Tassi[5], István Futó[6], Szabolcs Harangi[2]

[1]*Babes-Bolyai University, Faculty of Environmental Science and Engineering,*
Fântînele 30, Cluj-Napoca, 400294, Romania
[2]*MTA-ELTE Volcanology Research Group, Department of Petrology and Geochemistry, Institute of Geography and Earth Sciences, Eotvos University Budapest (ELTE),*
Pazmany setany 1/C, Budapest, H-1117, Hungary
[3]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 2, via V. Murata 605, 00143 Roma, Italy*
[4]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo,*
Via U. La Malfa 153, 90146 Palermo, Italy
[5]*Department of Earth Sciences, University of Florence, Via La Pira 4, 50121 Florence, Italy*
[6]*Institute for Nuclear Research, Hungarian Academy of Sciences,Bem tér 18/C, H-4026 Debrecen, Hungary*
Corresponding author: *calin.baciu@ubbcluj.ro*

The surface emissions of methane from geologic sources have been previously investigated, mainly within the important hydrocarbon-prone areas, as the Carpathian Foredeep, the Transylvanian Basin, and the Moldavian Platform (Etiope *et al*., 2004; Baciu *et al*., 2007; Baciu *et al*., 2008; Spulber *et al*., 2010; Frunzeti *et al*., 2012; Pop *et al*., 2015). In most of the cases, they occur as dry seeps, mud volcanoes, or hydrocarbon-rich springs. The gas composition is generally dominated by methane, accompanied by other light hydrocarbons and different amounts of other gases (CO_2, N_2, H_2S, etc.). Although in lower amounts and proportions, hydrocarbons may also be released from volcanic or non-volcanic geothermal areas. Methane emitted from geothermal areas has recently become a subject of investigation of our team, and studies focusing on its occurrence and origin are in progress.

The combined molecular and isotopic data offer insights on the origin of gas. In sedimentary hydrocarbon-prone areas, the methane is generally biotic, being derived either from the microbial activity (microbial methane), or from the thermal degradation of organic matter (thermogenic methane). In geothermal areas, a variety of pathways of methane production have been described, sometimes with significant implication of abiotic processes (e.g. Etiope, 2015).

The present work proposes two main objectives. The first is the assessment of methane, and possibly other light hydrocarbons content from gas manifestations and gas-rich springs from different geologic and tectonic settings across Romania. Detailed data on the participation of hydrocarbons to the geogenic gas emissions are presented. The second objective consists in constraining the origin of methane in relation with the geological environment, by using complex geochemical data.

Seventeen hydrocarbon gas seeps and more than 170 water sources from different structural contexts of Romania have been studied to different extents through molecular and isotopic analyses, aiming to evaluate the origin and post-genetic alterations of gas.

The seeps in the external area of the Eastern Carpathians, corresponding to the Flysch and Foredeep zones, and further on, the gas manifestations from the Moldavian Platform, show thermogenic origin, with different degrees of maturity, and some of them with indications of biodegradation. In the Southern Carpathian Foredeep the methane origin is also thermogenic. The Transylvanian gases are mainly microbial; thermogenic methane can be however found at the eastern edge of the basin, close to the Neogene volcanic belt. It is noteworthy that in the central part of the Transylvanian basin, the gases (Sarmasel, Deleni, Tauni) contain measurable amounts of C2+ alkanes, which suggest that the gas is not totally microbial. The presence of a thermogenic component may confirm the existence of a deeper petroleum system in Transylvania, as suggested by previous authors (e.g. Popescu, 1995). The isotopic measurements performed on dissolved gases from hydrocarbon-rich springs in the Transylvanian Basin confirm the microbial origin of gases (δ^{13}C-CH_4 = – 63‰), that towards the eastern margin changes to a sedimentary-thermogenic origin. Microbial methane is still present in the shallower strata.

The methane released in the area of Ciomadul volcanic complex is mainly thermogenic. The thermogenic methane may result from the thermal cracking of organic matter from sediments in the vicinity of the volcanic plumbing system, likely related to the Eastern Carpathian Flysch units, which were crossed by the magmas feeding the South Harghita volcanic range, including Ciomadul. The isotopic ratios show an enrichment in carbon-13 (δ^{13}C-CH_4 = – 6.5‰), that suggests the possible presence of a minor abiotic methane component. From this area towards the Carpathian Flysch and Carpathian Foredeep, the methane becomes more depleted in carbon-13, reaching typical values for thermogenic methane (δ^{13}C-CH_4 = – 49‰).

It is noteworthy that the type of methane found in springs (in dissolved or free form) is also influenced by the circulation of groundwater that may interact with the gases, in relation with the depth. A good example is the Transylvanian-Carpathian Transition zone where both types of biotic methane (microbial and thermogenic) have been found. In the geothermal areas of Herculane and Calimanesti-Caciulata, the methane is predominantly thermogenic, but the presence of a minor abiotic component is presumed, especially in the first case. On the Romanian side of the Pannonian Basin, microbial methane is present in the shallower reservoir, while in deeper strata the methane is thermogenic.

Keywords: methane; stable isotopes, carbon-13, gas emissions, Romania.

Acknowledgments: *This work was financially supported by the Romanian National Research Council, Project PN-II-ID-PCE-2011-3-0537, and by OTKA (Hungarian National Research Fund), Project K116528. The authors acknowledge support from the Deep Energy Community of the Deep Carbon Observatory.*

References

Baciu C., Caracausi C., Etiope G., Italiano F. (2007) Mud volcanoes and methane seeps in Romania: main features and gas flux. *Annals of Geophysics* 50:501-512.

Baciu C., Etiope G., Cuna S., Spulber L. (2008) Methane seepage in an urban development area (Bacau, Romania): origin, extent and hazard. *Geofluids* 8, 311-320.

Etiope G. (2015) Natural gas seepage: The Earth’s hydrocarbon degassing. Springer Int. Publ., pp. 199.

Etiope G., Baciu C., Caracausi A., Italiano .F, Cosma C. (2004) Gas flux to the atmosphere from mud volcanoes in eastern Romania. *Terra Nova* 16, 179-184.

Frunzeti N., Baciu C., Etiope G., Pfanz H. (2012) Geogenic emission of methane and carbon dioxide at Beciu mud volcano (Berca-Arbanasi hydrocarbon-bearing structure, eastern Carpathians, Romania). *Carpathian Journal of Earth and Environmental Sciences* 7(3):159-166.

Pop C.I., Ionescu A., Baciu C. (2015) Methane seepage from geologic sources on the Moldavian Platform (Eastern Romania). *Carpathian Journal of Earth and Environmental Sciences* 10(1):203-210.

Popescu B.M. (1995) Romania’s petroleum systems and their remaining potential. *Petroleum Geoscience* 1:337-350.

Spulber L., Etiope G., Baciu C., Malos C., Vlad S.N. (2010) Methane emissions from natural gas seeps and mud volcanoes in Transylvania (Romania). *Geofluids* 10, 463-475.

METHODOLOGICAL ASPECTS OF K-AR DATING IN APPLICATION TO SEDIMENTARY BASINS THERMAL HISTORY RECONSTRUCTION

Sylwia Kowalska[1], Stanisław Hałas[2], Artur Wójtowicz[2], Klaus Wemmer[3], Zbyszek Mikołajewski[4]

[1]*Oil and Gas Institute – National Research Institute, Kraków, Poland*
[2]*Mass Spectrometry Laboratory, Institute of Physics, Maria Curie-Skłodowska University, Lublin, Poland*
[3]*Isotope Geology Division, Geoscience Center, University of Göttingen, Göttingen, Germany*
[4]*PGNiG SA, Geology and Hydrocarbon Production Branch, Poland*
Corresponding author: *kowalska@inig.pl*

K-Ar dating of maximum diagenesis is widely used in geology for thermal history reconstruction in sedimentary basins. Various research centres give different magnitudes of measurement uncertainty (from 1 to 10 Ma) which should be taken into account. Usually the reported uncertainty responds only to standard operating procedures of an individual laboratory and is estimated by that laboratory. The main aim of this study was to find out what a realistic error should be considered when interpreting geological K-Ar dating results. For this purpose an interlaboratory comparison with the participation of four well-known laboratories was organized. Three of them are performing measurements by K-Ar method and one by Ar-Ar method with the use of the capsule technique specially adapted for very fine clay materials. The following scientists took part in the interlaboratory comparison: Stanislaw Hałas and Artur Wojtowicz from the University in Lublin, Poland (K-Ar), Klaus Wemmer from the University of Göttingen (K-Ar), Yakov Kapusta from ACTLAB laboratory in Canada (K-Ar) and Chris Hall from the University of Michigan in the USA (Ar-Ar). Test samples was previously analysed by Jan Środoń and Michał Banaś from Institute of Geological Science of Polish Academy of Sciences – Research Center in Krakow in Poland (Kowalska, 2008).

The research material consisted of Silurian and Ordovician bentonites from the Polish part of the East European Platform. Samples come from different boreholes drilled lately by PGNiG S.A. during intensive shale gas exploration in Poland. Silurian and Ordovitian strata in that region are very reach in volcaniclastic layers, which shows also different thicknesses from millimetres to more than 3 m.

Interlaboratory comparison was carried out on three test samples. From each test sample four different grain fractions <0.02, 0.02-0.05, 0.05-0.2 and 0.2-2 µm were separated at the Institute of Geological Sciences in Krakow. Samples were splited by quartering, encrypted and sent to the laboratories participating in the comparison. All the laboratories, despite of the Środoń and Banaś Lab, obtained very similar results for the three finest fractions (Table 1). The fraction 0.2-2 µm gave distinctly older ages, which proves an admixture of detritic material. The results of K-Ar and Ar-Ar dating show that dating of diagenetic age is possible for a fraction less than 0.2 µm. Based on the results of interlaboratory comparison, it is clearly seen that predo-minantly errors arise from the determination of potassium concentration.

Comparison of the results (Table 1) achieved from laboratories taking part in the research clearly indicates that the actual measurement errors range up to ±10 Ma. Significantly younger ages were obtained by the Ar-Ar method, what confirm the large influence of ^{39}Ar escape effect from the very fine grained samples, the so called “recoil effect" (e.g. Hall, 2013).

Table 1. *The results of interlaboratory comparison - K-Ar and Ar-Ar dating.*

Sample	Grain size [µm]	K-Ar [Ma]				Ar-Ar [Ma]
		Kraków (Poland)	**Lublin (Poland)**	**Göttingen (Germany)**	**Actlab (Canada)**	**Michigen (USA)**
1	<0.02	342	362	348.6	367	290
	0.05-0.02	287	354	348.3		296
	0.2-0.05	331	357	350.7		282
	0.2-2	361	384	355.6	387	319
2	<0.02	360	372	364.9		
	0.05-0.02	366	363	358.7		
	0.2-0.05	356	368	364.0		
	0.2-2	317	387	380.2		
3	<0.02	311	190			148
	0.05-0.02	320	196			
	0.2-0.05	364	212			
	0.2-2	325	272			

The above observations were confirmed by further studies carried out simultaneously for 60 bentonite samples from 10 other boreholes using only less than 2 µm fraction. It was also proved that in case of the Silurian and Ordovitian complex in Poland the thickness of bentonite layer do not influence the K-Ar results and all of them are suitable to date the maximum of thermo diagenesis. Very consistent results were achieved for the whole range of bentonites thicknesses.

Keywords: K-Ar, Ar-Ar, illite-smectite, Silurian-Ordovician bentonites, thermal history.

Acknowledgments: *The presentation is the result of research conducted in connection with the project: Construction of the Lower Paleozoic extent’s maps biostratigraphy and analysis of the Eastern European Platform for estimation of unconventional hydrocarbon deposits distribution, co-funded by the National Centre for Research and Development as part of the programme BLUE GAS – POLISH SHALE GAS. Contract No. BG1/GAZGEOLMOD/13.*

References

Kowalska S. (2008) Border of diagenesis and anchimetamorphism in Upper Proterozoic and Cambrian rocks of E part of Małopolska block established by clay mineral studies. PhD thesis, Institute of Geological Sciences PAN, Kraków, Poland, 238 pp.

Hall C. (2013) Direct measurement of recoil effects on ^{40}Ar/^{39}Ar standards. *Geological Society*, London, Special Publications 378: 53-62.

COMPLEX RADIONUCLIDES' UTILIZATION AS A DECISIVE CONTRIBUTION FOR NUCLEAR ENERGY REHABILITATION

Elena Agarwal[1], Iurie Bosneaga[2]

[1]*University of Academy of Sciences, Chisinau, Republic of Moldova,*
[2]*Institute of Applied Physics of Academy of Sciences, Chisinau, Republic of Moldova*
Corresponding author: *iubosneaga@gmail.com*

Sustainable development has no alternatives. We propose *Energy Strategy for the Sustainable Development (3D-Strategy*), based on the principles of *Decentralization, Diversification and Decarbonization*. Directly or indirectly this principles come from the thermodynamic analysis applied. The thermodynamic base of this analysis guarantees absolute objectivity (for example, independence from political and economical conjuncture factors - current fuel prices, etc.). We argue that especially long-term sustainability of the Nuclear Power can contribute roundly - together with the optimal mix of progressing renewables - for solving the most important challenges which humanity is facing – energy supply, food supply and climate change. Nuclear power generation has a huge potential for perfection, and most of it - is related to complex, secure and efficient radionuclides' utilization.

Presently in action nuclear power technologies generate "nuclear wastes" - on the front-end and, especially, on the back-end of the cycle. We firmly consider these collateral radionuclides as additional opportunities, but in no way - as an incorrigible drawback.

The problem of secondary ("waste") energy, or harmful (and taxable) thermal pollution - is common for all power plants, but it is more acute for NPPs (Nuclear Power Plants). In the report (Boşneaga, 2014) is presented a complex, integrated solution for this problem. "Waste" energy emissions are excluded – mainly due to application of thermal accumulators and large scale implementation of low-temperature food dehydration. Ionization and thermal potential of radionuclides and of the spent fuel - is used in two ways by this solution directly on the NPP site: for magnetohydrodynamic (MHD) additional electricity generation, with the respective facilitation of water vapor condensation on the outlet of the steam turbine, and also for ensuring microbiological security of the final food products. (In both cases are exploited the possibilities of cost-effective non-thermal ("cold") plasma generation - due to highly-radiating radionuclides).

There is one more possibility to improve drastically the current performances in nuclear power domain - due to rational spent radionuclides (spent fuel) utilization. We prove that it is necessary to ensure the progressive growth of heavy water NPPs, which could re-use the entire quantity of the spent fuel coming from the

"enriched uranium" NPPs - without reprocessing (Boşneaga, 2015). Such a secondary use of the "spent fuel" would permit substantial increase of the nuclear power generation - with relatively small capital investments and without any growth of the spent fuel quantity. In fact, spent fuel from the "enriched uranium" NPPs should be named "partially spent fuel", or "first stage spent fuel". For the large-scale "second stage" re-use of the enriched uranium in heavy water NPPs - we develop the efficient methods of obtaining the respective quantities of heavy water.

Keywords: radionuclides, spent fuel reprocessing derivatives, non-thermal plasma, MHD.

References

Boşneaga I. (2014) Integrated solution for energy and food problems - a way to sustainable development. *International Symposium on Food Safety and Quality: Applications of Nuclear and Related Techniques.* Vienna, Austria, 10-13 November 2014.

Boşneaga I. (2015) Huge non-spent potential of the "spent fuel"- the ways of its utilization. *International Conference on Management of Spent Fuel from Nuclear Power Reactors - An Integrated Approach to the Back-End of the Fuel Cycle*, Vienna, Austria, 15-19 June 2015.

XIVth Workshop of the European Society for Isotope Research
25 – 29 June 2017, Băile Govora, Romania

RADON CONCENTRATION MEASUREMENTS AS A TOOL FOR MAJOR TECTONIC LINES DETERMINATION IN THE CARPATHIANS

Leszek Jankowski[1], Sylwia Kowalska[2], Rafał Skupio[2], Marek Dohnalik[2]

[1]*Polish Geological Institute - National Research Institute, Kraków, Poland*
[2]*Oil and Gas Institute – National Research Institute, Kraków, Poland*
Corresponding author: *kowalska@inig.pl*

One of the essential elements of a petroleum system in the Carpathian mountains and a place where circulation process of fluids and bitumen occurs are major fault zones (Jankowski, 2015). These zones tend to be reservoir seals (closed for migration in compression regime) or reservoir migration paths (opened, usually in extensional regime). Recognition of fault type, its strike and locking depth, as well as tectonic system regime (from compressional to extensional), are crucial element of cartographic work and has an exceptional meaning for seismic interpretation process and for oil and gas exploration. The method of radon (^{222}Rn) concentration measurements in soil was tested as a tool to verify regional importance and precise localization of the most important tectonic zones (faults and overlaps) in the Polish part of the Carpathian mountains.

Radon (^{222}Rn) is an inert gas that does not stick to or react with any materials. Every radon nucleus decays through the sequence: polonium-218, lead-214, bismuth-214, polonium-214 and lead-210. With each transformation the nucleus emits characteristic alfa, beta and gamma radiation. The origin of ^{222}Rn in soils is associated with a number of different sources, among which the natural radioactivity of subsurface rocks and migration from the deeper zones of the earth's crust to the surface have the greatest meaning. As the majority of sedimentary rocks have relatively low radioactivity, due to this phenomenon it is possible to track the field radon anomalies connected with the presence of fault zones (Papastefanou *et al*. 2001; Inceöz *et al*., 2006; Vaupotič *et al*., 2010). The maximum increase in soil radon concentration is observed in areas directly localized over the fault lines even if it is covered with the thick soil profile.

Field measurements of ^{222}Rn in soil gas were carried out using RAD7 portable spectrometer developed by Durridge Company Inc. designed to detect alpha particles only. RAD7 uses a solid alpha detector - a semiconductor material (silicon), that converts alpha radiation directly to an electrical signal. The advantages of this detector are ruggedness and ability to electronically determine energy of each alpha particle. The measurement cell has a volume of about 0.7L. The system contains a built-in-pump with an air flow rate of 1 L/min, desiccant tubes, an infrared printer and set of pipes with additional dust and inlet filters. Device was connected to the Soil Gas Probe made by Durridge Company Inc. The probe was inserted to the ground on the depth about 50 cm, the measurement time was set for 10 min for each point. Before every test the cell with detector was purged to achieve fresh and dry air inside (humidity in the system during tests was lower than 6%). All of the measurements were performed in the stable weather conditions (similar temperature and no rain).

Test measurements ware conducted in the areas with well documented tectonic system by means of cartographic field works: in the Lanckorona - Żegocina zone, the Bieszczady melange zone (Jankowski, 2007), in the Grajcarek tectonic zone, in the Pieniny Klippen Belt and in the area of Węglówka - the northern border-zone of the Central Carpathian's Depression. These zones ware created as a result of secondary (accordingly to compressional faze of the Carpathian orogeny) tectonic deformation. Measurements ware done not only in the melange zones but also along transects perpendicular to that tectonic elements to refer background intensity.

The obtained results allowed not only for precise localisation of analysed fault zone, but it was also possible to define their hierarchy in Carpathian orogenic wedge. Obtained data show enormous differences of radon exhalation intensity between fault zones (thousands of Bq/m^3) and surrounding regions (less than hundred of Bq/m^3). The biggest radon concentration, more than 23000 Bq/m^3, was measured in the Central Carpathian's Depression. This value was recorded in the middle of tectonic structure, not in the northern or southern border fault zone, what was the most interesting finding of this project. Our studies showed also, that the Grajcarek tectonic zone is much more important migration pathway than normal fault separating Podhale Flysch from the Pieniny Klippen Belt region, as it was fought before. The Grajcarek fault zone, similarly to the Bieszczady melange, seems to be major tectonic zone responsible for creation of the huge tectonic melange of the Pieniny Klippen Belt.

Keywords: Radon concentration, Carpathian, faults, oil and gas deposits.

References

Inceöz M., Baykara O., Aksoy E., Doğru M. (2006) Measurements of soil gas radon in active fault systems: A case study along the North and East Anatolian fault systems in Turkey. *Radiation Measurements* 41: 349–353.

Jankowski L. (2007) Chaotic complexes in the Gorlice region (Polish Outer Carpathians). *Biuletyn PIG* 426: 27–52, in Polish with English abstract.

Jankowski L. (2015) The role of the chaotic complexes in the process of the Carpathian mountains creation – discussion approach. Prace Naukowe Instytutu Nafty i Gazu, *Państwowego Instytutu Badawczego*, 202, pp. 154, in Polish with English abstract.

Papastefanou C., Manolopoulou M., Stoulos S., Ioannidou Gerasopoulos E. (2001) Radon measurements along active faults in the Langadas basin, northern Greece. *Natural Hazards and Earth System Sciences* 1: 159–164.

Vaupotič J., Gregorič A., Kobal I., Žvab P., Kozak K., Mazur J., Kochowska E. (2010) Radon concentration in soil gas and radon exhalation rate at the Ravne Fault in NW Slovenia. *Natural Hazards and Earth System Sciences* 10 (4): 895-899.

