UFZ Centre for Environmental Research
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## UFZ-Report 02/2005

# European Society for Isotope Research

VIII Isotope Workshop, Extended Abstract Volume

June 25 to 30, 2005,
Leipzig, Germany

Gehard Strauch, Stephan M. Weise

UFZ Centre for Environmental Leipzig-Halle
Department of Hydrogeology, Department Isotope Hydrology

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European Society for Isotope Research - ESIR -

# VIII Isotope Workshop, Extended Abstract Volume

Gehard Strauch, Stephan M. Weise (Eds.)

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Department of Hydrogeology and Department Isotope Hydrology

# Contents

## Session 1: Contamination

### Chairman: D. Hunkeler

## Session 2: Geochemistry & Water

### Chairman: J. Hoefs

## Session 3: Ecology

### Chairman: L. Waasenaar

## Session 4: Sedimentology

### Chairman: M. E. Böttcher

## Session 5: Paleoclimatology

### Chairman: G. H. Schleser

# Conference Programme ESIR 8
June 25 - 30, 2005

## Sun, 26-06-05

| | | |
|---|---|---|
| 10.00 - 18.00 | Arrival | Conf. Office KUBUS |
| 14.00 - 18.00 | Sightseeing Tour | Meeting in the city |
| 18.00 – 20.00 | Registration | Conf. Office KUBUS |

## Mon, 27-06-05

| | | |
|---|---|---|
| 08:00 | Registration | Conf. Office KUBUS |
| 09:00 | Opening ESIR 8 | Conf. Site KUBUS<br>Organizers, G. Teutsch, Scientific Director of UFZ |

### Session 1: Contamination
Conf. Site KUBUS, Lecture Hall 1A

**Chairman: D. Hunkeler**

| | | |
|---|---|---|
| 09:30 | Compound-specific isotope methods in contaminant hydrogeology: State-of-the-art and challenges<br>*D. Hunkeler, Y. Abe (inv1)* | |
| 10:10 | Stable isotope study of a volatile hydrocarbons contaminated landfill site, Bonfol, Switzerland<br>*Thierry R. Oppikofer, Torsten W. Vennemann, Jorge E. Spangenberg, Markus Bill (o11)* | |
| 10:30 | Application of compound-specific stable carbon and hydrogen isotope analysis to characterize organic contamination of groundwater<br>*Jeroen Verhack, Jan Bronders, Ilse Van Keer, Rudy Swennen, Jan Schwarzbauer, Tom N.P. Bosma (o12)* | |
| ***10:50*** | ***Coffee break*** | |
| 11:20 | Evidences for in situ natural attenuation of Monochlorobenzene in an anaerobic contaminated aquifer<br>*Ivonne Nijenhuis, Sylvia Uhlig, Arno Kaschl, Marcell Nikolausz, Matthias Kästner, Hans-Hermann Richnow (o13)* | |
| 11:40 | Stable isotopes as expert witness in traffic accidents: assessing the likelihood between forensic samples of motor oils<br>*Jorge E. Spangenberg, Georges Pierrini, Christophe Champod, FrancoTaroni (o14)* | |
| 12:00 | Isotopic investigation of dissolved and sedimentary sulfur compounds for assessing in-situ biodegradation of petroleum hydrocarbons in a sulfate rich urban aquifer<br>*Kay Knoeller, Michael Schubert (o15)* | |
| 12:20 | Tracing the impact of river bank filtration on the transport of xenobiotica in urban groundwater by stable isotopes<br>*Karsten Osenbrück, Rolf Trettin, Kay Knöller, Gerhard Strauch, Hans-Reinhard Gläser, Monika Möder (o16)* | |
| ***12:40*** | ***Lunch break*** | ***UFZ Canteen*** |

## Session 2: Geochemistry and Water

Conf. Site KUBUS

**Chairman: J. Hoefs**

14:20 Isotope fingerprints in the earth sciences: a critical discussion
*Jochen Hoefs (inv2)*

15:00 Stable isotope ratio measurements using the Finnigan NEPTUNE multicollector ICPMS using high mass resolution
*Johannes Schwieters, Claudia Bouman (o21)*

15:20 The mineral isotope composition of two Precambrian carbonatite complexes from the Karelian - Kola region
*Marion Tichomirowa, Gerhard Grosche, Boris Belyatski, Elena Savva, Jörg Keller, Jens Götze, Wolfgang Todt (o22)*

