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Carbon, nitrogen and sulfur isotopes as evidence for an anomalous ocean during recovery from the End Permian mass extinction

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The Early Triassic carbon, sulfur, nitrogen, and strontium isotope records show patterns that, in concert, are unprecedented in the earth history. At the aftermath of the end-Permian mass extinction, the ocean chemistry underwent profound changes, as outlined by geochemical, sedimentological and paleontological observations. The Early Triassic carbon isotope record is marked by three positive excursions, outstanding not only by their abruptness, but also by their extreme magnitude, comparable only with Precambrian and Early Cambrian counterparts. The nitrogen isotope profile displays a negative excursion of 1.5‰ across the Lower – Middle Triassic boundary, mirroring the last carbon isotope excursion. The decrease in $\delta^{15}$N values indicates increased nitrate availability, consistent with the onset of an upwelling system indicated by sedimentological evidence. While the nitrogen isotope anomaly is likely to be local, confined to the North American upwelling zone, it suggests a sudden increase in ocean productivity, in agreement with the carbon isotope positive excursion. Another remarkable feature of the Early Triassic stable isotope record is represented by a large sulfur isotope shift, as recorded in sedimentary sulfates, however its timing and relationship with the carbon isotope record is poorly constrained.

Sulfur isotope profiles in the Moenkopi Formation in SW Utah and N Arizona show a large positive excursion at the end of the Lower Triassic possibly spanning the Lower-Middle Triassic boundary. Tentative correlations with the carbon isotope record from the Thaynes Formation, possible due to interfingering relationships between the Thaynes and Moenkopi formations, indicate a decoupling of the carbon and sulfur isotope cycles during the Early Triassic. Although it is difficult to reconstruct a scenario that would account for all geochemical anomalies described above, the stable isotope record is consistent with an Early Triassic stratified, stagnant ocean, low latitudinal temperature gradients, large carbon isotope gradients between deep, anoxic and surface waters, increased sulfate reduction in the anoxic zone that would lead to large fractionation of sulfur isotopes and formation of residual brines enriched in $^{34}$S. A reorganization of the ocean circulation system and onset of vigorous upwelling currents at the end of Early Triassic would mark the return to normal conditions and the final recovery after the end-Permian mass extinction.
Stable isotope fractionation of gamma hexachlorocyclohexane (lindane) during reductive dechlorination by sulphate-reducing bacteria

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Reductive dehalogenation of hexachlorocyclohexanes (HCHs) is the most likely degradation pathway in anoxic environments and stable isotope fraction analysis (SIFA) may be a promising tool for assessing the reductive dehalogenation of HCH in field studies. SIFA is taking advantage of the preferential transformation of lighter isotopomers during a degradation reaction, thus leading to an enrichment of heavier isotopes in the residual phase in the course of biodegradation. The isotope fractionation process can be quantified by the isotope fractionation factor \((\alpha)\) using the Rayleigh model.

In our study, we determined carbon isotope fractionation factors for the reductive dehalogenation of \(\gamma\) HCH using the sulphate-reducing bacteria (Desulfococcus multivorans DSM 2059 and Desulfovibrio gigas DSM 1382). Both strains are known for co-metabolic HCH dehalogenation. Degradation experiments with \(\gamma\) HCH in concentrations of 7–10 mg/L were carried out using benzoate (for D. multivorans) and lactate (for D. gigas) as electron donors, respectively.

\(\gamma\) HCH was reductively dehalogenated by both cultures in incubation times of up to three weeks. The main metabolites during biodegradation were benzene, monochlorobenzene and gamma tetrachlorocyclohexene (\(\gamma\) TCCH), detected by GC-MS, and thus, confirming the hypothesis of reductive dehalogenation under sulphate reducing conditions.

The rate of \(\gamma\) HCH biodegradation was strongly affected by the concentrations of the electron donors and sulphate in the growth medium. For example, D. multivorans degraded \(\gamma\) HCH completely only under sulphate limitation. In abiotic controls, \(\gamma\) HCH concentrations remained stable, and no metabolites were detected, hence demonstrating that \(\gamma\) HCH’s degradation by both strains was a biotic process.

The carbon stable isotope composition of \(\gamma\) HCH during biodegradation was monitored by GC-IRMS (Gas Chromatography-Isotope Ratio Mass Spectrometry). The first results indicate a carbon isotope fractionation \((\alpha C = 1.0037)\) of \(\gamma\) HCH by D. Gigas under sulphate limitation conditions.
Seasonal fluctuations in the past 5000 years: stable isotope record of molluscan shells (Balaton region, Hungary)

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Shell carbonate (Unionidae sp.) from archaeological excavations located at Ordacsehi (Southern part of the catchment area of the Lake Balaton, Central Hungary) were analyzed for stable C and O isotope compositions in order to obtain environmental and climatic information from the catchment area of Lake Balaton for the last 5000 years. Shell material from seven periods from Late Copper Age (~5000 yr BP) to Roman age (~12 yr BC to 400 yr AD) were studied in the same area. Beside bulk shell samples that reflect major climatic changes, sampling was conducted at cca. 1 mm resolution allowing observation of seasonal variabilities. As a comparison, shell material dated back to the Riss-Würm period was also studied in order to show variations related to glacial conditions.

The C and O isotope compositions show systematic variations both by means of bulk average and internal changes within individual shells. Bulk compositions reflect annual changes in temperature and water composition (i.e., recharge rate and evaporation efficiency), whereas the high-resolution data indicate seasonal (or even weekly) variations. Based on recent observations of the isotopic behaviour of Lake Balaton, the following conclusions were drawn. The late Copper period (Boleráz, 3000 BC) can be characterized with cooler and wetter condition, in agreement with pollen data. A warming trend can be observed from the Late Copper Period to the beginning of the middle Bronze Age. The Early Bronze period (Somogyvár-Vinkovci, 2600 BC) was probably warm, but the high seasonal fluctuations of the isotope curves within individual shells indicate a strong variation in precipitation amount and evaporation rate. The strong negative oxygen isotope shifts associated with the cold seasons in many of the shells suggest higher amounts of winter precipitation, whereas the significant positive shift within the main growing stages (warm seasons) indicate rather dry summers. Compared to the other periods studied, the Roman period – regarded usually as relatively warm – is characterized by rather stable conditions.

An interdisciplinary comparison with archaeological, historical and meteorological records is being undertaken in order to establish a complex climate change scenario for the last 5000 years in the Carpathian Basin.
Preliminary study of deuterium depleted water effect on the live cells by isotopic ratio mass spectrometry

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This preliminary study presents the models for deuterium depletion in plant germination, mouse blood and human blood, and the application of these models to study the effect of the depleted water on the live cells. The different deuterium contents of biological fluids involved in the experiments were measured by isotopic ratio mass spectrometry. We have found that the major effect of deuterium depleted water (DDW) was the inhibition of the cell division in plants, as in animal, or in human. To study the effect of the DDW on the plant, we have measured the deuterium content of the water extracted from plants that have consumed the DDW and we have compared with the plant that have consumed the normal water. For the plant, the effect of DDW was the decrease of growing rate, and decrease of germination rate of plants. Another effect of DDW on the plants was the decrease of the average length of stem and the decrease of the average length of roots. To study the DDW effect on the animals, particularly on the mice and Wistar rats, we have watched the content of the deuterium in blood for the animals that have drunk the DDW. The experiment confirms the inhibitory effect of the DDW in tumour grows. We have found the same effect of the DDW on the human. Also, we have found that the deuterium content in the blood of the patients with cancer disease is depleted by about 5-7 ppm compared with the healthy one. We suppose that the tumorous cells that have a higher speed of growth consume the deuterium from blood. As a result, for cancerous humans the deuterium content of blood serum is diminished compared with the healthy human. We propose to use the deuterium content of the blood in the cancer diagnosis and treatment.
The environmental and tectonic record of a continuous Cretaceous/Paleogene section from the Eastern Carpathians

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Marine red beds crop out in almost all the tectonic units of the Romanian Carpathians, extending from the Albian/Cenomanian boundary interval up to the end of the Cretaceous. A particular occurrence is known from the Romanian Carpathian bend area, including the Ialomia River basin, where the red bed deposition encompasses the late Campanian-Paleocene interval. The studied section is located in the Ialomia Valley (at the southern end of the Eastern Carpathians) and consists mainly of marls with abundant microfossils (foraminiferal and calcareous nannofossil assemblages). We sampled the section at 1-m intervals between meter 0 and 80, and each 20 cm interval for the upper part, a total of 112 samples being collected and investigated.

Stable isotopic, XRD mineralogical analysis, and nannoplankton investigations have been done across the section. The mineralogical bulk rock changes are not reflected by lithological changes in the studied section, suggesting that lithology is an incomplete record of the environmental conditions. Calcite is present in all samples, showing large variation, from values up to 70% down to 2%. In the early Maastrichtian, the values are higher, showing less variation with only two sharp drops toward lower values. During the late Maastrichtian, there are several intervals with low calcite concentrations. Generally, decreasing calcite content correlates well with decreasing ¹³C values, all the negative δ¹³C excursions being reflected by variations in calcite content. There are two intervals with constant low calcite content, the oldest within the late Maastrichtian between meter 40 and 60, and the youngest at the Cretaceous/Paleogene (C/P) boundary. Quartz and feldspars are plotted together; their content varies between 20 and 40% and shows no systematic fluctuations and long-term trends. The clay minerals consist of smectite, chlorite, and muscovite; no other clay minerals, as for example kaolinite, have been detected by XRD. Up to meter 27, the smectite is consistently close to 0%. During the early Maastrichtian, the clay mineralogy is dominated by the presence of chlorite and muscovite. In the late Maastrichtian, the smectite is increasing up to 40%.

The data gathered by us indicates significant paleobiogeographic fluctuations as well as enhanced tectonic uplift of the source area in the late Maastrichtian. The mineralogical content of the investigated section correlates with the isotopic composition. The strong correlation between the negative isotopic excursions, the low
carbonate and the high clay content is due to variation in the detritic input and/or productivity. The presence of smectite along the section indicates the absence of a strong diagenetic overprint.

Based on the multidisciplinary evaluation of the red beds outcropping in the Ialomița section, we propose the following interpretation. The lower Maastrichtian deposits are characterized by a monotonous red cherry bed lithological succession, high calcite content and generally constant δ13C values. In the latest early Maastrichtian, the increase of the Boreal nannofossil taxa is related to a cooling phase located at the upper part of the Chron 31r and towards the base of the Chron 31n.

Within the early/late Maastrichtian boundary interval, the δ13C values recovered concomitantly with a slight increase in the abundance of the Tethyan nannofossils, which are more related to warm surface waters. The calcite content shows high values. One of the most pronounced negative δ13C excursions covers the upper part of CC25a and also most of the CC25 b calcareous nannofossil Subzones, encompassing the upper part of the Chron 31n and the base of the Chron 30r. The carbonate content is low, clay minerals show high values suggesting higher detritic input and enhanced uplift and erosion in the continental source area. This interval corresponds to cool conditions as indicated by the high abundance of the Boreal calcareous nannofossils. Cooler conditions prevail up to the first occurrence (FO) of the nannofossil *Micula prinsii*. Above this bio-event, a progressive decrease of the Boreal nannofossils indicates a warmer climate just below the C/P boundary.

The C/P boundary is characterized by a negative excursion of the δ13C values, associated with constant low carbonate content and a significant drop in the nannofloral diversity, expressed by the mass-extinction of the Cretaceous taxa.

The youngest events recognized in the Ialomița Valley section are the four earliest Danian successive blooms, two of the calcareous dinoflagellate *Thoracosphaera* genus, which are intercalated with two blooms of the nannofossil *Braarudosphaera bigelowii*, the latter being associated with less negative δ13C isotopic values.

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Isotopic composition of spring waters from Croatian karst regions: Gacka River area

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The main springs of the Gacka River drainage area (Majerovo vrelo, Tonković vrelo and Pećina) have been studied by means of stable (18O) and radioactive (3H) isotope measurement. This area is situated in the Dinaric karst that comprises very important groundwater storage reservoirs. Since karst is characterized by high permeability, porosity and crevices in which water moves in complex subterranean networks, it is very sensitive to any kind of pollution. Gacka River is located in the Lika region at an altitude of about 400 m above sea level. Although its climatic conditions are mainly continental, the situation is complicated by the occasional influence of maritime Adriatic air masses. Water samples from the three springs (continuous sampling, some other springs occasionally) as well as precipitation were collected monthly in the period 2005-2006. Tritium measurements have been performed at the Laboratory for Measurements of Low-level Radioactivity of the Rudjer Bošković Institute, Zagreb, while stable isotope δ18O measurements were carried out at the new stable isotope facility (Environmental Physics Laboratory) at Rijeka University.

In the time period under study, δ18O in the Gacka precipitation is (–8.7 ± 2.1‰) with seasonal fluctuations typical for continental stations in the area. δ18O fluctuations in the spring waters are much smaller, indicating well-mixed waters. The three springs have fairly different δ18O-values although they are located at approximately the same altitude. This indicates that their catchments lie at different altitudes.

The spring water temperatures and flow rates show no direct correlation with the ambient temperature and the amount of precipitation. Large precipitation amounts in August and December 2005 have apparently no immediate effect on the spring δ18O-values. A weak seasonal variation again indicates a delayed response and good mixing.

The seasonal tritium distribution for the precipitation in the Gacka area is well correlated with that in Zagreb, the closest GNIP continental station. All three main springs show similar mean tritium concentrations, but much smaller seasonal variations than precipitation, indicating a short mean residence time and good mixing of infiltrated and ground water.

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Indoor radon and lung cancer risk in Romania

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After smoking, radon represents the second cause of risk in releasing of pulmonary cancer. This fact was clearly demonstrated by many cohort studies on miners working in uranium and non-uranium mines (National Research Council). In 2005 a big European pooled study has clearly shown the risk of lung cancer due to indoor radon exposure for all population (Darby et al., 2005).

The origin of the common cancer was still predominantly viewed as environmental in 1980. This view was based on the studies from the 1960's and 1970's, that identified large differences in the incidence of specific cancer among populations, and that showed that the immigrants acquired the pattern of cancer risk of their new country (Balmain et al., 2003). Cancer cells often lose their normal primary function and start behaving like rapidly growing embryonic cells rather than fully mature skin or liver or breast cells, in which growth is slow and regulated. They replicate without regard to the signals that normally indicate when it is appropriate to divide. These cells have damaged mechanisms for repairing DNA errors and often have even lost the fail-safe mechanisms that normally eliminate highly damaged cells.

In Romania, more than 1200 measurements for radon exposure are available at this moment (Cosma et al., 1996; Iacob et al., 2005). Based on these data and on the last radon - lung cancer risk factor from Balmain et al. (2003), we make an estimate of the annual rate of lung cancer cases due to radon exposure in Romania. Our data for Bihor and Cluj counties show the same relative radon - lung cancer risk as the above-mentioned study.

A small epidemiological pilot study regarding radon exposure and lung cancer risk in Transilvania was started in 2006 in the Stei area (Bihor county). Based on a number of measurements, a high radon exposure for population was estimated. The measurements were made using CR-39 track detectors and the average radon concentration was found to be of about 280 Bq/m³. The total number of cancer cases was 161 in the 1994 - 1998 interval for a population of about 24,000 and it may be extrapolated that for a 12-year period (1995 – 2007) this number is 320. If lung cancers are counted, as about 25% of the total cases are this means about 80 deaths are due to the lung cancer. This situation is similar with a region from Bulgaria where a small study has shown a risk for radon - lung cancer similar with other European studies (Preseyanov, 2001).

References

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Romanian wines characterization with isotopic analysis, in concordance with the Europeans standard

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Wine growing has been known for centuries long in Romania. The country has been favored by its geographical position in the south-eastern Europe, by its proximity to the Black Sea, as well as by the specificity of the local soil and climate. Alongside France, Italy, Spain, Germany, countries in this area like Romania could also be called "a vine homeland" in Europe. High quality wines produced in this region were object of trade ever since ancient times. For this reason, the Romanian wine industry has now a huge potential for a significant impact in the near future.

Under current European Union research projects, is necessary to develop the new methods of identifying evidence for wine adulteration and safety. The use of mass spectrometry (MS) to determine the ratios of stable isotopes in bio-molecules now provides the means to prove the botanical and geographical origin of a wide variety of foodstuffs – and therefore, to authenticate and eliminate fraud. The European Union, as a means of controlling adulteration of wine has officially adopted isotope analysis. Adulteration of wine can happen in many ways, e.g. addition of non-grape ethanol, addition of non-grape sugar, water or other unauthorized substances, undeclared mixing of wines from different wards, geographical areas or countries, mislabeling of variety and age.

The present paper emphasize the isotopic analysis for D/H, \(^{18}\text{O}/^{16}\text{O}\), \(^{13}\text{C}/^{12}\text{C}\) from wines, using a new generation Isotope Ratio MS, Finnigan Delta V Plus, coupling with a three flexible continuous flow preparation device (GasBench II, TC Elemental Analyser and GC-C/TC).

Authentication of wines is an important problem to which isotopic analysis has made a significant contribution. There is a strong need for reliable and validated methods to ensure compliance with such regulation and to protect the interests of the consumer.
Preliminary results in the study of the ecosystems in polar areas using stable isotopes

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This preliminary study was performed on ice and snow samples collected in the Antarctic area between the Growe Mountains (73° 06' 01'' S; 75° 14' 13'' E) and the coastal area (69° 23' 16'' S; 76° 22' 47'' E). The sampling interval was November 20, 2002 to March 24, 2003. The isotopic composition of hydrogen was carried out with a homemade mass spectrometer on the hydrogen gas obtained by quantitative reduction of water sample. The isotopic composition of oxygen was measured with an isotope ratio mass spectrometer type Atlas 86. All the samples have the specific values for the polar area. We have found the deuterium content in excess with negative values. These values ranged from -30‰ to -60‰. This result shows the evaporative origin of the samples. We have correlated the values of δD and δ¹⁸O with the temperature of the air at the time when the samples were collected and we have found that the decrease of the δD and δ¹⁸O values corresponds with the decrease of the temperature.
Isotope ratio mass spectrometry: analysis of wines from different Romanian regions

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The authenticity and geographical origin of some wines produced in Romania were investigated by isotope ratio mass spectrometry (IRMS) methods. We have developed the method for determining $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O in wine ethanol and water from wine. The determination of $^{13}$C/$^{12}$C of wine ethanol was performed in three steps: (i) 500 ml of a wine sample was distilled with a distillation apparatus with a constant reflux ratio of 10. The alcoholic distillate was collected with an ethanol content of about 93 % mass without significant isotope fractionation. (ii) The ethanol was converted into CO$_2$ by combustion in excess of oxygen. (iii) The carbon isotope ratio of the CO$_2$ obtained was analyzed by IRMS. The $^{18}$O/$^{16}$O isotopic ratio of the water of wine was determined by IRMS using CO$_2$, which was obtained after equilibration of wine and carbon dioxide. The samples of wine from the 2002, 2003, and 2004 vintages and from six different wine-growing regions of Romania were analyzed and the authenticity of these wines was tested.
$^{11}\text{B}/^{10}\text{B}$ measurements by negative ion mass–spectrometry

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A number of papers show procedures for simple and precise measurements of boron isotope composition in natural samples (Aggarwal & Palmer, 1995, and references therein).