CONTROL OF DECAY RATES OF NUCLEAR ISOTOPES BY COOPERATIVE EFFECTS BETWEEN THE BLOCKS OF THREE RADIATORS

Nicolae Enaki[1], Sergiu Bazgan[1], Tatiana Paslari[1], Ashok Vaseashta[1,2]

[1]*Institute of Applied Physics, Academy of Sciences of Moldova, Academiei str. 5, MD 2028*
[2]*International Clean Water Institute, NUARI, Manassas, VA USA*
Corresponding author: *enakinicolae@yahoo.com*

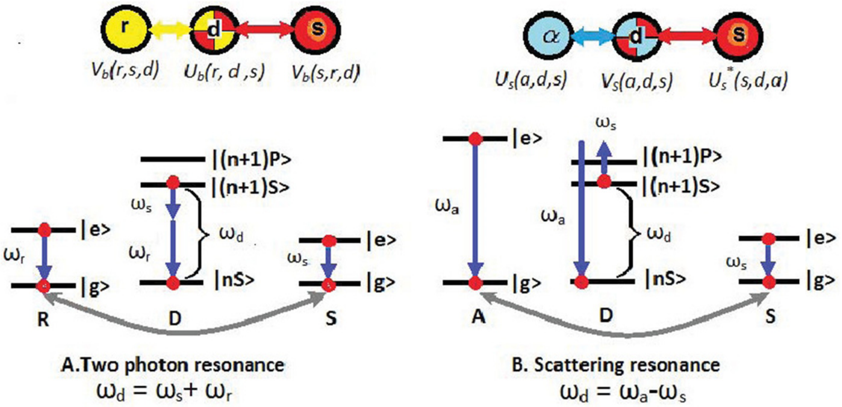
The non-linear and cooperative proprieties of Radioactivity of many elements recently became an open subject in the science due to its multi-quanta interaction with thermostat and vacuum field. For most radionuclide, single- and two-gamma transitions from meta-stable isomeric state to ground state are observed for the vast number of nuclei (or isotopes). This report is dedicated to the possibility of modification of the decay rate of the radionuclide studying the non-linear cooperative effects which appear between them during the decay time.

The nuclear medicine uses the radiation in the diagnostics and treatment of various tumours. In most cases, the information obtained after the radiation process can be applied to make a quick and accurate diagnosis of the patient's illness. From the physical point of view, in the isotope disintegration process it is attractive to change the decay rate of gamma-ray spontaneous emission of stored nuclei in the tissue. This allows us to accelerate or stop the emission rate in the small regions of organic tissue of the human body or in the laboratory. An example of the experimental problem connected to two channels of disintegration of Mo-99 in Tc-99 is described in (Vučina and Lukić, 2002). Here the parent nuclei Mo undergoes an isobaric transition to Tc-99 in two metastable states. It is constituted 80% of the nuclei go directly to first isomeric state and from 20% to go directly to the second isomeric level. Due to the long lifetime of Molybdenum -99 (66 hour) the hospitals are interested to buy this material as a radioactive isotope, and for practical application medical staff must use short life time isomer Tc-99m obtained from Molybdenum -99 (66 hour). It needs to transform rapidly the Mo in Tc in order to solve the problem of manipulation with two channels of decay processes. After this time period mentioned above the radioactive material becomes useless for treatment.

To avoid such a situation connected with the small decay time period, we propose to use two types of isotopes. For the first type, we named D isotope ensemble of nuclei with the long decay time (maybe one month). For second subsystem, we named R and S isotope type which the short decay time and is in two-photon resonance with the D nuclei subsystem as is represented in Figure 1. Firstly, the ill patient are treated with D nuclei with long time decay isotopes.

Achieving the attractive points of the tumours the D isotope (or isomer) nuclei are non-active from radioactivity points of view due to its long decay time. The ignition of this deposited excited nucleus may be organized with excited short living isomers. If this type of short living isomers achieved the same place in our body, the three particle cooperative decay effects between the long living isotopes (or isomers) and short lived isotopes (or isomers) described by Enaki in (Enaki, 2012a; Enaki, 2012b) becomes possible (see Figure 1 and Figure 2).

Hence, due to three particle cooperative effects between the nuclei, the radiation activity increases proportional to the number of radiators in tissue N_d N_r N_S multiplied by the square root of the decay rates of D- subsystem and decay rate of R-S subsystems. The priory estimation of this cooperative effect shows that it may reduce the decay rate of metastable D subsystem with some order of magnitude (for example instead of one-month decay rate for some minutes). The nuclei recoil effect together with gamma absorption may have the simultaneously the mechanical and optical actions on the affected tissue (see Figure 2).



A.Two photon resonance
$\omega_d = \omega_s + \omega_r$

B. Scattering resonance
$\omega_d = \omega_a - \omega_s$

Figure 1. *(a): Two-photon and (b): Scattering resonance with the D nuclei subsystem*

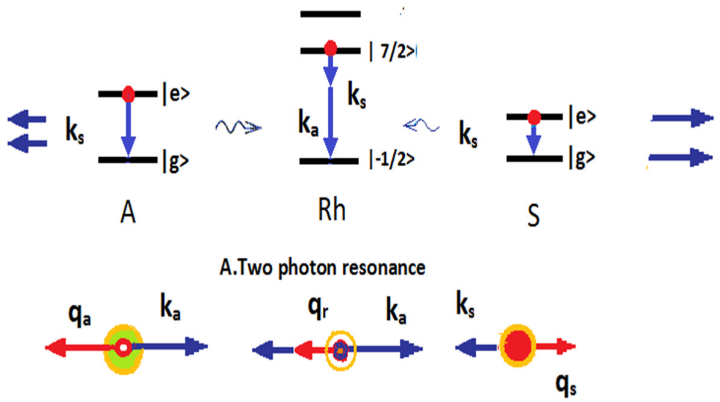


Figure 2. *(a): Two-photon resonance with short living isomers,*
(b): nuclei recoil effect together with gamma absorption

The connection between the nuclei scales and the dimension of the electronic bounds of the bio-molecules are proposed in order to establish and control the decay rate and two-quantum nuclei recoil. Several possible applications in medicine are proposed.

Keywords: nuclear isotopes, cooperative effects, bio-molecules, two-photon resonance.

References

Vučina J. and Lukić D. (2002) Radionuclidic generators for the production of technetium-99m and rhenium-188. *Facta Universitatis, Series Physics, Chemistry and Technology* 2(4): 235-243.

Enaki N. A. (2012a) Cooperative Resonance Interaction Between One-and Two-Photon Super-Fluorescence Trough the Vacuum Field. *Journal of Physics: Conference Series* 338(1): 12005-1 – 12005-12, ISSN 1742-6588, DOI: 10.1088/1742-6596/338/1/012005.

Enaki N. A. (2012b) Mutual cooperative effects between single- and two-photon super-fluorescent processes through vacuum field. *The European Physical Journal D* 66(4):98-1 – 98-21, ISSN: 1434-6060, DOI: 10.1140/epjd/e2012-20563-1.

ON SOME NEGLECTED MATTERS IN THE STABLE ISOTOPE SYSTEMATICS: THE ACID DIGESTION GRAIN SIZE EFFECT OF CARBONATES AND THE USE OF PROXIES FROM ‘COMPLETE SYSTEMS’

De Groot, Pier A.

Delta Isotope Consultancy, Oostham Belgium
pier.de.groot@telenet.be

In this lecture, a critical discussion on two ’neglected’ matters in stable isotope systematics will be presented.

The first matter concerns the grain size of ground carbonate samples for phosphoric acid digestion. From early on, with the development of the analytical method of oxygen (and carbon) isotope compositions in carbonates, it was recognised that different grain sizes of sample powders gave different oxygen isotopic results. For this reason, a specific grain size range was advised for the acid digestion method for oxygen isotope determination.

Although this effect was known, no explanation was given for this effect up to present in literature. We have to realise that only 2/3 of the oxygen is released by the acid digestion method, which basically causes the fractionation problem with different grain sizes.

In this lecture, an explanation for this isotope effect will be given. Consequences of using different grain sizes for the acid dilution method will be briefly discussed.

The second matter concerns the use of stable isotope proxies in systems where more parameters are involved. Question is if a single parameter (e.g. as a proxy) can be ‘lifted’ out of a complete, more complex system, while neglecting all other parameters.

Very commonly only selected parts of larger, complete systems are considered. If applying just a few variables of a complete system means the variables not included in the study must be fixed in value. However, if they do have influence on the isotopic distribution in the compounds of the system, this is neglected then. Moreover, experimentally determined isotopic fractionations as know from literature generally represent relatively simple systems with controlled values of variables, which rarely is true in more complex, natural systems. Experimental isotope fractionations are correct for the conditions as given. The quality of empirically obtained isotopic fractionations, however, depends on how well the variables of the system are defined. Now, extending this to the use of isotopic proxies, it has to be realised that in almost all cases it is assumed other variables are fixed, or they just are neglected. For instance, if we consider proxies for a specific stable isotope dataset, where first temperature and secondly salinity of

water is determined from the same dataset, an invalid procedure is applied. Probably both variables determined the isotopic distribution, but it is not certain which part of the isotopic distribution was induced by temperature and which by salinity. It will be shown that such interpretations are invalid and thus incorrect.

Keywords: stable isotopes, acid digestion, carbonates, fractionation, proxies, isotope systematics.

ISOTOPE EFFECTS IN CHEMICAL EXCHANGE REACTIONS OF URANIUM AND IN AMALGAMATION OF GADOLINIUM

Damian Axente and Cristina Marcu

National Institute for Research and Development of Isotopic and Molecular Technologies
400293 Cluj-Napoca, 67 – 103 Donat Str., Romania
Corresponding author: *Damian.Axente@itim-cj.ro*

In the chemical exchange reactions the isotope effects can not be expressed by using classical thermodynamics and therefore it appeals to the statistical thermodynamics, where the separation factor (α) is defined with the reduced partition function ratios.

The classical equilibrium constant of a chemical exchange, K_{cl}, equal to the ratio of the symmetry numbers of the reactants molecules, leads to a completely random distribution of the isotopes between two chemicals. Thus, there would be no isotope separation when K equals K_{cl}.

For the chemical exchange:

$$AX' + BX \leftrightarrow AX + BX'$$

the equilibrium constant is given by:

$$K = \frac{Q_{(AX)} \cdot Q_{(BX')}}{Q_{(AX')} \cdot Q_{(BX)}}; \qquad K = \frac{\left(\frac{s}{s'} \int\right)_{(AX/AX')}}{\left(\frac{s}{s'} \int\right)_{(BX/BX')}} \cdot K_{cl}\,; \qquad K = \propto \cdot\ K_{cl}$$

where: Q is the molar partition function for one mole of ideal gas molecules

$\left(\frac{s}{s'}\right)_{AX/AX'} \cdot \int AX/AX' = \frac{\left(\frac{Qqm}{Q_{cl}}\right)_{AX}}{\left(\frac{Qqm}{Q_{cl}}\right)_{AX'}}$ is the reduced partition function ratio (RPFR)

1/T dependence of the isotope effect:

$$\lim_{u \to \infty} lnb\,(u) = \frac{u}{2} \propto \frac{1}{T}; \qquad b(u) = \frac{1 - e^{-u}}{u\, e^{-u/2}}; \qquad u = \frac{h\nu}{kT}$$

is named “zero – point energy approximation” and is applicable at low temperatures and/or where vibration energy is high compared to the thermal energy.

At relatively high temperatures the temperature dependence of the isotope effect is given by:

$$\lim_{u \to 0} lnb(u) = \frac{u^2}{2u} \propto \frac{1}{T^2}$$

and the basis of substituted atoms masses dependence law of isotope effect is:

$$\ln\left(\frac{s}{s'}\right)\int \;=\frac{W_1}{24}\left(\frac{h}{kT}\right)^2\left(\frac{1}{m'}-\frac{1}{m}\right)\times\int(force\ constants)$$

where: m' and m are the masses of the substituted isotopic atoms; $W_{1\,=}$ modulating coefficient.

It was experimentally and theoretically established that the origin of uranium isotope effect in the $^{235}U/^{238}U$ exchange in the $U(IV)_{(S)}$ –$U(VI)_{(R)}$ system is not in the molecular vibration, but in the electron – nucleus interaction, known as the source of isotope shifts in atomic emission special lines:

$$^{235}U(IV)_{(S)} + {}^{238}U(VI)_{(R)} \leftrightarrow {}^{238}U(IV)_{(S)} + {}^{235}U(VI)_{(R)}$$

(Bigeleisen 1996) proposed the following relation for the separation factor (α) in the case of above mentioned chemical exchange:

$$\ln\propto\;=\;\ln\propto_0\;+\;\ln K_{anh}\;+\;\ln K_{BOELE}\;+\ln K_{hf}\;+\ln K_{fs}$$

where: $\ln\propto_0$ - (Bigeleisen *et al.* 1947) approximation of the $\ln\propto$; K_{anh} - the anharmonic vibration correction; K_{BOELE} - the correction to the Born – Oppenheimer approximation, the isotope mass shift; K_{hf} - the nuclear spin effect; K_{fs} - the nuclear field shift

The nuclear field shift term is opposite in sign from the vibration term in the $^{235}U/^{238}U$ exchange in $U(IV)_{(S)}$ –$U(VI)_{(R)}$ system and approximately three times as large as the absolute value of the latter.

The field shift term usually leads to an enrichment of the heavy isotope (^{238}U) in the species in which the electron density at the nucleus is minimum.

In the case of amalgamation of gadolinium the observed isotopic separation factor shows that the light isotope (^{156}Gd) is enriched in the amalgam phase, situation that can be explained by the field shift effect originated by interaction of "s" electrons with nucleus, (Fujii *et al*. 2009).

Keywords: isotope effect, chemical exchange, $U(IV)_{(S)}$ - $U(VI)_{(R)}$, Gd-amalgam systems.

References

Bigeleisen J. (1996) Nuclear size and shape effects in chemical reactions. Isotope chemistry of heavy elements. *Journal of the American Chemical Society* 118(15):3676-3680.

Bigeleisen J., Mayer M.G. (1947) Calculation of equilibrium constants for isotope exchange reactions. *Journal of Chemical Physics* 15(5):261.

Fujii Y., Nomura M., Suzuki T., Axente D. (2009) Isotope effects in electron exchange reactions of lanthanide and actinide elements including chemical uranium enrichment. *Revista de Chimie* 60(3):258-263.

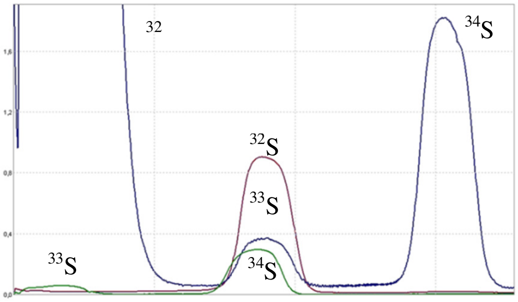
SIMULTANEOUS DETERMINATION OF δ^{34}S AND δ^{36}S ON SO_2 GAS

Tomasz Pieńkos, Stanisław Hałas, Andrzej Pelc

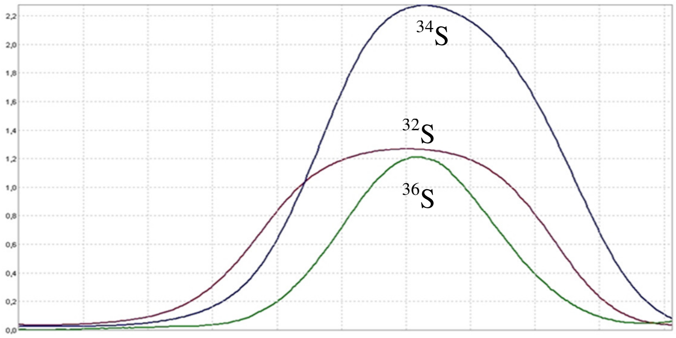
Mass Spectrometry Laboratory, Maria Curie-Sklodowska University, 20-031 Lublin, Poland
Corresponding author: *Andrzej.Pelc@poczta.umcs.lublin.pl*

In this study we have applied SO_2 gas to the multiple isotope analysis (i.e. simultaneous analysis of sulfur isotope ratios: $^{33}S/^{32}S$, $^{34}S/^{32}S$ and $^{36}S/^{32}S$) using S^+ ion beams. So far such analysis is performed on SF_6 gas, the preparation of which requires the use of a fluorination line (Ono *et al.,* 2006) and a mass spectrometer with enhanced resolving power to resolve isotope peaks $^{33}SF_5$ from $^{32}SF_5$ at masses 128 and 127. On the other hand SO_2 gas can be easily prepared from sulfides (Robinson and Kusakabe, 1975) and from sulfates (Halas and Wolacewicz, 1981). Moreover, a great advantage of the isotope analysis on S^+ instead on SO^+ or SO_2^+spectra is that there is no need to keep constant oxygen isotopic composition in the SO_2 gas. Usually sulfide and sulfate samples prepared to SO_2 have different oxygen, but it doesn't matter in the case of analysis on S^+.

In the patent application (Halas *et al.,* 2016) we have described a new ion source which can be applied for analysis of gases. The new ion source significantly enhances the generation of positive and negative ions in comparison to commonly used Nier type by more than 2 orders of magnitude. The analyzed gas is admitted from a dual inlet system to the ion source through separate capillaries connected to the pneumatically operated changeover valve as described by Halas (1979). Prepared SO_2 samples were purified from water and O_2 which eliminates interference at mass 32 peak. Nevertheless a contamination at peak 33 was observed, most likely from hydrogen desorbed inside the vacuum system. For this reason we were not able to determine δ^{33}S, because of formation of $^{32}SH^+$ ions which interfere with $^{33}S^+$, thereby measured delta value was unstable in time. This was not the case with the smallest peak 36.



The two figures present the plots of mass spectra recorded in three independent Faraday cups for simultaneous collection of the 32-33-34 or 32-34-36 triplets. The ion currents were measured with aid of AD549LH electrometers as voltages on the high-ohm resistors of 0.2, 5 and 500 GΩ, with respective capacitors yielding a common time constant of 1.5 s. The obtained precision (1σ) on positive ion beams was better than 0.1‰ and 0.01‰ for δ^{36}S and δ^{34}S, respectively.



Results of test measurements are shown in the Table below. In both tests the measurement time (averaging of the ion currents) was 12 s, whereas in zero enrichment test additional break of 12 s was applied after each switch from sample to standard and vice versa to avoid any detectable cross contamination of the admitted gases. The length of this break was tested by analysis of a sample differing in δ^{34}S from the working standard by more than 20 permil. The details of the design of the innovative ion source, vacuum system and electronic controllers will be presented.

Test measurement	Mean δ^{34}S [‰]	Mean δ^{36}S [‰]	N
Standard vs. standard	-0.003 ± 0.008	-0.31 ± 0.10	20
Zero enrichment	-0.020 ± 0.007	0.16 ± 0.13	26

N is the number of subsequent integrations of the ion currents.

Keywords: sulfur isotopes, delta-34, delta-36, sulfur dioxide, S^+ ions.

Acknowledgments: *We thank most sincerely to Dr. Keith Hackley for the donation of an old mass spectrometer to UMCS, on the basis of which we were able to develop the new instrument. This study was supported by NCN project 2013/11/B/ST10/00250*.

References

Hałas S. (1979) An automatic inlet system with pneumatic changeover valves for isotope ratio mass spectrometer, *Journal of Physics E: Scientific Instruments* 12: 418-420.

Hałas S., Pieńkos T., Pelc A., Wójtowicz A. (2016) Patent descriprtions P.416375 and P.417560.

Halas S. and Wolacewicz W. (1981) Direct extraction of sulfur dioxide from sulfates for isotopic analysis, *Analytical Chemistry* 53: 686-689.

Ono S., Wing B., Johnston D., Farquhar J., Rumble D. (2006) Mass dependent fractionation of quadruple stable sulfur isotope system as anew tracer of sulfur biogeochemical cycles, *Geochimica et Cosmochimica Acta* 70: 2238-2252.

Robinson B. and Kusakabe M. (1975) Quantitative preparation of sulfur dioxide, for ^{34}S/^{32}S analysis, from sulfides by combustion with cuprous oxide. *Analytical Chemistry* 47:1179-1181

MICROAREA δ^{18}O ANALYSIS IN BIOAPATITES ON HIGH RESOLUTION ION MICROPROBE SHRIMP IIe/MC

Zbigniew Czupyt and Mateusz Rechowicz

Polish Geological Institute - National Research Institute, Warsaw, Poland
Corresponding author: *zbigniew.czupyt@pgi.gov.pl*

SHRIMP IIe/MC - Sensitive High Resolution Ion Microprobe is one of the Secondary Ion Mass Spectrometers family. Similar to other SIMS instruments, the SHRIMP bombards a sample under vacuum with a beam of primary ions that sputters secondary ions which are focused, filtered, and measured according to their energy and mass. The SHRIMP is the most productive geochemical instrument of its class. It is designed for continuous round-the-clock data acquisition in order to maximize scientific returns. The simple ion optics and robust design results in ease of operation and instrumental setup compared to other ion probes. It is a highly versatile workhorse for a wide range of geochemical and geochronological investigations.

Until now, SHRIMP IIe has been applied to a variety of geological and geochemical purposes including U-Th-Pb geochronology of uranium bearing minerals, but also stable isotopes analyses (eg carbon, sulphur and oxygen) in biogenic and inorganic materials; and to diagnosis isotope anomalies in meteorites and lunar soil. There are two main types of analysis which dominate current SHRIMP usage. These are uranium-lead geochronology, and isotope ratio determination. These analytical techniques can be used to solve a wide variety of geological, environmental, or technological problems.