***15:40 Coffee break***

16:10 Isotope geochemistry as a tool for investigation of the origin of increased salinity in the Cambrian-Vendian aquifer system in northern Estonia
*R. Vaikmäe, E. Karreo, E. Kaup, A Marandi, T. Martma, L. Vallner (o23)*

16:30 Development of methods for recovery of water from fluid inclusions for stable isotope analysis
*Yuri Dublyansky (o24)*

16:50 Determination of $\delta$D and $\delta^{18}$O in brackish and saline natural waters. Part I: The question of distillation of water samples prior to isotopic analysis.
*Adam Porowski, Peter Kowski (o25)*

17:10 Isotopic evidences for a new type of groundwater in the Kinneret basin, Israel
*C. Siebert, S. Geyer, P. Möller (o26)*

***19:00 Conference Dinner*** ***Leipzig Zoological Garden***
23:00 back

## Tue, 28-06-05

## Session 3: Ecology

Conf. Site KUBUS

**Chairman: L. Wassenaar**

08:30 Global application of stable hydrogen isotopes to wildlife forensics
*Leonard I. Wassenaar, Keith A. Hobson, Gabriel J. Bowen (inv3)*

09:10 Nitrogen isotope ratios as indicator of organic production
*Hilmar Förstel, Angelika Basu, Markus Boner (o31)*

09:30 Effects of clear cutting and soil preparation on natural $^{15}$N abundance and N concentration in the needle and soil of two boreal conifer tree species
*S. P. Sah and H. Ilvesniemi (o32)*

09:50 Carbon isotopes distribution along pine needles (Pinus nigra)
*Lidia Barszczowska, Mariusz-Orion Jedrysek (o33)*

***10:10 Coffee break***

10:40 Potential of natural fouling communities for assimilation of fish farm derived particulate nitrogen: a case study in Gulf of Aqaba (Red Sea)
*Sonja Lojen, Timor Katz, Anat Tsemel, Ehud Spanier, Dror L. Angel (o34)*

| | | |
|---|---|---|
| 11:00 | $CO_2$ concentration and $\delta^{13}C$ through time in sets of monthly air samples from down-town Parma and from the Parma and Taro river valleys, Italy<br>*Antonio Longinelli (o35)* | |
| 11:20 | Carbon isotope discrimination affected by atmospheric pollutants<br>*Ralf Wagner (o36)* | |
| 11:40 | Turnover of soil organic carbon - The microbial perspective<br>*Christiane Kramer, Gerd Gleixner (o37)* | |
| 12:00 | C and O isotope working standards from $C_3$ and $C_4$ photosynthates<br>*Jorge E. Spangenberg (o38)* | |
| ***12:20*** | ***Lunch*** | ***UFZ Canteen*** |
| 13:30 | Excursion | Freiberg<br>20:00 back |

## Wed, 29-06-05

## Session 4: Sedimentology

Conf. Site KUBUS

**Chairman: M. E. Böttcher**

| | | |
|---|---|---|
| 09:00 | Authigenic sulfur phases as recorders for black shale-triggered anaerobic oxidation of methane: Results from ODP Leg 207<br>*M.E. Böttcher, Brumsack H.-J., A. Hetzel, A. Schipper (inv4)* | |
| 09:40 | Microbially-derived methane in coalbed gases: compound-specific carbon-isotopic study of coalbed gases from the Illinois Basin, USA<br>*D. Strapoc, A. Schimmelmann, M. Mastalerz (o41)* | |
| 10:00 | Early diagenesis of sulphur in recent estuarine sediments (Authie Bay, N France)<br>*Sonja Lojen, Nevenka Mikac, Cedric Gabelle, Michel Wartel (o42)* | |
| 10:20 | Sulfur and oxygen isotopes of Lower Miocene nonmarine evaporites in the Upper Silesian Coal Basin<br>*S. Halas, T.M. Peryt, I. Pluta (o43)* | |
| ***10:40*** | ***Coffee break*** | |
| 11:10 | Ordovician and Silurian carbon isotope trend: a state of art report based on the East Baltic data<br>*Tõnu Martma, Dimitri Kaljo (o44)* | |
| 11:30 | Variations of $\delta^{13}C_{TOC}$ values of clastic sediments from Thuringia related to biogeo-chemical carbon cycle<br>*Karin Bräuer, Knut Hahne, Birgit Mingram, Ulrich Wand (o45)* | |
| 11:50 | Basin-Scale changes in Upper Cretaceous paleosols: paleoenvironmental implication for the Maastricht deposits, South Carpathians.<br>*Ana-Voica Bojar, Dan Grigorescu, Franz Ottner, Zoltan Csiki (o46)* | |
| ***12:10*** | ***Lunch*** | ***UFZ Canteen*** |
| 14:00 | Poster Session | Conf. Site KUBUS |
| 17:00 | Advisory Board Meeting | incl. Poster Evaluation |
| 18:00 | General Assembly | President, Gen. Assembly<br>incl. Poster Award |