In our measurements of boron isotope composition, we used in the single ion source PtRh and Re filaments and BaCl$_2$ as an activator. By monitoring spectrum at mass 26 (CN$^-$ ions) using PtRh filament, we observed a significant interference at mass 42 (BO$_2^-$ with CNO$^-$ ions). Platinum is a good catalyst for organic ion production. This effect can be reduced by burning off all the organics during loading the sample by heating it in air to a dull red color (700ºC). The use of rhenium filament leads to a lower interference effect, but after burning off the organics, we have to use a temperature considerably higher to get sufficient ion current, because the rhenium material suffers some oxidization.

For the NIST–SRM 951 standard and Mediterranean Seawater we have obtained 4.0300 ± 0.0028 and 4.1760 ± 0.0090 for $^{11}\text{B}/^{10}\text{B}$ ratio, respectively. These results are in good agreement with literature values (Sonoda et al., 2002; Gonfiantini et al., 2003). An example of a mass spectrum obtained with our TIMS is shown in the figure to the right.

References


Possible paleoclimatic record from fossil hydrothermal systems in the Ross Sea area (Antarctica)

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During Cenozoic time, diffuse alkaline magmatism related to the rifting in the Ross Sea Embayment intruded the northeastern region of the Wilson Terrane, Antarctica. Plutons with syenitic-monzonitic to gabbroic compositions provided the necessary heat source for local hydrothermal systems to occur in fractured rocks.

Oxygen and hydrogen isotope investigation of altered granitoids along the Ross Sea coastline were undertaken to constrain the characteristics of Eocene fossil hydrothermal systems. The δ¹⁸O values, as low as 4‰ in K-feldspar of country rocks, and the δD values of biotite/amphibole in the range of -100‰ to -200‰, indicate that these minerals interacted with meteoric-dominated hydrothermal waters. The δ¹⁸O and δD values of minerals were used to reconstruct the isotopic composition of the meteoric - hydrothermal waters.

Altitude, latitude, local climate conditions and tectono-thermal histories were similar for the different outcrops; thus the hydrogen isotope composition of hydrothermal minerals was used as a proxy for paleoclimatic reconstructions, provided the water-vapor hydrogen fractionation in the atmosphere is temperature-dependent. Isotopic compositions for recharge hydrothermal waters could be calculated for a fairly continuous time interval, between 52 and 26 Ma. These compositions suggest that cold-climatic episodes were recorded in hydrothermally altered rocks, coherently with the climate evolution defined by high-resolution oceanic proxies.
Radioisotopes used for medical applications

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Radionuclides are often used in medicine diagnosis, clinical chemistry, molecular biology, and other life science fields. The isotopic neutron sources of $^{241}$Am - $^9$Be and $^{239}$Pu - $^9$Be and the cyclotron are normally used for the production of some radioisotopes of medical interest such as: $^{116m}$In, $^{56}$Mn, $^{198}$Au, $^{61,64}$Cu.

The $^{64}$Cu and $^{61}$Cu radioisotopes are often used in nuclear medicine for PET imaging and radio-immunotherapy of tumors by the way of deuteron particle bombardment of enriched $^{64}$Zn target. The radioisotope $^{64}$Cu is both a positron and a beta emitter and is already used for labeling of PET imaging radiopharmaceuticals.

In order to study the production of $^{64}$Cu and $^{61}$Cu, the stacks consisting of $^{64}$Zn foils, Ti monitor foils and Al catcher foils were irradiated at a Scanditronix MC40 cyclotron with a 19.5 MeV deuteron beam energy. The activities of the various product isotopes in the foils were analyzed by $\gamma$-spectrometry with HPGe detectors. The average deuteron energies in the foils were calculated with the SRIM 2003 code. Theoretical excitation functions calculated with the Alice91 code were compared with the experimental ones and a reasonable agreement was found. This study provides the first experimental data regarding the deuteron induced $^{64}$Zn(d,2p)$^{64}$Cu and $^{64}$Zn(d, an)$^{61}$Cu reactions on enriched $^{64}$Zn.
Application of sulphur isotope ratio for evaluation of SO$_2$ emission in the combustion process

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Historical data for Europe show increasing emissions, and consequently deposition, of sulphur, up to a factor of 2 in 1950 and 3.5 in 1980 in comparison to pre-industrial levels (Posch et al., 1996). Attention now focuses on global environmental issues, in particular on the contribution on European emissions of precursors to climate changes.

There are no known methods besides sulfur isotope abundance ratio measurements used to investigate the fate of anthropogenic sulfur in the environment.

The stable isotopes sulfur composition in compounds of anthropogenic origin, present in atmosphere, biosphere, hydrosphere, groundwater, soil, etc., may differ from those originating from natural sources. The sulfur cycle plays a key role in the hydrochemical development of lignite and coal mining districts. Identification of sulfur sources and transformations is essential to investigation of pollutants in the mining areas. Sulfur isotope ratio can be treated as an environmental tracer, and may be applied to study the sulfur pollution distribution from coal mining and combustion processes, in the environment.

The study presented in this paper uses a different approach. One of the study reports on sulfur isotope ratio in lignite and products from lignite combustion measurements. This subject is important because products from combustion, ash and gypsum are stored in open corridors of the mine. Sulfur, which occurs in these products, can be diluted by rain and finally can be detected in groundwater. This process may cause changes of sulfur isotope composition. The objective of this study was to use sulfur stable isotopes as a marker in monitoring pollutants pathways in the biggest Polish complex electro power – coal mine Belchatow. Major goals were identification of sulfur sources and its influence for the surrounding area.

Reference

Speleothem carbon isotopes and ecosystem changes

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The carbon isotopic values ($\delta^{13}C$) of speleothem carbonate are related to the primary sources of carbon in the cave seepage water. These sources are soil carbon dioxide, sourced from root respiration and microbial respiration and tied indirectly to atmospheric carbon dioxide by photosynthesis, and carbonate bedrock. Timescales of major karst development are typically on the order of $10^4$-$10^6$ years, implying that variations in speleothem $\delta^{13}C$ on shorter timescales could likely be due to changes in the soil carbon pool, which is tied to vegetation. $C_3$ and $C_4$ photosynthetic pathways produce large differences in the $d^{13}C$ values of plant tissue. $C_3$ plants have $\delta^{13}C$ values averaging ca. $-26\%$o, whereas $C_4$ plants average ca. $-12\%$o. $C_4$ plants are typically warm-season grasses and a few herbs found in tropical and temperate grasslands, whereas $C_3$ plants are mostly trees, shrubs, cool-season grasses, and most herbs. Within their ranges, both proportion and biomass of $C_4$ plants in North American grasslands are highly correlated with mean annual temperature and less strongly correlated within mean annual precipitation.

A cautionary note in interpreting speleothem $\delta^{13}C$ values is necessary, however, because other processes may mask the primary environmental signal of vegetation. These processes largely fall into the category of kinetic processes and/or evaporative conditions during calcite crystallization. Hendy (1971) distinguished such kinetic effects from the more desirable ‘isotopic equilibrium’ condition, that is, the condition defined by sufficiently slow degassing rates, and with no evaporation, such that the fractionation of heavy and light isotopes between aqueous and solid phases is only a function of temperature. There is no absolute test for the absence of these masking processes. However, a necessary condition for their absence is a demonstration that two or more speleothems have similar isotopic profiles. Replication is possible among spatially separated speleothems only if these masking processes have affected different drips in exactly the same way. As this is unlikely, replication provides a test for these additional processes. Thus, if different speleothems record identical isotopic compositions through time, this suggests that kinetic/vadose zone processes are not significant, and that the record can be interpreted as a primary environmental record, and possibly one of vegetation change.

Tropical and temperate grasslands throughout the Americas, Africa, and Asia occupy large areas of the Earth and many include $C_4$ grasses. Grasslands and savannas may have important links to climate through the carbon cycle, as the deep root systems of many grassland species sequester large amounts of carbon in the soil. $C_4$ grass distribution in the past and its role in the carbon cycle has been little studied. Carefully interpreted, high-resolution speleothem $d^{13}C$ records are capable of providing reconstructions of past vegetation trends into regions and time periods for which basic data are lacking.
Reference

Diurnal variations of sulphate concentration and sulphur isotopic composition (δ^{34}S) of sulphate ion in the Sulejow reservoir

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The research concerns diurnal variations of dissolved sulphate ion concentration (C(SO\(_4^{2-}\))) and sulphur isotopic composition (δ\(^{34}\)S (SO\(_4^{2-}\))) of this ion. Series of daily water samples were collected twice: in summer (July 26\(^{th}\) - 27\(^{th}\) 2006) and winter (February 2\(^{nd}\) - 3\(^{rd}\) 2007) from the Sulejow dam reservoir (Central Poland).

Clear, regular diurnal variations of sulphate ion concentration have been observed in both summer and winter. C(SO\(_4^{2-}\)) varied from 20.2 mg dm\(^{-3}\) at 02:00 to 23.6 mg dm\(^{-3}\) at 10:00 in summer and from 18.31 mg dm\(^{-3}\) at 02:00 to 27.63 mg dm\(^{-3}\) at 20:00 in winter. Similar, but less distinct, diurnal variations of sulphur isotopic composition (of about 1‰) have been noted. δ\(^{34}\)S (SO\(_4^{2-}\)) varied between 4.44‰ at 10:00 and 5.39‰ at 02:00 in summer and between 2.21‰ at 08:00, and 3.31‰ at 20:00 in winter.

Average values of C(SO\(_4^{2-}\)) in both investigated seasons were near identical, i.e. 22.4 mg dm\(^{-3}\) in winter and 22.6 mg dm\(^{-3}\) in summer. The average value of δ\(^{34}\)S (SO\(_4^{2-}\)) in winter was 2.80‰, in contrast to higher summer values achieving 4.87‰, indicating an enrichment of sulphates in heavy sulphur isotopes in summer compared to winter. It could be caused by the supply of sulphate ion enriched in heavy sulphur isotopes from tributaries or from the surrounding crop fields in summer. Simultaneously, the increase of the δ\(^{34}\)S (SO\(_4^{2-}\)) value in summer was negatively correlated with the sulphate ion concentration. This appears to indicate an assimilative sulphate reduction by phytoplankton during the period of intensive cyanobacterial bloom. In this process, lighter sulphur isotopes are preferentially assimilated, leading to an enrichment of heavier isotopes in the residual sulphate.

Positive correlation between C(SO\(_4^{2-}\)) and δ\(^{34}\)S (SO\(_4^{2-}\)) (R\(^2\) = 0.44, n = 7) was noticed in winter, suggesting an extra pool supply of sulphate ion enriched in heavy sulphur isotopes. A potential source of these sulphates could be the oxidation process in the bottom of the reservoir or external sources such as tributaries or surrounding coniferous forests.
230Th and 231Pa-excess geochronology of manganese nodules

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The geological age of a manganese nodule, collected from the Clarion-Clipperton region of the North Pacific Region has been determined by means of 230Th and 231Pa-excess radiometric methods. The distribution of the α-activity over a transverse section of the nodule has been performed by using cellulose-acetate CR 37 detectors, while the concentration of the fissile elements has been achieved, for the same section, by means of muscovite detectors, following neutron irradiation. For both cases we have obtained a map of trace distribution, whose density is higher on marginal zones and decreases gradually towards the background for the lower part of the nodule and abruptly for the upper one.

By taking into account the radial distribution of traces, we have calculated for the external layers, rich in traces, an average growth rate of 20 mm/Ma. More details are presented concerning the experimental technique as well as the peculiarities of trace distribution over the entire investigated section.
Modeling seasonal variations of carbon isotope compositions ($\delta^{13}C$) in tree-rings and CO$_2$-respired by the trunk

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Carbon isotope composition ($\delta^{13}C$) of plant material and respired CO$_2$ are widely used to assess the effect of climatic conditions on plant ecophysiology. First of all, these are largely affected by the atmospheric CO$_2$ signature (about -8‰) and by fractionation processes occurring within the plant, in particular during photosynthesis (Farquhar et al., 1989) and respiration (Tcherkez et al., 2003). $\delta^{13}C$ is usually interpreted using a model of photosynthetic discrimination described in Farquhar et al. (1989). However, this model does not fully explain $\delta^{13}C$ seasonal variations in tree-rings (Porté & Loustau, 2001) and CO$_2$ respired by the trunk (Maunoury et al., 2007). Carbon allocation and compartmentalization among tree organs have a role in this seasonal variability (Damesin & Lelarge, 2003). For example, starch is generally $^{13}C$-enriched compared to soluble sugars. Its synthesis, mobilization for growth and turnover directly influence the $\delta^{13}C$ of the other compounds.

A model integrating known C fractionation processes, carbon allocation and C stock compartmentalization among tree organs has been developed. This model is coupled with CASTANEA (Dufrêne et al., 2005), a forest ecosystem model simulating carbon balance (photosynthesis, growth and respiration) and drought effects on canopy stomatal conductance from climatic data at a half-hourly time-scale. Five organs are described: leaves, branches, trunk, coarse roots and fine roots. C stocks are split into starch and soluble sugars within each organ. Simulated isotope compositions are compared to measurements carried out in an oak forest (Barbeau, France) during the year 2003. These measurements consist of the $\delta^{13}C$ of total organic matter, soluble sugars and starch in leaves and branches, the $\delta^{13}C$ of total organic matter in tree-rings and the $\delta^{13}C$ of CO$_2$ respired by the trunk.

The proposed model will improve our understanding of the factors influencing C isotope compositions variability in tree-ring bulk matter and respired CO$_2$. The development of a discrimination model that allows the simulation of $\delta^{13}C$ in both respired CO$_2$ and tree-rings will have implications for separating the different ecosystemic respiration components and improving paleoclimatic reconstruction (dendroclimatology).

References


Reconstructing the Holocene climate record in western USA based on $\delta^{18}$O and $\delta^{13}$C in speleothems

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The Pacific Northwest region of the United States is strongly influenced by the Pacific Ocean, which has been one of the strongest sources of regional-to-global climate variability during the Holocene. Although the modern spatial patterns of climate fluctuations affecting the Pacific basin at seasonal, interannual, and decadal timescales are reasonably well understood, the relative brevity of the instrumental record (~120 years) and of the tree ring record (~1000 years) limits our understanding of how this variability may have changed on longer timescales. Given the major influence that the Pacific Ocean exerts on regional-to-global climate, it is particularly important to address this question in order to understand the past role of the Pacific on past climate of North America, as well as its potential role in future climate change.

Here we present a high-resolution reconstruction of Holocene climate using stable isotopes in speleothems from Oregon Caves National Monument (OCNM) in southwestern Oregon, USA (42ºN, 123ºW). OCNM is strongly influenced by air masses originating in the Pacific Ocean and is strategically situated in an area where storm track are entering North America.

$\delta^{18}$O measurements of meteoric waters collected above the cave site indicate a temperature-dependent fractionation of 1.3‰/°C, which is higher than the fractionation between water and calcite (-0.2‰/°C), suggesting that the $\delta^{18}$O of OCNM speleothems is strongly influenced by temperature. The climate of southern Oregon is characterized by relatively warm and dry summers associated with high pressure over the North Pacific, and cool and wet winters that occur in response to an intensification of the Aleutian low pressure cell. Because of seasonality of precipitation our speleothem record reflects mostly changes in the cool season climate. The speleothem reconstruction indicate that for the past 9000 years the climate of southwestern Oregon was characterized by a general warming trend, consistent with an increase in winter insolation at 45ºN. Superimposed on this trend there is higher frequency variability at centennial to multi-decadal timescales, which for the past 1000 years seems to be correlated with tree-ring reconstructions of Northern Hemisphere temperature. The period corresponding to the Medieval Warm Period (~800 to 1300 AD) is characterized by two warm periods centered at 1010 and 827 AD interrupted by a cooler period centered at 955 AD. Similarly, the Little Ice Age (~1350 to 1850 AD) is not very clearly expressed in our record, this period being characterized by significant decadal and centennial variability with both warmer and cooler intervals.
Molecular and isotopic records of the Permian-Triassic transition at the Mt. Velebit, Croatia

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During the Middle/Late Permian and Early Triassic, a continuous shallow water deposition took place at the eastern shelf of the Pangaea. Part of these carbonate rocks outcrop today in the central part of the Mt. Velebit, Croatia. The prevailing rock type is dolomite (70 to 99 wt% of CaMg(CO₃)₂), represented by two lithological units: Transitional Dolomite and Sandy Dolomite, with a narrow intercalation of oolitic dolomite in between.