One of the δ^{18}O isotope ratio determinations, are measurements in bioapatites like conodonts human and animal teeth (enamel). Organisms through their life absorb elemental and isotopic composition from surrounding environment. Also dental tissues, with high apatite share, keep an oxygen isotopic signal from period of enamel successive mineralization. Temperature dependent oxygen isotope fractionation between biogenic apatite and ingested water is influenced by specific physiology of an organism but also by climatic and geographical factors. It makes possible to use δ^{18}O values of tooth enamel as indicators of paleotemperature and ancient environmental proxy, applicable for bioarcheological research. However, one of the essential issues is the difficult choice between the preservation of dental remains and the use of destructive techniques. This problem can be solved by in situ analysis on ion microprobes. The technique that offers a high spatial resolution of microsampling with sensitive detection of isotopic ratios can effectively support the interpretation of δ^{18}O variability in the past. Ion microprobe is a good tool for low-destructive measurement of δ^{18}O oxygen isotopic ratios in thin incremental layers of tooth enamel with a spatial resolution of a few micrometers.

Keywords: geochronology, stable light isotopes, microprobe, mass spectrometry.

TIMS ION SOURCE FOR ALTERNATE ISOTOPE RATIO DETERMINATION OF TWO SAMPLES

Adrian Pacek, Stanisław Hałas, Tomasz Pieńkos

Mass Spectrometry Laboratory, Maria Curie-Skłodowska University, 20-031 Lublin, Poland
Corresponding author: *adrian.pacek@poczta.umcs.lublin.pl*

There are two essential difficulties in Thermal Ionization Mass Spectrometry (TIMS) analysis of isotope ratios: *mass discrimination effect* and *cross contamination*. The first one can be overcome by use of high-mass compounds as a loading form to ion source e.g. phosphate in case of lithium (Chan, 2004), but the second one remained unsolved by far.

We describe a new triple filament ion source for TIMS. Our ion source enables alternate lithium or potassium isotope analysis of two samples without any visible cross-contamination. Essentially it is an improved version of well-known triple filament ion source, thus it is equipped with two evaporation filaments (rhenium) and one ionization filament (platinum/iridium) installed in parallel between them in front of the extraction slit (Figure 1).

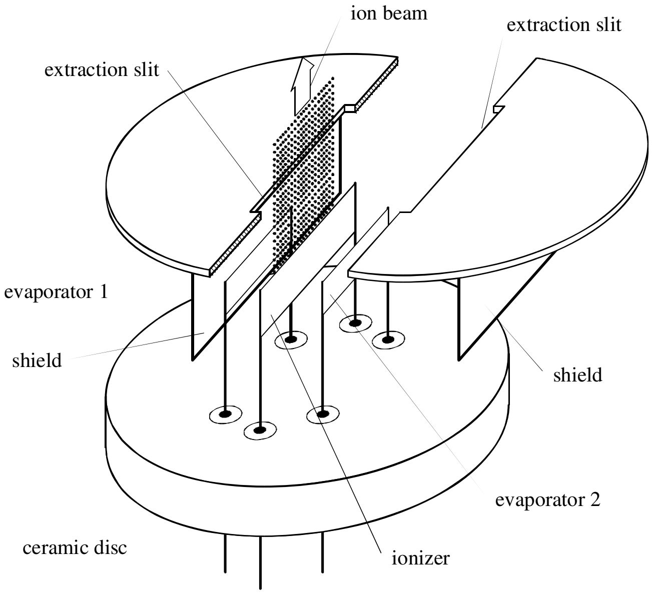


Figure 1. *Simplified schematic diagram of the triple filament ion source of TIMS. The right-half of extraction slit with shield is shifted to allow visibility of the filaments*

All the three filaments are connected to separate current stabilizers, which allow independent control of their temperatures. Due to high work function of platinum (5.65 eV) the ionization filament does not require very high temperatures to get stable ion currents. The most important original concept is to use the platinum filament in double role: as ionizer and a barrier preventing any *cross contamination* of isotopically different samples loaded on the two separate evaporators. The second role was fulfilled by its larger size in comparison to evaporators. Therefore, isotopically different samples can be measured one after another alternately without venting the mass spectrometer chamber.

The results of measurements for two potassium samples extremely di-fferent in isotope compo-sition are shown in the Table 1. Measurements were conducted alternately without venting spectrometer chamber. One is natural sample with isotope ratio $^{39}K/^{41}K$ of 13.59 and the second is ^{41}K spike with the isotope ratio of 0.0522. The analysis was conducted for over 100 minutes, nevertheless no *cross contamination* for at least over 5 hours of further alternate analysis has been noticed. Mass spectra of a natural sample and the ^{41}K spike are shown in Figure 2 and Figure 3, respectively.

Table 1. *The sequence of measured isotopic ratios of two extremely different potassium samples loaded on different evaporators*

		$R_{natural}$	R_{spike}			$R_{natural}$	R_{spike}
Minutes	***5***	13.57			***55***	13.60	
	10		0.0529		***60***		0.0521
	15	13.58			***65***	13.59	
	20		0.0522		***70***		0.0521
	25	13.51			***75***	13.61	
	30		0.0523		***80***	0.0522	
	35	13.56			***85***		13.59
	40		0.0522		***90***	0.0521	
	45	13.56			***95***		13.61
	50		0.0521		***100***	0.0523	

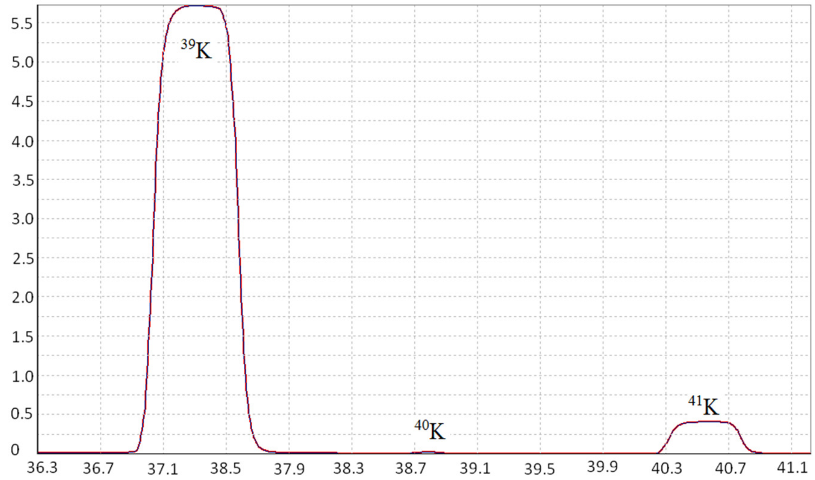


Figure 2. *Mass spectrum of K natural*

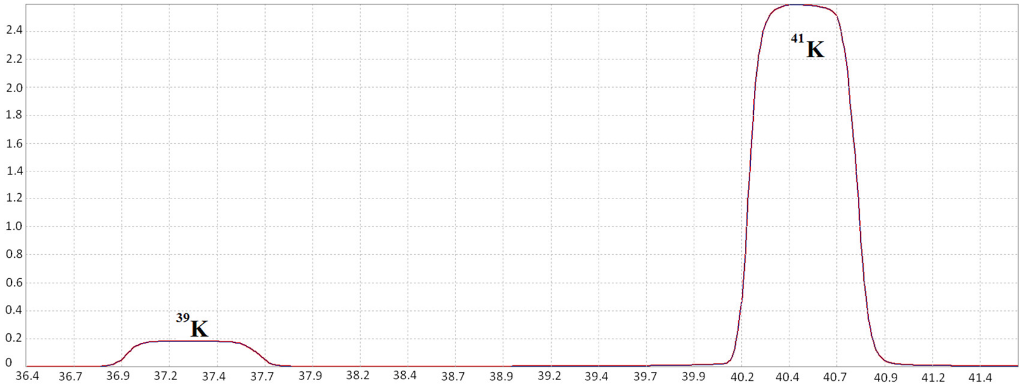


Figure 3. *Mass spectrum of* ^{41}*K spike*

Our new ion source allows measuring the isotope ratio of li-thium or potassium with accuracy of half per mil or better. A high sen-sitivity of such analysis is confirmed by the presence of the peak ^{40}K in potassium spectrum. Possibility of alternate sample-standard analysis may lead to detect the variability of potassium isotopic ratio in terres-trial samples, which has never been reported by far.

In the full presentation during the conference we will also present the schematic diagrams and photos of our ion source, numerical simulations of the ion beam forming in the ion source and some lithium isotope analysis in different water samples.

Keywords: TIMS, ion source, lithium, potassium, isotope ratio.

References

Chan L.-H. (2004) Chapter 6 in: de Groot P. A. (editor), *Handbook of Stable Isotope Analytical Techniques*, vol.1, *Elsevier*, Amsterdam.

Hałas S., Pacek A., Pieńkos T., Patent application W.125814 of 05.12.2016, Thermoemission ion source for a mass spectrometer.

PUSHING RESEARCH BOUNDARIES: BENEFITS OF TEMPERATURE RAMPED GAS CHROMATOGRAPHY IN EA-IRMS

Oliver Kracht, Christopher Brodie, Andreas Hilkert, Charles Douthitt

Thermo Fisher Scientific, Bremen, Germany
Corresponding author: *oliver.kracht@thermofisher.com*

The Thermo Scientific^{TM} EA IsoLink^{TM} IRMS System has fundamentally improved analysis by EA-IRMS using *temperature ramped gas chromatography* with a single GC column and a patented helium management system that reduces cost per analysis. These innovative features open doors to push research boundaries at new levels, especially for the analysis of very small concentrations and on very high C/N and C/S ratio samples.

This presentation will principally focus on the advantages of using *temperature ramped gas chromatography*. Traditionally, gas chromatography in EA-IRMS employed a GC column held at an isothermal temperature as the gases eluted. However, using *temperature ramped gas chromatography* in the EA IsoLink IRMS System, a feature common in GC-MS and GC-IRMS, the temperature of the GC column can be quickly changed as analyte gases are eluting, improving peak separation, peak fidelity, analysis of very small sample amounts and precision of replicate measurements. We will discuss these improvements in peak separation, background determi-nation, troubleshooting of the combustion, pyrolysis and chromatographic processes, blank determination and analysis of very small sample concentrations. Our improved GC technique is illustrated in Figure 1, which shows a chromatogram of a NCS analysis on wood (C/S ratio of 7900:1) from a single sample drop. Complete baseline separation of each analyte is achieved with sound background correction and peak fidelity, including for very large (7000 µg C) and very small (11 µg N and 1 µg S) analyte amounts. For 5 replicate measurements on wood, $\delta^{13}C = -24.10 \pm 0.06‰$; $\delta^{15}N = 3.20 \pm 0.23‰$ and $\delta^{34}S = 5.92 \pm 0.26‰$.

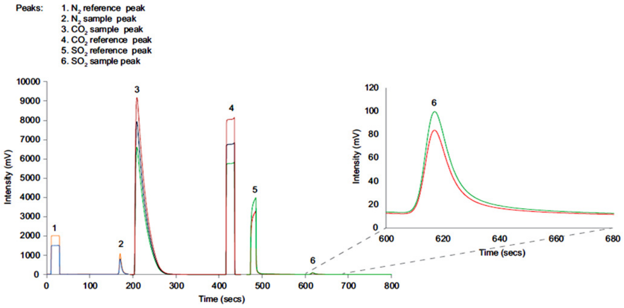


Figure 1. *Gas chromatography using a single GC column ensures analysis of samples with C/S ratios >7000: (e.g. wood) when analysing NCS from a single sample drop. Analysis time is less than 10 minutes using 1.4 liters of helium*

RoAMS - THE NEW AMS CENTER IN BUCHAREST

Tiberiu Bogdan Sava, Iuliana Stanciu, Corina Anca Simion, Gabriela Odilia Sava, Doru Pacesila, Bianca Stefan, Alexandru Vasiliu, Vasile Mosu, Ilie Maria

Horia Hulubei - National Institute for Physics and Nuclear Engineering,
30th Reactorului Str., Magurele Ilfov 077125, Romania
Corresponding author: *tiberiu.sava@nipne.ro*

We present an insight of the new RoAMS facility at the Horia Hulubei - National Institute for Physics and Nuclear Engineering, starting with its official foundation in 2013. The HVEE 1MV Tandetron was installed to perform multi-isotopic AMS analysis, especially to determine infinitesimal quantities from the 14C, 26Al, 10Be, 129I, 239,240,242Pu isotopic species. Simultaneously, the radiocarbon group started to set-up the sample preparation laboratory for various material types, relying mainly on a modern automated graphitization station, produced by Ionplus AG. We present the measurement results for the reference and standard materials, along with the results for the SIRI (Sixt International Radiocarbon Inter-Comparison) proficiency test samples. Also, some of the typical inherent problems specific to radiocarbon dating laboratories and their solutions are listed. There are also presented the ongoing and future projects regarding the AMS measurement of the actinide species for environmental studies and nuclear forensics purposes.

RADIONUCLIDES' IONIZING POTENTIAL - AN INDISPENSABLE COMPONENT OF ENERGY-EFFICIENT COLD PLASMA MICROBIOLOGICAL DECONTAMINATION

Elena Agarwal[1], Iurie Bosneaga[2]

[1] *University of Academy of Sciences, Chisinau, Republic of Moldova,*
[2] *Institute of Applied Physics of Academy of Sciences, Chisinau, Republic of Moldova*
Corresponding author: *iubosneaga@gmail.com*

Microbiological decontamination is a challenging problem for the "homo urbanus" civilization. Many factors indicate the evident exacerbation of this problem - continuous population growth combined with the increasing degree of its urbanization and mobility, intensification of the anthropogenic pressure upon the environment, amplified by periodical natural disasters and different scale technogenic catastrophes. Also eventual biological terrorism's threats should be taken into account.

Among many others - the problem of microbiological decontamination (sterilization) of the gigantic quantities of potable and waste water is a particularly pressing one - it ranks on the economic importance energy problem, and on the social importance - surpasses it. Because of the large volumes - the demand of energy efficiency for the process of decontamination becomes an imperative.

Nowadays microbiological sterilization represents a set of relatively expensive physical and chemical methods, with the domination of heat sterilization method. But virus-type small-size infections need another - special tough treatment. Relatively newly discovered heat-resistant *prions* (portmanteau of ***pr***otein infect***ion*** - "mad cow disease") put in difficulty microbiologists - because of the absence of efficient sterilization methods for this extremely stable infection.

We propose thermodynamic approach for sterilization problem solution optimization (Agarwal E., 2015). The main conclusion derived is that all the "physical" methods, which introduce high-potential - Gibbs' free energy ΔG - into the system under sterilization (thermal, high-pressure, US, UV, ionizing radiation etc.) do not ensure reliable (secured) sterilization. Most of the physical methods of sterilization provoke "endothermic" structural destructions (respectively, for them $\Delta G>0$), but there always remains a certain possibility of reparation, or even creation of new mutations - viable (virulent) forms. Gain of free energy from the environment is the main (obligatory) condition for maintaining of life, but is not generally relevant for sterilization. This idea is confirmed inclusively by high-level survival of dried microorganisms in conditions of long-time cosmic (orbital) irradiation.

We consider that the most efficient method for obtaining safe (sterile) medium is a chemical spontaneous exothermic irreversible reaction of oxidation, which leads to the destruction of organic matter. Here you have an example of such a reaction - sugar (glucose) oxidation. Release of low-potential energy *Q* (“dead” energy) makes this reaction irreversible (respectively, for it $\Delta G<0$):

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + Q \qquad (1)$$

So, the problem of energy-efficient reliable sterilization could be reduced to efficient oxidation.

Methods of ensuring energy-efficient oxidation of the medium under sterilization. Choosing the best oxidizing agent can be done using data from Table 1. The data presented show that fluorine is the most powerful oxidizer. Fluorine, however, is so active that any manipulations with it are extremely dangerous (with respect to fluorine, only diamond and some species of glassy carbon are stable). As well, large scale use of fluorine could induce new ecological problems. So, oxygen is the most indicated oxidizer. Oxygen is ecologically perfect, being the most abundant element on Earth and also the main component of tissues. (Unfortunately, in many cases, chlorine and its derivatives were chosen as the main sterilizing agents, and this is unhealthy - from many points of view).

We consider that cold (non-equilibrium) plasma chemical reaction of oxidation is the best energy-efficient method for irreversible sterilization, without any chance of eventual “adaptation” for microorganisms: being the shortest way of obtaining sterility, it transforms finally the organic compounds in gas phase.

Table 1. *Constants of atoms (molecules), characterizing oxidation and dissociation capacity [1998, 1977]*

Molecule type	**F_2**	**Cl_2**	**O_2**	**O_3**	**N_2**
Bond (dissoc.) mol. energy, *eV (kJ/mol)* &respec.rad.λ (λ_{max} dissociation limit)	1.61 (155.0) (λ_{max}= 772.0 nm) $F_2+h\nu\rightarrow F+F$	2.52 (242.6) (λ_{max}= 493.3 nm) $Cl_2+h\nu\rightarrow Cl+Cl$	5.12 (493.6) (λ_{max}= 242.4 nm) $O_2+h\nu\rightarrow O+O$	1.11 (107.0) (λ_{max}=1117.3 nm) $O_3+h\nu\rightarrow O_2+O$	9.81 (945.3) (λ_{max}= 126.6 nm) $N_2+h\nu\rightarrow N+N$
Electron affinity, *eV*	3.45 (for atom F)	3.61 (for atom Cl)	1.47 (for atom O) 0.44 (for mol. O_2)	2.26 (for mol. O_3)	-0.21 (for atom N)
Ionization energy (for atoms, molecules), *eV*	17.42 ($F+h\nu\rightarrow F^++e$) 15.70 ($F_2+h\nu\rightarrow F_2^++e$)	12.96 ($Cl+h\nu\rightarrow Cl^++e$) 11.48 ($Cl_2+h\nu\rightarrow Cl_2^++e$)	13.62 ($O+h\nu\rightarrow O^++e$) 12.08 ($O_2+h\nu\rightarrow O_2^++e$)	12.52 ($O_3+h\nu\rightarrow O_3^++e$)	14.53 ($N+h\nu\rightarrow N^++e$) 15.58 ($N_2+h\nu\rightarrow N_2^++e$)
Electronegativity, atoms(by L Pauling)	3.98	3.16	3.50	3.50	3.05
Covalent radius of atoms, *nm*	0.064	0.099	0.066	0.066	0.074

Most of the physical methods of sterilization are indicated to be used only as a supplement, together with the mandatory oxidation. Thus, molecular oxygen (eventually, electrically charged) should be an obligatory component of the plasma sterilizer.

Cold non-equilibrium plasma ensures maximal chemical activity and energy efficiency. Microwaves are one of the best methods of obtaining dense active cold plasma: the higher is the frequency and applied power, the higher is the grade of non-equilibrium and plasma density. Another cost-efficient possibility for cold plasma generation - is the use of radionuclides (coming from re-processing of the spent nuclear fuel), or even of the spent nuclear fuel itself. Microwaves could be present in the technology as a supplement to radionuclides - in the cases, when the density of the active cold plasma should be increased.

Additionally electro-hydrodynamic (EHD) pumps - based on radionuclides' ionization and dynamic potentials - could be used in the process of microbiological decontamination.

Keywords: microbiological decontamination (sterilization), non-thermal plasma, radio-nuclides.

References

Agarwal E., Bosneaga I., Bologa M. (2015) About the basic solutions for cold plasma decontamination. *Report for the VIIIth International Conference Plasma Physics And Plasma Technology (PPPT – 8)*, Minsk, Belarus, 14 - 18 September, 2015. Contributed Papers, V2, p.501 -504, ISBN 978-985-7137-19-0 (Vol 2).

Khimicheskaya entsiklopediya (1998) *Izdatel'stvo "Bol'shaya Rossiyskaya Entsiklopediya"*, Moskva (in Russian).

Rabinovich V.A., Khavin Z.Y.A. (1977) *Kratkiy khimicheskiy spravochnik*. Izdatel'stvo "Khimiya" (in Russian).

NEW DESALINATION PROCEDURE FOR THE ROUTINE DETERMINATION OF ^{18}OXYGEN AND ^{2}HYDROGEN ISOTOPIC COMPOSITION OF SALINE WATERS AND BRINES

Adam Porowski

Institute of Geological Sciences of Polish Academy of Sciences (INGPAN)
Twarda 51/55, 00-818 Warszawa, Poland
adamp@twarda.pan.pl

The routine techniques for determining the oxygen and hydrogen isotope ratios in water call for CO_2-H_2O equilibration and H_2O reduction on hot metal (i.e. Zn, Cr, U) respectively, and mass spectrometric analysis is then performed on the evolved gases of CO_2 and H_2. The precise determination of the isotopic composition of brines and various saline solutions with application of the routine techniques is still problematic and technically often impossible due to detrimental influence of dissolved salts.

The difficult and challenging problem of brines desalination and water extraction from salt solutions to determine of its O and H isotopic composition with application of routine methods in our approach comes down to the elimination of negative influence of chloride salts of alkaline earth metals – i.e. Mg and Ca. Magnesium and calcium chlorides are usually the main compounds of natural saline waters and brines in the Earth’s crust, they are highly soluble in water, highly hygroscopic, and form hydrous precipitates. The thermal dehydration of hydrates $MgCl_2(H_2O)_x$ does not occur straightforwardly, and practically is not possible with application of simple vacuum distillation (e.g. Florkowski, 1985; Horita and Gat, 1988; Horita, 1988; Porowski and Kowski, 2008).

The new desalination procedure combines the chemical precipitation of Mg^{2+} and Ca^{2+} ions in form of insoluble fluorides, and the vacuum extraction of water from non-hygroscopic precipitates. The method consists of two technical steps, namely: (*1*) chemical conversion and precipitation, and (*2*) distillation and extraction. The first step is based on the quantitative chemical conversion of chloride forms of Ca^{2+} and Mg^{2+} ions to fluoride forms. The conversion causes the transformation of highly soluble and highly hygroscopic chloride salts of Ca and Mg to practically insoluble and non-hygroscopic fluoride salts.