## Thur, 30-06-05

## Session 5: Paleoclimatology

Conf. Site KUBUS

**Chairman: G. H. Schleser**

08:30 Stable isotopes as proxies for the reconstruction of past climates
*G.H. Schleser (inv5)*

09:10 A stable isotope record of an ice core from Akademii Nauk ice cap, Severnaya Zemlya, Russian Arctic
*Diedrich Fritzsche, Rainer Schütt, Hanno Meyer, Heinrich Miller, Frank Wilhelms, Lev M. Savatyugin (o51)*

09:30 Stable isotope investigations on tree-ring cellulose of Late Glacial pine chronology of Reichwalde (Lusatia). Effects caused by destruction of fossil woods.
*M. Haupt, R. Wagner, T. Boettger (o52)*

09:50 Effect of river regulation on the isotopic characteristics of river water and molluscs
*István Fórizs (o53)*

***10:10 Coffee break***

10:40 Stable isotope study on the carbonate phases of the Basaharc loess-paleosol profile (Hungary)
*Bernadett Bajnóczi, Erzsébet Horváth (o54)*

11:00 Geochemical and isotopic variations in recent freshwater carbonates in Krka river, Croatia; Implication for climate reconstruction
*Sonja Lojen, Baghdad Oudanne, Barbara Vokal, Wolfgang Papersch, Neven Cukrov (o55)*

11:20 Environmental isotope studies in Croatia
*Ines Krajcar Bronic (o56)*

11:40 Holocene isotopic shift of atmospheric sulfur - a case history from Hungary
*István Horváth, István Veto (o57)*

12:00 Final Statements Strauch/Weise

## Session 1

# Contamination Studies

# Compound-specific isotope methods in contaminant hydrogeology: State-of-the art and challenges

D. Hunkeler, Y. Abe
Centre of Hydrogeology, University of Neuchâtel, Rue Emile Argand 11, 2007 Neuchâtel, Switzerland

## 1 Introduction

Compound-specific isotope analysis has rapidly advanced as a new tool to evaluate transformation processes in the subsurface. An increasing number of laboratory studies have shown that chemical and biological transformation of organic compounds is often associated with significant isotope fractionation, while physical processes have little effect on isotope ratios. These results provide the basis for application of the method at field sites as a tool to demonstrate and possible quantify contaminant transformation. The reliability of the approach depends on how robust the isotope fractionation factor for a given transformation process is and on the availability of adequate mathematical tools for interpretation of field isotope data. In the presentation, the factors that control the magnitude of isotope fractionation during biodegradation are discussed as well as strategies for quantitative evaluation of isotope data in the field.

## 2 Magnitude of isotope fractionation during biodegradation

There is a general consensus that isotope fractionation during biodegradation originates from an kinetic isotope effect associated with the initial enzymatic transformation of the substrate. There is a wealth of information available on isotope effects for different reactions from studies in organic chemistry and enzymology. A first insight into the magnitude of isotope fractionation for different reactions can be gained by calculating expected isotope effects for splitting different type of bonds. If only differences in vibrational energy between analogous bonds with different isotopes are taken into account and tunneling is neglected, these estimates are denoted as Streitwieser semi-classical limits and are reported in Table 1 for some common bonds (6). Thereby, it has to be noted that in organic chemistry and enzyme studies, isotope effects are usually expressed by the ratio of the rate of the light ($k_L$) to the heavy isotope ($k_H$) and are therefore usually > 1:

$KIE = k_L / k_H$ (i) while in geosciences, the inverse ratio is used:

$\alpha = k_H/k_L$ (ii) Alternatively, isotope fractionation is expressed in terms of an isotopic enrichment factor $\varepsilon=(\alpha-1)\cdot 1000$.

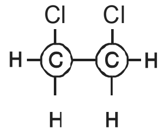
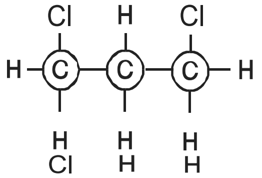
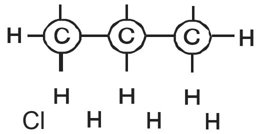
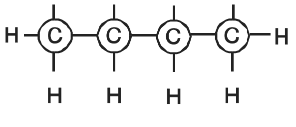
According to these estimates, the magnitude of the isotope effect is larger for the element with the larger relative mass difference in the bond as is most apparent for C- versus H-isotope fractionation in a C-H bond. For a given element in different bonds, the expected isotope effect is the larger, the heavier the atom is to which the element of interest is bound. Thus for example, a large carbon isotope effect is expected for splitting a C-Cl bond ($\varepsilon$=-53.9) than for splitting a C-H bond ($\varepsilon$=-20.6).