Detailed paleontological, isotopic, organic, and inorganic geochemical studies have been carried out for this section, in order to investigate the environmental changes. Fossil communities show the evidence of two biotic crises, one that coincides with a lithological change in the Upper Permian, and the other accompanied with the pronounced negative shift in ¹³Cᵩ by up to 3‰ (VPDB), which is probably the consequence of global extinction at the Permian-Triassic transition. Upper Permian values for ¹³Cᵩ vary between −0.8 to +2‰, with an average of +1.2±0.5‰, while Lower Triassic values range from −1.3 to +0.9‰, with an average of 0.0±0.5‰. At the transition level, ¹³Cᵩ is +1.4 to 0.6‰, and on average 0.4±1.4‰. ¹⁸Oᵩ values in the Upper Permian range from −3.2 to −1.3‰, with an average of −2.6±0.4‰, and in the Lower Triassic from −3.2 to −2.2‰, with an average of −2.7±0.3‰. This uniform slow decrease in ¹⁸Oᵩ values is probably due to an enhanced terrigenous input towards the P/Tr transition and in the Lower Triassic. Upper Permian ¹³C for kerogens vary from −27.3 to −24.4‰, average −25.8±0.9‰. The values at the transition level are −27.0 to −27.1‰, and the Lower Triassic values range from −29.1 to −26.4‰, with an average of −27.5±0.4‰. The range of ~4.7‰ is probably a result of the variations in the primary composition of the organic matter. A constant decrease in the values of ¹³Cᵩ is accompanied with the negative trend of ¹³C for carbonates. The value of ¹³Cᵩ-ker shows the same trend as the ¹³Cᵩ and ¹³Cᵩ, indicating lower productivity at the Permian-Triassic transition, and a primary source for inorganic and organic signals, with no secondary change. ¹⁵N values for the Upper Permian samples are −0.7 to +8.2‰, with an average value of +3.7±2.8‰, for the transition samples −0.7 to +0.8‰, average 0.0±1.0‰, and for the Lower Triassic samples +0.3 to +6.9‰, average +3.8±2.0‰. Altogether, values for the ¹⁵Nker vary between −2.4 and +8.2‰, pointing to a mixed contribution of ¹⁵N-rich marine (~7‰), mostly in the Upper Permian, ¹⁵N-depleted terrestrial (~0‰) organic materials
towards the transition, and cyanobacteria (−2 to +4 ‰) at the transition level and in the Lower Triassic.

The distribution of $n$-alkanes (C$_{13}$ to C$_{34}$), acyclic isoprenoids (C$_{21}$ to C$_{28}$), hopanes and steranes indicate input of bacterial and algal biomass, however there is no pronounced change between the Late Permian and Early Triassic samples. Odd long-chain $n$-alkanes (maximizing at C$_{26}$) and C$_{39}$ steranes confirm the important contribution of continental debris. Results of compound-specific C isotope analyses of alkanes indicate an increase in $^{13}$C values after the transition, showing gradual recovery of biota after the extinction event.
Compound-specific stable isotope analysis (CSIA) for monitoring *in situ* benzene biodegradation in contaminated aquifers

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Benzene is a groundwater pollutant of specific concern, since it causes a significant health risk due to its widespread occurrence, relatively high water solubility and toxicity. Biodegradation is the only *in situ* process leading to a decrease of benzene concentrations in groundwater coupled to a sustainable mass removal of the contaminant. Therefore, the evaluation of *in situ* biodegradation of benzene is essential for the implementation of groundwater management strategies such as Natural Attenuation (NA).

In recent years, compound-specific stable isotope analysis (CSIA) has gained more and more attention as a tool for characterizing and assessing *in situ* biodegradation of organic pollutants in contaminated aquifers. This concept relies on the stable isotope fractionation occurring during the microbial degradation leading to an enrichment of heavier stable isotopes in the residual fraction of a contaminant. Thus, the observation of isotope ratio shifts for carbon, hydrogen or other elements that are involved in cleavage or generation of chemical bonds during the initial step of microbial transformation can be used as an indicator for *in situ* biodegradation.

In the present study, CSIA was applied to investigate biodegradation of benzene within an aquifer located in the area of a former hydrogenation plant close to the city of Zeitz (Saxony-Anhalt, Germany). Based on multi-level sampling, we determined the vertical and horizontal distribution of carbon and hydrogen isotope ratios of benzene within the contaminant plume. Furthermore, the carbon and hydrogen isotope fractionation associated to microbial benzene degradation was investigated in laboratory experiments with anaerobic enrichment cultures from the field site and aerobic pure cultures. In agreement with recently published studies, our results showed that aerobic and anaerobic benzene degradation lead to nearly the same carbon isotope fractionation but to significantly different hydrogen isotope fractionation. Hence, it is possible to distinguish between aerobic and anaerobic benzene biodegradation in the field by means of carbon and hydrogen isotope ratio analyses. Our field data provided evidence for anaerobic degradation of benzene especially at the fringe of the contaminant plume. Changes in carbon isotope ratios were used to quantify the *in situ* biodegradation of benzene using the Rayleigh equation. Furthermore, the applicability of the Rayleigh equation for the assessment of *in situ* biodegradation was investigated and showed limitations and advantages of this concept. In conclusion, our investigations show that CSIA is a useful tool for monitoring *in situ* biodegradation of benzene in contaminated aquifers.
Isotopic composition of precipitation sulphates as an indicator of pollutant origin in Wrocław (SW Poland) precipitations

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This paper describes results of isotopic analyses of (i) hydrogen and oxygen in water (δD_H2O and δ18O_H2O) and (ii) sulphur and oxygen of sulphates (δ34S_sulphate and δ18O_sulphate) from precipitation collected during a one-year period (May 25th, 2004 to May 25th, 2005) in Wrocław (SW Poland). The city of Wrocław has ca. 640,000 inhabitants and is situated on the Odra River on the foreground of the Sudety Mountains. The average annual precipitation reaches 583 mm, and predominant wind directions in Wrocław are south and west.

Monitoring the concentration of sulphates in precipitations has been carried out by the Institute of Meteorology and Water Management (IMWM department of Wrocław) for several years. The IMWM data present only information about the quantity of sulphates in precipitation and do not inform about the origin of pollutants. Our sulphate concentration measurements, ranging from 1.84 to 19.66 mg/l (average 9.17 mg/l), combined with isotopic analyses, allowed us to answer two questions: (i) what is the equation of LLWM (Local Meteoric Water Line) in Wrocław; and (ii) what are the main sources of sulphates in the Wrocław precipitation.

The obtained δD_H2O and δ18O_H2O values of the precipitation in Wrocław range from -115.3 to -8.3‰ (average -52.9‰) and from -16.3 to -0.8‰ (average -8.2‰), respectively. The resulting equation for LMWL for Wrocław is δD = 6.83*δ18O + 3.10, (r²=0.97, n=32). The rotation of the LMWL in relation to the Global Meteoric Water Line (GMWL) may vary annually and seasonally depending on variations in conditions (summer versus winter) of formation of the source water vapor (mostly over the North Atlantic). Accordingly, there are positive correlations between δD_H2O and δ18O_H2O values and air temperature (r²=0.44 and 0.49, respectively).

The δ34S_sulphate varies from 1.1 to 4.2‰ (average 2.5‰) and δ18O_sulphate varies from 9.0 to 16.7‰ (average 13.8‰). The data of oxygen isotopic analyses of water and sulphates indicate two main sources of sulphates in Wrocław precipitation:

1. low-temperature sulphates forming in situ in Wrocław from atmospheric SO2 and precipitation water, supported by δ34S_sulphate ~2.5‰ and a positive correlation between δ18O_sulphate and δ18O_H2O (r²=0.82);
2. high-temperature sulphates forming in rapid SO3 high-temperature hydration in the immediate proximity of industrial chimneys, supported by a much different δ34S_sulphate than the locally typical value of 2.5‰ and by
the much weaker correlation between $\delta^{18}$O$_{\text{sulphate}}$ and $\delta^{18}$O$_{\text{H}_2\text{O}}$ of the local precipitation water ($r^2=0.49$).

We hypothesize that the first, low-T generation of sulphates forms from local sulphur and oxygen reservoirs, whereas the second high-T generation is allochthonous and is probably transported from industrial centers outside of Wroclaw.
Sulfur isotopes of Precambrian sulfates and sulfides in the Fedorovskaya Formation (Aldan Shield, Yakutia)

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The isotopic analyses of Precambrian sulfates and sulfides may provide important information about the chemical compositions of Precambrian oceans with respect to the evolution of the Earth's biosphere and atmosphere. Sedimentary sulfates in Precambrian rocks are direct evidence that free oxygen was an important component in the atmosphere-hydrosphere system at that time and they may be reflections of evaporite deposition in old sedimentary basins.

Rocks with sulfates were early identified in the Fedorovskaya Formation on the Aldan Shield by Vinogradov et al. (1975). Geological exploration works at the Seligdar apatite deposit and prospecting of analogous objects in other sectors of the Aldan Shield revealed a wide distribution of sulfur-containing phases in metamorphic sedimentary rocks of the Fedorovskaya Formation, which are represented by carbonate and calc-silicate varieties. They conformably intercalate with gneisses and crystalline schists and have similar structural styles. The rocks are metamorphosed to the granulite and amphibolite facies, and their U-Pb age is 1.8 – 2.0 Ga.

This paper presents results of the systematic study of sulfur isotopic compositions in sulfur containing mineral phases, which commonly are heterogeneous and composed of several generations. Gypsum, anhydrite, celestine, and pyrite for the analyses were collected from the borehole cores of the Seligdar, Mustolaakh, Birikeen and Chukurdan apatite deposits. Samples of barites and scapolites came from outcrops of the Hematitovoe and Bish deposits, accordingly.

First generations of anhydrite form concordant layers, lenses or segregations in marbles, gneisses and geologically oldest sulfate-bearing apatite-carbonate rocks underlying the Seligdar ore body. Last generations of the sulfates form pods and branching veinlets in the apatite–bearing carbonate rocks of the Seligdar deposit with a thickness of 1.5 – 5 cm, and veins up to 3 – 5 m thick. Fine-grained and platy gypsum, white and pink in color, predominates over anhydrite, which concentrates toward the axial portions of the veins and forms aggregates of tabular burred crystals of lilac color. At the Mustolaakh, Birikeen and Chukurdan deposits sulfates were sporadically found in borehole cores as separated nets and clear late veins.

Three generations of barite and scapolite occur in barite-quartz-hematite ores and apatite-scapolite-diopside ores. Minerals of the first generations are smaller in size (1 – 2 mm), scattered in the ores, while minerals of the last generations form big crystals (up to 5 cm).

The studied minerals are characterized mainly by positive δ³⁴S values (up to +32.1‰) while pyrites have δ³⁴S values from -3.5 up to +3.9‰. Very low, but positive δ³⁴S
values (0.2 – 3.6‰) are determined for scapolites and relatively low values (5.7 – 10.6‰) for barites. Isotopic compositions of first generation anhydrites give $\delta^{34}$S values from 5.4 to 6.9‰. The following generations have distinctly higher values, from 20.3 to 32.1‰. The studied gypsums and celestines are characterized by similarly high $\delta^{34}$S values (22.5 - 30.1‰) and (24.0‰), respectively.

The isotopic investigations showed that the first generations of minerals commonly have more heavy sulfur isotopic compositions. Preserved primary sedimentary rocks generally contain the original sulfates, which is in accordance with the C and O isotopic records of coexisting carbonates, universally enriched in $^{13}$C. Apatite-sulfate-carbonate rocks are the products of complex alternation of sedimentary processes at different basin salinity regimes, occasionally marked by the decomposition of older sediments under subaerial conditions. High $\delta^{34}$S values in the later generations of sulfates are connected with the enrichment of the later carbonates in light carbon and oxygen isotopes. They were produced by post sedimentation alterations under the effect of surface waters and/or metasomatic processes.

Reference

About isotope equilibrium between vapor and liquid phases

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Being inspired by a discussion with Professors Max Wolfsberg and Gábor Janscó, I would like to reconsider the topic on isotope equilibrium between vapor and liquid phases. I will present a novel viewpoint, which may significantly simplify the mathematical description of $10^3 \ln a$ over the whole temperature range, i.e., from melting to the critical point of liquid.

Some examples of such calculations for geochemically important fluids will be presented.
Flexible inlet system for on-line compound-specific \( \delta D \) and \( \delta^{13}C \) analyses of natural gases

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Compound-specific \( \delta D \) and \( \delta^{13}C \) values in natural gases can provide geochemical diagnostics for (i) processes involved in formation of natural gas, (ii) biodegradation of gas species, and (iii) fractionation via migration/diffusion. The relative concentrations of individual components of natural gases (e.g., \( H_2 \), \( CO_2 \), methane, ethane, propane, \( i \)-butane, \( n \)-butane) may vary over several orders of magnitude. The determination of hydrogen and carbon compound-specific stable isotope ratios requires that the hydrogen and carbon dioxide peak heights for each component are properly adjusted to match the dynamic range of the stable isotope mass-spectrometer. We present a custom-built gas inlet system (GASIS) linked with a Delta Plus XP mass-spectrometer that provides flexibility, ease of operation, and economic use of small gas samples with wide ranges of analyte concentrations.

The overall on-line GC-IRMS system consists of (i) a customized GASIS inlet system and two alternative reactors, namely (ii) an oxidative Cu-Ni-Pt reactor at 950ºC, and (iii) a reductive graphitized \( Al_2O_3 \) reactor at 1420ºC. In addition, the system is equipped with (iv) a liquid nitrogen spray-cooling unit for -20ºC cryo-GC-focussing, and (v) a Nafion® dryer. The GASIS inlet system's three injection loops allow flexibility in the volume of injected analyte gas (e.g., from 0.06 µl to 500 µl) in order to measure reproducible \( \delta D \) and \( \delta^{13}C \) values for gases at concentrations ranging from 100% down to 10 ppm. We calibrate our GC-IRMS system with two isotopically different methane reference gases from cylinders, as well as with isotopically defined \( CO_2 \) and \( H_2 \) reference gases (all calibrated off-line against VSMOW, SLAP, NBS-19 and L-SVEC). We use our two methane reference gases for generating regression lines, monitoring the \( H_3 \)-factor, as well as for correcting for day-to-day variability as part of the analytical routine procedure. Pre-analytical daily conditioning of reactors is necessary; the oxidative reactor requires overnight oxidation at 550ºC, and the reducing reactor receives an initial graphitic coating of the \( Al_2O_3 \) ceramic tube via carbonization of injected hydrocarbon gas. Practical environmental and geochemical applications will be discussed.
Diurnal variations in the photosynthetic activity of cyanobacterial bloom on a freshwater dam reservoir: an isotopic study

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The aim of our study was to assess the role of the cyanobacterial bloom in a lowland artificial freshwater reservoir. The investigated Sulejowski reservoir was constructed in 1973 by damming the Pilica River (central Poland). It is a typical eutrophic lake with annual summer blooms, which constitute a serious constraint to using the reservoir as a drinking water source and recreation center.

Sampling has been carried out on a diurnal basis (sampling every 4 hours during 32 hours) at the time of the most intensive bloom on the July 26-27 2005 (depths: 0 m, 3 m, 6 m). The following geochemical parameters have been measured: the isotopic composition of the oxygen dissolved in water (δ¹⁸O(DO)), of the oxygen from the water molecule (δ¹⁸O(H₂O)) and of the dissolved inorganic carbon (δ¹³C(DIC)), dissolved oxygen concentration (DO), dissolved inorganic carbon concentration (DIC), as well as the content of organic matter (OM), the total nitrogen concentration (TN) and the total phosphorus concentration (TP). This was done to better understand dynamics of photosynthesis, respiration, and decomposition as well as to trace the diurnal variations in cyanobacteria biological activity. DO varied at night from 10.10 to 10.39 mg/l and during the day from 10.49 to 13.85 mg/l as a result of photosynthesis. It can be expected that cyanobacteria activity results in a measurable isotopic effect. The δ¹⁸O(DO) varies in the range of 15.5 to 20.2‰, which is significantly lower than δ¹⁸O(DO) representing air-water equilibrium (δ¹⁸O(DO)ₑₒₚ = 24.2‰). Such a pronounced enrichment in ¹⁸O is due to photosynthetic oxygen production by cyanobacteria. Cyanobacteria decompose water (δ¹⁸O(H₂O) ranges from -8.65 to -8.14‰), hence adding ¹⁸O - depleted DO. The lowest δ¹⁸O(DO) value has been obtained at 10:00 in the surface water sample (16.0‰), and at 14:00 in the sample from 3 m depth (15.5‰), whereas the highest δ¹⁸O(DO) value has been obtained at 2:00 at the depth of 1m (20.9‰). The δ¹³C(DIC) values vary between -6.48 (at 14:00) and -10.58‰ (at 22:00). The minimum in δ¹³C(DIC) value corresponds to rather high δ¹⁸O(DO) value (19.1‰), the maximum values of TN, TP and OM, and the largest amount of cyanobacterial cells observed. All of these were caused/accompanied by an intensive process of decomposition of cyanobacterial cells.

The presented results allow us to state that the most intensive photosynthesis occurs at the surface at 10:00, but at deeper sites it occurs at 14:00. This delay is probably due to the vertical migration of cyanobacterial cells resulted from increasing insolation. We believe that the decomposition process takes place overnight, but our results show that the significant maximum is at about 22:00.
Partition of sulfur and oxygen isotopes in sulfate from crystalline aquifers of the Sudety Mountains (Poland)

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The crystalline massifs from the Sudety Mnts (SW Poland) are apparently contaminated by polluted precipitation resulting from the combustion of fossil fuels in the Black Triangle (BT), one of the largest polluted areas in SW Poland. The acid rains generated in the BT have been proposed as a main cause of the elevated sulfate content in surface waters and groundwater in the Sudety Mountains and have involved for decades a significant decrease in pH, particularly at higher altitudes. The hydrogeochemical analysis, however, has shown that a large portion of the sulfate in surface waters and groundwater from the area might be controlled by in situ processes, such as biological activity in soil and rock weathering in the local water flow system.