In the second step the simple vacuum distillation can be applied to extract the water from solution and precipitates without fractionation of water molecules. The vacuum distillation is the most time-consuming step in the whole procedure of water desalination. However, its application after chemical transformation of Mg and Ca chloride salts into fluorides, allows recovering all the water from solution-precipitate mixture without oxygen and hydrogen isotope fractionation in reasonable temperature range (up to about 300 - 350°C in our experiments).

The precision and accuracy obtained in the determination of $\delta^{18}O$ and $\delta^{2}H$ of water extracted from artificial Mg and Ca solutions (up to 3 – 4 M) as well as natural brines (including Dead Sea water) is comparable with that usually obtained for fresh waters.

Keywords: brines, desalination, saline waters.

Acknowledgments: *This research was supported by National Science Center (NCN), Grant No 4610/B/T02/2009/36. I thank the authorities of the INGPAN for organizational support of the research. I would also like to express my gratitude to: dr Elena Kayukova, Institute of Earth Sciences, Saint Petersburg State University, for help in collecting brines from evaporitic lakes; dr Elena Dubynina, Moscow State University, for providing a fresh sample of the Dead Sea water.*

References

Florkowski T. (1985) Sample preparation for hydrogen isotope analysis by mass spectrometry, *International Journal of Applied Radiation and Isotopes* 36:991-992.

Horita J., Gat J.R. (1988) Procedure for the hydrogen isotope analysis of water from concentrated brines, *Chemical Geology (Isotope Geoscience Section)* 72:85-88.

Horita J. (1988) Hydrogen isotope analyses of natural waters using an H_2-water equilibration method: a special implication to brines, *Chemical Geology (Isotope Geoscience Section)* 72:89-94.

Porowski A., Kowski P. (2008) Determination of $\delta^{18}O$ and $\delta^{2}H$ in saline oil-associated waters. The question of vacuum distillation of water samples prior to isotopic analysis, *Isotopes in Environment and Health Studies* 44:225-236.

ICP-MS/MS: A NEW TOOL FOR ISOTOPIC ANALYSIS

Lecornet Gregory, **Lener Jean-Pierre**

Agilent Technologies France S.A.S. 3 avenue du Canada, Z.A. Courtaboeuf, 91970 Les Ulis, France
Corresponding author: *Gregory.lecornet@agilent.com*

As is widely known, ICP-MS is not only able to provide elemental, but also isotopic information. These isotope ratio measurements can even be affected by spectral interference to a larger extent, as for this type of analysis at least two isotopes of the same element need to be measured interference-free. In 2012, the introduction of a new type of quadrupole-based ICP-MS device (ICP-tandem mass spectrometer) has improved the control over the cell chemistry and has brought the concept of chemical resolution as a means to avoid spectral overlap to a higher level. The use of ICP-MS/MS for both the determination of natural variations in isotopic composition and for isotope dilution mass spectrometry (IDMS) have been reported on in literature (Eduardo Bolea-Fernandez, Lieve Balcaen, 2017; Ian *et al*., 2016; K. Johan Hogmalm, Thomas Zack, 2016).

We will show the capability of this new instrument for geochronology (Rb–Sr system) and for the analysis of medium to long-lived nuclides (e.g. Ni-59, Sr-90, Tc-99 I-129, Cs-135,…) in decommissioning materials (concrete, soil, sediment, metal etc.).

Keywords: ICP-MS, Tandem mass spectrometry.

References

Bolea-Fernandez E., Balcaen L. (2017) Overcoming spectral overlap via inductively coupled plasma-tandem mass spectrometry (ICP-MS/MS). A tutorial review *Journal of Analytical Atomic Spectrometry* 34: 250-257.

Croudace I. W., Russell B.C. (2016) Plasma source mass spectrometry for radioactive waste characterisation in support of nuclear decommissioning: a review, *Journal of Analytical Atomic Spectrometry* 32, 494-526.

Hogmalm K. J., Zack T. (2016) In situ Rb–Sr and K–Ca dating by LA-ICP-MS/MS: an evaluation of N_2O and SF6 as reaction gases, *Journal of Analytical Atomic Spectrometry* 32, 305-313

HYDROGEN STABLE ISOTOPES DETECTION WITH CARBON NANOTUBE BASED SENSOR

Eusebiu Ilarian Ionete[1], **Stefan Ionut Spiridon**[1], **Bogdan Florian Monea**[1],
Daniela Ebrasu-Ion[1], **Oana Romina Botoran**[1], **George Stoian**[2], **Ashok Vaseashta**[3]

[1]*National Research and Development Institute for Cryogenics and Isotopic Technologies – ICSI Rm. Valcea, 4 Uzinei Street, Rm. Valcea, Romania*
[2] *National Institute of Research and Development for Technical Physics Iasi, Iasi, Romania*
[3]*Institute for Advanced Sciences Convergence & Int'l Clean Water Institute, Manassas, VA, USA, and Molecular Science Research Center, Orangeburg, SC, USA*
Corresponding author: *eusebiu.ionete@icsi.ro*

Stable hydrogen isotopes detection, fast and accurate, at an entire pallet of different concentrations is an important desire of technological designers. In the case of semi-industrial or industrial facilities who process hydrogen or are implicated in the process of protium/deuterium/tritium separation (e.g heavy water detritiation plants) the fast distinction between them is an absolute necessary tool for human operator's safety.

The presented sensor platform approach is based on deposition of a hydrogen high affinity metal, namely palladium (Pd), on purified and functionalized single wall carbon nanotubes (SWCNTs) known for their good electronic, chemical-stability and sensitivity characteristics.

The obtained devices where tested for different concentrations of protium and deuterium mixtures in air from low concentration up to the explosion limit, of 4%.

Using Principal Component Analysis multivariate method applied to different adsorption/desorption characteristic we determined a clear separation between Protium and Deuterium with an increasing trend in the case of Deuterium.

Hydrogen gas, as well its alternative forms (e.g. deuterium, protium or tritium), is widely used in many applications and industrial facilities. Gas sensors capable to operate in confined space or inaccessible areas, at room temperature and with low power consumption (Dhall, Jaggi, and Nathawat, 2013) is one of the most desired goals of many researchers in this field. Deuterium detection, especially at tritium removal facilities (TRF), monitoring/ controlling of any leaks is of essential importance for the operating staff.

Carbon nanotubes (CNTs) with their extraordinary properties, such as high surface area over its geometrical dimensions and mechanical strength present themselves as a serious contender for gas sensors, with a very high sensitivity and low response time (Kumar, A.L.M. Reddy, S. Ramaprabhu, 2008). By using SWCNTs functionalized with Palladium (Pd) for H/D detection, we tried to take advantage of the Pd high affinity to hydrogen and the high specific area of SWCNTs.

Materials and Methods - SWCNTs where cleaned, functionalized and prepared for deposition of palladium, before being drop casted onto a support over gold interdigitized electrodes (IDEs). FTIR spectroscopy was employed in order to investigate the nature of surface groups attached to CNTs after functionalization process. The investigation was performed using a Frontier FT-NIR spectrometer having a diamond ATR accessory in domain of 650-4000 cm^{-1}.

The technique employed for palladium deposition is based on the simple reaction of chemical reduction (Toebes, van Dillen, and de Jong, 2001). The morphological analysis of the drop-casted SWCNTs deposited on the sensor substrate was performed using scanning electron microscopy (SEM) and the results are presented in Figure 1.

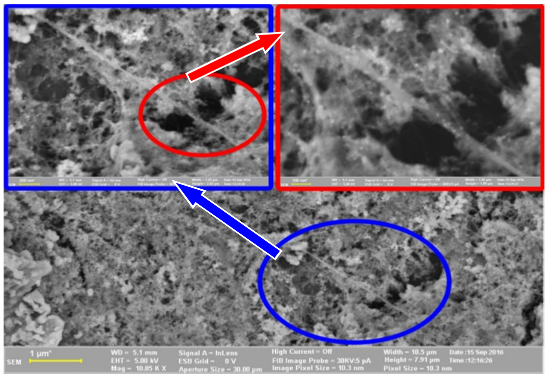


Figure 1. *SEM image of Sensor with a network of Pd functionalized SWCNTs*

Results - The sensors responses after exposure to Protium and Deuterium in different concentrations, ranging from 0.1 up to 4% were measured employing a customized system, also capable to provide the gases for investigation and for the regeneration process. The tests for H/D detection were carried out in air atmosphere with different H/D levels. Figure 2 shows the results of tests for hydrogen and deuterium gas sensing, respectively.

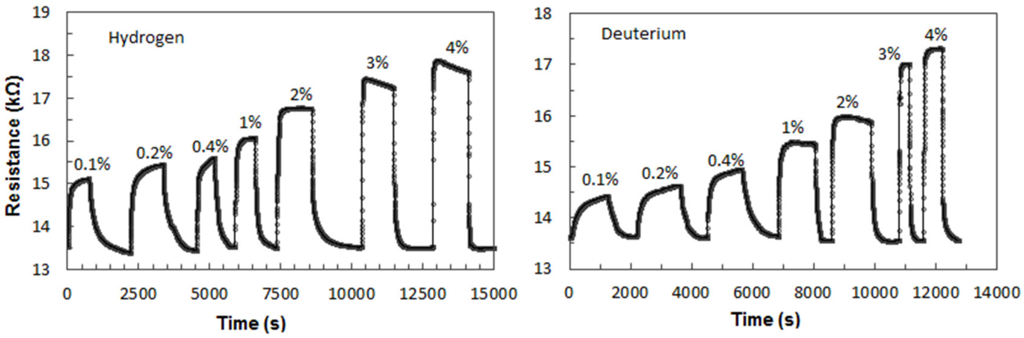


Figure 2. *Variation of sensor resistance for different hydrogen and deuterium concentrations of 0.1%, 0.2%, 0.4%, 1%, 2%, 3% and 4%.*

A principal component analysis (PCA) method was applied to our measurements. In this study, our system is realized from 14 observations (7 different hydrogen concentrations and 7 different deuterium concentrations) and 14 variables representing the angle tangent at the law of resistance variation (Figure 3) or extended version with 919 variables representing the recorded resistance per second for each individual concentration (Figure 4).

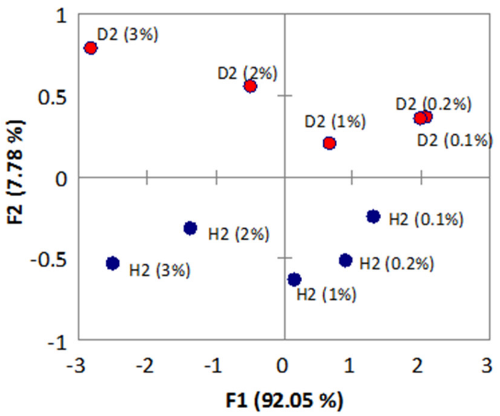


Figure 3. *Principal component analysis map determined for the first two principal components, PC1 and PC2*

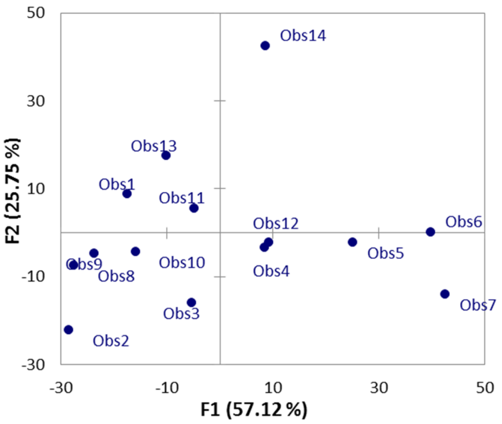


Figure 4. *Principal component analysis map determined for 919 variables*

Conclusion - We have developed a new sensor, based on Pd/SWCNTs sensible substrate, specific for hydrogen isotopes, Protium and Deuterium detection and differentiation.

The Pd/SWCNTs compound showed very good sensibility toward H/D gas, with a strong affinity toward protium giving us the opportunity to declare that a sensor capable to differentiate between the two isotopes, protium and deuterium, can be created using our method and technology. It can also be used as a potential hydrogen detection tool.

Keywords: hydrogen isotopes; sensor; carbon nanotubes (CNTs); sensing mechanisms

References

Dhall S., Jaggi N., Nathawat R. (2013) Functionalized multiwalled carbon nanotubes based hydrogen gas sensor, *Sensor and Actuators A- Physics* 201: 321-327.

Kumar M. K., Reddy A. L. M., Ramaprabhu S. (2008) Exfoliated single-walled carbon nanotube-based hydrogen sensor, *Sensor and Actuators B-Chemistry* 130:653-660.

Toebes M. L., van Dillen J. A., de Jong K. P. (2001) Synthesis of supported palladium catalysts, Journal of Molecular Catalysis A: Chemical *173(1):*75-98.

ESTIMATION OF THE PURIFICATION TECHNIQUES OF THE SAMPLES FROM THE WINES FOR TRITIUM ANALYSIS USING LIQUID SCINTILLATION COUNTING

Irina Vagner, Carmen Varlam, Ionut Faurescu, Denisa Faurescu, Diana Bogdan, Diana Costinel, Violeta Niculescu

National Research and Development Institute for Cryogenics and Isotopic Technologies – ICSI Rm. Valcea, 4 Uzinei Street, Rm. Valcea, Romania
Corresponding author: *irina.vagner@icsi.ro*

In this paper we estimated, using deuterium measurements, tritium measurements and content of organic carbon, the influence of the purification technique over the aqueous samples resulted from wine distillation, in order to determine tritium concentration from wines, as free water or tissue free water. Tritium measurement from aqueous fraction of the wines of known vintage can be a useful tool in reconstruction of the tritium activity in certain areas (Takahashi *et. al*., 1969; Kozak and Biro, 1984; Krajcar-Bronic *et. al*., 1998), which together with C-14 activity makes possible to date the time of the harvest of the wine (Schonhofer, 1997). Also the evaluation of the aqueous component of the wine or other alcoholic beverages (Kimura *et. al*., 1998; LLNL, 2016; Baglan *et. al*., 2015) represents an important part in the process of dose calculation and can provide information about the presence and movement of tritium release to the environment. It was shown (Roether, 1967) that tritium content in wine samples is not determined exclusively by water taken up by the roots, but is also influenced to a large extent by direct exchange with atmospheric moisture.

The methods applied in this study are described in the following. First step of wine samples treatment was the separation of the aqueous fractions using fractionate distillation. The aqueous fractions obtained were purified, in order to perform tritium analysis using liquid scintillation counting according to ISO 9698: 2010, using four techniques: chemical treatment and distillation, chemical treatment and lyophilisation, treatment using clinoptilolite zeolitic tuf (material usually used as adsorbent in water purification) followed by lyophilisation and lyophilisation without any other prior treatment.

Estimation of the purification techniques applied was done by determining the organic carbon content in each purified sample, from which we concluded that aqueous fractions purified using chemical treatment and distillation as well as the ones purified using chemical treatment and lyophilisation had the lowest content in organic carbon, showing an advanced removal of the organic compounds from the samples.

Isotopic ratio $^2H/^1H$ from the purified aqueous samples was determined, using the CF-IRMS technique, in order to establish the isotopic fractionation that might appear during purification process. Lyophilisation without any other treatment is the method used for purification of aqueous fractions from wine prior to $^2H/^1H$ isotopic ratio analysis. Comparing with the above mentioned method, the lyophilisation with chemical treatment had the closest results for $^2H/^1H$ isotopic ratio, the sample purified with the other two methods recording massive isotopic fractionation, the highest fractionation being recorded for samples treated with clinoptilolitic tuff.

In conclusion the most reliable purification method used for wine aqueous fractions, according with the results obtained for organic carbon content and $^2H/^1H$ isotopic ratio is chemical treatment followed by lyophilisation.

Keywords: tritium measurement, liquid scintillation counting, aqueous component of wines.

Acknowledgments: *This paper was prepared in connection with the work done for Experimental Cryogenic Pilot for Tritium and Deuterium Separation and under the national project PN 16360401: ,,Assessing the impact of different ecosystems on stable isotopes and multi-element composition of plants – researches on geo-seasonal variability"*

References

Baglan N., Kim S.B., Cossonnet C., Croudace I.W., Fournier M., Galeriu D., Warwick P.E., Momoshima N., Ansoborlo E. (2015) Organically Bound Tritium analysis in Environmental Samples, *Fusion Science and Technology* 67 (2), 250-253.

Kimura S., Miyamura T., Maeda S., Iwamoto A. (1998) Development of a Method for Tritium Measurement in Ethylalcohol and Application to Individual Component of Sake, *Japanese Journal of Toxicology and Environmental Health* 44 (6), 428-441.

Kozák K., Biró T. (1984) Reconstruction of environmental tritium levels from wine analysis. *Health Physics* 46(1), 193-203.

Krajcar-Bronic I., Horvatincic N., Obelic B. (1998) Two Decades of Environmental Isotope Records in Croatia: Reconstruction of the Past and Prediction of Future Levels, *Radiocarbon* 40 (1), 399-416.

International Standard Organization - ISO 9698: 2010. Water Quality – Determination of Tritium Activity Concentration – Liquid Scintillation Counting Method, 2nd Ed.

Lawrence Livermore National Laboratory – LLNL, 2016. UCRL-TR-50027-15 - Environmental Report 2015, available to *https://saer.llnl.gov.*

Roether W. (1967) Estimating the tritiu input to groundwater from wine samples: groundwater and direct run-off contribution to central European surface waters" in *IAEA Proceedings Series "Isotopes in Hydrology",* Symposium held in Vienna, 14-18 November 1966, STI/PUB/141, 73-91.

Schönhofer F. (1997) Low-Level Measurements with Liquid Scintillation Spectrometry Development and Application in "*Methods and Applications of Low-Level Radioactivity Measurements, PROCEEDINGS OF WORKSHQP ROSSENDORF/ DRESDEN, 7-8 NOVEMBER 1996*", Editor: J. Fietz.

Takahashi T., Nishida M., Ohno S., Hamada T. (1969) Tritium Concentration in Wine, Rain and Ground Water, *Radioisotopes* 18 (12), 560-563.

INFLUENCE OF WOOD DECAY ON THE ISOTOPIC COMPOSITION OF TREE RINGS

Viorica Nagavciuc[1,2,3], **Zoltán Kern**[2], **Aurel Perşoiu**[3, 4], **Ionel Popa**[5]

[1] *Faculty of Forestry, Ştefan cel Mare University, Suceava, Romania*
[2] *Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences MTA, Budapest, Hungary*
[3] *Stable Isotope Laboratory, Ştefan cel Mare University, Suceava, Romania*
[4] *Emil Racoviţă Institute of Speleology, Cluj Napoca, Romania*
[5] *National Research and development Institute for Silviculture Marin Dracea, Câmpulung Moldovenesc, Romania*
Corresponding author: *nagavciuc.viorica@gmail.com*

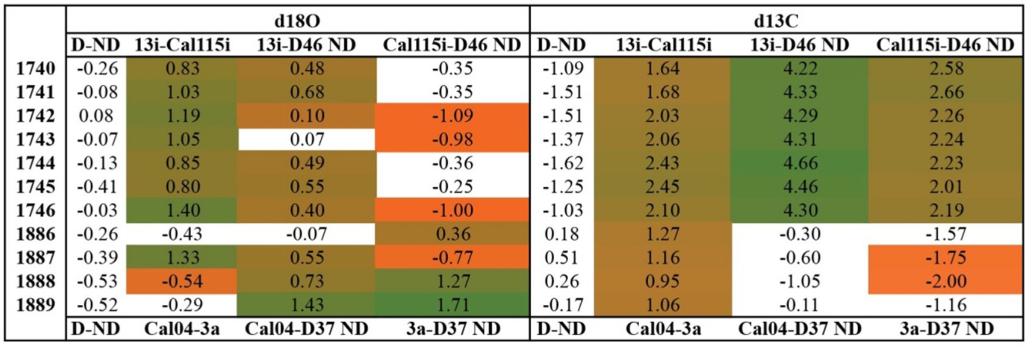
Stable isotopic composition of tree rings is a high-resolution proxy indicator of past climatic changes, as a result of precise dating, annual resolution, and strong relationship with climate. However, in order to create long chronologies (thousands of years), analysis of both living and dead trees is required. Sub-fossil trees can be recovered from bogs, river gravel or from natural ecosystems with a very low rate of decomposition, thus preserving the timber in good conditions for many years (McCarroll and Loader, 2004). However, uncertainties appear in the stable isotopic composition of the wood, as decaying process can affect the stable isotopic composition of the wood or its different constituents. However the knowledge in this respect (Kłusek and Pawełczyk, 2014; Savard *et al.*, 2012) is very limited.

The aim of this study is to determine the potential of decayed wood as palaeoclimatic indicator by analysing the isotopic composition of decayed and non-decayed wood retrieved from the same tree, in Swiss stone pine (*Pinus cembra*) from the Eastern Carpathian Mountains, Romania.

For this study, we have selected two sub-fossil Swiss pine stone trees, with both decayed and non-decayed wood for the same year (samples D46 and D37, with the analyzed rings corresponding to AD 1740-1746, and AD1886-1889, respectively), and compared the results of the isotopic analyses with those from other four trees with non-decayed wood, only (samples 13i, Cal115i, Cal04, 3a).

The intra-ring (Figure 1) variability measured on both decayed and non-decayed wood ranges between 0.08 ‰ and -0.41 ‰ for $\delta^{18}O$ and between -1.03 ‰ and -1.62 for $\delta^{13}C$, while the inter-tree (Figure 1) variability ranges from -1.09 ‰ to 2.26 for $\delta^{18}O$, and from -2 ‰ to 4.66 ‰ for $\delta^{13}C$.