The above values only apply if the bond is considered in isolation which is generally not possible in substrates isotopically labeled at natural abundance. In a fraction of the molecules, the heavy isotope will not be located at the reactive site; thus, no isotope effect occurs even though a heavy isotope is present. This effect is discussed using transformation of haloalkanes by haloalkane dehalogenase as an example

Table 1 Streitweiser semiclassical limits for isotope effects at 25°C. Modified from (6).

| Bond | Frequency (cm$^{-1}$) | Isotope | KIE | α | ε |
|---|---|---|---|---|---|
| C-H | 2900 | $^{12}$C/$^{13}$C | 1.021 | 0.979 | -20.6 |
| | | $^{1}$H/$^{2}$H | 6.44 | | |
| C-C | 1000 | $^{12}$C/$^{13}$C | 1.049 | 0.953 | -46.7 |
| C-Cl | 750 | $^{12}$C/$^{13}$C | 1.057 | 0.946 | -53.9 |
| C-Cl | 750 | $^{35}$Cl/$^{37}$Cl | 1.013 | 0.987 | -12.8 |
| C-N | 1150 | $^{12}$C/$^{13}$C | 1.060 | 0.943 | -56.6 |
| C-N | 1150 | $^{14}$N/$^{15}$N | 1.044 | 0.957 | -42.1 |
| C-O | 1100 | $^{12}$C/$^{13}$C | 1.061 | 0.943 | -57.5 |
| C-O | 1100 | $^{16}$O/$^{18}$O | 1.067 | 0.937 | -62.8 |

Table 2 Whole molecule isotope effect and bond-specific isotope effect for dehalogenation of chlorinated ethanes by Xanthobacter autotrophicus GJ10.

| Compound | Isotope effect for whole molecule | | Bond-specific isotope effect |
|---|---|---|---|
| 1,2-Dichloroethane<br>1,2-DCA |  | 1.0301 | 1.0567 |
| 1,3-Dichloropropane<br>1,3-DCP |  | 1.0204 | 1.0567 |
| Chloropropane<br>CP |  | 1.0174 | 1.0484 |
| Chlorobutane<br>CB |  | 1.0135 | 1.0487 |

For haloalkanes, no isotope effect occurs despite the presence of a heavy isotope if it is located at a non-reactive position (such as the middle carbon in 1,3-DCP) or if several identical reactive site are present in the molecules (such as in 1,3-DCP) and the heavy isotope occurs at the reactive site that is not undergoing reaction.

For these reasons, a decreasing whole-molecule isotope effect is generally expected with increasing number of atoms of the element of interest and an increasing number of reactive sites. Indeed, for chlorinated alkanes, the whole-molecule carbon isotope effect decreases with the number of carbon atoms (Table 2). The whole-molecule isotope effect can be corrected for the number of atoms at non-reacting position and the number of equivalent reactive sites to obtain bond-specific isotope effect (3). The bond-specific isotope effects are in a similar range for all compounds and correspond quite well to the estimation of the isotope effect associated with splitting a C-Cl bond, which is expected to be 1.057 (Table 1). For CP and CB, the bond-specific isotope effect is slightly smaller than for the other two compounds.

For the interpretation of calculated bond-specific isotope effects, it has to be taken into account that they can be affected by other factors than the molecule size and number of reactive sites. If the transformation step is preceded by slow transport or binding step, the kinetic isotope effect will be partly masked. Such steps may have contributed to the somewhat smaller values for CP and CB. The calculation of bond-specific isotope effects and comparison with theoretical values makes it possible to gain insight into factors that control the magnitude of isotope fractionation and in return may also be used to predict maximum isotope effects for a given compound and for given reaction mechanism.

## 3 Evaluation of field data

For one step transformation processes, the evaluation of field data is usually based on the Rayleigh equation which is given in its simplest version, using carbon isotopes as an example, by:

$\Delta\delta^{13}C = \varepsilon * \mathrm{In}\,(C/C_0) = \varepsilon\,\mathrm{Inf}$ (iii)

where $\Delta\delta^{13}C$ is the shift in carbon isotope ratio, $C_0$ the initial concentration, C the concentration at the sampling point and ε is the isotopic enrichment factor.