Between 2001 and 2005, we have analyzed sulfate content, $\delta^{34}$S(SO$_4^{2-}$) and $\delta^{18}$O(SO$_4^{2-}$) values to calculate the amount and isotope characteristics of sulfate coming from rock weathering, anthropogenic pollution and biological activity, and also to describe the major sources of sulfate from surface waters and groundwater in two crystalline massifs of the Sudety Mountains. The massifs are Rudawy Janowickie and Śnieżnik Massif, intensively exposed for anthropogenic pollution. We have found that diversified lithology among the crystalline rocks (granites, gneisses, micaschists) might importantly influence the sulfate content in surface waters and groundwater. The main sulfate load in the studied waters has been connected with the relatively shallow zone of weathered rocks and the local system of water flow. Moreover, the sulfur isotope composition of sulfur-bearing minerals (mostly pyrite) directly influences the value of $\delta^{34}$S(SO$_4^{2-}$), from 2.56 to 3.58‰. The second important source of sulfate in analyzed waters has come from acid rains. This sulfate is characterized by slightly higher values of $\delta^{34}$S, from 3.27 to 7.63‰ comparing to rock weathering, and the highest $\delta^{18}$O values from 8.74 to 14.84‰. Based on the oxygen isotope mass balance equation, we calculated that the contemporary sulfate input from anthropogenic pollution might constitute even 1/3 part in the waters under study. The input of this sulfate is the highest during wet seasons, after rainy periods and/or snow melting. With time, however, this sulfate is intensively recycled in the zone of weathered rocks, mainly due to biological transformation, and this process involves a general decrease of $\delta^{18}$O(SO$_4^{2-}$) value. The biological source of sulfate (soil in coniferous and deciduous forest, marsh) has shown a relatively small range of $\delta^{34}$S, from 1.87 to 4.13‰, but on the other hand, the appearance of peat bogs might locally cause the enrichment of sulfate in heavier sulfur and oxygen isotopes, up to 5.69 and...
7.83‰, respectively. The importance and oxygen isotope characteristics of the sulfate input from the canopy throughfall, which probably delivers significant amounts of sulfate during wet seasons, is still unknown.

<table>
<thead>
<tr>
<th>The source</th>
<th>Sulfate content [mg/l]</th>
<th>$\delta^{34}$S(SO$_4^{2-}$) [%]</th>
<th>$\delta^{18}$O(SO$_4^{2-}$) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline rocks</td>
<td>up to 1450.78</td>
<td>2.56 to 3.58</td>
<td>-5.17 to -6.53</td>
</tr>
<tr>
<td>Precipitation</td>
<td>0.33 to 6.50</td>
<td>3.27 to 7.63</td>
<td>8.74 to 14.84</td>
</tr>
<tr>
<td>Peat bogs</td>
<td>20.30 to 21.06</td>
<td>5.69 to 7.83</td>
<td>7.54 to 10.03</td>
</tr>
<tr>
<td>Soil, marsh</td>
<td>not analyzed</td>
<td>1.87 to 4.13</td>
<td>not analyzed</td>
</tr>
</tbody>
</table>

In general, a strong altitude-dependence of the $\delta^{34}$S(SO$_4^{2-}$) and $\delta^{18}$O(SO$_4^{2-}$) values suggest that sulfate isotope composition is mainly controlled by *in situ* processes occurring in the zone of weathered rocks (oxidation/dissolution of sulfur-bearing minerals and biological transformation) and mixing of waters of different origin such as geogenic, anthropogenic and biological. In the table above we present typical values of sulfate content, $\delta^{34}$S(SO$_4^{2-}$) and $\delta^{18}$O(SO$_4^{2-}$) values found in different sources of sulfate in surface waters and groundwater from the crystalline massifs of the Sudety Mountains.
Stable isotopic investigations on travertines from the Gerecse Mountains (Hungary)

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The aim of this study was to collect stable carbon and oxygen isotopic signals from the most significant travertine occurrences of the Gerecse Mountains, to derive both paleohydrological and paleoclimatic information about the area from the Pliocene until nowadays. So far, more than 230 samples were investigated from ten quarries.

During the Pliocene and the Quaternary, the area of the Gerecse Mountains was characterised by a strong hydrological activity. As a result, many local travertine deposits were formed on different terrace levels of the Danube River. The spring activity changed during the Pleistocene and the centre of the discharge moved to other parts of the Gerecse Mountains. In the Late Pliocene, the Western and Eastern Gerecse were the main discharge points of the karstic water. Later on, in the Early Pleistocene, the Central Gerecse became the centre of the travertine deposition, but in the Middle Pleistocene the springs dried up. In the Late Pleistocene and during the Holocene, the spring activity stopped almost completely, except for the Western Gerecse (Scheuer and Schweitzer, 1988).

Looking at the carbon stable isotopic compositions, a clear difference can be observed between the Western, Middle and Eastern part of the Gerecse Mountains (Fig. 1), which can be interpreted by local differences during the deposition of the travertines.

The lowest δ¹³C values (-7‰<δ¹³C<-2.5‰, PDB) are characteristic to the Western Gerecse, whereas the travertines of the Middle Gerecse show significantly higher δ¹³C values (-2.5‰<δ¹³C<1‰, PDB). Travertines collected from the Eastern Gerecse (Kő
Hill, Muzsla Hill) were formed during the Pliocene and have characteristically higher \(\delta^{18}O\) values (21‰<\(\delta^{18}O\)<23.5‰, SMOW) than the younger travertines of the Middle and Western Gerecse which could be related to a change in the paleoclimatic conditions during the deposition of travertines.

**Reference**

\( \delta^{18}O \) of cellulose organic fraction combined with \( \delta^{18}O \) of calcite and \( \delta^{18}O \) of diatoms in lake sediments: a new tool for paleoclimate reconstructions on continents?

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Lake sediments are among the most valuable climatic archives on continents. Studies aimed at reconstructions of continental climates based on lake sediments are usually of interdisciplinary character, comprising physico-chemical, biological and isotopic tools. Isotope methods are considered as particularly useful (Leng et al., 2006). \( \delta^{18}O \) isotope composition of bulk carbonate fraction of lake sediments was often used to infer relative changes of lake water temperature in the past, while \( \delta^{18}O \) of cellulose organic fraction served as proxy for \( \delta^{18}O \) of lake water. \( \delta^{18}O \) of diatoms was tested as a proxy for temperature or isotopic composition of lake water (Leng and Barker, 2006).

Laminated sediments of Lake Gosciaz located in central Poland have been a subject of extensive interdisciplinary investigations aimed at reconstructing environmental and climatic changes in central Europe during the Lateglacial and the Holocene (Ralska-Jasiewiczowa et al., 1998). A recent study carried out on these sediments was aimed at a systematic comparison of the carbonate and diatom "isotope thermometers" in a lacustrine environment. Five absolutely dated sections of the Gosciaz lake sediment column, comprising 100-150 years each and ranging from Lateglacial to the Late Holocene, were selected for this study. Each section was split into 10-year samples. The following isotope parameters were analysed in each sample: \( \delta^{13}C \) and \( \delta^{15}N \) of bulk organic fraction, \( \delta^{18}O \) of cellulose organic fraction, \( \delta^{18}O \) and \( \delta^{13}C \) of authigenic calcite and \( \delta^{18}O \) of diatoms (if available).

The \( \delta^{18}O \) of the cellulose organic fraction gave an insight into changes of the \( \delta^{18}O \) of lake water in the past. The inferred \( \delta^{18}O \) of the lake water varied from ca. -13.5‰ during the Younger Dryas (ca. 12100 cal. years BP), to ca. -6.5‰ in the Early Holocene (ca. 9000 cal. years BP) and -9.2‰ during the Late Holocene (ca. 3800 cal. years BP). These large apparent changes of \( \delta^{18}O \) in lake water were most probably caused by two factors: (i) a stepwise change of \( \delta^{18}O \) of the local precipitation at the transition from Younger Dryas to Holocene (approximately 2.5-3‰) and (ii) changes in the \( ^{18}O \) evaporative enrichment of the lake water induced by changes of its hydrological balance.

These inferred changes of \( \delta^{18}O \) in lake water were used to assess effective epilimnion temperatures of the lake derived from measured \( \delta^{18}O \) of calcite and \( \delta^{18}O \) of diatoms, assuming thermodynamic equilibrium during calcite precipitation and formation of
diatom silica. The epilimnion temperatures derived from $\delta^{18}O$ of calcite vary in a large range: from ca. 5°C during Younger Dryas to ca. 25°C in early Holocene, whereas the epilimnion temperatures derived from $\delta^{18}O$ of diatoms are systematically lower and less variable.

This work was supported by grant from State Committee of Scientific Research (project No. 2P04E 002 26) and by the statutory funds of the AGH University of Science and Technology (project No.11.11.220.01).

References


Technical improvements in continuous flow–isotope ratio MS applications

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Continuous flow applications have revolutionized isotope ratio mass spectrometry (IRMS) within the last 20 years. Today continuous flow techniques can be found in all fields of application having improved sample size, throughput, and variety of isotope information, overall precision and ease of use.

Bulk stable isotope analysis (BSIA) is the most widely used continuous flow technique. By coupling elemental analyzers for combustion and for high temperature conversion to the IRMS the isotope ratios of H&O, N&C as well as S can be analyzed in the μg range. All type of organic and a wide range of inorganic samples as well as water can be analyzed.

Continuous improvements on the ease of use and reliability of BSIA applications are a substantial part in enhancing this technique. Reducing the gas amount of the high flow system EA, the injection of reference gases and adjustment of signal intensities by dilution are parameters to deal with. Moreover, varying the reference gas signal intensities allows the determination of linearity and H³+ factors for optimal delta value calculations providing additional parameters to contribute to precision and accuracy requirements in the daily laboratory routines.

Today’s needs for multi-element analysis not only require the possibility to inject up to five reference gases but must also cover a high range of analyte abundances using dilution and amplifier gain switch techniques. The unequal distribution of elements in a substance as well as differences in sample weights demand a quick and flexible response to varying signal intensities by dilution and amplifier adjustments. Accompanied effects of varying signal intensities influencing stability, precision, and accuracy have to be addressed.

Examples for multi-element isotope analysis, throughput, and dynamic ranges together with the requirements on sample size, precision, and accuracy will be discussed.
Stable isotope studies of Plio-Pleistocene fauna from Dmanisi, Georgia

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Establishing environmental context is crucial in human palaeontology because it provides both the essential contextual framework as well as clues to external influences, evolutionary drivers and trends. This is a particular issue with the first known hominins to have emerged beyond Africa approximately 1.75 Ma ago at the site of Dmanisi in Georgia. Morphologically the Dmanisi hominins, although variable, closely resemble the very earliest members of the genus Homo in Africa. The question then arises about how early humans, adapted over millions of years to tropical and savanna environments in Africa, coped with the temperate, harsher conditions of the southern Caucasus. We do not, however, understand the prevailing climate conditions in this part of the world very well, except for limited environmental information from the Eurasian faunal assemblage that suggests a mosaic of forest and open landscape. It has been suggested that possibly the ancient Dmanisi environment was warm enough to support some C₄ savanna grasses. Here we show that this was not the case; based on stable carbon isotope analyses of enamel, the floral cover was entirely C₃, although there is a hint that this situation may have changed later. Although the distinguishing power of C₃ and C₄ flora is lacking, a combination of carbon and oxygen isotope ratios serves to distinguish the niches of some fauna. For instance the influence of closed forest habitats is suggested for bears, which have the lowest ¹³C/¹²C ratios. Preliminary high-resolution data from tooth crowns show that δ¹⁸O fluctuated by 3-4‰ seasonally, and small but patterned seasonal trends can be distinguished in δ¹³C amongst both grazing and browsing fauna.
Oxygen and sulfur isotope fractionation associated with pyrite oxidation by H₂O₂

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Radiolysis of water as a consequence of natural radioactivity and cosmic rays can produce a mixture of strong oxidants, including hydrogen peroxide (H₂O₂) and hydroxyl radicals (HO·), as well as molecular hydrogen (H₂). Subsequent radiation-induced chemical oxidation reactions are particularly significant in geologic environments where the fugacity of molecular oxygen is negligible. Oxidation by radiolytically generated reagents can be observed in modern groundwater associated with uranium ore bodies and can be inferred for ancient groundwaters. Prior to development of an O₂-rich atmosphere on Earth, radiolytic oxidants could have reacted with pyrite and provided local sources of partially to fully oxidized sulfur species available for microbial metabolism.

We evaluated sulfur and oxygen isotope effects associated with reactions between pyrite and radiolytic oxidants using sealed-quartz-tube experiments that utilized aliquots of 60 mg of freshly crushed, sieved and cleaned mineral pyrite and 10 mL of deoxygenated water with micromolar concentrations of H₂O₂. Reactions proceeded for 1 to 10 days at 4 to 150ºC. Primary oxidation products were dissolved sulfate, elemental sulfur, and iron sulfate. X-ray diffraction patterns and images from scanning electron microscopy reveal anhedral to subhedral hydrated iron sulfates in globular clusters of about 10-30 μm in diameter on pyrite surfaces. δ³⁴S values remained unchanged for partially reacted pyrite, but showed distinct enrichment of ³⁴S in produced sulfate and depletion of ³⁴S in elemental sulfur.

¹⁸O-labeled experiments exhibit a complicated dependence of the oxygen isotopic composition of sulfate on temperature of reaction, and thus suggest competing oxidation mechanisms for pyrite at different temperatures. Distinct oxygen isotopic signatures for produced sulfate are related to different pathways of oxygen incorporation from H₂O₂, H₂O, and O₂ from decomposition of H₂O₂.

Our experiments demonstrate that radiolysis is an effective mechanism for the production of oxidizing species in subsurface environments over geologic time. Recognizing geochemical signatures of radiolytic oxidation is particularly important for diagnosis and understanding of biotic and abiotic reaction pathways in environments where molecular oxygen is negligible, and for assessing potential sources of chemical energy for microbial metabolism in the deep subsurface of Earth and Mars.
Oxygen isotope evidence for unusually high evaporation rates from Budzisławskie Lake (Central Poland)

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Here we present the results of oxygen isotopic analyses carried out on water samples from Budzisławskie Lake (Central Poland). The lake has neither tributaries nor outflows, being supplied most probably only by precipitation waters (no evidence for groundwater supply). For several years a serious decrease in water level has been observed in this lake (e.g., in the hydrological year 2003/2004 the water table has lowered with about 0.3 m). The total annual rainfall of the year 2003 was as low as 344 mm, and in the year 2004 it raised to 440 mm – this area shows a significant water deficit (average annual precipitation in Poland is about 550 mm).

Our study was aimed at determining the possible reasons for the observed water loss. The oxygen isotopic analyses of the water have been done in order to estimate the rate of evaporation from the lake’s surface and its direct catchment. The water samples of Budzisławskie Lake have been collected on 3rd October 2005 from 3 sampling points and from 3 different depths at each sampling point (9 samples analyzed). The $\delta^{18}$O values vary between -2.36‰ and -1.78‰ (an extremely high value compared to typical $\delta^{18}$O values for lake waters in Poland, averaging -9‰, or to precipitation waters averaging -10.1‰). Such a large enrichment in heavy oxygen isotopes in the Budzisławskie Lake is, in our opinion, due to intensive evaporation. Using the Rayleigh distillation model we calculated that 56% of the water supplied by precipitation evaporated from the lake and from its direct catchment. We assumed that water from precipitations (falling directly into the lake and coming through its direct catchment) is the only water supply for the lake and that there is no outflow (e.g., to groundwater). Consequently, it can be calculated that the evaporation was responsible for an up to 6 m decrease of the water level of Budzisławskie Lake.

More precise investigations must be carried out at least in an entire hydrological year and the local isotopic composition of rainfall waters should be observed with respect to seasonal variations and isotopic mass balance.
Fructans: stable isotope biomarkers of agaves

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Stable isotopes are new tools that enable the understanding of biochemical, physiological and metabolic processes. Agaves have been used for centuries to elaborate Mexican alcoholic beverages. Stable isotope values have been used to establish the authenticity of some of these beverages (Aguilar-Cisneros et al., 2002; Bauer-Christoph et al., 2003). However, in the last decade, we have learned that fructans are a group of carbohydrates that present wide health-promoting benefits as prebiotics, lipid metabolism regulators, cryo- and osteoporosis protection agents, to mention some. Agaves are CAM (Crassulacean Acid Metabolism) plants that accumulate fructans as a reserve of carbohydrates. Therefore, carbon and oxygen stable isotopes from Agave fructans might be used as biomarkers, to help establishing some of their roles in health-related aspects. The purpose of this work was to establish the potential of Agave fructans (agavins) as biomarkers based on their stable isotope characteristics. Fructans from Agave species collected from different geo-climatic conditions were extracted and purified using the method of Lopez et al. (2003).

Delta values for carbon and oxygen were obtained using an elemental analyser and GC-IR-MS, respectively. Stable isotope values allowed the differentiation among fructans obtained from Agave species and Dasylirion spp. The values from agavins fitted perfectly with previously reported values for CAM plants, with the exception of Dasylirion spp (-10.52 to -12.51‰ for δ¹³C and 27.94 to 36.6‰ for δ¹⁸O). Moreover, δ value differences were observed among agavins obtained from different Agave species and other plants. On top of this, the influence of geo-climatic factors on a specific Agave species was found, e.g. δ¹⁸O values for A. angustifolia from Oaxaca (35.28‰) and Sonora (28.42‰).

This work demonstrates the usefulness of stable isotopes as biomarkers on fructans origin. Therefore, the role of fructans involved in a specific health-related issue might be established accurately by the delta value carried on in one or few of their degradation products.

References

Impact of traffic pollution on *Pinus pinea* tree-ring: $\delta^{13}$C and $\delta^{15}$N analysis

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The increasing amount of nitrogen deposition, in particular of NO$_x$, from fossil fuel combustion has several implications on global biogeochemical cycles. Many N-fertilization experiments showed contrasting results at the plant and stand scale. Consequently, the question arises: did vegetation benefit from this increase of atmospheric [NO$_x$] and how is it possible to detect on long term their eco-physiological effects?

The objective of our study was to apply a promising approach to detect possible effects of atmospheric NO$_x$ fertilization on *Pinus pinea* trees, growing close to traffic pollution. Specifically, we examined the time-related trend in the growth residuals through Carbon and Nitrogen isotopic and dendrochronological analysis. The isotopic signatures in tree rings have been used in several studies to assess the long-term records of climatic change or the tree physiological responses to ecological stress factors. Nitrogen is present in tree rings, although in relative low concentration, and the isotopic signature of N isotopes might provide useful information on N cycling processes.

In this study great effort has been done to develop a methodological system to chemically remove the mobile N in wood, that contributes to inter-ring transfer of N, and to perform isotopic measures on low N concentration (<0.06%) in tree rings.