The $\delta^{18}O$ intra-tree variability is only marginally larger than the analytical precision, but somewhat higher for the $\delta^{13}C$ variability. The intra-tree variability is less than that reported in the literature (0.5-1.5 ‰, (Leavitt, 2010; Li *et al.*, 2015) for $\delta^{18}O$; however, for $\delta^{13}C$ it is larger than the reported values (0.7-1.2 ‰, (Leavitt, 2010; Leavitt and Lone, 1991; Leavitt and Long, 1986). The differences in $\delta^{13}C$ (up to 1.5 ‰) imply the possible alteration of the original isotopic signal due to wood decay.



	d18O				d13C			
	D-ND	13i-Cal115i	13i-D46 ND	Cal115i-D46 ND	D-ND	13i-Cal115i	13i-D46 ND	Cal115i-D46 ND
1740	-0.26	0.83	0.48	-0.35	-1.09	1.64	4.22	2.58
1741	-0.08	1.03	0.68	-0.35	-1.51	1.68	4.33	2.66
1742	0.08	1.19	0.10	-1.09	-1.51	2.03	4.29	2.26
1743	-0.07	1.05	0.07	-0.98	-1.37	2.06	4.31	2.24
1744	-0.13	0.85	0.49	-0.36	-1.62	2.43	4.66	2.23
1745	-0.41	0.80	0.55	-0.25	-1.25	2.45	4.46	2.01
1746	-0.03	1.40	0.40	-1.00	-1.03	2.10	4.30	2.19
1886	-0.26	-0.43	-0.07	0.36	0.18	1.27	-0.30	-1.57
1887	-0.39	1.33	0.55	-0.77	0.51	1.16	-0.60	-1.75
1888	-0.53	-0.54	0.73	1.27	0.26	0.95	-1.05	-2.00
1889	-0.52	-0.29	1.43	1.71	-0.17	1.06	-0.11	-1.16
	D-ND	Cal04-3a	Cal04-D37 ND	3a-D37 ND	D-ND	Cal04-3a	Cal04-D37 ND	3a-D37 ND

Figure 1. *Intra- and inter-tree variability of δ^{18}O and δ^{13}C, calculated as the differences between the measured isotopic values in decayed and nondecayed. The D-ND columns show the inter-tree differences, measured between decayed (D) and non-decayed (ND) wood on tress D46 and D37. The inter-tree variability was calculated on non-decayed wood, only. The color shading varies from maximum (dark green) to minimum (orange) variability. White cells indicate samples with lower variability than that found between the decayed and non-decayed samples.*

The inter-tree differences for δ^{18}O are between the reported (1-2 ‰) values of (Leavitt and Wright, 2002; Treydte *et al*., 2006; Wright and Leavitt, 2006), but are larger for δ^{13}C; (Leavitt, 2010) and (Porté and Loustau, 2001) reporting differences in the 1-3 ‰ range. However, the inter-tree differences are larger than the intra-tree ones, thus suggesting that oxygen and carbon isotopic compostion changes during wood-decay processes are affecting the original isotopic signal to a degree that should not impart the usefulness of stable isotopes in tree rings in palaeoclimatic research.

The small differences of inter-ring and inter-tree variations of δ^{18}O and an exceeding moderate value of δ^{13}C, suggest what the stable isotopic compositions represent a good indicator proxy for paleoclimatic reconstructions, with the recommendation to avoid the decayed wood when it is possible.

Keywords: tree rings, δ^{13}C, δ^{18}O, decayed wood.

Acknowledgments: *LP2012-27/2012, CLIMFOR 18SEE, PN-II-RU-TE-2014-4-1993*

References

Kłusek M. and Pawełczyk S. (2014) Stable Carbon Isotope Analysis of Subfossil Wood, *Geochronometria* 41(4):400-408, doi:10.2478/s13386-013-0168-8.

Leavitt S.W. (2010) Tree-ring C–H–O isotope variability and sampling, *Science of the Total Environment* 408(22):5244-5253, doi:http://dx.doi.org/10.1016/j.scitotenv.2010.07.057.

Leavitt S.W. and Lone A. (1991) Seasonal stable-carbon isotope variability in tree rings: possible paleo-environmental signals, *Chemical Geology: Isotope Geoscience Section* 87(1):59-70, doi:10.1016/0168-9622(91)90033-S.

Leavitt S.W. and Long A. (1986) Stable-carbon isotope variability in tree foliage and wood, *Ecology* 67(4):1002-1010, doi:10.2307/1939823.

Leavitt S.W. and Wright W.E. (2002) Spatial expression of ENSO, drought, and summer monsoon in seasonal $\delta^{13}C$ of ponderosa pine tree rings in southern Arizona and New Mexico, *Journal of Geophysical Research: Atmospheres* 107(18):1-10, doi:10.1029/2001JD001312.

Li Z., Nakatsuka T. and Sano M. (2015) Tree-ring cellulose $\delta^{18}O$ variability in pine and oak and its potential to reconstruct precipitation and relative humidity in central Japan, *Geochemical Journal* 49(2):125-137, doi:10.2343/geochemj.2.0336.

McCarroll D. and Loader N.J. (2004) Stable isotopes in tree rings, *Quaternary Science Reviews* 23(7-8):771-801, doi:http://dx.doi.org/10.1016/j.quascirev.2003.06.017.

Porté A. and Loustau D. (2001) Seasonal and interannual variations in carbon isotope discrimination in a maritime pine (Pinus pinaster) stand assessed from the isotopic composition of cellulose in annual rings., T*ree Physiology* 21: 861-868.

Savard M.M., Bégin C., Marion J., Arseneault D. and Bégin Y. (2012) Evaluating the integrity of C and O isotopes in sub-fossil wood from boreal lakes, *Palaeogeography, Palaeoclimatology, Palaeoecology* 348–349:21–31, doi:10.1016/j.palaeo.2012.06.003.

Treydte K.S., Schleser G.H., Helle G., Frank D.C., Winiger M., Haug G.H., Esper J. (2006) The twentieth century was the wettest period in northern Pakistan over the past millennium., *Nature* 440(7088):1179-1182.

Wright W.E. and Leavitt S.W. (2006) Boundary layer humidity reconstruction for a semiarid location from tree ring cellulose $\delta^{18}O$, *Journal of Geophysical Research: Atmospheres* 111(18):1-9, doi:10.1029/2005JD006806.

NANOMATERIALS AND CONVERGING TECHNOLOGIES: SCENARIO IN RISK ASSESSMENT, SAFETY AND SECURITY BY DESIGN

Ashok Vaseashta[1,3], **Antonietta Gatti**[2], **Marina Turcan**[3],
Nicolae Enaki[3], **Eusebiu Ilarian Ionete**[4]

[1]*Institute for Advanced Sciences Convergence & Int'l Clean Water Institute, Manassas, VA, USA, and Molecular Science Research Center, Orangeburg, SC, USA*
[2]*Istituto per lo Sviluppo e la Tecnologia dei Materiali Ceramici- Consiglio Nazionale delle Rìcerche, c/o Nanodiagnostics, Via E. Fermi 1/L, 41057 San Vito (Modena), Italy,*
[3]*Institute of Applied Physics, Academy of Sciences of Moldova, Academiei str. 5, MD 2028*
[4]*National Research and Development Institute for Cryogenics and Isotopic Technologies – ICSI Rm. Valcea, 4 Uzinei Str., 240050 Rm. Valcea, Valcea, Romania*
Corresponding author: *prof.vaseashta@ieee.org*

From a technology standpoint, nanomaterials offer significant advantages due to their unique characteristics resulting from reduced dimensionality. Furthermore, advances in material synthesis have provided the means to control or even manipulate the transitional characteristics. Consequently, various "designer" materials with desired properties have recently been fabricated. Dual-use nature of technology coupled with the ability to functionalize with a plethora of biological configurations pose a significant safety and security concerns. Furthermore, a life cycle analysis of nanomaterials is largely unknown; and nanomaterials resulting from the laboratories, manufacture, and even incidental events pose serious concerns. Too little is known about the release of nanosized by-products from nanomaterials-waste after incineration at the end of their life-cycle. As an example, aquatic contamination occurs for multiple reasons ranging from taking the water sources for granted, negligence in waste disposal, deliberate contamination, and technological innovations outpacing development of effective guidelines for life-cycle management and regulations to properly recycle/reuse/disposal of commercial nano-products.

Notwithstanding such concerns, the beneficial uses of nanomaterials offer a challenging scenario for policy-makers, researchers, and industrialists alike to propose and implement viable alternatives for sustainable development in terms of keeping up with the latest technological innovations, social responsibility, and "being green". With so much at stake, it is prudent to challenge conventional wisdom and investigate a new set of strategies that employ nexus of technological innovations, in conjunction with "acceptable" risk assessment and a strategic transformation in "use, reuse, and recycle" as effective management tools to address "design safety, security, and sustainability". "Safety and Security by design" employ strategic transformations towards ensuring that humans and a safe environment can simultaneously exist on the Earth. We have investigated life-cycle-

assessment based on the characterization, assessment, and management of risk to assess impacts on human and environmental health from a safety and security standpoint. We present strategic solutions to a life-cycle-based approach to nanomaterials and potential toxicity of nanosized particles using model of the sea urchin Paracentrotuslividus, Zebra Fish and their offspring. Passage through membranous barriers via the digestive tract to the coelomic fluid is the subject of ongoing study using biomarkers, such as coelomic fluid inside coelomocytes (uptake), cholinesterase activity, and using expression of stress-related proteins (HSP70) and Gonads morphological features. Aquatic (nano)ecotoxicity is arguably the least understood and requires systematic investigation. Ongoing research aims to detect, counter, and mitigate potential security threats and is at the core of our current and ongoing investigations, hence we further present a strategic thrust to identify, assess, and recommend revolutionary strategic solution pathways using field-ready technologies, sensor platforms, and foresight tools, already developed by the authors, to offer possible solutions pathways.

Keywords: safety, security, sustainability, nanomaterials, decision support, neural networks

References

Vaseashta A. (2014) Advanced sciences convergence based methods for surveillance of emerging trends in science, technology, and intelligence, *Foresight* 16(1):17-36.

Vaseashta A. (2015) Life Cycle Analysis of Nanoparticles – Risk, Assessment, and Sustainability, *DEStech Publications, Inc.*, ISBN: 978-1-60595-023-5

Vaseashta A. (2012) The Potential Utility of Advanced Sciences Convergence: Analytical Methods to Depict, Assess, and Forecast Trends in Neuroscience and Neurotechnological Developments and Uses; Ashok Vaseashta. In *Neurotechnology: Premises, Potential, and Problems*, edtd. J. Giodano, CRC Press.

THE EXODUS OF HARAPPANS FROM RAJASTHAN AND GUJARAT, INDIA: REVISITING A PLAUSIBLE REASON

Ashish Sarkar

School of Petroleum Technology, Pandit Deendayal Petroleum University,
Gandhinagar, Gujarat, India
ashish29s@yahoo.co.in

Human race is always inquisitive about its lineage, beginning and rise of the civilisation. And hence the quest for history of human civilization is being continuously chased. One of the well understood oldest yet mature civilizations is the Indus valley civilisation, which spans between 2300 and 1750 B.C. (based on uncalibrated ages; Bridget and Allchin, 2003). As there are various uncertainties about ^{14}C dating (Agarwal, 1982), calibration of these dates are required to convert them to calendar years to normalise all the available global data.

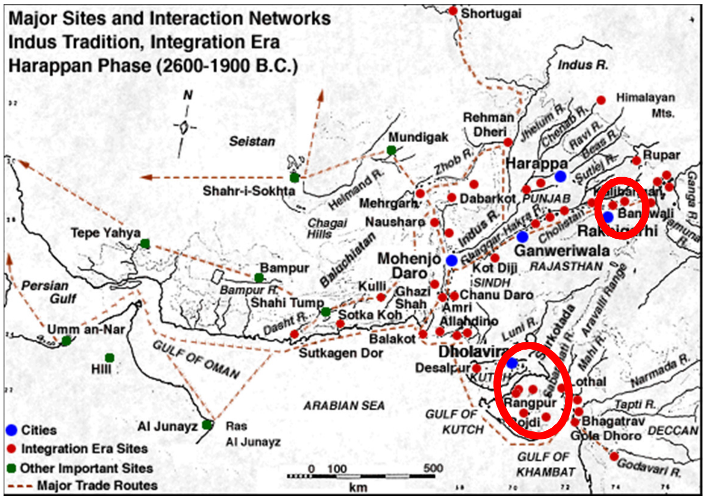


Figure 1. *Harappan Sites (Source: https://www.harappa.com/har/ancient-indus-sites.html); Areas under discussion in the present work have been encircled in red.*

In the present work the ^{14}C dates available from the artifacts retrieved from various Harappan sites in the western Indian states of Rajasthan and Gujarat (Figure 1) viz. Kalibangan (29.4701°N, 74.1328°E), Lothal (22.5227°N, 72.2488°E), Rojdi (22.2587°N, 71.1924°E), and Surkotada (23.635173°N, 70.841339°E) have been calibrated to calendar years based on Stuiver *et al*. (2017). Nearly all the calendar ages are within a range of about 5000 and 4400 calendar years BP, which goes well with the Harappan culture.

A perpetual question about the disappearance/end of the Harappan cultures, why suddenly the people living in these locations evacuated their establishments? Among the many causes for such exodus from these neatly designed human establishments nearly at the same time, climate change is attributed towards the major cause. At present the region under question in the States of Rajasthan and Gujarat witness a semiarid climate and receives less than or close to 300 mm annual rainfall. Juyal *et al*. (2003, 2006) have noted that the southern extension of Thar desert reached close to the Orsang Basin (22°5' N, 73°35' E) during the Last Glacial Maxima and then started retreating/shrinking northward. These areas still have been in the arid conditions during nearly 5 ka BP, which is also evident from huge and well designed water harvesting systems in all these Harappan establishments.

Sarkar *et al*. (2000), from a marine core in eastern Arabian Sea, based on normalized $\delta^{18}O$ in *Globigerinoides sacculifer*, a planktonic foraminiferal species, demonstrated that though from 10 ka BP till 2 ka BP the Indian monsoon shows an increasing trend, it had intermittent decrease in monsoonal activity in the Indian subcontinent. It has been noted that at about 5.7 ka BP, the monsoon had been the weakest during the whole Holocene. Since then the monsoon showed enhancement continuously till 4.7 ka BP. Since then the monsoon began decreasing, which probably compelled the inhabitants in those establishments to leave their loved homes.

Keywords: Harappan, exodus, planktonic foraminifera, monsoon, radiocarbon dating.

Acknowledgements: *Dr. Navin Juyal of Physical Research Laboratory, Ahmedabad, India for useful discussions; Dr. Ravi Bhushan of Physical Research Laboratory, Ahmedabad, India for helping to calibrate the radiocarbon ages to calendar years.*

References

Agarwal D.P. (1982) The archaeology of India. Scandinavian Institute of Asian Studies *Monograph Series* No. 446. Curzon Press. 268-269.

Allchin B. and Allchin F.R. (1996, Reprint 2003) The rise of civilization in India and Pakistan. Cambridge University Press.

Juyal N., Chamyal L.S., Bhandari S., Bhushan R., Singhvi A.K. (2006) Continental record of the southwest monsoon during the last 130 ka: evidence from the southern margin of the Thar Desert, India. *Quaternary Science Reviews* 25:2632-2650.

Juyal N., Kar A., Rajaguru S.N., Singhvi A.K. (2003) Luminescence chronology of aeolian deposition during the Late Quaternary on the southern margin of Thar Desert, India. *Quaternary International* 104:87-98.

Sarkar A., Ramesh R., Somayajulu B.L.K., Agnihotri R., Jull A.J.T., Burr G.S. (2000) High resolution paleomonsoon record from the Eastern Arabian Sea. *Earth and Planetary Science Letters* 173(3-4):209-218.

Stuiver M., Reimer P.J., Reimer R.W. (2017) CALIB 7.1 [WWW program] at http://calib.org, accessed 2017-3-15.

RADIOCARBON DATING OF PUTINEIU AND PERETU ORGANIC SEDIMENTS AS A PRE-SCREENING TOOL IN PALINOLOGY; LIMES TRANSALUTANUS CASE STUDY

**Corina Anca Simion[1], Constantin Haită[2], Tiberiu Bogdan Sava[1],
Iuliana Mădălina Stanciu[1], Odilia Gabriela Sava[1], Oana Gaza[1], Doru Păceşilă[1],
Bianca Maria Ştefan[1], Eugen S. Teodor[2]**

[1]Horia Hulubei National Institute for Research and Development in Physics and Nuclear Engineering – IFIN-HH Bucharest-Măgurele, Romania
[2]National History Museum of Romania, Bucharest, Romania
Corresponding author: anke@nipne.ro

The project named "Interdisciplinary technology for archaeological field survey. Case Study on Limes Transalutanus south of Argeş River" concerns the *limes* sector located between Argeş River and Danube (155 km). The Roman frontier has functioned there in the first half of the third century AD. Some features of the military facilities – as the presence/absence of the boundary palisade – put problems difficult to understand. We tried to explain the uneven design through some properties of the environment – today broadly changed. In order to test our hypothesis, we needed some core drillings for palynology, which also provided datable samples.

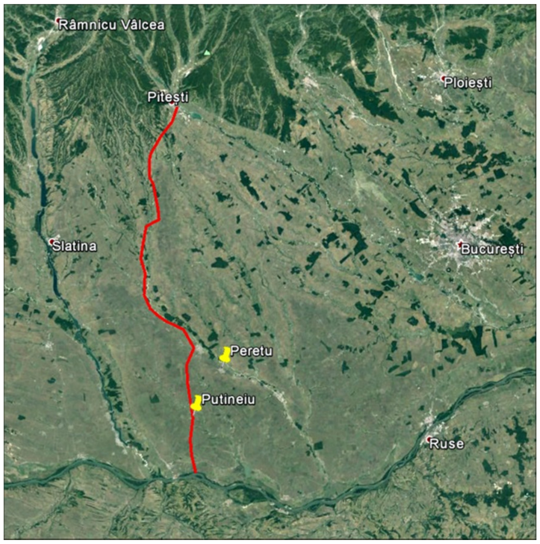


Figure 1. *Sample sites of Putineiu and Peretu, image from Google Earth®. Red line for the Roman frontier (south of Argeş River).*

The case study began with two ponds/marshy areas, at Putineiu and Peretu (see Figure 1 above and Table 1 below). Radiocarbon dating of bulk samples is useful for suggesting a relative date for each layer of soil and sediments, as established by sedimentology. Estimating the age of humic fractions or other significant materials gives us directions in understanding the history of alluvial activity, unexpected events in the past, structure of vegetation, and presence of forested areas in the proximity of the Roman frontier.

Table 1. *Sample characterization of Putineiu and Peretu marshy areas.*

No.	Coring/ Sampling point	Sampling depth (cm)	Material	Remarks	Conventional radiocarbon age (BP) and error, bulk sediments	Conventional radiocarbon age (BP) and error, fractions
1	C1/ Putineiu I	86	Organic sediment	Fine silt	1788(35)	4861 (101) – HA1 4823 (44) – HA2 2601 (59) – HA2 bis 4463 (30) – pure HM 3325 (42) – HM on solid phase
2	C1/ Putineiu I	140-144	Organic sediment	Fine silt	2942(37)	4976 (58) – HA1 4638 (38) – HA2 6799 (197) – HA2 – bis 6163 (44) – pure HM 4611 (119) – HM on solid phase
3	C1/ Putineiu I	216-220	Organic sediment	Fine silt	4613(41)	4478 (113) – HA2 – bis 6451 (38) – pure HM
4	C2/ Putineiu II	218	Organic sediment with wood fragments	Fine silt	3874(40)	1845 (37) – humic fractions 1227 (21) – HM on solid phase
5	C5/ Peretu	85	Organic sediment	Fine silt	169(32)	-2067 (18) – Non Hydrolyzable Phase of Humic Acids (NHPHA) -6 (26) – wood remains
6	C5/ Peretu	265	Fine fragments of shells	Fine silt	42722(755)	21066 (209) – HM on solid phase

Bulk sediments were directly dated using AMS method at RoAMS Laboratory, IFIN-HH. The initial calibration curves helped us to choose the most promising cores as a source of pollen or to identify the layers formed by natural deposition which, probably one of them corresponds to historical period of interest. Sequential separation of humic acids, humine, hydolyzable and non hydrolyzable humic acids fractions, organic low temperature and inorganic high temperature components, together with shells fragments, modern and old wood fragments were dated as fractions of bulk sediments. The differences between initial estimation of the age and the real situation are in Table 1.

Concluding remarks - Dating bulk samples isn't reliable on alluvial sediments, therefore one needs separation, and check if the individual dates of humic fractions (humic acids and humine) are close enough each other; this is the case for sample 1, which is a sediment formed in Roman Age and bulk dating gives us a reliable age. If a larger gap occurs between these dates, it could be due to a refreshment of the layer with organic compounds leaked from upper strata (and possibly bringing pollen); this would be the case for sample 2. When samples are collected from sediments still older, different fractions would have net different chronology, and humic acids are lacking (also pollen), as for the sample 3. Although the sample 4 is taken in the same area and at the same depth as the sample 3, and it has a higher organic content than the previous sample, the results on humic fractions highlight that the soil is immature, reshuffled, and will be also useless for palynology. Dating fractions and other materials separated from samples 5 and 6 offer a much disturbing situation; sample 5 is characterized by massive organic remains, especially vegetal debris, but associated with unknown place of formation and decomposition scenario, elsewhere, upstream on the riverside, and can't be associated with the Roman Period. Completely other case is the sample 6; we have isolated two different sediments, both containing fragmented shells, with very different determined age, dealing with a reshuffle or a reservoir effect, or both. In this case one needs mass spectrometry for delta C-13, in order to highlight the reservoir effect. The last sample is more like a blind test for the others (verifying the age of the layer in the absence of organic compounds), also useless for palynology.