The Rayleigh equation can be used in different ways to evaluate field data: First, $\Delta\delta^{13}C$ can be plotted against $\ln C/C_0$. If biodegradation is the main degradation process, a linear relation should be obtained with a slope corresponding to the isotopic enrichment factor from laboratory experiments. However, often the contaminant concentration is also affected by dispersion and field based isotopic enrichment factors are smaller than laboratory derived values as for example observed for anaerobic MTBE degradation (8). Second, the fraction of compound remaining f (or the fraction removed 1-f) can be calculated based of shifts in isotope ratios and isotopic enrichment factors derived from laboratory experiments. Finally, the Rayleigh equation combined with the first order rate law (5) provides a simple means to estimate first order degradation rates from field data:

$k = (\Delta\delta^{13}C) / (\varepsilon * t)$ (iv)

where t is the travel time between source and sampling point. To illustrate the application of equation (iv), first order degradation rates were calculated based on published field isotope data from petroleum hydrocarbon contaminated sites (Table 3). The calculated rates are close to mean rates estimated for other fields using different methods.

Table 3 Estimation of first order degradation rates from field isotope data using equation 4 and comparison with reported rates.

| Compound | $\delta^{13}C_0$ | $\delta^{13}C$ | t | $\varepsilon_{reported}$ | f | k (1/d) | $k_{literature}$ |
|---|---|---|---|---|---|---|---|
| MTBE(7) | -25.7 | 1.8 | 1518 | -13 (8) | 0.12 | 0.0014 | 0.0014 (2) |
| Benzene (4) | -25.9 | -24.7 | 80 | -2.4 (4) | 0.60 | 0.0065 | 0.0036 (12) |
| Benzene (10) | -28.7 | -27.7 | 97 | -2.4 (4) | 0.65 | 0.0045 | 0.0036 (12) |
| Toluene (4) | -21.9 | -18.5 | 80 | -1.5 (4) | 0.10 | 0.030 | 0.059 (12) |
| Toluene (10) | -27.9 | -13.9 | 97 | -1.5 (4) | 0.0003 | 0.083 | 0.059 (12) |
| o-Xylene (4) | -25.9 | -16.3 | 80 | -1.8 (4) | 0.005 | 0.068 | 0.039 (12) |
| o-Xylene (10) | -28.3 | -26.9 | 97 | -1.8 (4) | 0.39 | 0.010 | 0.039 (12) |
| m/p-Xylene (4) | -23.4 | -19.2 | 80 | -2.8 (4) | 0.22 | 0.019 | 0.025/0.014 (12) |
| m/p-Xylene (9) | -27.6 | -21.9 | 94 | -2.8 (4) | 0.13 | 0.023 | 0.025/0.014 (12) |

## 4 Conclusions

The availability of an increasing number of laboratory studies on isotope fractionation during biodegradation in conjunction with new data evaluation methods have provided detailed insight into factors that control isotope fractionation during biodegradation. These studies demonstrate that the observed fractionation is compound- as well as pathway-specific. While new data evaluation methods potentially make it possible to predict whole molecule isotope effects for compounds that have not yet been investigated, the influence of slow preceding steps is still difficult to quantify. The occurrence of pathway-specific isotope fractionation can complicate evaluation of isotope data at field sites. However, recent studies have shown that dual isotope studies, an well-established approach for inorganic compounds such as nitrate, is a powerful approach to identify degradation mechanisms; thus, to select appropriate enrichment factors for quantification of biodegradation (8, 13). While different strategies for quantitative evaluation of isotope data have been developed, they all rely on the Rayleigh equation which assumes a homogeneous, well-mixed contaminant pool. At field sites, this assumption is generally not valid since contaminants travel at different velocities due to the physical heterogeneity of the subsurface. The uncertainty associated with geological heterogeneity remains to be investigated. The discussed approaches to evaluate field data are only valid for one step processes. However, for a number of important contaminants such as chlorinated ethenes transformation processes usually involve multiple steps. Recently, analytical and numerical models that incorporate isotope fractionation in multistep processes were developed which aid in the interpretation of isotope data from such processes (1, 11).