Preliminary results on two mature *Pinus pinea* individuals, exposed to large amount of traffic exhaust for 20 years will be showed. A consistent decrease in the ring width starting from 1980 with a slight increase in $\delta^{13}$C value has been found as a consequence of environmental stress. Moreover, the decrease in $\delta^{15}$N values of tree rings with time could be the results of increased atmospheric deposition of isotopically light nitrate, reflected in the plant uptake.

Our results confirm the potential utility of nitrogen analysis in tree rings as a tool to assess the long-term trend in the biogeochemical behavior of nitrogen and open a bright outlook for further studies.
Effects of water stress and girdling on intra-annual δ¹³C of tree-ring: a functional approach

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Growth and δ¹³C of tree rings are often used to understand tree functioning during its life and its responses to environmental factors. The model used to interpret δ¹³C signals is the model of Farquhar (1982), which is based on leaf discrimination during photosynthesis. Recent studies have shown the existence of post-photosynthetic fractionations (e.g., during respiration).

Our objective is to study the link between leaf and ring, in term of the δ¹³C signal. More precisely, we would like to understand how an environmental constraint (like water stress) or an artificial stopping of C allocation from leaves to ring, could have an impact on the current year ring δ¹³C, by a change in quality and quantity of leaf assimilates available for ring growth. We will examine the impact of these two constraints on the ring growth, the intra-annual pattern of ring δ¹³C and the trunk respiration (i.e., CO₂ efflux and δ¹³C).

An experiment has been conducted on young oaks (Quercus petraea, 2 years old), under controlled conditions. Two types of stress have been applied during the period of vegetation season:

• A water stress applied in July, at the end of the radial growth, like under field conditions;
• A girdling applied just after budburst, when leaves were not mature and radial growth has begun.

- Water stress decreased trunk growth (-27% compared to controls), even if applied at the end of the growth period. A decrease of carbon assimilation and stomatal conductance were associated to this stress. Concerning the girdling, the impact on growth was first a stop of trunk growth. But after several weeks, tissues were regenerated and girdled trees showed a similar growth as controls, but postponed. As a consequence, growth conditions (weather, photosynthesis...) were not the same than for controls.

- Both water stress and girdling had an impact on trunk respiration (divided by 2 in one week for girdled trees) and on δ¹³C of CO₂ respired by trunk: CO₂ respired by stressed trees was ¹³C enriched compared to the one respired by controls (up to +5.6‰ for girdled trees and +3.7‰ for water stressed trees). This ¹³C enrichment is assumed to be due to:
  • for girdled and water stressed trees: a shift in respiration substrates from photosynthetic sugars to reserve (i.e., starch, which is ¹³C enriched; Brugnoli et al., 1988).
• only for water stressed trees: a change in discrimination during photosynthesis, because of stomata closure, leading to $^{13}$C enriched assimilates compared to controls.

Tree rings have been cut in fine sections of 60 µm, in order to allow high-resolution **intra-annual** $\delta^{13}$C (of total organic matter) measurements. Values obtained varied between $-25$ and $-27.5\%$ for controls, between $-21.5$ and $-24.7\%$ for girdled trees and between $-22.9$ and $-25.3\%$ for water stressed trees. The pattern and range of values, obtained for controls, were consistent with results on the sessile oak of Helle and Schleser (2004). For water stressed, an increase of latewood $\delta^{13}$C was observed which did not occur for control and girdled trees. For girdled trees the decrease in $\delta^{13}$C during early wood synthesis, observed for control and water stressed trees, was later in the season and less strong.

These results confirm that carbon pools available for ring growth have been affected by the two stresses, due to both a change of carbon fluxes (i.e., respiration and photosynthesis) and a modification of carbon pools $\delta^{13}$C (because of a change of discrimination during photosynthesis and/or a shift in respiration substrates).

**References**


Stable isotope ($\delta^{13}C$ and $\delta^{18}O$) and calcareous nannoplankton records of Cretaceous Oceanic Anoxic Events: first evidence in the Southern Carpathians, Romania

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Over the last decades, the study of $^{13}C$ and $^{18}O$ isotopes was used to reveal Cretaceous Anoxic Oceanic Events. Such events were firstly described by Schlanger and Jenkyns (1976), being represented by sediments exceptionally rich in organic carbon (black shales). Several black shale sequences were proved coeval in different regions, indicating a widespread deposition of C$_{org}$-rich sediments during time-intervals named Oceanic Anoxic Events (OAEs). During the OAEs, several positive $\delta^{13}C$ excursions occurred, related to the increased burial of organic carbon, caused by high productivity in the oceans and/or dysoxic to anoxic conditions in the deep and intermediate waters. Among the Cretaceous Anoxic Events, the Oceanic Anoxic Event 2 (OAE2 or Livello Bonarelli), placed within the Cenomanian/Turonian boundary interval, is one of the best studied and one of the longest in duration (Jarvis et al., 2006).

So far, the Cretaceous OAEs were not evidenced in the Romanian Carpathians, even if the lithological overprint of these events (i.e., black shales) is known for a long time. This paper presents a first record of the OAE2 in Romania, in the Ohaba-Ponor section (in the Hațeg region), where the isotopic studies, correlated with paleobiological ones point out this event. A positive excursion of the $\delta^{13}C$ was recorded in the Hațeg region in sediments encompassing the Cenomanian/ Turonian boundary interval, where values increase up to 2.2‰, then decrease to 0.1‰ within the earliest Turonian. This interval of positive $\delta^{13}C$ excursion represents the regional expression of the OAE2. Additionally, the calcareous nannoplankton distribution pattern and the $\delta^{18}O$ fluctuations between -2 and -6‰ identified in the same interval indicate temperature changes of the surface water.

References

Distribution of stable isotopes in surface water along the Danube River in Serbia

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The activities on the Danube water quality survey in its middle course (elevation 74 – 62 m asl) were carried out during a 5-day sampling campaign in August 2004 using the research ship-laboratory “ARGUS”. 10 locations were chosen on the Danube on the whole length of its flow through Serbia from Bačka Palanka (Nestin, 1287 km to confluence with the Black Sea) to Golubac Branjica (1040 km) and one on the Tisa (Title, 9.5 km to confluence with the Danube). In this stretch the river collects the water mass from its principal tributaries, namely the Tisa River with the largest drainage area of 157 000 km\textsuperscript{2}, the Sava River with largest mean annual discharge of 613 m\textsuperscript{3}/s and the Velika Morava River, creating substantial changes in the regime. Collected samples from mid-river section were analyzed for chemical parameters (dissolved oxygen (DO), total alkalinity, nitrate (NO\textsubscript{3}), sulfate (SO\textsubscript{4}\textsuperscript{2})), ammonium (NH\textsubscript{4}), nitrates (NO\textsubscript{2}), calcium (Ca\textsuperscript{2+}), and magnesium (Mg\textsuperscript{2+}), stable isotopes (\textsuperscript{2}H and \textsuperscript{18}O) in addition with air and water temperature, pH and conductivity measurements. Hydrogen and oxygen stable isotope were used in combination with measured hydrochemical parameters to determine the transport processes in river systems.

Danube river water data ranged from −80‰ to −66‰ for \textsuperscript{2}H, and from −11.2‰ to −9.3‰ for \textsuperscript{18}O with δ values increasing downstream. The isotopic signature of the adjacent tributaries (Tisa, Sava and Velika Morava) sampled at the locations (Titel, Ostružnica and Ljubičevski most, respectively) close to their confluence with the Danube just about the time of campaign, were enriched (\textsuperscript{2}H ranged between −67‰ and −63‰, and \textsuperscript{18}O between −9.3‰ and −8.9‰) with respect to the Danube water. The longitudinal non-homogeneity of the Danube water was evident by the \textsuperscript{18}O signal below the confluence with the Tisa River at 8 km downstream (Čenta). It was estimated that the mixing process between them was 83%. The orthogonal regression generated the regional river water line (RRWL) from individual sites along the Danube \textsuperscript{2}H = 7.5 (± 0.3) \cdot \textsuperscript{18}O + 4.3 (± 2.8) (r = 0.99, n = 16, σ = 1.06) which is close to the local meteoric water line. The d-excess values ranged between 7.3 and 10.7‰. The \textsuperscript{18}O – water temperature gradient of 0.35 ‰/°C agrees well with values obtained for precipitation samples in this region. DO, as the most well established indicator of water quality fluctuated from the level required to protect aquatic organisms in surface waters from 5.7 mg/L (in the lowland Tisa River) to 10.6 mg/L (in the Danube before the Tisa confluence). The correlation between DO and water temperature was low (r = 0.36) probably due to the relatively short water temperature range (21.2 – 24.4°C). On contrary, observed strong negative correlation (r = 0.94) between DO and \textsuperscript{18}O corresponds to the biological condition of a river.
Isotopic signature of Llandoverian open marine bedded cherts from Bardo Syncline, Holy Cross Mountains, Central Poland: preliminary results

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Introduction

Layers of bedded cherts play a key role in paleoenvironmental reconstructions, because: (1) they precipitate either: syngenetically and/or during the early diagenesis stage, and (2) their preservation potential is very high. These features are especially important when examining older rocks (or sections) with comparably low preservation potential (e.g., fine grained sediments). Such a situation exists in the Bardo Syncline, in the Holy Cross Mountains, where bedded cherts are interlayered with siliceous clay-shales and mud-shales, the so-called “Silurian Graptolitic Shales” (SGS). Previous investigations of one of the authors, based on petrographic methods (Ochmański, 2006), led to the hypothesis of volcanic-activity-related genesis of these cherts. This paper shows the results of isotopic analysis of δ¹³C and δ¹⁸O, which strongly support this theory.

Geological setting

The Holy Cross Mountains (HCM) are a small range in Central Poland (Fig. 1). They consist of a Paleozoic core and a Mesozoic marginal cover. Within the Paleozoic core, two regions can be distinguished: the Lysogóry Region (LR) in the North, and the Kielce Region (KR) in the South. They are divided by a deep tectonic lineament known as the Holy Cross Fault. Their position during the early Silurian is still under discussion, but most data shows that they were distant from each other (Nawrocki et al., 2007).

The Upper Ordovician - Lower Silurian rock column consists mostly of fine-grained sediments. Lower Silurian strata are known as SGS and they can be found in both regions, but bedded cherts occur only in KR, within the Zbrza Fm. (Fig. 2). They are interlayered with non-altered siliceous clay-shales. The Zbrza Fm. rests comfortably on mudstones and siltstones of the Zalesie Fm. (local spatial equivalent of the Wólka Fm.), and is covered by claystones and clayshales of the Deźniak Fm. All listed units do not show any sign of post-depositional alteration.

Numerous bentonite layers can be found within underlaying (Chlebowski, 1971), and overlaying (Tomczyk, 1962; Chlebowski, 1978; Ochmański, unpublished) sediments.

![Fig. 1. Simplified geological map of HCM, showing exposures of Silurian strata. Bardo Syncline is pointed with arrow. Solid line outlines the so-called “Paleozoic Core of HCM.](image-url)
Methods

Two sections, Bardo - Stawy and Zalesie, were examined bed by bed. The exact position of all chert layers within each profile was measured and oriented and whole-rock samples were collected. Samples for isotopic analyses were cut out from the inner parts of the samples collected to avoid weathered and/or altered fragments. In order to obtain TOC concentrations, samples were powdered using a ball mill and carbonates were removed by reacting them with 2N HCl overnight at room temperature. TOC and $^{13}$C values were obtained with a continuous flow EA-MS system (Costec EA and Delta Plus XP Finnigan mass spectrometer). $^{13}$C values were calibrated using acetanilide, our internal standard calibrated against VPDB. $^{18}$O values range from: 22.3‰ to 27.8‰ VSMOW, with the average of 24.6‰. No trend with respect to stratigraphic position or thickness of layers of bedded cherts can be observed.

Discussion

Comparison of obtained results with previously cited data (Schidlowski, 2000, Fig. 2) points to the following, potential natural sources of organic matter: (1) higher plants, (2) eukaryotic algae, (3) anoxygenic photosynthetic bacteria, (4) methanogenic bacteria, and (5) methanotrophic bacteria. Higher plants must be excluded, as they did not exist at the time. Taking into account the presence of fossilized cyanobacteria within recognized structures (Kremer and Kaimierczak, 2005), which typically record isotopic signatures of $^{13}$C down to – 27‰ PDB, we assume the following biota that might have participated in formation of these cherts: anoxygenic photosynthetic bacteria and/or methanotrophic bacteria and/or methanogenic Archaea (= methanogenic bacteria sensu: Schidlowski, 2000). All these organisms are commonly present within the lower sections of present-day and fossil microbial mats.

Fig. 2. Rock succession in Kielce region (A) and Bardo Syncline (B).
The oxygen isotopic signatures, 24.6‰ on average, show values distinctly lower than previously cited values for this age, with $\delta^{18}O > 30\%$ (Robert and Chaussidon, 2006, Fig. 1). The $\delta^{18}O$ variation of ~7‰ among our samples is similar to all cited data (either: Archean or Phanerozoic) for deep-sea cherts (Knauth and Lowe, 2003). Robert and Chaussidon (2006) made the assertion that all cherts showing values < 6‰ than highest $\delta^{18}O$ values found in cherts at a given age (presented by Knauth and Lowe, 1978) do not preserve their original isotopic signature. This statement seems to be inappropriate in our case, as very sensitive for temperature changes under-, inter-, and over-laying sediments do not show any sign of alteration. Therefore, lower values of $\delta^{18}O$ may reflect syndepositional or early diagenetic conditions.

$\delta^{18}O$ values obtained result in estimated temperatures of precipitation of the cherts ranging from 40 to 80°C. Such values correspond to values estimated by Knauth and Lowe (1978) for Precambrian cherts rather than for the post-hirnantian glaciation sea-water of Llandoverian age. Therefore we attribute the isotopic signature to local conditions. The presence of bedded cherts only in KR (and absence in LR) supports this hypothesis. Local warming at such scale can be caused by syndepositional local volcanic activity. The presence of bentonite layers, deposited not further than 40 km from the source (Chlebowski, 1971) within under- and over-laying sediments strongly supports this theory.

Biogenic genesis of the investigated cherts can be overruled, as radiolarian remains occur not only within cherts, but also within interlayered shales. Therefore radiolarian skeletons cannot be the source of silica precipitated in chert layers. Horizons enriched in radiolarian remains are more likely a result (radiolarian blooms) of a sudden influx of volcanogenic silica into the basin, than a cause of precipitation.

Conclusions

Preliminary results of isotopic investigations of bedded cherts in the Bardo Syncline, HCM, show and/or confirm:

1. The presence of microbial mats within sediments deposited;
2. Their benthic and multilayered character,
3. The preservation of the original syndepositional signature;
4. Warming up of the seafloor or shallow subsurface during deposition or early diagenesis due to local occurrences of volcanic activity;
5. Differences in the isotopic signature of particular bedded chert layers may reflect: (1) temperature, and/or (2) volume of hydrothermal influx, and/or (3) distance from source of hydrothermal influx.

Assuming that our conclusions are correct, we propose the following model of bedded chert precipitation:

Bedded cherts precipitated as result of local, temporal influxes of silica-rich hydrothermal fluids, resulting from volcanic activity during deposition and/or at an early diagenetic stage, and before decomposition of microbial mats.

REFERENCES


Gypsum deposits in Central Italy caves: speleogenetic considerations

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The main caves in Central Italy - Monte Cucco and Frasassi - are made up of tridimensional maze systems developed in a Jurassic carbonate bank, on the external side of anticlines where they are dissected by thrust faults. The internal morphologies of the passages, galleries, and shafts present solutional galleries characterized by cupolas and blind pits, anastomotic passages, roof pendants, and phreatic passages situated at different levels. All the caves present gypsum deposits often associated with clays.

In the Gola di Frasassi caves, in the galleries that reach the phreatic zone where mineralized waters (rich in sulphuric acid) are rising, microcrystalline gypsum forms on the limestone walls. Gypsum deposition is related to the reaction between the sulphuric acid (produced by microbial or abiotic sulphur oxidation) and the carbonate host rock.

Large microcrystalline gypsum deposits partially fill the fossil passages in the Faggeto Tondo and Monte Cucco caves, while isolated gypsum blocks are known in many other karst systems in Central Italy.

Mineralogical analyses show the presence of gypsum and some other rare associated minerals such as fluorite, barite, and celestine. Sulphur isotopic analysis ($\delta^{34}$S) both on the newly formed and fossil cave gypsum deposits give a $\delta^{34}S$ average value of -13.5‰. The similarity in the cave morphologies, mineralogy, and isotopic value of the gypsum suggests a common speleogenetic mechanism for these caves.
Isotopic investigations of cave drip waters and precipitations in Florida, USA

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Precipitation and in-cave drip waters from speleothems at three caves that transect N-S the Gulf coast of the Florida peninsula have been collected to quantify the variability of the isotopic signal. The study aims to isolate the primary factors that control that isotopic variability both at the site and at regional scale. In addition to weekly water samples, instrumentation inside and outside each cave monitors hourly data on temperature and relative humidity; acoustic loggers acquire data on drip rates beneath active speleothems attached to unfractured blocks of the aquifer matrix. The relationship between the isotopic composition (δ¹⁸O and δ²H) of cave waters and meteoric sources is critical for reconstructing paleoclimates using speleothem data. This study will serve as a first of its kind in the southeastern US where the impacts of confounding variables such as temperature, vapor source, storm frequency, and intensity, distance from shore, and soil/water/rock interactions are poorly understood.

Determining precipitation sources will shed light on how the climate of the Florida Peninsula is affected by regional weather patterns such as the Atlantic Multi-decadal Oscillation, El Niño, and the Intertropical Convergence Zone. For example, rainfall from tropical systems in the summer show a depleted δ¹⁸O signal when compared to frontal precipitation events during the winter. δ¹⁸O signals of precipitation and cave drip waters show positive correlation. The drip water δ¹⁸O signal is slightly subdued from interaction with water stored in the epikarst.
Stable isotopes in cave ice: what do they tell us?

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Introduction

In the context of recent climate changes, our understanding of the climate of the past two millennia has become more important, as the changes we witness can be placed in a longer-term context, helping us decipher both natural and anthropogenic forcing on the climate system.