Keywords: radiocarbon dating, humic fractions, palinology, Limes Transalutanus

Acknowledgments: *This work was partially supported by the core program of IFIN-HH with ANCSI Bucharest under contract PN 16 42 03 02 and UEFISCDI Project PN-II-PT-PCCA-2013-4-0759.*

RADIOCARBON DATING OF SINGLE AMINO ACIDS ISOLATED BY HPLC METHOD FROM ARCHAEOLOGICAL BONE SAMPLES

Oana Gaza[1,2], Catalin Stelian Tuta[1], Tiberiu Bogdan Sava[1], Dan Gabriel Ghita[1], Corina Anca Simion[1], Iuliana Madalina Stanciu[1,2], Doru Gheorghe Pacesila[1], Vasile Mosu[1]

[1] *Horia Hulubei National Institute for Research and Development in Physics and Nuclear Engineering – IFIN-HH Bucharest-Măgurele, Romania*
[2] *Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest Romania*
Corresponding author: *oana.gaza@nipne.ro*

Bone consists of approximately 75-80% hydroxyapatite and the rest of 20% is organic material. Approximately 85-90% of the organic component is type I collagen. Archaeological bones are usually dated by radiocarbon measurement of extracted collagen.

The standard procedure for measuring an organic sample using AMS technique consists in extracting and graphitization of the collagen, following a very complex sequence of chemical transformations from bone to graphite. The two main stages of the preparation are pretreatment stage, in which the organic material is extracted from the bone and the graphitization stage, in which the extracted material is transformed to graphite that is inserted in a matrix of iron powder through a reduction process of the CO_2 obtained from the combustion of the organic sample. The whole process is done using a fully automated graphitization unit developed by Swiss Federal Institute of Technology, Zürich, Switzerland.

However, low collagen content, preservation, can be significantly influenced by the burial environment. Under these conditions, the bone collagen can be chemically and/or physically degraded over 90%, and consequently the number of bone samples suitable for AMS radiocarbon dating can be considerably reduced. Because of that, we are trying to improve the classical pretreatment methods by using a High Pressure Liquid Chromatography (HPLC) system for the separation and identification of individual fractions of amino acids from raw collagen.

Dating amino acids from bone collagen can reduce the measurement error and the degree of contamination, leading to more accurate results.

Keywords: collagen, amino acids, HPLC, AMS, radiocarbon dating.

APPLICATIONS OF STABLE ISOTOPES AS INDICATORS IN FOOD QUALITY AND AUTHENTICITY STUDIES

Roxana Elena Ionete, Oana Romina Botoran, Raluca Popescu, Diana Costinel

National Research and Development Institute for Cryogenics and Isotopic Technologies –
ICSI Rm. Vâlcea, 4 Uzinei Str., 240050, Râmnicu Vâlcea, Romania
Corresponding author: *roxana.ionete@icsi*

The quality (e.g. taste, texture, flavor, etc.) of many foodstuffs is owed to the specific conditions encountered in the cultivation area. Moreover, people are tempted to confer food consumption an aura of romance and tradition, mainly for certain products like wine, oil or honey, and this because local characteristics of climate and soil combine to produce crops with certain specific features. In food retail business also frauds may appear, such as dilution of the product with water to increase the volume, additions of flavours without declaring it on the label, addition of other raw materials, non-compliance with the recipe, especially for traditional products, etc. Thus, many consumers demand for a guarantee of the product in terms of naturalness and authenticity.

As any organic matrix, food consists of chemical compounds which contain the main bio-elements hydrogen (H), carbon (C), nitrogen (N), oxygen (O) and sulphur (S), occurring as mixtures of stable isotopes. Their isotope ratios depend on those of local primary compounds, geological and climatic conditions and on anthropogenic influences at the site of the substances´ formation (e.g. irrigation, fertilization, pollution). As the individual elemental isotope ratios react differently on these influences, they provide more or less independent but complementary information regarding the origin.

Table 1. *Overview of fractionation processes in the environment relevant for food authenticity (Kelly, Heaton and Hoogewerff, 2005; Laursen et al., 2016)*

Isotope ratio	Fractionation processes	Information
$^{2}H/^{1}H$	Evaporation, condensation, precipitation, transpiration	Geographical, water addition, fertilization rate
$^{13}C/^{12}C$	CO_2 asimilation, stomatal conductance	Geographical, botanical origin (C3 and C4 plants), fertilization rate
$^{15}N/^{14}N$	N transformation processes, atmospheric loss	Agricultural practice -fertilizer type and rate
$^{18}O/^{16}O$	Evaporation, condensation, precipitation, transpiration	Geographical, water addition, fertilization rate
$^{34}S/^{32}S$	S transformation processes	Geographical (marine), fertilizer type
$^{87}Sr/^{86}Sr$	Age of the rock and Rb/Sr ratio - radiogenic decay of ^{87}Rb	Geographical, geology

Applications of stable isotopes as markers for food quality and authenticity is based on the fact that several processes and reactions (e.g. biological, biochemical, physical, chemical) cause isotope fractionation, generating thus a unique isotopic signature. The most widely used analytical techniques for measuring this isotopic fingerprint are the isotope ratio mass spectrometry (IRMS) and nuclear magnetic resonance (NMR). Useful information on the geographical origin, organic production of food or the flavours natural origin can be achieved by combining isotope ratio analysis ($^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{2}H/^{1}H$, $^{15}N/^{14}N$, $^{34}S/^{32}S$) of food products with the elemental profiling and analysis of $^{87}Sr/^{86}Sr$ by inductively coupled plasma mass spectrometry (ICP-MS) or compound specific analysis by GC-IRMS or HPLC-IRMS and site-specific natural isotope fractionation nuclear magnetic resonance (SNIF-NMR).

Stable isotope analysis is used to detect the geographical origin of raw materials by linking the stable isotope pattern of products with those of the natural environments from which they derivate.

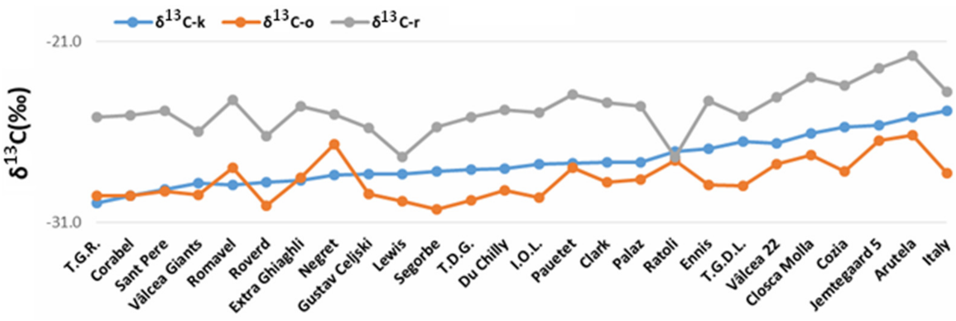
For example, a reliable tool to differentiate some Romanian wines by their production district was proved to be the combined isotopic - elemental fingerprinting (Dinca *et al.*, 2016). Discriminant analysis, using as independent values C and O stable isotope ratios and minerals, allowed to classify approximately 90.37 % of the investigated wines and additionally, to verify the influence of the vintage year. It was highlighted that $\delta^{18}O$ had the strongest relationship with the climatic conditions and location.

In case of honey has been demonstrated that the combination of isotopic ratios ($^{13}C/^{12}C$ of honey and $^{13}C/^{12}C$ and $^{15}N/^{14}N$ from the protein fraction extracted from honey) with multivariate analysis, can be a reliable tool to differentiate the floral origin of honey. Also, SNIF-NMR as complementary technique to IRMS may provide useful information for honey samples differentiation, since the $(D/H)_I$ values in the ethanol obtained by fermenting honeys is specific to a given botanical and geographical origin (Dinca *et al.*, 2015).

Also, stable isotope analysis represents a potential tool for assessing the food agricultural origin (organic versus conventional), since the studies showed that $\delta^{15}N$ could be a good indicator for revealing the fertilization history of a plant (Laursen *et al.*, 2016), but for a reliable authentication of agricultural origin of plants, a multi-isotopic analysis (H, C, N, O, S) is recommended.

Summarizing the information given by stable isotopes in food authentication studies, we can state as a general rule that (*i*) hydrogen and oxygen isotope data in food products are linked to those of waters from the specific geographical origin, (*ii*) carbon is related with the climatic conditions, plants photosynthesis pathways (C3- or C4- plant species) and water use efficiency of crops, (*iii*) nitrogen is linked with the agricultural practices (organic or conventional – use of fertilizers), (*iv*) sulphur is correlated with the geology (volcanic activity) and distance from the sea, while (*v*) strontium is related to geology. An important issue in food authentication using stable isotopes is the existence of reference databases of genuine samples, in a statistically sufficient number and representative for the assessment to be considered (e.g. geographical area, frauds detection, or agricultural practices), to which “unknown origin samples” to be compared.

Starting from these considerations, some preliminary data of an ongoing research on characterization and differentiation of hazelnut (*Corylus avellana* L.) cultivars using NMR, C/H/N analysis and $\delta^{13}C$-IRMS are presented. Thus, 26 hazelnut cultivars (native and foreign) grown in Valcea county (Romania) were used in this investigation. Oil was extracted from kernels and afterwards the fatty acids composition and IV (iodine value) was measured by NMR, while the elemental composition (C/H/N) and $\delta^{13}C$ of the kernel, extracted oil and residue was determined.



Chemometrics was applied to the data in order to identify similarities and differences between the cultivars. A very well separation of hazelnuts according their cultivars geographical origin, the most important parameters for the discrimination being the C% and H% of the oil and N% of the kernel and oil. For this discriminant analysis, the $\delta^{13}C$ of the kernel, oil and residue correlated well, indicating an influence of the geographical origin on the $\delta^{13}C$ fingerprint of the hazelnut. Similar to other published data, the oil had a depleted carbon-13 composition compared to that of the kernel (mean of -1‰); in consequence, the residue had an enriched carbon-13 composition (mean of +4‰).

Keywords: food authenticity, geographical origin, stable isotopes

References:

Dinca O.R., Ionete R.E., Popescu R., Costinel D., Radu G.L. (2015) Geographical and botanical origin discrimination of Romanian honey using complex stable isotope data and chemometrics, *Food analytical methods* 8(2):401-412.

Dinca O.R., Ionete R.E., Costinel D., Geana I.E., Popescu R., Stefanescu I., Radu G.L. (2016) Regional and Vintage Discrimination of Romanian Wines Based on Elemental and Isotopic Fingerprinting, Food Analytical Methods 9(8): 2406-2417.

Kelly S., Heaton K., & Hoogewerff J. (2005). Tracing the geographical origin of food: The application of multi-element and multi-isotope analysis. *Trends in Food Science & Technology*, *16*(12), 555-567.

Laursen K.H., Bontempo L., Camin F., Rosmann A. (2016) *Advances in isotopic analysis for food authenticity testing*, in Downey G. (Ed.). (2016). Advances in food authenticity testing. Woodhead Publishing.

CHEMOMETRIC DISCRIMINATION OF TRANSYLVANIAN VEGETABLES BASED ON THEIR ISOTOPIC AND ELEMENTAL FINGERPRINT

Dana Alina Magdas, Ioana Coralia Feher, Adriana Dehelean, Gabriela Cristea, Cezara Voica, Stelian Radu, Romulus Puscas

National Institute for Research and Development for Isotopic and Molecular Technologies,
Mass spectrometry, Chromatography and Applied Physics Department
Corresponding author: *alina.magdas@itim-cj.ro*

Authenticity represents an important food quality criterion and for this reason, reliable testing methods are widely requested by food producers, processors, consumers and authorities. The significant increase of consumer demand for organic food products had determined the development of combined analytical methods to discriminate different regimes of vegetables producing (organically versus conventionally growing conditions and also, greenhouse grown vegetables from those produced in the field). The prices differences among various categories has created a financial enticement to mislabel and try to pass off for instance, cheaper conventional products as organic.

This work presents the isotopic composition and elemental profile of more than 100 vegetables samples grown in different agricultural regimes in Transylvanian farms. The sample set was tested from stable isotopes ratios ($^{2}H/^{1}H$, $^{18}O/^{16}O$, $^{13}C/^{12}C$ and $^{15}N/^{14}N$) and multielemental content point of view. The used techniques for this study were: Isotope Ratio Mass Spectrometry (IRMS) for isotope measurements whereas, for elemental profile Coupled Plasma Mass Spectrometry (ICP-MS). The best markers association for the differentiation of organic from and conventional vegetables, as well as for geographical origin discrimination were made by applying chemometric techniques first ANOVA and then, for a more clearly identification, LDA.

Our main objectives were the identification of the best markers combination that are able to classify vegetable samples according to growing conditions organic vs. conventional and also greenhouse vs. field.

Keywords: Vegetables, stable isotopes, elemental profile, agricultural practices.

Acknowledgments*: The financial support for this work was provided by the Executive Agency for Higher Education, Research, Development and Innovation (UEFISCDI), in the frame of HUMAN RESOURCES Program, Contract no: 159/01.10.2015.*

APPLICATION OF CHEMOMETRIC TOOLS FOR THE DETERMINATION OF AUTHENTICATION APRICOT BRANDIES IN SERBIA

Maja M. Lojović[1], Biljana V. Marošanović[1], Aleksandra P. Bauer[1], Strahinja Z. Kovačević[2], Sanja O. Podunavac-Kuzmanović[2], Lidija R. Jevrić[2]

[1]*SP Laboratorija A. D., Industrijska 3, Becej, Serbia*
[2]*Faculty of Technology, University of Novi Sad, Novi Sad, Serbia*
Corresponding author: *Biljana.Marosanovic@victoriagroup.rs*

Mass production and intensive marketing leads to many food products losing their authenticity, uniqueness and characteristic of the region from which they come.

Apricot brandy is national, Serbian, alcoholic beverage with a great tradition, and by the quantity and quality of produced brandy Serbia occupies a leading position in the world and as such it becomes the subject of forgery. Counterfeiting is related to increasing ethanol content by adding sugar from sugar beet (C3 plant) or sugar cane and corn (C4 plant).

In order to successfully detect counterfeits in the production of fruit brandies we use the method of determining the stable isotopes of carbon ($\delta^{13}C$), hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) by Elemental Analyzer (FlashEA 1112 HT) - Isotope Ratio Mass Spectrometry (ThermoFinnigan DELTA V Advantage).

In order to monitor changes in the relationship of stable isotopes $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$ formed the base of data based on the value of laboratory control samples apricot brandy, without sugar and with the addition of 3%, 5%, 10% and 20% sugar from sugar beet.

To detect forgeries, SP Laboratorija analyzes commercially available alcoholic beverages, brandy produced in our laboratories of different varieties of apricot and different geographical origin (South and North Serbia), as well as alcohol derived from corn and sugar cane.

Application of chemometrics, established a correlation between the concen-tration of sugar values (derived from sugar beet) and $\delta^{2}H$ values. The value of percentage of added sugar was transformed in the negative logarithm of the molality (-log B) of added sugar to obtain a linear relationship between the variables. By applying this equation, it is possible to calculate the amount of added sugar in the unknown sample. Combined results of $\delta^{2}H$ and $\delta^{13}C$ values gives important information about botanical origin of ethanol and possibility of distinguishing between fruit spirits and spirits with non-fruit origin (made from beet sugar, corn, cane sugar).

Keywords: Authenticity, apricot brandy; isotopic analysis; chemometrics.

Reference

Podunavac-Kuzmanović S.O., Jevrić L.R., Kovačević S.Z., Marošanović B.V., Lojović M.M. (2015) Chemometric approach to determination of the authenticity of different types of Serbian and Macedonian brandy. *Glasnik hemičara, tehnologa i ekologa Republike Srpske* 11:11-16.

IDENTIFICATION AND CHARACTERIZATION OF SOME SEED EXTRACTS BY USING ISOTOPIC DILUTION-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Ramona Bleiziffer[1], Sonia Suvar[1], Paula Podea[1], Andreea Maria Iordache[2], Ramona Zgavarogea[2], Cornelia Mesaros[3], Monica Culea[1]

[1]*"Babes-Bolyai" University, 1M Kogalniceanu St, Cluj-Napoca, Romania*
[2]*National Research and Development Institute for Cryogenics and Isotopic Technologies – ICSI Rm. Valcea, 4 Uzinei Str., 240050, Rm. Valcea, Romania*
[3]*University of Medicine and Pharmaceutics, 38 Gh. Marinescu st, Târgu Mureş, Romania*
Corresponding author: *culea_monica@yahoo.com*

The phytochemicals from fruis and vegetables have health benefits to lower the risk for the development of health problems. Their contribution is of interest for protection against cardiovascular diseases, cancer, diabetes, obesity, constipation. The aim of this study was to compare the content of amino acids and metals and the antioxidant activity of different seeds used as food supplements. Isotopic dilution - gas chromatography coupled with mass spectrometry (ID-GC-MS) was applied for quantitative determination of free amino acids of some seed extracts (e.g. linseed, poppy, grape, hemp, nuts, pumpkin, sesame, watermelon, chia, etc). ^{15}N-Glycine (99 atom % ^{15}N) was added as internal standard and matrix calculation or regression curves were used in the quantitative work. Method validation, using amino acid standards following the extraction and derivatization procedure (n = 3), gave precision lower than 20% (R.S.D.) and L.O.D. value 1ng. Good linearity results for amino acids were found, the regression coefficient beeing over 0.99 for the majority of analyzed amino acids.

A DSQ Thermo Finnigan quadrupole mass spectrometer coupled with a Trace GC was used. Also elements (metals and minerals) content was determined by inductively coupled plasma quadrupole mass spectrometry (ICP-Q-MS), a Varian ICP-MS 820 instrument. The antioxidant attributes of the seed's extracts were evaluated using DPPH (1,1-diphenyl-2-picrylhydrazyl) free radical scavenging antioxidant assays. The study characterized the variation of the free amino acids and essential amino acids within the different samples associated with their essential and toxic elements content and antioxidant capacity. The amino acids, minerals and metals content and antioxidant properties proved their nutritional quality to be used as food supplements.

Keywords: Antioxidant, ICP-Q-MS, Metals, Seed extracts.

References

Culea M., Iordache A.M., Horj E., Mesaros C., Bleiziffer R. (2016) GC-MS Methods for Amino Acids Determination in Different Biological Extracts, *Studia UBB Chemia* 61:213-222.

ISOTOPIC AND ELEMENTAL ANALYSIS – A TOOL TO DIFFERENTIATE BETWEEN GREENHOUSE AND FIELD VEGETABLES COMMERCIALIZED ON ROMANIAN MARKET

Gabriela Cristea, Dana Alina Magdas, Cezara Voica, Ioana Feher, Romulus Puscas

National Institute for Research and Development of Isotopic and Molecular Technologies,
67-103 Donat, 400293 Cluj-Napoca, Romania
Corresponding author: *gabriela.cristea@itim-cj.ro*

In this study more than 100 vegetable samples from the Romanian market were investigated in order to: *i*) distinguish isotopic and elemental fingerprint of vegetable grown in greenhouses compared to those grown on field (radish – *Raphanus sativus*, and broccoli – *Brassica oleracea*), and *ii*) differentiate, by mean of stable isotopic ($\delta^{13}C$, $\delta^{18}O$ and $\delta^{2}H$) and elemental point of view, the agriculture type (organic versus conventional) that was used for their production (vegetable marrow – *Cucurbita pepo*). The measurements of $\delta^{13}C$ from vegetable samples were carried out on an Elemental Analyser (Flash EA1112 HT, Thermo Scientific), coupled with an isotope ratio mass-spectrometer IRMS (Delta V Advantage, Thermo Scientific). For $\delta^{18}O$ and $\delta^{2}H$ analysis, the equipment was a Liquid-Water Isotope Analyzer (DLT-100, Los Gatos Research). An Inductively Plasma Mass Spectrometer (ICP-MS, Perkin-Elmer Elan DRC-e) was used for the concentration content measurements of elements. The correlations between isotopic and elemental determinations were made by using the linear discriminate analysis. $\delta^{13}C$ values ranged between - 31.8 ‰ and - 27.4 ‰ for radish samples, and between - 28.1 ‰ and - 23.5 ‰ for vegetable marrow. The isotopic composition of $\delta^{2}H$ varied from -90 ‰ to -7.0 ‰, function of sample geographical origin.

Keywords: isotope ratio mass spectrometry, inductively coupled plasma - mass spectrometry, vegetable, greenhouse, linear discriminate analysis.