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# Stable isotope study of a volatile hydrocarbons contaminated landfill site, Bonfol, Switzerland

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[2)]Office des Eaux et de la Protection de la Nature, République et canton du Jura, Les Champs-Fallat, 2882 Saint-Ursanne, Switzerland

## 1 Introduction

Between 1961 and 1976 about 114'000t of chemical waste were deposited in the industrial landfill site of Bonfol (ILSB), Jura, NW Switzerland. The site is located in a former clay pit in a quaternary clay formation. About 5 % of the waste consists of volatile organic compounds (VOC), notably chlorinated aliphatic hydrocarbons, as well as chlorinated and non-chlorinated aromatic hydrocarbons. As part of a pilot study, the distribution of the VOC contamination in the groundwater by means of organic and isotopic geochemistry was investigated.

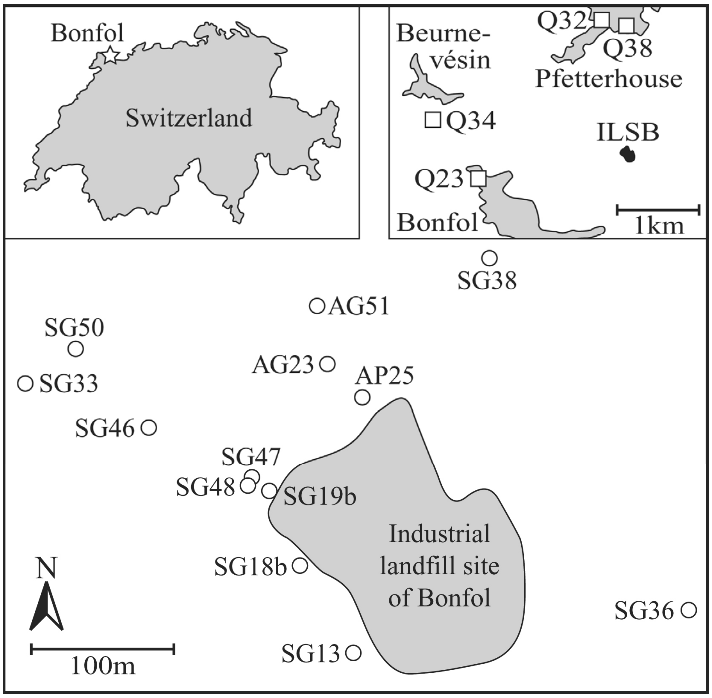

Fig. 1 Localisation of the sample sites and the industrial landfill site of Bonfol, Switzerland (Abbreviations: Q = karst springs, SG = boreholes in the gravel aquifer, AG and AP = boreholes in quaternary clay formation)

## 2 Sampling and methodology

Four domains were sampled in October 2003, April 2004 and October 2004: i) four karst springs (Q in Fig. 1) in the region of Bonfol, ii) ten boreholes (SG in Fig. 1) in the underlying gravel aquifer, where a plume of VOC is caused by a leak of the landfill site, iii) three boreholes in a sable lens within the clays (AG and AP in Fig. 1), polluted by the leachate, and iv) five sites in the waste water purification facility, where the landfill leachate is cleaned.

The isotopic composition of water ($\delta^{18}O_{water}$, $\delta^{2}H_{water}$ expressed vs. V-SMOW) and dissolved inorganic carbon (DIC, $\delta^{13}C_{DIC}$ expressed vs. V-PDB) were measured with a ThermoQuest Finnigan GasBench II connected to a Delta Plus XL isotope ratio mass spectrometer (IRMS) and an H-Device coupled to a Delta S IRMS. VOC aliquots were extracted from the water samples by a headspace technique, which is an isotopically non-fractionating procedure for sampling of most VOC (Slater et al., 1999). VOC identification and quantification were performed by gas chromatography with mass spectrometric detection (GC/MSD; Agilent HP6890 coupled to an Agilent HP 5973 MSD). The carbon isotope composition of some individual VOC was obtained by gas chromatography coupled to a combustion interface and an isotope ratio mass spectrometer (GC/C/IRMS; Agilent G1530A/ThermoFinnigan GC Combustion III/Delta Plus XL).

## 3 Results and discussion

The isotopic composition of the water in the karst springs (samples Q) show highly variable values of $\delta^{18}O$ and $\delta^{2}H$ in the range from −8.0 to −9.9‰ and −55 to −70‰, respectively. Seasonal variation with higher δ values in autumn has been identified, indicating rapid flow rates within these aquifers. The $\delta^{13}C$ values of DIC vary between −14.6 and −17.3‰ with concentrations between 2.6 and 7.2 mmol/l. This range of $\delta^{13}C$ values corresponds to groundwater in equilibrium with soil $CO_2$ ($\delta^{13}C_{CO2} \approx -23‰$) at a pH of 6.5. A pollution of 10.0 ppb trichloroethylene (TCE) and 2.4 ppb tetrachloroethylene (PCE) has been detected in the spring Q32, 1.6 km north of the ILSB. The concentrations of TCE and PCE in these samples are too low for accurate measurement of the $\delta^{13}C$-value by GC/C/IRMS. Therefore, we could not determine the origin of these pollutants as suggested by Beneteau et al. (1999).