So far, ice cores proved to be one of the most reliable sources of palaeoclimatic information, as they can provide an accurate view of past atmospheric composition and circulation, air temperature and precipitation amount, and magnitude of solar variability. They are available from Polar Regions, as well as from tropical and mid-latitude mountain glaciers, but are missing from a large fraction of the Earth surface.

Recently, at the First International Workshop on Ice Caves (Cluj Napoca, 2004), a new direction emerged in ice core science: the use of ice deposits from caves in palaeoclimatic reconstructions. Previous studies (Racoviță and Onac, 2000; Holmlund et al., 2005; Luetscher et al., 2005) suggested that ice accumulations in caves might contain palaeoclimatic information, therefore we have tested this hypothesis on the ice block from Scărișoara Cave.

This paper is concerned with various aspects regarding stable isotope measurements on rainfall, newly formed and fossil cave ice, and on cryogenic cave calcite (CCC) deposited during the ice formation.

Site description

Scărișoara Ice Cave hosts the world’s second largest cave ice block (100,000 m³, 22 m thick), with an age of more than 1200 years (Holmlund et al., 2005).

The entrance of the cave is located on the edge of the Scărișoara Plateau (Arieș catchment area, Apuseni Mts.), at 1165 m asl. The cave formed in thickly bedded limestones of Upper Jurassic age (Bucur and Onac, 2000).

The cave consists of four main sections: The Great Hall, The Church, The Little Reserve and The Great Reserve (Fig. 1); the ice block is located in the Great Hall, from where it reaches into the three lateral rooms: The Church, and The Little and Great Reserve.

From a climatic point of view, the cave has a complex structure, with four meroclimatic zones (Racoviță, 1984): a transition meroclimate in the entrance shaft, a glacial zone in the vicinity of the ice block, a periglacial one at certain distances from the block, and a warm meroclimate in the non-glaciated parts of the cave. The repartition of these meroclimates is reflected by the thermal pattern of the cave: while in the Great Hall the mean annual temperature is around –0.9ºC, it increases to –0.2ºC in the Great Reserve and 4.3ºC in the Coman passage (Fig. 1).

The climate of the region is continental temperate, showing a strong influence of the westerlies. The mean annual precipitation varies around 1200 mm, the highest values being recorded in spring and early summer months, while October is the driest month. The mean annual temperature is approximately 6.5ºC.

Fig. 1. Location of Scărișoara Ice Cave (black asterisk); cross-section through Scărișoara Ice Cave.
Methods

Precipitation and snow were collected between December 2004 and August 2006, while in January 2005 newly formed ice was collected from different parts of the cave. Air temperature and precipitation amount were measured outside the cave on a daily basis during the same period. Additionally, samples of ice were collected from each centimeter at different depths (0-0.5 m, 11.01-11.24 m, 21.90-22.15 m) from an ice core recovered in February 2003 in the Great Hall of the Scărișoara Ice Cave.

The stable isotope composition of water was measured at Joanneum Research, Graz, Austria, using automatic equilibration lines and a Finnigan MAT Delta Plus Mass Spectrometer.

CCC samples (fine-grained carbonate powder with grain size generally 1 to 5 mm) trapped within the ice at certain horizons were sampled along the vertical ice wall in the Little Reserve of Scărișoara using ice screws. CCC isotope composition was measured at the stable Isotope Laboratory, Institute of Earth Science, Graz University using a Kiel device and a Finnigan Delta Plus Mass Spectrometer. The standard deviation of both $\delta^{13}C$ and $\delta^{18}O$ is 0.06 and 0.1‰. The data are given vs. PDB for both $\delta^{18}O$ and $\delta^{13}C$.

We also used additional CCC data from Žák et al. (2007) for samples collected from three settings: 1) around ice stalagmites, 2) from the apex of ice stalagmites, and 3) from the upper surface of the main ice block.

Results and discussions

Stable isotopes in precipitation and ice

Stable isotope data from precipitation show a positive correlation between $\delta^{18}O_{prec}$ and air temperature (Fig. 2), with a slope of about 0.89‰ °C⁻¹. This value is in good agreement with the results of Rozanski et al. (1992) and Fricke and O’Neil (1999), who have found that slopes at European sites range from 0.2 to 1.1‰ °C⁻¹.

The Local Meteoric Water Line (LMWL) at Scărișoara ($y=8.14x+10.227$) is similar to the Global Meteoric Water Line (GMWL) ($y=8x+10$). Forizs et al. (2004) and Kern et al. (in press) have obtained similar values at two nearby sites, Focul Viu and Bortig ice caves.

The $\delta^{18}O$ values of cave ice are higher than the ones from precipitation, and show lower amplitudes and reduced seasonal variations (Table 1). As shown by Forizs et al. (2004), these higher values are determined by the formation of ice between December and May, when the $\delta^{18}O$ values of precipitation are above the annual mean. Moreover, evaporation at relative humidity lower than 100% could cause additional fractionation. Racoviță (1994) showed that the relative humidity in the cave could drop below 90% during winter months, when cold and dry air quickly infiltrates in the cave. Moreover, positive temperatures could occur in ice caves during winter months (Persoiu et al., 2007), so fractionation due to evaporative processes is likely to occur and affect the initial isotopic record.

The smoothing of the stable isotope values for cave ice recovered from the ice block is supposed to be determined by both diffusion through the ice body and melting-refreezing processes, active during the formation of ice.

Table 1. Mean, maximum, and minimum values of $\delta^{18}O$ for precipitation and ice.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{18}O$ values (% VSMOW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation</td>
<td>Mean 12.84 Amplitude 19.67 Maximum -12.07 Minimum -22.74</td>
</tr>
<tr>
<td>New ice</td>
<td>Mean -8.76 Amplitude 3.01 Maximum -7.06 Minimum -10.07</td>
</tr>
<tr>
<td>Ice core</td>
<td>Upper section Mean -11.07 Amplitude 3.24 Maximum -9.50 Minimum -12.74</td>
</tr>
<tr>
<td></td>
<td>Middle section Mean -9.80 Amplitude 0.86 Maximum -9.44 Minimum -10.20</td>
</tr>
<tr>
<td></td>
<td>Lower section Mean -11.20 Amplitude 1.27 Maximum -10.78 Minimum -12.05</td>
</tr>
</tbody>
</table>

Stable isotopes in cryogenic cave carbonate (CCC)

CCC is formed during the spring, when water resulted from snow melting at the surface enters and freezes inside the cave into thin layers, enabling the quick escape of CO₂ from solution under open system conditions (Žák et al., 2004, 2007). The fine-grained CCC deposited during this process show a large increase of the $\delta^{13}C$ values compared to the normal range from speleothems in the area. These are typically accompanied by either no increase, or moderate

![Image](image_url)
increase of the δ18O values. The variability of the δ13C values within the cave is as large as 11%, while the δ18O maximum variation is 5%. The calcite samples collected from the ice block show the same values of both δ13C and δ18O as modern calcite (Fig. 3). Also, a clear trend (not shown) towards heavier carbon isotope composition with increased depth is visible, as well as highly variable δ13C values in various ice layers.

The data suggest that the variation in the δ13C values of cryogenic calcite may be influenced by: CO2 degassing, melting and refreezing processes, and variation in DIC values of infiltration waters.

![Fig. 3. Stable isotope values for cryogenic cave calcite](image)

**Fig. 3. Stable isotope values for cryogenic cave calcite** from Scărișoara Ice Cave (“new” - newly formed calcite, “old” – calcite trapped inside the ice block >500 yrs.). Data for “new” calcite from Zák et al. (2007).

**Conclusions**

Stable isotope investigations have been carried out on precipitation, cave ice and cryogenic calcite at Scărișoara Ice Cave, Romania. The δ18Oprec has been found to be positively correlated with the air temperature (r = 0.7), while the LMWL is similar to the GMWL (δD = 8.14δ18O+10.227). δ18O in ice have higher values than in precipitation, due to the formation of ice mainly from winter precipitation, when the average δ18O is lower than the annual mean. Melting-refreezing processes affect the ice, also reflected by the lower values and smoothed amplitudes of δ18O.

The cryogenic cave calcite formed during rapid water freezing has a characteristic isotopic signal, with a significant increase in δ13C and a moderate increase in δ18O compared to typical values for speleothems from the area. Older CCC shows the same pattern, but long term variations are also visible and may be related to changes in the climatic conditions during its formation. The identification of the relation between the stable isotope values of C and O in cryogenic calcite and air temperature is required in order to make this proxy useful in the reconstruction of past climate variations in the area.

Romania’s climate during winter and early spring months, when both air temperatures and precipitations are favorable for the ice accumulation (Perșou, 2004), is mainly controlled by variations of the North Atlantic Oscillation (Bojariu and Paliu, 2000), the main mode of climate variability in Europe (Vinther et al., 2003). Preliminary observations have shown that there is a good correlation between the external air temperature and the precipitation amount in the area, and the NAO index (which measures the difference in air pressure between Iceland and the subtropical Atlantic from the Azores through the Iberian Peninsula), so that if the transfer function between δ18O and δ18H values of cave ice and precipitation is found, there is a good potential to use this proxy to reconstruct past climatic changes in the area. Dating of the ice, as well as stable isotopes measurements of ice, dripwater and CCC are in course, in order to decipher the above-mentioned relationship.

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Chlorine has two stable isotopes, $^{35}\text{Cl}$ and $^{37}\text{Cl}$, with natural abundances of 75.77% and 24.23%, respectively. The isotope ratio $^{37}\text{Cl}/^{35}\text{Cl}$ has been applied to tracing the circulation of chlorine compounds in the environment and their degradation in physico-chemical and biological processes. By the investigation of the $^{37}\text{Cl}$ we can distinguish the origin of Cl-bearing substances. Recently, significant differences between naturally occurring Cl-bearing compounds and anthropogenic chlorinated organic substances were confirmed (Stewart and Spivack, 2004). It is particularly interesting because chlorinated organic compounds, including the common solvents (e.g., perchloroethylene, carbon tetrachloride) are among the most frequently detected groundwater pollutants. These substances are known or suspected to be carcinogenic or mutagenic for humans. They are readily transported by groundwater and are not reduced to acceptable level (for consumption) by most water supply treatments.

By using a single focusing mass spectrometer with two collectors we have measured chlorine isotope ratios in our laboratory. The mass spectrometer is equipped with the dual inlet system, electron impact ion source, magnetic sector and detecting system (where ions are collected and then ion currents are processed by computer).

The chloromethane gas was used to determine the chlorine isotope ratio in our studies. This gas is very comfortable for this type of investigations as it is less reactive than HCl or chlorine, and has no memory effect in the inlet and vacuum systems of the mass spectrometer (Eggenkamp, 2004). To produce the chloromethane gas from a studied water sample the following steps were done: (i) the precipitation of silver chloride from water, (ii) reaction of silver chloride with iodomethane, (iii) cryogenic separation of chloromethane from the remaining reagents.

The obtained chloromethane gas was then admitted into to the mass spectrometer where during the electron - molecule collisions a few of ion beams were formed. We measured the ion currents at m/q equal 50 and 52, at which the most efficient formation of $^{35}\text{Cl}$ and $^{37}\text{Cl}$ ion species is recorded. In this contribution we present our first results of chlorine isotope ratios measured in water samples. Aliquots of chloromethane gas produced from 15 mg of silver chloride were analyzed. Preliminary results are promising, since a standard error of $\delta^{37}\text{Cl}$ of 0.1‰ was achieved.

References


Effects of different soil preparations methods on the foliage N dynamics in Finnish boreal forests: $^{15}$N natural abundance isotopic method approach

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In this paper, we report on the impacts of clear cutting and soil preparations on the foliage N dynamics. We used natural $^{15}$N abundance to study this. The clear cutting is a common silvicultural practice in Finland and half of forest cuttings are regenerated from seeds. In order to provide better seed bed conditions and to improve environmental conditions for seedling growth, site preparation methods such as ploughing, burning, fertilization etc. are commonly used, but the effects of the rapid increase in slash and the removal of trees and the site preparation methods on the $^{15}$N fractionation, especially on long-term basis, have rarely been studied. This study concerns on the study about the impacts of the different site preparation methods on the foliage N concentrations and $^{15}$N. The different methods of site preparations studied were:

i) Slash burning,
ii) Ploughing,
iii) Ploughing and fertilizer and,
iv) Fertilizer alone and control (no treatment).

The $\delta^{15}$N values of plant foliage N closely reflected the management practice (fertilization, burning and ploughing) of different boreal forests in the medium term (20–25 years). Furthermore, the foliage N dynamics related to management practices are explained in this study in more details. Finally, from our study we conclude that the long-term effects of different management practices can be studied through the natural abundance of $^{15}$N isotopes in foliage of boreal forests, provided that there is no significant atmospheric N deposition.
Isotopic study of late diagenetic ore mineralization in the Bleiberg lead-zinc deposit (Eastern Alps, Austria)

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The strata-bound Pb-Zn deposit of Bleiberg (Carinthia, Austria) is hosted by Triassic platform carbonates of Carnian age. Today, the mining activities are finished. Bleiberg is the largest deposit in the Alps. So far 2.2 million tons (Pb:Zn = 1:1) have been mined.

The age of the deposit is synchronous with these Carnian rocks. Brigo et al. (1972) supposed a Triassic (Carnian) age of the mineralization in the Bleiberg Pb-Zn deposit and his affiliated deposits. Sulphur isotope data (Schroll & Rantitsch, 2005), lead isotopes and rubidium/strontium ages (Schroll et al., 2006) and the detection of fossil sulfate-reducing bacteria (Kucha et al., 2005) support this supposition. The pre-burial deposed ores were heated up to ca. 130°C during the Jurassic and Cretaceous (Rantitsch, 2001, 2003). Re-mineralization processes during this interval depend on the availability of fluids. The dewatering of gypsum that contains 20% H₂O is an important source of diagenetic fluids. Gypsum is transformed into anhydrite at temperatures around 55°C (Bilo, 1986). Blue anhydrite of diagenetic origin is common in evaporitic limestones. This also happened in the lagoonal Wetterstein formation in the Antoni mine (Bleiberg). According to the thermal model (Rantitsch, 2001, 2003) this diagenetic process lasted during Jurassic times. Irregular metasomatic bodies of blue anhydrite are hosted by the lagoonal Wetterstein limestone. Locally the anhydrite intruded into pre-existing ore bodies. The border anhydrite - limestone is rimed by a coarse-grained brownish sphalerite and/or calcite. The sphalerite is intimately associated with pyrite, marcasite, fluorite and quartz. The pre-existing sphalerite - galenite ores partly show re-crystallization.

Methods
The ore association and wall rock were investigated by different isotope methods: δ¹³C, δ¹⁸O (carbonate and anhydrite), δ³⁴S (sphalerite, galenite and anhydrite), δ³⁴S, δ¹⁸O (anhydrite) and ⁸⁷Sr/⁸⁶Sr.

Results
The blue anhydrite is enriched in heavy sulphur in comparison with coeval δ³⁴S different from syn-sedimentary anhydrite. The δ¹⁸O values of blue anhydrite and calcite indicate disequilibrium. δ¹³C and δ¹⁸O of the precipitated calcite are consistent with diagenetically formed calcite (prismatic type). The δ³⁴S difference of sphalerite
(rim) and blue anhydrite does not correspond to a realistic equilibrium temperature as suggested (Schroll & Rantitsch, 2005). $^{87}$Sr/$^{86}$Sr values of anhydrite and calcite are not too different from coeval seawater strontium. This is in agreement with the $^{34}$S and $^{18}$O data of anhydrite.

The isotope studies give an insight of this diagenetic mineralization process. The activities of the diagenetic fluids remain restricted to a limited area of the lagoonal facies of Wetterstein limestone, which is poor on silicate and organic matter. The ratio of fluid to carbonate was low. The precipitation of sphalerite was abiogenic. The notice of secondary ore forming processes at Bleiberg is an interesting aspect. However, the supposed isotope equilibrium could not be established (Schroll & Rantitsch, 2005).

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References

A Sr-O-H isotopic study of the Apuseni Mountains
Neogene magmatic province, Romania

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Neogene magmatism in the Apuseni Mountains of Romania was active between 15
and 7 Ma, with an isolated final eruption at 1.6 Ma. Several groups of magmatic rocks
can be distinguished on the basis of ages, trace elements, and isotopic compositions.
Most are of calc-alkaline affinity, despite the fact that the region is located 200 km
from the Carpathian subduction trench. However, adakite-like calc-alkaline magmas
were also erupted and the youngest eruptions were of alkaline affinity.

In this study we present 27 new oxygen isotope data, 15 hydrogen and 17 new Sr
isotope analyses on mineral separates and groundmass from samples from the
Apuseni Mountains. All the analyzed rocks lack olivine but contain phenocrysts of
clinopyroxene, amphibole, biotite and sometimes-abundant plagioclase.