Acknowledgments: *The financial support for this work was provided by the Executive Agency for Higher Education, R & D and Innovation, UEFISCDI, PN-II-RU-TE, contract no. 159/2015.*

COMPARISON OF AMINO ACIDS AND ANTIOXIDANT CAPACITY OF SOME HERB EXTRACTS

Andreea Maria Iordache[1], Ramona Bleiziffer[2], Sonia Suvar[2], Paula Podea[2], Cornelia Mesaros[3], Monica Culea[2]

[1]National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI Rm. Valcea, 4 Uzinei Str , 240050, Romania
[2]"Babes-Bolyai" University, M. Kogalniceanu Str, Cluj-Napoca, Romania
[3]University of Medicine and Pharmaceutics, 38 Gh. Marinescu str, 540000 Târgu Mures, Romania
Corresponding author: *iordache_andreeamaria@yahoo.com*

Herbs and spices contain relatively high amounts of phytochemicals with health benefits beyond basic nutrition related to lower the risk for the development of health problems as cardiovascular diseases, cancer, diabetes, obesity, constipation. The aim of this study was to compare the amino acids and antioxidant capacity of different herb extracts. Isotopic Dilution-Gas Chromatography - Mass Spectrometry (ID-CG-MS) have been applied for the characterization of 15 plant extracts from Botanical Garden of University of Medicine and Pharmacy Tg. Mureş (e.g. Elderberry, Celery, Caraway, Basil, Comfrey, Howthorn, Lemon Verbenon, Celandine, Thyme, Artemisia, Mint, Curry, Sage, Rosemary, Nettle, etc). The GC-MS method was developed for the determination of free amino acids from the different herb extracts. The samples were dried and crushed and extracted in 6% trichloroacetic acid and then purified on an ion-exchange solid phase. Quantitation of amino acids was performed by adding ^{15}N-glycine 99 atom % as internal standard. Amino acids were derivatized as trifluoroacetic butyl esters, separated on a nonpolar capillary chromatographic column and analysed using a quadrupole mass spectrometer. The method was repeatable for most of the amino acids (coefficient of variation was in the order of 20%), and good accuracy and limits of detection were obtained. A DSQ Thermo Finnigan quadrupole mass spectrometer coupled with a Trace GC was used for the analytical investigation. The antioxidant attributes of the herb extracts were evaluated using DPPH (1,1-diphenyl-2-picrylhydrazyl) free radical scavenging antioxidant assays. The study characterized the variation of the free amino acids and essential amino acids within the different samples associated with their essential amino acids and antioxidant capacity. Essential amino acids varied from 0.05 mg/g (Basil) to 1.35 mg/g (Nettle). The amino acids and antioxidant properties proved their nutritional quality to be used as food supplements.

Keywords: Amino acids, Antioxidant capacity, Herb extracts, ID-CG-MS.

References

Hodisan T., Culea M., Cimpoiu M.C., Cot A. (1998) Separation, identification and quantitative determination of free amino acids from plant extracts, *Journal of Pharmaceutical and Biomedical Analysis* 18:319-323.

Culea M., Scrob S., Suvar S., Podea P., Has I., Muste S. (2015) Determination of Amino Acids in Corn Seed by Gas Chromatography–Mass Spectrometry, *Analytical Letters* 48(1):37-46.

ASSESSMENT OF DEUTERIUM IN PLANTS GROWN WITH WATERS OF DIFFERENT CONCENTRATIONS IN DEUTERIUM. REMARKS

Diana Costinel[1], Roxana Elena Ionete[1], Raluca Popescu[1], Ooana Romina Botoran[1], Radu Tamaian[1], Gallia Butnaru[2]

[1] *National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI Rm. Valcea, 4 Uzinei Str , 240050, Romania*
[2] *University of Agricultural Sciences and Veterinary Medicine of Banat from Timişoara, Romania*
Corresponding author: *Diana.Costinel@icsi.ro*

An investigation of deuterium distribution in plants grown in various media conditions, meaning waters with different concentrations in deuterium, associated with different type of soil or magnetic nano particles (MNPs), is presented in the current work.

A first experimental study was performed on two *Vitis vinifera* (L) genotypes. The influence of two natural factors, water - tap water (TW) with 140 ppm Deuterium content and deuterium depleted water (DDW) with 30 ppm Deuterium content, and electromagnetic field, was assessed. The experiment was conducted during one year period, in two stages – first in laboratory conditions (in jars containing only the liquid mixtures in which the cuttings storage mater was activated and the organogenesis was initiated) until root formation took place, followed by the second stage in greenhouse conditions, when the autotrophic stage started (the plants uses all its organ equipment - roots and leaves, to provide their growth nutrients). During the first stage of work, no nutrients were added in the experimental solutions. A total of 10 cuttings of first year shoots belonging to different *Vitis Vinifera* (L) varieties were put into liquid media (500 cm^3/jar) in three experimental groups and one control (C), each in four replications. TW, DDW and mixture of each water type with MNPs ($\theta = 0.23\times10^{-3}g/100cm^3$ concentration) were used.

The organogenesis of each *Vitis vinifera* L pointed out a particular behaviour during the experiment. The majority of plantlet traits were positive influenced by the 30 ppm D concentration. When kept in DDW and DDW&MNPs, an earlier formation of leaves and root and a higher number of surviving stocks happened. Also, the deuterium content in leaves of plants grown with DDW or DDW associated with MNPs increased almost 4 times comparative with those of plants grown with TW, when the Deuterium increased insignificant (approximatively with 3 ppm).

A second experiment performed in laboratory conditions was aimed to evaluate the deuterium content in the roots, haulms and leaves of plants depending on the water (natural and depleted in Deuterium) and type of soil used as growing media. The experimental biological materials were represented by garlic (*Alium sativum*)

and monocotyledonous flowering plants. Two different soils, humus active – Agro, soil enriched with humic acid and organic matter, and universal earth – BioFlo, mixture between brown peaty and red peaty, moderate organic matter level, were used as growth substrate. For watering, water with two different Deuterium concentrations, 26 ppm and 145 ppm, has been applied.

The amount of Deuterium (expressed in ppm) was determined by isotope ratio mass spectrometry (IRMS) in waters extracted from various sections of the plants. Enrichment in Deuterium was found in the following order: leaves > roots and haulms > water used. In the experiments with DDW, the Deuterium content increased at almost 4 - 5 times in leaves comparative with that from the DDW and in root and haulm the concentration was approximatively 3 times higher. When normal water (145 ppm) was used, the Deuterium in leaves increased with 2 ppm, while in roots and haulms we found a slight decreasing in deuterium with 3 ppm. Significant differences between these two batches we observed when the substrate - soil humus active, was changed with universal earth.

Remarks: during both experiments, the enrichment of Deuterium in leaf tissue can be explained by the evapo-transpiration process. Deuterium increased slowly when plants entered into vegetation, but increased significant in leaves, with a few dozen of ppm. If using a growth medium with low Deuterium concentration (e.g. 26 ppm) combined with humus active soil, the Deuterium content in leaves may increase at several times. This behaviour can be attributed to plant adaptation/acclimatization as response to the abiotic factor, deuterium depleted water. The majority of plantlet traits were positive influenced by the low D concentration in growth medium.

Keywords: deuterium, tap water, deuterium depleted water

Acknowledgment: *This study has been financed by the Romanian Ministry of Education and Research, National Authority for Scientific Research for the financial support, under the NUCLEU Program, project PN 16360401 ,,Assessing the impact of different ecosystems on stable isotopes and multi-element composition of plants – Researches on geo-seasonal variability''.*

TRACEABILITY OF HEAVY METALS AND STRONTIUM-LEAD ISOTOPE CHARACTERIZATION IN SOIL-WINE SYSTEMS FROM DEALU BUJORULUI VINEYARD, ROMANIA

Florin-Dumitru Bora[1], Cezara Voica[2], Elena Postolache[1], Alina Donici[1*]

[1]Research Station for Viticulture and Enology Targu Bujor, Galaţi, Romania
[2]National Institute for Research and Development of Isotopic and Molecular Technologies,
67-103 Donat, 400293 Cluj-Napoca, Romania
Corresponding author: *donicialina79@gmail.com*

Determination of the elemental composition of soils and wines is useful for many reasons. Firstly, the concentration of elements from soils and wines is useful information to viticulturists and oenologists for controlling the process of obtaining high and quality wine (Pohl, 2007). Secondly, the elemental composition could be used as a wine fingerprint and represents one of the criteria for evaluating the authenticity of wine (Grindlay et al., 2008).

The chemical composition and sensory characteristics of wine are highly influenced by geographical origin, grape variety, ecoclimatic conditions, vintage and processing conditions (Marini *et al*., 2006). In addition to details on wine composition and nutritional value, many wine consumers now expect information on the origin territory of wine products, as the geographical origin of a wine can be an important criterion ensuring the quality of product.

Establishing the geographical origin of wines is an issue of major concern for countries around the world, in order to protect quality products in case of false statements regarding their geographical origin. This can lead to actions that may have negative economic impact to wine industry (Versari *et al*., 2014; Geană *et al*., 2016).

In the present research, we determined the heavy metals (Pb, Sr, Cd, Ni, Co, Cu, Ni, Hg, As, Cr) content from vineyard soil (0-10 cm, 10-20 cm, 20-30 cm, 30-40 cm, 40-50 cm, 50-60 cm, 60-70 cm, 70-80 cm, 80-90 cm, 90-100 cm, 100-110 cm and 110-120) and from wine. Also the isotopic ratio $^{87}Sr/^{86}Sr$ and $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ from soil and wines was established, in order to highlight reliable markers for wine geographical origin. For thus, we used as samples a selection of wines obtained in the Dealul Bujorului Vineyard, from Muscat Ottonel, Fetească Albă, Fetească Regală, Fetească Neagră, Merlot and Cabernet Sauvignon vine varieties, during three consecutive years 2014-2015-2016.

The determination of heavy metals was performed on mass spectrometer with inductively coupled plasma, (ICP-MS) iCAP Q Thermo scientific model, based polyatomic species before they reach the quadrupole mass spectrometer, using a PFA micro flow concentric nebulizer.

The instrument was daily optimized to give maximum sensitivity for M^+ ions and the double ionization and oxides monitored by the means of the rations between $Ba^{2+}/^{Ba+}$ and Ce^{2+}/CeO^+, respectively, these always being less than 2%. The experimental conditions was: argon flow on nebulizer (0.85 L/min), auxiliary gas flow 0.80 L/min, argon flow in plasma 15 L/min, lens voltage 7.31 V; RF power in plasma 1100 W, spray chamber temperature (2.53±1.00°C). Accuracy was calculated for the elements taken into consideration (0.5-5.0%). The precision for isotopic determination of such an instrument is about 0.05%.

Regarding the concentration of heavy metals from Dealu Bujorului vineyard soil, the highest concentrations were recorded on surface of the soil profile [for Cu of 546.01 ± 9.15 mg/kg (0 - 10 cm) and 521.37 ± 4.59 mg/kg (10 - 20 cm)) and for Ni of 9.01 ± 2.05 mg/kg (0 - 10) and 8.37 ± 1.59 mg/kg (10 - 20 cm)] but these concentrations decrease with increasing depth of the soil profile [for Cu of 315.28 ± 6.19 mg/kg (100 - 110 cm) and 213.41 ± 0.31 mg/kg (110 - 120 cm)) and for Ni of 6.32 ± 1.47 mg/kg (100-110) and 5.35 ± 0.79 mg/kg (110 - 120 cm)]. Exception to this rule do Pb that with increasing of depth of the soil profile also increases concentration of Pb from vineyard soil [Pb, 8.21 ± 2.32 mg/kg (0 - 10 cm) and 9.75 ± 1.23 mg/kg (10 - 20 cm)], but from the depth of the soil profile from 100 - 120 cm concentration decreases [Pb, 5.16 ± 0.94 mg/kg (100 - 110 cm) and 6.43 ± 0.59 mg/kg (110 - 120 cm)]. Reporting concentration of heavy metals in soil at national and international regulations we can say that, except Cu (546.01 ± 9.15 mg/kg (0-10 cm)), all metals contents were found in quantities below the limits imposed by the legislation.

In all tested wine samples, the toxic metals contents were found in quantities below the limits imposed by legislation. The highest concentration of heavy metals for wine was found at Fetească Neagră [Cd (0.12 ± 0.11 μg/L) (2014), Pb (0.13 ± 0.50 μg/L) (2015)] and Merlot [Cd (0.14 ± 0.14 μg/L) (2014), Pb (0.13 ± 0.52 μg/L) (2015)] compared to white wines Fetească albă [Cd (0.11 ± 0.01 μg/L) (2016), Pb (0.11 ± 0.10 μg/L) (2014)] and Fetească albă [Cd (0.10 ± 0.10 μg/L) (2015), Pb (0.11 ± 0.06 μg/L) (2015)]. Their relatively large ranges of variation were due to the diversity of Romanian areas from which they are originating, with diverse quality of the soil but also as a result of anthropogenic impact.

The higher mean of $^{87}Sr/^{86}Sr$ isotopic ration was obtained at the Merlot variety [1.3605 ± 0.0416 (3.7979%, 2015)] and Cabernet Sauvignon [1.3378 ± 0.0240 (1.7939%, 2015)]. A possible explanation for the higher mean of $^{87}Sr/^{86}Sr$ isotopic ration for wine can be the mineral consistency of the vineyard soil and its different eco-climatic conditions. In the wine from Muscat Ottonel variety we obtained a minimum mean of $^{87}Sr/^{86}Sr$ isotopic ratio of 0.7134 ± 0.0259 (3.6062% 2014). Regarding $^{206}Pb/^{207}Pb$ isotopic ratios, based on analyses we can say that Muscat Ottonel variety (2015) Fetească Albă variety (2014) and also Fetească Regală variety (2016), shows traces of pollution comes from cars (automobile emissions) (if $^{206}Pb/^{207}Pb$ = 1.1000 - 1.1400 [automobile emissions]) and Cabernet Sauvigon variety (2014 and 2015), shows traces of atmospheric pollution with lead on vine (if

$^{206}Pb/^{207}Pb$ = 1.1700 - 1.1210 [atmospheric pollution]). The higher mean of $^{208}Pb/^{206}Pb$ isotopic ratios was obtained at the Fetească Neagră variety 2.3520 ± 0.1880 (4.5927% 2016), Cabernet Sauvignon variety 2.4098 ± 0.0817 (3.4294% 2014) and Cabernet Sauvignon variety 2.3337 ± 0.0267 (1.1423% 2015).

Keywords: elemental composition, wine, $^{87}Sr/^{86}Sr$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ isotope ratio, geographical origin.

Acknowledgments: *This paper was published under the frame of the Romanian Ministry of Agriculture and Rural Development, project ADER no. 14.2.2. "Quantitative studies on assessment and monitoring contaminants, on the chain of viticulture and winemaking to minimize the amount of pesticides and heavy metals as principal pollutants".*

References

Geană E.I., Sandru C., Stanciu V., Ionete R.E. (2016) Elemental profile and $^{87}Sr/^{86}Sr$ isotope ration as fingerprints for geographical traceability of wines: an approach on Romanian wines. *Food Analytical Methods* 10(1):63-73.

Grindlay G., Mora S., Maestre S., Gras L. (2008) Application of a microwave-based desolvation system for multi-elemental analysis of wine by inductively coupled plasma based techniques. *Analytica Chimica Acta* 624(1-2):24-37.

Marini F., Bucci R., Magri A.L., Magri D.A. (2006) Authentification of Italian CDO wines by class-modeling techniques. *Chemometrics and Intelligent Laboratory Systems* 84:164-171.

Pohl P. (2007) What do metals tell us about wine? *TrAC Trends in Analytical Chemistry* 26(9):941-949.

Versari A., Laurie V.F., Rici A., Laghi L., Parpinello G.P. (2014) Progress in authentication, typification and traceability of grapes and wines by chemometric approaches. *Food Research International* 60:2-18.

APPLICATION OF CHEMOMETRIC TECHNIQUES IN STABLE ISOTOPE EVALUATION

Oana-Romina Botoran, Roxana Elena Ionete, Diana Costinel, Raluca Popescu

National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI,
Uzinei Street no. 4, 240050, Râmnicu Vâlcea, Romania
Corresponding author: *oana.dinca@icsi*

Nowadays, food science follows the same unique pattern as all the applied experimental science: partially or even completely automated, leading to defining authenticity and traceability concepts as multivariate issues. At present, a complete and precise range of technical possibilities exists for stable isotope ratio measurements, but superior performance with respect to the accuracy and precision of isotopic data interpretation is represented by the multivariate pattern recognition techniques. Although this instrumentation and its statistical aspects are rather complex and sensitive, these methods provide the output required for extracting the useful information from such data, facilitating the considerations of inter-correlations between the measured isotope ratios and providing the isotopic pattern of a geographic, botanic or varietal origin (Figure 1).

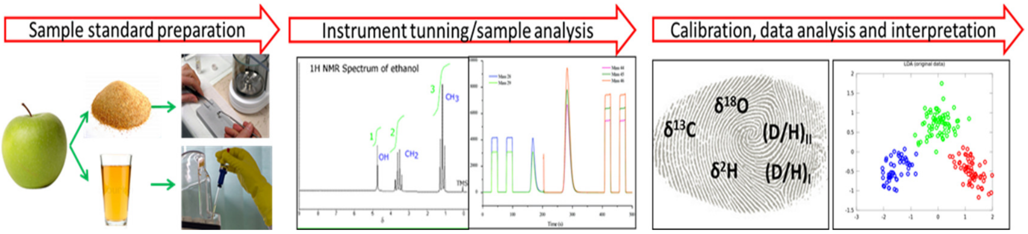


Figure 1. *Exemplified work flow of stable isotope ratio analysis*

The principal objective of this study was to demonstrate that combining isotope data with multivariate analysis, in developing a data base, may cover many different aspects of the authenticity assessment, including the discrimination by variety or geographical origin, adulteration, and the control of production process and mislabeling. Pattern recognition methods based on $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{2}H/^{1}H$ and D/H isotopic ratio from 258 fruits samples (17 different varieties) were used for different purposes, such as data exploration and development of predictive models. Depending on the particular purpose, the output of these models was qualitative or quantitative and a proper validation of the predictive models was included in order to provide a reliable prediction. Dealing with vast amount of raw data, as in the classification of the 258 fruit samples, the main problem was to extract the best information from the stable isotopes values: to classify the fruits into categories and, especially, to predict the category of fruits of unknown category and to evaluate the correctness of this assignment.

In order to develop the database using stable isotope ratio as sigle parameters in combination with multivariate statistics, as a standard procedure for the extraction of latent information and to provide a fast data overview, an univariate statistical analysis was performed to explore each variable from the data set, separately and to describe the pattern of response to the variable, concluding that all the isotopic parameters are relevant for the botanical discrimination. Further, discriminat analysis was selected to sort the samples into predefined classes and subsequently to enable classification of unknown fruit samples. This model is based on the existence of a calibration set, known as "training samples", where the botanical origin and authenticity is guaranteed, as well as geographical, geological and climatic reference information. Categories formed by different variety origin of fruits also includes differences due to geographical origin, soil, compositin, climate and harvesting periods specific for each type of fruit in particular.

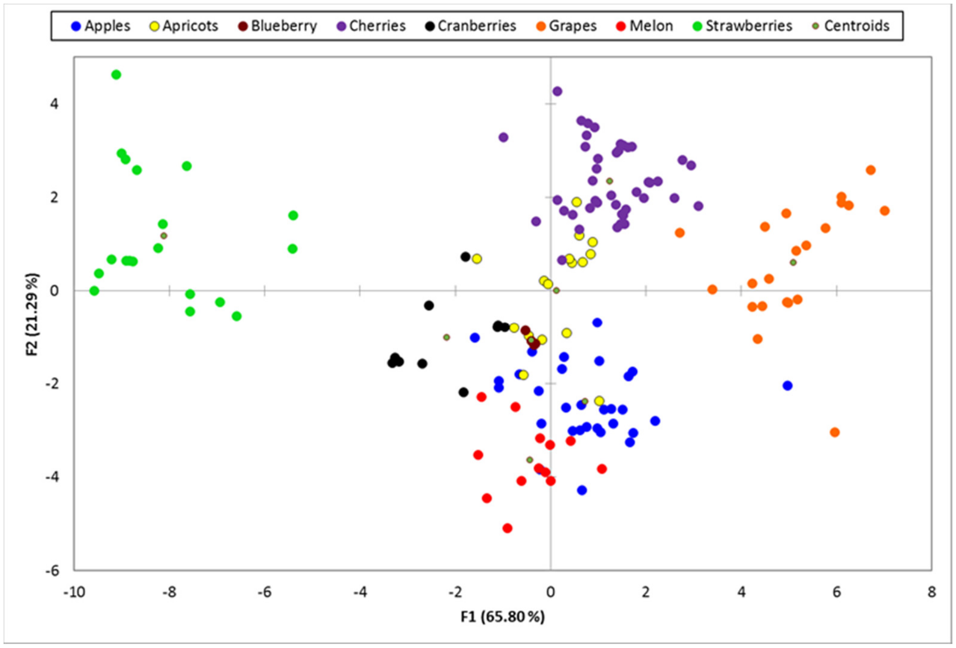


Figure 2. *Discriminat analysis of fruit botanical origin for which the confusion matrix for the cross-validation results was higher than 80%*

Applying discriminant analysis, with stable isotopes ratio as independent variables and variety as dependent variable, we have obtained a total rate classification of 86.60% and a cross-validation rate of 63.32%. Although the separation was good, some fruits overlap, therefore another discriminant analysis was performed using as dependent variable only the fruits for which the confusion matrix for the cross-validation results was higher than 80%. In this case, a confusion matrix for the sample estimation of 96.16% was obtained and a confusion matrix for the cross-validation of 92.26% (Figure 2).

The excellent prediction rate achieved through discriminant analysis for classifying fruits from different harvesting periods and producing regions from Romania according to their botanical origin, gives further evidence of the ability that multivariate statistical analysis, based on stable isotopes data, has in confirming the provenance. However, as new types of adulteration will inevitably appear, the need for combining the isotope data with other variables may arise, and therefore it is expected that multivariate statistical techniques to become an important complementary tool used in food authentication.