The $\delta^{18}O$ values of water samples in the gravel aquifer (samples SG) range from −8.9 to −9.5‰ and the $\delta^{2}H$ values from −63 to −66‰. This aquifer is homogeneous and does not show any systematic seasonal variation. The range measured in the gravel aquifer is similar to that of the regional sources (samples Q), but the mean values show a slight depletion in oxygen-18 and deuterium. This isotopic shift could be explained by the distinct altitude of the recharge areas of the gravel and karst aquifers and the associated different isotopic composition of precipitations. The concentrations of DIC (1.4 to 3.6 mmol/l) are much lower than in the karst aquifer. The $\delta^{13}C_{DIC}$ values vary between −15.0 and −20.5‰ with a mean value of −19.7‰, compatible with a lower influence of marine carbonate dissolution. Mixing processes between waters from different zones in the gravel aquifer have been identified. Waters from zones with low permeability (wells SG38 and SG18b) have higher concentrations of DIC and more positive $\delta^{13}C_{DIC}$ values than samples taken in regions with higher permeability. TCE, PCE, tetrachloromethane, chloroform and chlorobenzene have been detected in borehole SG19b. A plume of TCE and PCE can be followed downstream. The decrease of their concentration downstream reflects most likely dilution, dispersion and evaporation effects in the aquifer. It appears that very little or no degradation by aerobic micro-organisms occurs, as no degradation products were detected.

The $\delta^{2}H$ values in pore water from the clay formation (samples AG and AP) show nearly no variation in the three boreholes (−60.6 to −61.6‰). The $\delta^{18}O$ values decrease significantly with increasing distance to the ILSB (from −7.8 in AP25 to −8.7‰ in AG51).

Apparently high $^{18}$O-concentrations near the landfill site can be caused by the occurrence of VOC. Many VOC contain ions of masses 44 to 46 in their mass spectra, and can, therefore, contribute to m/z 46 in the ion source. Equilibration techniques using the Finnigan GasBench may provide false results for heavily contaminated samples. A thermal conversion/elemental analyser (TC/EA) would be more suitable for such samples. The $\delta^{18}$O values increase with VOC contamination. Concentration of total aromatic and aliphatic hydrocarbons decrease from 4460 ppb (AP25) to 1905 ppb (AG23), and finally to 57 ppb (AG51). The value for sample AP25, ~15 m from ILSB, is nearly as high as in the landfill leachate (5151 ppb). Dichloromethane, TCE and PCE are the only aliphatic hydrocarbons detected in borehole AG23 with concentrations below 3 ppb. No aliphatic hydrocarbons were found ~60 m from ILSB (sample AG51). The front of the contamination can be followed by higher concentrations of the more mobile aromatic hydrocarbons in boreholes AG23 and AG51, at least up to ~60 m from ILSB. We did not study samples more distant from the ILSB.

Apparently the pollutants are not affected by biodegradation, since the isotopic composition of the carbon in the VOC show no significant variation between the leachate and boreholes AP25 and AG23. The concentration of DIC and the s24d$^{13}C_{DIC}$ values increases with distance to ILSB in samples AP25 (3.0 mmol/l, −9.7‰) and AG23 (12.3 mmol/l, −5.7‰). A more important $CO_2$ contribution from dissolution of marine carbonates in this sand lens of the clay formation might explain these variations of the DIC.

The leachate of the ILSB is collected in a basin before it gets cleaned. 39 VOC have been identified. Their concentrations were slightly variable with time. The $\delta^{13}$C values were 0.6 to 0.9‰ lower in October 2004 relative to April 2004. This could be related to pulsed introduction of the leachate and variable residence times in the basin. Degradation processes in the basin produce a fractionation of the carbon isotopes, leading to an enrichment in $^{13}$C. Table 1 shows several $\delta^{13}C_{VOC}$ values measured in the leachate in October 2004, and are compared to published values.