A comparison of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in whole-rocks, mineral separates and
groundmasses reveals that the whole-rocks tend to have slightly higher values than
amphibole or clinopyroxene separates. Clinopyroxene phenocrysts in all the measured
rocks show an extremely restricted range of $^{18}\text{O}$ values between 5.5 and 5.6‰. These
values are similar to $^{18}\text{O}$ values of clinopyroxene in mantle peridotite xenoliths
worldwide. Most mafic minerals, as pyroxene and amphiboles show a narrow range of
$^{87}\text{Sr}/^{86}\text{Sr}$ and $^{18}\text{O}$, but plagioclase and groundmass show a shift toward both higher
$^{87}\text{Sr}/^{86}\text{Sr}$ and higher $^{18}\text{O}$ values. Magmas older than 13.5 Ma are characterized by the
highest $^{87}\text{Sr}/^{86}\text{Sr}$, values in their phenocryst phases, volcanic rocks younger than 13.5
Ma have lower $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{18}\text{O}$ ratios, with a narrow range for pyroxene and
amphibole mineral separates, indicating closed system fractional crystallization. A
larger scatter of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{18}\text{O}$ values is found in plagioclase phenocrysts and
groundmasses, indicating that occasionally crustal assimilation occurred. The $\delta D$
values for hydrogen-bearing phases such as amphibole, biotite, and groundmass show
variations up to 20% within a location, indicating fractional crystallization in a closed
system. For all samples a trend of decreasing $\delta D$ in the source with time is observed,
the $\delta D$ values varying between $-126$‰ to $-66$‰.
Low $\delta^{18}$O and $^{87}$Sr/$^{86}$Sr ratios for mafic minerals in the volcanic rocks in the Apuseni Mountains generally indicate a low degree of source enrichment, which does not support the operation of subduction processes. Moreover, the data fall in the same field as primitive oceanic arc lavas revealing that the range of $\delta^{18}$O is not evidently associated with “slab-derived fluid” (high Ba/La) or “sediment-derived melt” (high La/Zr) signatures. Petrological and geochemical analysis of the complex succession of magmas in the Apuseni Mountains province demonstrates that normal calc-alkaline and adakite-like magmatism can be generated in a non-subductional environment, in this case associated with an extensional setting related to Miocene block rotations.
Chlorine isotope geochemistry

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Chlorine is an unusual element. It is neither siderophile, nor chalcophile, nor lithophile. Rather it is generally highly partitioned into aqueous fluids. There are two stable isotopes of Cl, masses 35 and 37. The latter comprises ¾ of the total, leading to a non-integer molecular weight (this was very significant for physicists in the early 20th century, who were trying to understand the structure of atoms). Chlorine isotope geochemistry was first investigated by Hoering & Parker (1961). He found that there was very little variation in the $^{37}$Cl/$^{35}$Cl ratios of natural materials. In the mid 1990s, a new series of studies were made, where large variations in the $\delta^{37}$Cl values of terrestrial and meteoritic materials were found. We have revisited the chlorine isotope system, modifying existing analytical procedures so that 20 mg samples of Cl can be analyzed on a gas source mass spectrometer using CH$_3$Cl as an analyte. Precision is ±0.14‰. We have measured the $\delta^{37}$Cl values of the major terrestrial and extraterrestrial reservoirs. Mantle samples include pristine mid ocean ridge basalt glasses, and several sub-continental mantle samples. The major crustal reservoirs for Cl are the oceans and evaporites, and these have been thoroughly investigated previously. Four primitive carbonaceous chondrites have also been measured. We find that the chlorine isotope composition of the Earth’s mantle and crust are indistinguishable from each other, with $\delta^{37}$Cl values of 0.0±0.2‰, and are only slightly higher than the values measured for carbonaceous chondrites of -0.3±0.5‰ (Fig. 1).

Fig. 1. $\delta^{37}$Cl values of selected terrestrial and chondritic samples (from Sharp et al., 2007).
The results indicate that there was no fractionation between crust and mantle during planetary degassing, and minimal, if any, fractionation between the nebular reservoir and the newly forming planets. Sedimentary samples from 3.85 Ga to recent show no correlation between $\delta^{37}$Cl value and age, discounting a two-stage accretionary history for Earth, if the late veneer had a different isotopic composition from the earlier accreted material. Previously published data define distinct reservoirs for the mantle, crust and chondrites covering over 5‰ – such results cannot be reconciled with the constant $\delta^{37}$Cl value of sediments through time. These previously published data (TIMS) appear to have been compromised by an analytical artifact.

References


Paleoclimate reconstruction derived from speleothem strontium and $\delta^{13}$C in Central Florida

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A speleothem from central Florida, USA was analyzed for its variability for trace elements of strontium and carbon isotopes. Thermal ionization mass spectrometry of uranium-thorium isotopes indicates the speleothem was precipitated during the last 4,000 years. Sr concentration is negatively correlated with $\delta^{13}$C, as a function of soil productivity. Coeval changes in the Sr content and $\delta^{13}$C signals, as induced by soil productivity, are explained by changing precipitation above the cave. Both proxies record a 170-180 year solar cycle that has also been found in marine records from the Gulf of Mexico and elsewhere. Consequently, this result provides evidence of an extraterrestrial driven modulator of precipitation in central Florida.
Origin of petroleum in metalliferous Lower Cambrian black shales, Yangtze platform, South China: insight from isotopes and biomarkers

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In this communication we report the results of the first molecular and compound specific isotopic analysis of carbonaceous matter in mineralized Lower Cambrian black shales from the margin of the Yangtze Platform in South China. These black shales are in places strongly enriched in Ni, Mo, V, Co, Cr, Au, U, As, Pb, Zn, Cu, Re, and PGE. Several models have been put forward for explaining such extreme metal enrichment. These include enrichment by diagenetic fluids, hydrothermal exhalation, extraterrestrial impact, synsedimentary enrichment from seawater, and discharge of petroleum into the basin.

The TOC content of the analyzed samples is between 5.5 and 8.2 wt%. The Rock-Eval S₁ (free hydrocarbons, HC) and S₂ (pyrolytic HC) parameters are less than 0.2, suggesting high thermal maturation or extensive oxidative/bacterial degradation of the organic matter. The n-alkanes in the C₁₁ – C₃₁ range (maximum at C₁₆, bimodal distribution with further maxima at C₂₂ or C₂₆ in some samples, slight even-over-odd dominance), pristane (Pr) and phytane (Ph) in roughly equal proportion, and alkylcyclohexanes in the range C₁₁ – C₂₈ are the main resolvable compounds in the GC/MS chromatograms of the saturated HC from all samples. Some samples contain also hopanes and steranes, with the latter dominating over the former. Relatively consistent Pr/n-C₁₇ and Ph/n-C₁₈ ratios point to a relatively uniform environment and little differences in maturation/alteration and migration effects between samples. The aromatic HC fractions of all samples mainly contain oxidized compounds. Pure aromatic HC such as alkylbenzenes, naphthalene, and alkylnaphthalenes were detected only in very minor concentrations.

The δ¹³C (vs. VPDB) and δ¹⁵N (vs. Air) ratios of the kerogen range respectively from –31.5 to –35.4‰ and from –1.4 to 0.6‰. The δ³⁴S (vs. V-CDT) values of molecular sulphur from extracts of black shale samples range between 13.9 and 15.8‰. Most of the n-alkanes' and isoprenoids' δ¹³C values across the C-number range are between –33 and –25‰. In all samples pristane and phytane are depleted in ¹³C by up to 6‰ compared to C₁₇ and C₁₈ n-alkanes. All these results are best explained by derivation of hydrocarbons from algal and bacterial mats that were deposited in a saline, anoxic marine environment. The new data do not support an abiotic origin of that petroleum, proposed previously. Combined with sedimentological and S isotopic evidence, a low-energy, restricted basin setting appears most likely. A genetic link between metal enrichment and bitumen formation seems obvious from field relationships, textures and the unusual metal enrichment can be explained by the relatively high metal solubility in petroleum.
Direct evidence for the existence of dairying farms in prehistoric (< 3922 BC) Central Europe

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The chemistry of organic residues from archaeological potsherds was used to get further insight into the dietary trends and economies at the Constance lake-shore Neolithic settlements of Arbon Bleiche 3/Switzerland (3384-3370 BC) and Hornstaad-Hörnle IA/Germany (3922-3902 BC). These are, at present, the oldest archaeological samples analyzed at the Institute of Mineralogy and Geochemistry, University of Lausanne.

The approach includes δ¹³C and δ¹⁵N of the bulk organic residues, fatty acids distribution and the δ¹³C of individual fatty acids. Fat samples of modern animals that have been fed exclusively on C3 forage grasses, and samples of vegetable oils were analyzed in order to test the origin of the fat in the archaeological ceramics (Spangenberg et al., 2006). These reference samples are the modern equivalent of animal and vegetable fats, which may have been consumed in a mixed ecology community with hunting, fishing, gathering, breeding, shepherd, and agrarian activities. The animal fat samples include adipose samples of pig, cattle, calf, lamb, deer, and fish, milk fat samples of cow, goat, and sheep. The analyzed plant oil samples include olive, pumpkin, sunflower, sesame, maize, rape, hazelnut, walnut, and groundnut oils. The used combined chemical and isotopic approach provides valuable information to complement archaeological indirect evidence about the dietary trends obtained from the analysis of faunal and plant remains. The total nitrogen content (~15 wt%) and C/N ratios (5.7 to 19) of the organic residues are in the range of cooked/alkalized protein-rich food. The small variations of the δ¹³C and δ¹⁵N values within the range expected for degraded animal and plant tissues, is consistent with the archaeological evidence of animals, whose subsistence was mainly based on C3 plants. The overall fatty acid composition (C9 to C24 range, maximizing at C14 and C16) and the stable carbon isotopic compositions of palmitic (C16:0), stearic (C18:0) and oleic acids (C18:1) of the organic residues indicate that the studied Arbon Bleiche 3 and Hornstaad-Hörnle IA sherds contain fat residues of plant and animal origin, most likely ruminant (bovine, ovine). Several samples plot in the δ¹⁴C16:0 vs. δ¹³C18:0 and δ¹³C18:1 vs. δ¹³C18:0 fields of ruminant milk, and young suckling calf/lamb and pig adipose. These data provide direct proof of milk and meat consumption and farming practices for a sustainable dairying during the Neolithic in central Europe.
Reference

The geochemical characterization of organic matter in sediments of the Mrah Area, Syria

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The Mrah area belongs to the Palmyride region in central Syria. The main target of the exploration was the sediments of the Kurrachine Dolomite Formation. Geochemical prospects of the Mrah-2 well are focusing on the determination of possible source rocks and hydrocarbon occurrences through the well profile. Stable carbon isotopes have a special significance as a part of geochemical investigations, in order to estimate the origin of organic matter and point to genetic relations between hydrocarbons and their precursors.

Geochemical examinations of the rocks have shown generally low organic carbon content (average 0.25%). The increased values of total organic carbon (TOC>0.3%) are linked to claystone/shale layers within the Middle Triassic sediments, but with no source rock characteristic due to restricted petroleum generating capability (S2<2 mg HC/g rock) (Fig. 1). The low hydrocarbon generation potential of the Middle Triassic sediments is the result of oxic to suboxic depositional conditions, which altered hydrogen rich organic matter into unfavorable organic facieses.

The microscopic examination of kerogen has demonstrated the predominance of amorphous, unstructured organic matter with only sporadic inputs of vitrinite, fusinite and reworked vitrinite. Considering all optical examinations and maturity parameters, organic matter is determined as the terrestrial organic matter in high maturity stage of catagenesis (1.2 to 1.3% Ro) (TAI from 3 to 4) (Fig. 2).

Fig. 1. TOC, Hydrocarbon potential and HI-Tmax plot (cuttings and cores from Mrah-2 well).

The microscopic examination of kerogen has demonstrated the predominance of amorphous, unstructured organic matter with only sporadic inputs of vitrinite, fusinite and reworked vitrinite. Considering all optical examinations and maturity parameters, organic matter is determined as the terrestrial organic matter in high maturity stage of catagenesis (1.2 to 1.3% Ro) (TAI from 3 to 4) (Fig. 2).
The presence of bitumen was registered in the form of lamination and impregnation. The bitumen yields are rather high and vary from 787 to 3193 ppm. High EOM/TOC ratios (average 329 mgHC/gTOC) and high content of the n-alkanes (average 87%) point to their secondary, migrated origin. The gas chromatographic results presumed thermally altered bitumens originated from marine algal material deposited in an either reducing or slightly oxic deposition environment. The fingerprint of bitumens shows differences in their molecular parameters and highlights the differences in the type of organic matter and their precursors, as well as the environmental conditions and the thermal maturity level. Dissimilar bitumen characteristics could be explained as the result of hydrocarbon migration processes during different geological periods.

Generally, kerogens are isotopically lighter, which relates to the terrestrial material organic facies ($\delta^{13}C$ -26.72; -28.29‰). The positive genetic relationship of kerogen related to associate bitumen is detected only for two samples (2874-2880 and 2993-2995 m). Bitumens from deeper sequences are negatively correlated to kerogens, which suggests secondary, migrated origin of bitumens (Fig. 3) The evident shift towards less negative values in kerogen from the 2993-2995 m sample can be influenced more probably by the contamination with organic material insoluble in organic solvents, than by the radical altering of the organic source material. Deducing from the pyrolysis results, the visual analysis of isolated kerogen, the gas chromatographic analysis of bitumen and stable isotope analysis of kerogen, contamination with organically originated mud additives has been proven.

Fig. 3. The stable carbon isotope composition of kerogens and bitumens from Mrah-2 well.

References


The $\delta^{18}O$ record of a Holocene stalagmite from V11 Cave, NW Romania

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Stable isotope analyses on a Holocene stalagmite from V11 Cave yield a paleoclimate record for the last 9200 years. The stalagmite chronology is based on seven high precision U-Th ages obtained by thermal ionization mass spectrometry (TIMS).

The V11 Cave is located in the SE part of Varasoaia Glade (Bihor Mountains, NW Romania), at 1254 m a.s.l. The cave is formed in Anisian limestones and dolomites, has 1166 m of surveyed passages and a vertical extension of 67 m (−37 m; +30 m) (Damm, 1993). The cave area is a typical karst plateau with sinkholes and ponors, with vegetation mainly consisting of spruce stands and alpine herbs (Bodnariuc et al., 2002). The present-day climate of the area is predominantly influenced by west-northwest oceanic air masses. The mean annual temperature is 5°C and the mean annual precipitation exceeds 1200 mm. The mean annual temperature and the relative humidity in the cave, measured between 2003 and 2004, are 6.5°C and 97–98%, respectively (Tamas et al., 2005).

The S139 stalagmite has 20.5 cm in length, and a fairly constant diameter of 5-6 cm, except for the first two cm at the top (3 cm in diameter). S139 was active when sampled, growing on the wall of a small room, which intersects the main passage some 30 m from the cave entrance and about 20 m below the surface. It is composed of pure white calcite with columnar fabric, with few pores and hardly visible growth.

Fig. 1. a) V11 Cave location in Romania (gray circle); b) Cave map with position of S139.
laminae, and shows no signs of recrystallization. At 25 mm from the top, a short growth hiatus occurs, associated with dissolution of the central part of the sample. Another small concavity is noticed at 60 mm from base, indicating dripwater corrosion, but with limited extension (3 mm) in depth. Such features may be explained by the faster-dripping unsaturated water feeding the stalagmite during summer, fact noticed during dripwater sampling in 2003-2004.

Seven calcite subsamples (0.8-2 g weight, 3 mm thick) were taken for the TIMS dating. Chemical separation followed procedures from Tamas and Causse (2001) and Constantin et al. (2007). Uranium and thorium ratios were measured in peak jumping mode on a Finnigan-MAT262 mass spectrometer.

All samples show relatively high uranium contents, ranging from 3.5 to 5 ppm. No correction for detrital contamination was performed, as $^{230}$Th/$^{232}$Th ratios obtained are fairly high (660 – 9000). The lower $^{230}$Th/$^{232}$Th value for the top subsample (~107) is obviously due to the small amount of $^{230}$Th. The ages range between 9257±23 yr and 52±3 yr BP, the latter obtained for the first 3 mm from the stalagmite top. A growth hiatus is recorded between 2178 and 929 yr BP. The average growth rate for the whole stalagmite is 22 mm/ky, but faster growth is recorded in the intervals 9.2-8.4 ky BP (36 mm/ky) and 7.2-6.4 ky BP (93 mm/ky).

203 samples for stable isotope analyzes were taken at 1 mm along the growth axis and 3 growth layers were checked for kinetic isotopic fractionation. Tests for equilibrium deposition show little correlation between $\delta^{18}$O and $\delta^{13}$C values along the stalagmite ($r^2 = 0.2$), however on the last growth interval, from 929 yr. to present, we found a strong co-variation between the two records ($r^2 = 0.8$). The maximum variations of $\delta^{18}$O values within the growth layers were 0.14‰, 0.3‰, and 0.34‰ respectively. All these data point to calcite deposited under equilibrium conditions with respect to oxygen and carbon isotopes (Hendy, 1971) along most of the stalagmite.

![Fig. 2. Ages and position of samples for U-Th dating on S139 and the $\delta^{18}$O record.](image)

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The δ¹⁸O values range between -6.40‰ and -8.25‰ PDB along the stalagmite growth axis, with a mean value of -7.64‰. δ¹³C values vary between -3.5‰ and -7.14‰ PDB. A comparison of the S139 record with isotope data obtained from two other stalagmites (S22 and S117) sampled from the same cave (Tamas et al., 2005) shows there is a good correlation between the three records over the common 9.2 ky – 5.6 ky period. Two small drops to values < -8‰ centered at 9.2 and 8.2 ky are ascribed to cold events detected in the Greenland ice cores and other paleoclimate proxies (e.g., von Grafenstein et al., 1999; Bond et al., 2001). Between 7.8 and 2.1 ky, the oxygen record slightly increases, but has lesser variation. The last growth interval, from 900 yr to present, is marked by a sharp increase of δ¹⁸O and δ¹³C values at around 700 yr BP As a whole, the isotope record allows comparison with pollen and paleovegetation data from the area.

References


Estimation of environmental radionuclide concentration in soils, a comparison of methods for the annual radiation dose determination in luminescence dating

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A study was made to compare and test the performance of several methods for the annual radiation dose determination in luminescence dating. The following techniques were compared: instrumental neutron activation, high-resolution gamma spectrometry, and alpha spectrometry.

In the case of instrumental neutron activation, ²³⁸U, ²³²Th, and ⁴⁰K concentrations were determined using the Zirconium standardization method. Detailed analysis was carried out using high-resolution gamma spectrometry, the activities of different nuclides (²³⁴Th, ²²⁶Ra, ²¹⁴Pb, ²¹⁴Bi, ²¹⁰Pb, ²²⁸Ac, ²⁰⁸Tl) in the uranium and thorium chains being measured, as well as ⁴⁰K. The advantage of this method is that radioactive equilibrium or disequilibrium in the uranium series can be checked. In the present work, the direct measurement of ²²⁶Ra, which can give extra information on the interpretation of the radioactive equilibrium, was implied. Since there is a serious spectral interference (up to 43%) on its 186.2 keV gamma line (by ²³⁵U at 185.7 keV) the correction procedure was outlined. Radon loss due to sample preparation was also investigated and an average loss of 15% was observed. Thus we stress upon the need for storing the samples for three weeks before measurement in order for the radioactive equilibrium to be reached again. A constant underestimation of ²¹⁴Bi activities compared to ²¹⁴Pb was observed. Since ²¹⁴Bi and ²¹⁴Pb should be in equilibrium, this can be attributed to summing-out effects. We recommend that in the case that no corrections are made to derive the activity of radon daughters from the activity of ²¹⁴Pb instead of computing average value including also ²¹⁴Bi. Moreover, concentrations of ²¹⁰Po, ²²⁶Ra, and ²³⁸U were determined through alpha spectrometry measurements.