Keywords: botanical origin, chemometrics, fruits, stable isotopes.

Acknowledgment: *This work was supported by the project PN16360402, grant No. 23N/2016 from the Romanian Ministry of Research and Innovation.*

References

Dinca O.R., Ionete R.E., Popescu R., Costinel D, Radu G.L. (2014). Geographical and botanical origin discrimination of Romanian honey using complex stable isotope data and chemometrics. *Food Analytical Methods* 8:401-412;

Dinca O.R., Ionete R.E., Costinel D, Geana I.E, Popescu R., Stefanescu I., Radu G.L. (2016). Regional and vintage discrimination of Romanian wines based on elemental and isotopic fingerprinting. *Food Analytical Methods* 9(8):2406-2417;

Botoran O.R., Ionete R.E., Costinel D., Popescu R., Geana E.I., Miricioiu M.G. (2016). Influence of climate and origin on the isotopic and elemental profile of fruits. *Journal of Biotechnology* 231:77-78.

ORGANIZERS

Govora Bai, ROMANIA 2017
ESIR
EUROPEAN SOCIETY FOR ISOTOPE RESEARCH

THE NATIONAL RESEARCH AND DEVELOPMENT INSTITUTE FOR CRYOGENICS AND ISOTOPIC TECHNOLOGIES
ICSI Rm. Valcea

EXHIBITORS AND SPONSORS

Thermo SCIENTIFIC

Agilent Technologies

CAMECA®
SCIENCE & METROLOGY SOLUTIONS

nu

O.F. Systems
PERFORMANCE MATTERS

SC OFICIALI IMPERIUM SRL

analytikjena
An Endress+Hauser Company

Leco®
Delivering the Right Results
© 2016 LECO Corporation

XEROSERVICE

expert trade

COMALTRONIC
automatizări-alarme-supraveghere video-control acces

REDOX
RESEARCH & ANALYTIC
www.redox.ro

APPLICATION BRIEF

AB30356

EA-IRMS: Simultaneous δ^{13}C, δ^{15}N, and δ^{34}S Analysis of Wood with the EA IsoLink IRMS System

Christopher Brodie, Oliver Kracht,
Alexander Hartwig, Andreas Hilkert,
Charles Douthitt
Thermo Fisher Scientific, Bremen, Germany

Key Words

C/S Ratio, C/N Ratio, EA IsoLink, Gas Chromatography, NCS Analysis, δ13C, δ15N, δ34S, Wood

Goal

To demonstrate simultaneous NCS analysis on wood samples, with a C/S ratio > 7000:1, using the EA IsoLink IRMS System.

Introduction

A prominent challenge in analyzing sulfur in sample matrices with very high C/S ratios (e.g. > 5000:1), such as wood, is the very low amount of sulfur in the sample alongside the extremely high carbon amounts. In addition, simultaneous NCS weight% (wt%) and isotopic analysis of very high C/S ratio samples has been a significant analytical challenge due to difficulties in complete baseline separation of N_2, CO_2 and SO_2, the analysis of high amounts of carbon relative to small amounts of nitrogen and sulfur, and EA-IRMS system sensitivity.

Figure 1. Thermo Scientific EA IsoLink IRMS System.

Analytical Configuration

For analysis, 5 replicates of approximately 12–16 mg of dried, homogenized wood were weighed into tin capsules, along with 2 mg of V2O5 and introduced to the reactor from the Thermo Scientific™ MAS Plus Autosampler, where it was combusted with 41 ml of oxygen. Analysis time is less than 10 minutes, using less than 1.5 liters of helium per sample, and it is based on standard sensitivity mode of the Thermo Scientific™ Delta V™ Series Isotope Ratio Mass Spectrometer.

Simultaneous NCS analysis of wood

Using the Thermo Scientific™ EA IsoLink™ IRMS System (Figure 1), simultaneous NCS analysis is demonstrated on wood samples (C/S ratio ≥ 7000:1). Table 1 shows excellent precision on simultaneously measured wt% N, wt% C, wt% S, δ13C, δ15N and δ34S values. The analysis shows that for a sample containing very small nitrogen and sulfur amounts, alongside extremely high carbon amounts, precision of 0.26‰ for n = 5 is achieved on 1 μg S, which equates to less than 0.007% or 70 ppm of sulfur.

thermo scientific

Table 1. Data from simultaneous NCS analysis of wood samples.

Sample	Weight (mg)	wt% C	wt% N	wt% S	δ^{13}C (‰)	δ^{15}N (‰)	δ^{34}S (‰)	µg C	µg N	µg S	ppm S	C/S Ratio
Spruce	12.69 (11.72–14.24)	54.954 ±1.086	0.088 ± 0.003	0.007 ±0.0002	-24.10 ± 0.06	3.20 ± 0.23	5.92 ± 0.26	7036.48	11.14	0.89	70	7905
Iroko	15.63 (15.00-16.07)	32.018 ± 0.814	0.123 ± 0.01	0.005 ± 0.0005	-26.43 ± 0.04	10.13 ± 0.32	6.36 ± 0.27	5004.75	19.20	0.71	70	7048

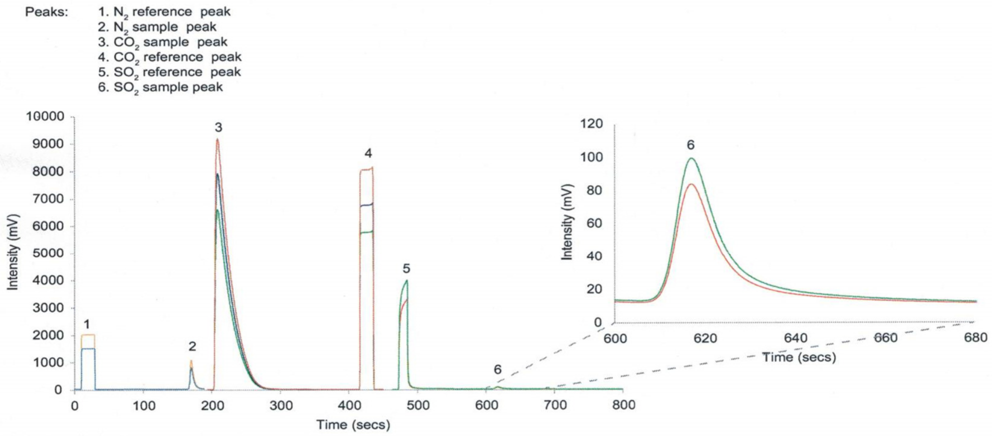


Figure 2. Isotope chromatogram for simultaneous NCS measurements on a spruce wood sample.

From a single sample, complete baseline separation of N_2, CO_2, and SO_2 peaks is achieved and sharp peak shapes with no peak tailing is ensured by temperature ramped continuous flow gas chromatography (Figure 2). The excellent dilution capabilities for high CO_2 amounts in the presence of very low N_2 and SO_2 amounts, using the Thermo Scientific™ ConFlo IV™ Universal Interface, makes simultaneous NCS analysis routine on very high C/S, C/N, and C/N/S ratio sample matrices.

However, the sample weight required for simultaneous NCS analysis of wood samples will vary. This depends on the sulfur content of sample. The data presented in Table 1 are application data and are not warranted because they exceed product specifications. The warranted product specification for δ13C is ±0.1‰ (1 sd) for 50 µg of carbon, δ15N is ±0.15‰ (1 sd) for 50 µg of nitrogen and δ34S is ±0.3‰ (1 sd) for 10 µg of sulfur measured on Sulfanilamide.

Summary

From a single sample with a high C/S, C/N and C/N/S ratio, outstanding precision, low cost per sample, and short analysis times are ensured for wt% and isotopic measurements in simultaneous NCS mode by the EA IsoLink IRMS System. The method presented here demonstrates simultaneous NCS analysis on wood samples with a C/S ratio > 7000:1 and a nitrogen and sulfur content of <20 µg and 1 µg, respectively.
Cost per analysis is reduced by the Helium Management (HeM) Module, using less than 1.5 liters per sample.

Find out more at **thermofisher.com/EAIsoLink**

ThermoFisher SCIENTIFIC

LEAVE INTERFERENCES BEHIND WITH MS/MS

Agilent 8900 Triple Quadrupole ICP-MS

PUT YOUR ICP-MS RESULTS BEYOND DOUBT.

The 2nd generation Agilent 8900 ICP-QQQ has a unique tandem MS configuration, so can operate in MS/MS mode to control reaction chemistry in the collision/reaction cell. This leads to more consistent, reliable and accurate results in demanding applications in industrial and research laboratories.

The Agilent 8900 also works superbly in helium collision mode, and has robustness and productivity to match Agilent's market-leading quadrupole ICP-MS systems, making it the world's most powerful and flexible multi-element analyzer.

Superior performance

- Accurate trace-level analysis of previously "difficult" elements, Si, P, S, Cl...
- Resolution of isobaric overlaps, beyond capability of high-resolution ICP-MS
- Fast TRA for reliable analysis of nanoparticles, including SiO_2 and TiO_2

Unparalleled flexibility

- Innovative Method Wizard automates method development, including for nanoparticle analysis
- Unique MS/MS scan modes aid research and method development
- Sample introduction and collision/reaction cell configurations to suit any application

Proven ICP-QQQ Technology

Since the launch of Agilent's unique 8800 ICP-QQQ in 2012, triple quadrupole ICP-MS has enabled hundreds of labs around the world to do more than ever before:

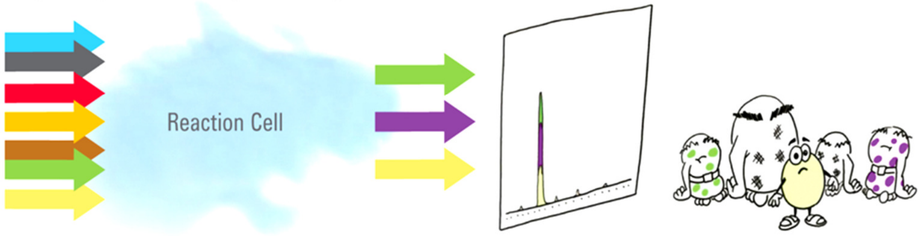
- Monitor lower levels of contaminants in advanced materials and high-purity semiconductor process chemicals
- Quantify unknown proteins and peptides, by measuring the sulfur and phosphorus heteroelements
- Characterize silica and other nanoparticles in complex environmental, food and biological samples, even at the sub-50 nanometer scale
- Accurately determine selenium, arsenic and their species at lower levels in complex sample matrices

Agilent Technologies

The MS/MS advantage for reaction gas methods

ICP-QQQ provides superior control of interferences by operating in MS/MS mode. An additional mass filter (Q1), placed before the collision/reaction cell, prevents non-target masses from entering the cell. With MS/MS, reaction chemistry is controlled and consistent, so analyte ions or product ions are measured free from interference, even in complex and variable samples.

Conventional quadrupole ICP-MS (ICP-QMS)

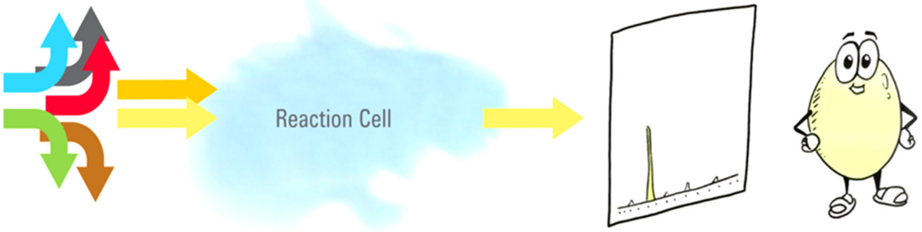


No mass filter before cell. All ions enter the cell.

Reaction chemistry varies with sample composition. Non-target ions can pass through cell or may react to form new product ions at the target analyte mass.

Many different ions and product ions can contribute to the measured signal, leading to variability and inaccuracy.

Agilent triple quadrupole ICP-MS (ICP-QQQ) with MS/MS



Quadrupole mass filter (Q1) rejects all non-target masses before the cell.

Analyte and on-mass interferences are separated by consistent and predictable reaction chemistry.

Only the target analyte ions/product ions contribute to the measured signal, so results are accurate and reliable.

For more information:
Contact your local Agilent
representative or visit:
www.agilent.com/chem/8900icpqqq

Published June 1, 2016
5991-6994EN

Agilent Technologies

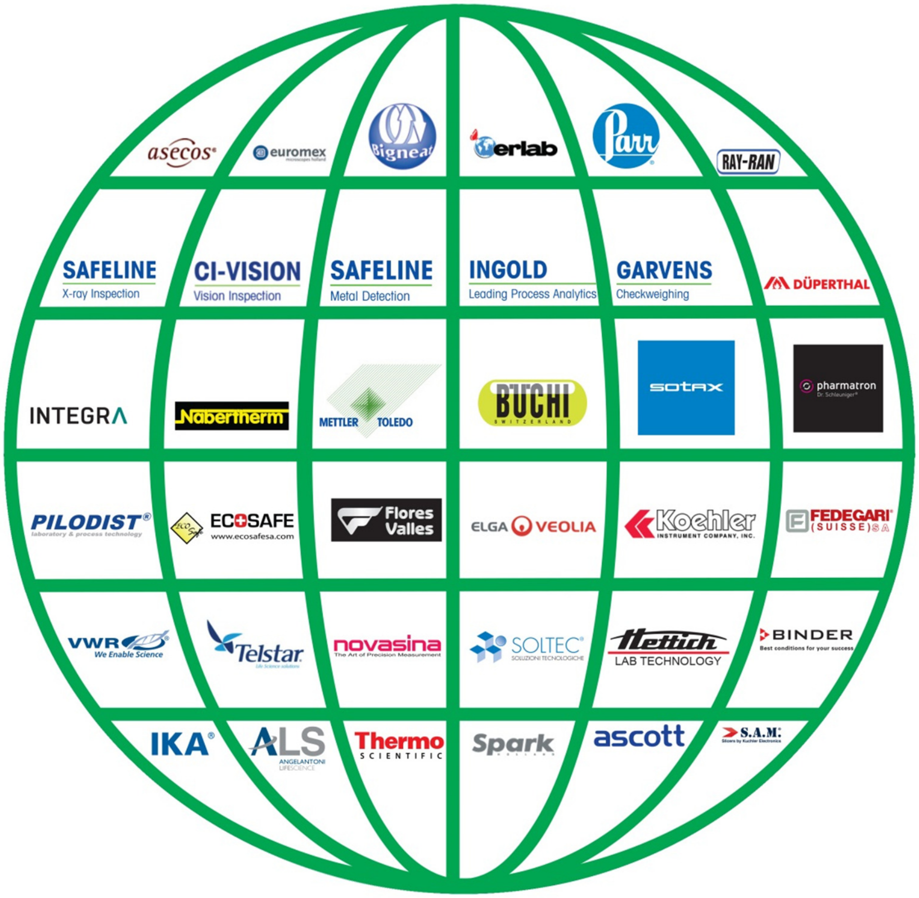
O.F. Systems
PERFORMANCE MATTERS

O.F. Systems is a company with Romanian private capital, having as main activity the supply of laboratory equipment, process equipment and industrial scales.

Since the company's establishment in 1992, the policy O.F. Systems has been and remains strictly customer oriented.

The company's competitiveness is defined by two parameters:

- O.F. Systems’s team and their individual performance
- The quality of its suppliers



O.F. Systems is the company where any specialist can find reliable information, providing not only laboratory equipment but also good ideas, practical solutions rather than theoretical approaches, service, and a „know how” based on its team experice.

O.F. Systems provides industry professionals with complete integrated solutions, in order to increase efficiency and competitiveness, from designing a laboratory to its smallest details, coupled with maintenance services and post warranty service.

Over the years O.F. Systems added to the partnership with METTLER TOLEDO (the company represents exclusively, for 25 years, METTLER TOLEDO products in Romania) more successful collaborations with top manufacturers, representative for the market: Buchi, Sotax, ThermoScientific, Elga, Parr, etc.

„To converge to an idea is just the beginning, staying together is only progress, but to work together to that common vision is the true measure of success. Commitment, dedication, teamwork, innovation and continuous learning are the values that created the base for a collaboration of over 25 years. Together, METTLER TOLEDO and O.F. Systems are confident in continuing this success.”

O.F. Sytems SRL

strada Al. Serbanescu, nr. 25, bloc. 7N, et. 2, ap. 9, sector 1, Bucuresti, Romania ▌
tel. +40 0745281346 ▌ fax +40 21 2320831 ▌ http://www.ofsystems.ro/

O.F. Systems
PERFORMANCE MATTERS

analytikjena
An Endress+Hauser Company

Analytik Jena is a provider of instruments and products in the areas of analytical measuring technology and life science. Its portfolio includes the most modern analytical technology and complete systems for bioanalytical applications in the life science area. Comprehensive laboratory software management and information systems (LIMS), service offerings, as well as device-specific consumables and disposables, such as reagents or plastic articles, complete the Group's extensive range of products.

Tradition with innovative power Analytik Jena takes pride in a long history and tradition of developing high-end analytical instrumentation, which dates back to the inventions made by Ernst Abbe and Carl Zeiss in Jena over 150 years ago. Within the last 25 years Analytik Jena has become one of the most innovative manufacturers of analytical measuring technology that serves the demands of routines laboratories as well as of sophisticated niche applications worldwide.

Analytik Jena stands for high-end analytical instrumentation with superior quality made to the demands of our customers. Innovative technology that convinces with a unique analytical performance is continuously developed and manufactured at R&D and production sites throughout Germany. Analytik Jena`s "Made in Germany" high-performance analysis systems fulfill the needs of its customers: Highest quality, unparalleled precision and innovative technology, durability and robustness. Proven Carl Zeiss technology combined with modern, innovative solutions for working even more precisely, quickly, efficiently and economically.

Analytical instruments produced by Analytik Jena includes:

- High-Performance ICP-MS: PlasmaQuant® MS / MS Elite
- High-Resolution Array ICP-OES: PlasmaQuant® PQ 9000 / PQ 9000 Elite
- Atomic Absorption Spectroscopy: novAA®, ZEEnit, contrAA®
- Atomic Fluorescence Spectroscopy: mercur
- Sample Preparation: microwave digestion systems (TOPwave®)
- UV VIS Spectroscopy: SPECORD® and SPEKOL®
- Photochemiluminescence: PHOTOCHEM®
- Sum Parameter Analysis: - multi N/C®–TOC/TN, multi X®–AOX/TOX, EOX, POX
- Elemental Analysis: Carbon, Sulfur, Nitrogen and Chlorine (multi EA® series)

Powerful, patented technology The PlasmaQuant® MS is the world's highest performing quadrupole ICP-MS with unsurpassed sensitivity of over 1.5 million counts/second/ppb.

The PlasmaQuant® MS is optimized for routine applications in environmental including waters, wastes, soils and sediments, food and agriculture, chemicals and petrochemicals as well as for quality control in the semiconductor industry where plasma robustness to handle complex sample matrices is paramount.

The PlasmaQuant® MS Elite is designed for maximum sensitivity to deliver lowest possible detection limits for research applications. It measures the smallest nanoparticles and detects drug-tracing elements at below partsper-trillion level. The Elite is also perfect for laser ablation analysis, isotopic-ratio measurements and chromatography techniques to separate analyte species.

The unique resolving power, unmatched sensitivity and exceptional matrix tolerance of the PlasmaQuant® PQ 9000 Elite consistently offer the lowest detection limits and highest ease of use in demanding applications. Warranting the highest precision it is the first choice for advanced material analysis, research and quality control labs facing complex matrices including refractory, ferrous and highpurity metals, rare earths and petrochemicals. With a clear emphasis on wide applicability, simplicity and cost-effectiveness the PlasmaQuant® PQ 9000 ensures excellent plasma performance, detection limits and accuracy in general applications. Fulfilling the demands of agricultural, food and environmental analysis it is a convincing all-rounder with enhanced productivity and operator comfort.

Analytik Jena brings an innovation on the market – the contrAA® series – which exceeds the performance of conventional AA spectrometers in all parameters. The HR-CS AAS contrAA® 800 D it's a new instrument concept, using a high-intensity xenon short-arc lamp as continuum radiation source, a high-resolution double monochromator (a prism and an Echelle grating) and a CCD array detector. It finally closes the gap between ICP-OES and AAS.

HR-CS AAS contrAA® 800 F for flame and hydride techniques, contrAA® 800 G for graphite furnace technique and contrAA® 800 D for flame, hydride and graphite furnace techniques are capable of analyzing liquid as well as direct solid samples. This instruments combines intelligent design with premium functionality and persuasive performance characteristics:

- Just one light source for all elements
- Sequential multi-element routine as standard
- Unique simultaneous background correction
- solid AA® – direct solid AAS Solid and paste like samples, as powders, cream or viscous oils can be analyzed directly in the graphite furnace.

Thanks to their unique precision, innovative technologies and durability an increased number of companies are putting their trust in technology from Analytik Jena AG. We can mention in here companies like: Abbott, Akzo Nobel, Altana, AstraZeneca, Braun, BASF, Baxter, Bayer, BMW, Boehringer Ingelheim, BP, Buderus, Coca-Cola, Dea, Degussa, Dow, Esso, Fresenius Fuji, Gsk, Henkel, Honeywell, Knoll, The Linde Group, Mercedes, Merck, Mitsubishi Motors, Nissan, Novartis, Roche, Samsung, Sanofi Avensis, Sasol, Schering, Schott, SGS, Shell, Siemens, Solvay, Thyssenkrupp, Volskwaggen, Wacker and many more.

https://www.analytik-jena.de

analytikjena
An Endress+Hauser Company

Author index