Analyses were carried out on five different soil samples taken from the archaeological site of Lumea Noua, Alba Iulia. The importance of these samples is related to the fact that they surrounded ceramic materials of archaeological interest which were collected for luminescence dating, thus the nuclide concentrations measured in this work will be directly used in the process of obtaining the age of this pottery. The matrix dose rate for quartz inclusions was calculated. The obtained values for the five samples range between 2 and 2.5 μGy/year.
The results obtained through gamma spectrometry and neutron activation are in agreement within error limits, the advantage of the latter being that it is more precise, while the advantage of the first over the latter being the conclusions upon equilibrium that can be drawn. As work is still in progress we refrain ourselves from drawing far-reaching conclusions at the time of writing. The final results will be presented and discussed at the conference.
Development of the Nano-EA-irMS: a novel method for analyzing the isotopic composition of large organic compounds

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Existing methods for the compound-specific stable isotope analysis (CSIA) require introduction of individual compounds to an isotope ratio mass spectrometer via gas (GC) and liquid chromatographic (LC) interfaces. While these methods are robust, there are limitations on the size and polarity of analyzable compounds.

To measure the isotopic composition of a broader range of compounds (especially tetraether membrane lipids and pigments), we developed a system to reduce the minimum sample size using elemental analysis mass spectrometry (EA-irMS) of individual compounds. EA-irMS sample size requirements are artificially high because high carrier gas flow rates effectively dilute the sample gas. To take advantage of the universal applicability of EA-irMS, we have designed a system to reduce sample size requirements by cryogenically trapping sample gas (CO₂, N₂, H₂, and CO) from the high-flow EA effluent on a custom 0.75 ID silicosteel trap packed with 5Å MolSieve (Restek, Bellefonte, PA USA). The sample gas is then diverted to a low-flow helium stream (1 ml/min), thus reducing the carrier gas:sample gas ratio.

We tested this system with standards for nitrogen (IAEA N₂-ammonium sulfate and in-house sediment standard), carbon (C₄₁ alkane and ANU sucrose), and hydrogen (NBS-22 oil, C₄₁ alkane, androstane). In each case, instrument background and/or memory effects led to both systematic and non-systematic variations in the measured isotope values. In the nitrogen system the background magnitude is quite stable with a coefficient of variation of 2.3%, so we were able to obtain consistent isotopic results for standards. The carbon background is less consistent, having a coefficient of variation of 7.4%, hence the system requires larger carbon samples for accurate analysis. Possible sources for noise in nitrogen background are small leaks or impurities of the oxidation gas; the carbon background is primarily from the silver sample cups. Nonetheless, nano-EA sensitivity is 1.5 to 3 orders of magnitude greater than conventional EA for carbon (100 nmol C) and nitrogen (60 nmol N).

In the hydrogen system, isotopic composition of the H₂ background is variable but consistently small. We hypothesize that sample gas partially charges a pool of exchangeable H₂ on the surface of the reactor and controls its isotopic composition. The isotopic composition of this reservoir is then imparted to both background and
subsequent sample gases. Molecular modeling suggests the reservoir is associated with hydrogen exchange on the glassy carbon surface at high temperatures. This memory effect has been observed in conventional TC-EA systems, but is much more pronounced in the Nano-TC-EA systems. Reducing and controlling this memory effect is essential to future δD analysis, yet the sample size required to overcome the background is still at least 2 orders of magnitude (>100 nmol H) smaller than the requirements for conventional EA analysis.
Dilution factor for Danube - Black Sea Canal water in Agigea - Black Sea area using tritiated wastewater from NPP Cernavoda

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The Danube - Black Sea Canal is situated in the southeastern part of Romania. It takes its waters from Danube, upstream Cernavoda town, and flows into the Black Sea at Agigea. The main uses of the channel are numerous, but navigation and nuclear power generation at the Cernavoda Nuclear Power Plant can be mentioned. In addition, the canal is highly urbanized. The maximum weigh-carrying of the canal is 70 million t/year. Agigea is the most important harbor of the Canal and due to intense activity, the risk of accidents is relatively high.

In this study we propose to use tritiated liquid effluents from CANDU type NPP Cernavoda as tracers, to study the mixing coefficient between the freshwater of the canal and the Black Sea waters. Tritiated water can be used to simulate the transport and dispersion of solutes in the Danube - Black Sea Canal because it has the same physical characteristics as water. Measured tracer-response curves produced from injection of a known quantity of soluble tracer provide an efficient method of obtaining necessary data. We established the tritium level in the monitored zone Agigea - Black Sea by monthly sampling the canal water and precipitation between May 2005 and May 2006. The average tritium concentration for the Black Sea near Agigea was 12.5 +/- 2.2 TU. During the NPP evacuation we established inside the canal lock at Agigea a well-mixed tritium concentration of 174.07 +/- 6.2 TU. Using waters lock as a tracer we established a dilution factor of 1:4.28 inside the Agigea harbor, and a dilution factor of 1:2.17 for the open sea. The “Grigore Antipa” INCDM used these primary parameters in their dispersion simulation for the Agigea - Black Sea area.
State-of-the-art in the primary isotope measurement: what is an “absolute isotope amount ratio measurement“?

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Stable isotope measurement techniques are considered as one of the fastest growing analytical areas, especially due to the large range of their applications. However, most frequently, the explored matter is extremely sensitive to small variations in isotope ratios and therefore a high analytical precision of the measurements is required.

Fortunately, in most cases, valuable information can be obtained from 'differences' in isotope amount ratios and most of the related analytical instrumentation (mass spectrometers) has therefore been developed in this direction.

Based on Nier's original configuration, more and more sophisticated “delta” Isotope Ratio Mass Spectrometers (IRMS) were designed and built, with large mass ranges and increased measurement precisions. The principle of such machines is to perform ratios of ion current ratio measurements on samples and “reference sample” under identical conditions and so reporting “delta” value differences in per mil. By applying this approach it is obvious that the quality of such δ-measurements is mainly depending of the “degree” of obtaining (and keeping) perfect “identical” conditions in the mass spectrometer concerned. This kind of methodology has however some fundamental weaknesses:

- In nearly all the circumstances, reference samples are artifacts and they are subject to inhomogeneity and instability issues over time. For isotope studies, it will therefore be practically impossible to guarantee good inter-comparability of results (in time and space).
- Reference samples (exception in some cases; i.e. nitrogen in air) will be physically exhausted sooner or later. Such situation will require the elaboration of a difficult “transfer” procedure of the carrier “value” to its successor.
- Particular situations require the knowledge of absolute isotope amount ratios, as in the re-determination of the Avogadro constant.

The philosophy of 'absolute' isotope ratio measurement at IRMM is totally opposite to usual “δ-measurements”. Instead of being concentrated to assure “identical conditions” in the mass spectrometer (for reference and sample), here the approach is to maximize and control the isotope fractionation process in the molecular gas flow from the inlet system to the ion source. Therefore, even if the basic processes that take place are practically identical as in any other commercial gas IRMS - electron impact ionization, the formation and focusing ion beams in the source, magnetic deflection and detection (Faraday/with the subsequent Secondary Electron Multiplier)
- the concept is to relate the dynamics of the measured ion currents to a known physical process in an extremely stable and known environment.

The goal of this paper is to fully describe the principle of “absolute” isotope amount ratios measurements and to clarify the mathematics behind the data treatment.
A new evaluation of the Oxygen correction algorithm for carbon and oxygen isotope amount measurements on CO₂ gas

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Carbon isotope amount measurements are intrinsically related to the oxygen isotopic composition, as most mass spectrometric measurements are made on CO₂ gas at mass-to-charge 44 to 46. The large number of isotopomers however is making the calculation of carbon or oxygen isotope abundance rather tricky.

Oxygen has three stable isotopes, of which two are rare both with natural abundance of only ~0.037 and ~0.2 amount %, for respectively ¹⁷O and ¹⁸O. The variations around these abundances are dependent of fractionation processes in nature. It is therefore rather difficult to achieve the oxygen isotope abundances only by theoretical calculations or assumptions, even if the sample history is well known. To trace back past events however, values for the oxygen isotope abundances could help.

Current mass spectrometric measurements (via commercial δ instruments) are performed at mass-to-charge 44, 45, and 46 (mass-to-charge 47 is minor abundant and being so, difficult to measure via commercial machines) i.e. insufficient equations are available in this way to determine the carbon and oxygen isotope abundances.

A typical procedure to overcome this problem is to complete the set of two equations with an additional one, which describes the relationship (as assumed) between the three oxygen isotopes in the sample:

\[ \frac{^{17}R_{\text{sample}}}{^{18}R_{\text{sample}}} = \left( \frac{^{17}R_{\text{reference}}}{^{18}R_{\text{reference}}} \right) \cdot a \cdot \frac{^{18}R_{\text{sample}}}{^{18}R_{\text{sample}}} \]

In absence of any “mass-independent” fractionation process, which is nearly the case for all environmental and geochemical (natural) applications, it could be safely assumed that ¹⁷O variations are following the ¹⁸O ones according to the upper relationship. The two “constants” involved are subject for discussion as the fractionation factor l could have a value between 0.500 and 0.5305 while \(a\) is based on previous measurements. However, different ¹⁷Oxygen-¹⁸Oxygen algorithms are currently used; all based on different determinations of ¹⁷Oxygen as well as on different values for ¹ value. As this “correction” algorithm has a significant effect on the carbon and oxygen isotopic abundances, only absolute values for oxygen isotopes can help.

The work here is therefore focused especially on the “absolute” C and O isotope amount ratios measurements performed on the different CO₂ gases from various carbonates. All amount ratios are calibrated via “synthetically prepared mixtures of enriched isotopes”, which makes any correction for the oxygen variation superfluous. The final relationship obtained between the oxygen isotopes ¹⁷O and ¹⁸O allows to calculate the fractionation factor l and the constant \(a\) in the upper equation.
Effect of DDT on the diet-tissue fractionation factoring in various tissues of the perch *Perca fluviatilis*

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In ecotoxicological studies, stable isotopes (\(^{15}\)N and \(^{13}\)C) are more and more used as a complementary method of dietary analysis, to describe trophic links and to assess food-web structure. Stable isotopes are regarded as indicators of organic matter sources able to describe trophic links and matter transfer along a food chain. These studies allow an accurate determination of the trophic level, based on the calculation of the diet-tissue fractionation factor. However the latter, determined for the whole organism or for particular tissues, may vary substantially *in natura*. Vanderklift and Ponsard's (2003) analyses point to several important sources of variation in \(^{15}\)N enrichment such as tissues, diet, taxon, main biochemical form of nitrogen excretion or nutritional status. The potential effect of pollutants on the diet-tissue fractionation factor is seldom taken into account. Therefore we raised perch, *Perca fluviatilis* in controlled conditions, and fed them for 6 weeks with commercial pellets contaminated with DDT, an ubiquist contaminant. DDT exhibite estrogenic activity stimulates production of liver microsomal enzymes that lead to hydroxylation of steroids in experimental animals which may have adversely affected reproductive success and development. In the present study, \(^{13}\)C and \(^{15}\)N were analysed in lipid-free tissues (liver, gills, white muscle), showing various metabolic activities.

Reference

The study of the isotopic composition of milk and dairy products

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The stable isotope composition of food is strictly connected with environmental conditions (climate, geographical position, geology) and anthropogenic factors (fertilizers, pollutants etc). The bases are isotopic effects (biological, physical and chemical), which are responsible for different isotopic compositions in nature: soil, air and water.

The Isotope Ratio Mass Spectrometry (IRMS) methods play a very important role in food authenticity and origin control. The measurements of bio-element (hydrogen, nitrogen, carbon, oxygen, and sulfur) composition provide a very sensitive tool to food control. The isotopic methods of origin and authenticity control were recently implemented in the European Union for wine, juice, and honey.

The aim of our study is to explore the relationship between the isotopic composition of milk, dairy products and their origin. The effect of differentiation of the isotope composition of milk is connected with the different compositions of cow diet (maize, grass, etc.) and the different compositions of drinking water. Seasonal and regional variations of cow diet composition cause seasonal and regional variations of isotopic composition of the milk and finally dairy products (see Table below and Fig. 1).

<table>
<thead>
<tr>
<th>Chemical component</th>
<th>Source</th>
<th>Element</th>
<th>Isotope Ratio</th>
<th>Critical factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Drinking water</td>
<td>Oxygen</td>
<td>$^{18}\text{O}/^{16}\text{O}$</td>
<td>hydrogeology, geographical origin</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrogen</td>
<td>$^{2}\text{H}/^{1}\text{H}$</td>
<td></td>
</tr>
<tr>
<td>Casein</td>
<td>Fodder: grass, hay</td>
<td>Carbon</td>
<td>$^{13}\text{C}/^{12}\text{C}$</td>
<td>plants: C3, C4 metabolism</td>
</tr>
<tr>
<td>Lactose</td>
<td>maize or beet</td>
<td>Nitrogen</td>
<td>$^{15}\text{N}/^{14}\text{N}$</td>
<td>fertilizers: organic or synthetic</td>
</tr>
<tr>
<td>Fat</td>
<td></td>
<td>Sulfur</td>
<td>$^{34}\text{S}/^{32}\text{S}$</td>
<td>geology, air pollutants</td>
</tr>
<tr>
<td>Minerals</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. What does determine the water isotopic composition of dairy products?  
Schematic way from the farm to the consumer.
In the frame of the project, many samples of milk and dairy products from main regions of milk production are gained. The collected samples are measured using an IRMS DELTA\textsubscript{plus} (Finnigan, Germany) with peripheral units: GasBench, H/Device and Elementar Analizer.

The correlations between stable isotope composition $^{18}$O/$^{16}$O $^{13}$C/$^{12}$C, $^{15}$N/$^{14}$N and $^{2}$H/$^{1}$H in milk components is analyzed. The variability of the parameters related to environmental factors such as geology, climate, and anthropogenic factors are studied. Finally, on the base of the collected results, the regional distribution of isotopic parameters will be drawn. In the future we will propose the method of origin control for some dairy products for the database of authentic value of stable isotope composition.

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Boron isotope study about the anthropogenic influence on the urban water cycle

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Boron is used as a conservative tracer in aqueous environment because of its high solubility (predominantly as boric acid), its natural presence in nearly all water, and because of its occurrence in anthropogenic impacted water systems. Particularly the latter one is in focus on studies of anthropogenic impacts on urban water. To understand the interaction of urban surface and groundwater, boron and particularly their stable isotopes, ¹¹B and ¹⁰B, are increasingly applied as tracer and marker for urban geochemical processes.

Here, we present a study on the urban water components of the city of Leipzig, Germany, with the aim to use boron and its isotopes as tracer for anthropogenic influences. The results of this urban catchment of Leipzig are then compared with data from the urban influenced river catchment of the Hérault watershed in France.

At both sites, a multi-isotope approach is used for analysing the stable isotopes of H/O from water, S/O from sulphate, N/O from nitrate, and boron isotopes in connection with hydrochemical data. Results of water samples from rivers, groundwater wells, and effluents from sewage water treatment plants are discussed in order to find relations of anthropogenic impacts on the water system.
Origin of groundwater in the Budapest thermal karst regime by preliminary environmental isotope data

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The fault-line of Danube at Budapest is the discharge area of a regional thermal karst water flow regime, where the warm (deep) and the luke-warm (relatively shallow) components are mixed. The chemistry of the karstic water varies in a wide range, but the relatively high sodium content (up to 200 mg/l) is characteristic mainly for the warm component. According to the regional karst water flow model (Tóth, 2007) the water of the warm component reaches considerable depth where it mixes with a small portion of very saline fossil seawater while it is warmed up to about 80 to 100 °C.

Our goal is to determine the origin of water by stable (H, O) and radio- (¹⁴C) isotope measurements and validating the hydraulic flow model by these isotopic data.
Fig. 1. Oxygen isotopic composition ($\delta^{18}O$) vs. (Na+K)/(Na+K+Ca+Mg) meq.% parameter of 27 thermal water samples taken in the area of Budapest, Hungary.

See the text for the explanation of the Mixing lines 1 and 2.

In Hungary, the average $\delta^{18}O$ value of groundwater infiltrated during the Holocene is between -10‰ and -9‰, while infiltrated during the latest glaciation (at the end of the Pleistocene) it is between -14.8‰ and -11‰ (Stute and Deák, 1989).

The so far studied samples fall into two groups according to their $\delta^{18}O$ values (Fig. 1). Samples of one group (dominantly warm component) have $\delta^{18}O$ values between -13 to -11‰ clearly indicating that these waters were infiltrated during the Ice Age. It is interesting to note there is a negative linear correlation between the $\delta^{18}O$ and Na+K milliequivalent percent parameters. According to sporadic radiocarbon age data (Deák, 1979, 1980) the oldest thermal water of the studied area is about 20 ka, around what time there was the last glacial minimum (LGM). Since the $\delta^{18}O$ value of the water infiltrated during the LGM in Hungary is close to -14‰ (Stute and Deák, 1989), the samples in the first group were infiltrated after the LGM. In this case the more negative the $\delta^{18}O$ value the older age has the water. If we accept the hydraulic model (Tóth, 2007) that these water samples are mixture of deep circulated meteoric water and a small amount very saline fossil sea water, we can infer, that the older the water the greater is the ratio of fossil sea water component (greater Na+K meq.% means greater sea water component). On Fig. 1 “Mixing line 1” shows this mixing.

The other group of samples (dominantly luke-warm component) is characterized by $\delta^{18}O$ values around -10.5‰, which may indicate that these waters were infiltrated during the transition from the Ice Age to the Holocene or these samples are mixture of Holocene infiltrated water (shallow circulating flow system) and water from the first group (deep circulating system) when both components are moving up to the surface. This process is indicated on Fig. 1 by the “Mixing line 2”. Further radiocarbon measurements will help to determine whether this group of samples is a mixture of two components or not.

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References


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