Table 1: $\delta^{13}$C values of aliphatic and aromatic hydrocarbons

| Substance | $\delta^{13}$C [‰] this study | $\delta^{13}$C [‰] from literature |
|---|---|---|
| TCE | −30.82 ± 0.41 | −27.37 to −31.90 [1)] |
| PCE | −22.68 ± 0.30 | −23.19 to −37.20 [1)] |
| Benzene | −23.56 ± 0.27 | −23.87 to −29.40 [2)] |
| Toluene | −25.07 ± 0.17 | −25.76 to −29.03 [2)] |
| Xylene | −26.02 ± 0.23 | −26.09 to −26.56 [2)] |

[1)]Shouakar-Stash et al. (2003), [2)]Harrington et al. (1999)

Except for TCE, the $\delta^{13}$C values of the VOC in the leachate are higher than the values measured by Harrington et al. (1999) and Shouakar-Stash et al. (2003) for pure compounds from different manufacturers. This $^{13}$C enrichment of the VOC could be related to degradation processes in the ILSB. An isotopic shift associated to evaporation cannot be excluded.

The first step of cleaning of the leachate is mainly biodegradation in a filter with anaerobic micro-organisms that degrade about 92% of the aliphatic hydrocarbons and 34% of the aromatic hydrocarbons. After having passed by two evaporation basins, in which aerobic bacterial degradation occurs, no VOC were detected. The anaerobic biodegradation seems to produce dichlorethylene and vinylchloride from other chlorinated ethenes, and benzene from alkyl- and chloro-aromatic compounds. After the filter most VOC concentrations were too low for $\delta^{13}C$ analyses. For benzene a $^{13}C$-enrichment of 0.9‰ is observed. This indicates that benzene was biodegraded in the anaerobic filter. The DIC in the water after the anaerobic filter shows high concentrations (17.7 mmol/l) and high $\delta^{13}C$ values (−1.0 to −3.7‰), most probably related to a high biologic activity in the filter with preferential metabolic assimilation of isotopically light carbon. In the evaporation basins the DIC concentrations decrease to 2.2 and 5.3 mmol/l. These values correspond to the concentrations measured in the karst springs (samples Q) and in the gravel aquifer (samples SG). In the first basin the $\delta^{13}C_{DIC}$-value decreases to about −15‰, which falls in the range of the karst springs. In the second basin the $\delta^{13}C$-value increases to −9.1 to −11.1‰. This isotopic shift reflects mixing of water from the first basin with precipitation water ($\delta^{13}C_{DIC} \approx -2$ ‰). The $\delta^{18}O_{water}$ values (−8.3 to −9.9‰) and $\delta^{2}H_{water}$ values (−57 to −64‰) are within the range of the karst springs (samples Q). They show high variations between the three sampling campaigns. Hence, the isotopic composition of the water in waste water purification facility is greatly influenced by the last precipitation event.

## 4 Conclusions

The cleaning of landfill site waters contaminated by VOC through evaporation and biodegradation processes can be traced by changes in the concentrations and isotopic compositions of DIC and individual VOC. The changes in the isotopic composition of water reflect mixing and recharge processes.

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# Application of compound-specific stable carbon and hydrogen isotope analysis to characterize organic contamination of groundwater

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Stable isotopic analysis is being increasingly applied to investigate and monitor the sources, transport, and fates of organic contaminants in environmental systems including groundwater. This interest has been largely due to recent demonstrations of the ability of isotopic analysis to differentiate sources of, and to demonstrate degradation of, contaminant organic compounds in the environment (e.g. Hunkeler *et al.*, 2001; Morasch *et al.*, 2002; Shouakar-Stash *et al.*; 2003; Slater, 2003).

Soil investigations carried out at and around a former paint and varnish factory near the city of Vilvoorde (Belgium) indicated that at shallow depth (< 6 m) a VOC (volatile organic carbons) contamination is mainly characterized by the presence of BTEX components whereas at greater depth also chlorinated hydrocarbons (VOCl's) were detected. With respect to the BTEX pollution at least two pools of light non-aqueous phase liquids (LNAPL) are considered of being the source of the contamination (figure 1). The presence of the VOCl's is related to multiple sources distributed over neighbouring sites. Because of mixing of the pollutants it is very difficult to distinguish the contribution of each of the delineated sources using molecular analytical data. A differentiation is also necessary when remedial actions have to be defined since liabilities are an important aspect for the problem owner(s).

In order to distinguish the impact of the two source zones on the BTEX contamination at the site and to evaluate the presence of degradation processes, compound specific stable carbon and hydrogen analyses were carried out on groundwater samples and pure product. Samples were taken from more than 20 wells located both in the potential source zones as downstream. The results of these analyses will allow to define a difference between different types of pollutant plumes. The method and the approach for the selected site including the results will be discussed during the presentation.

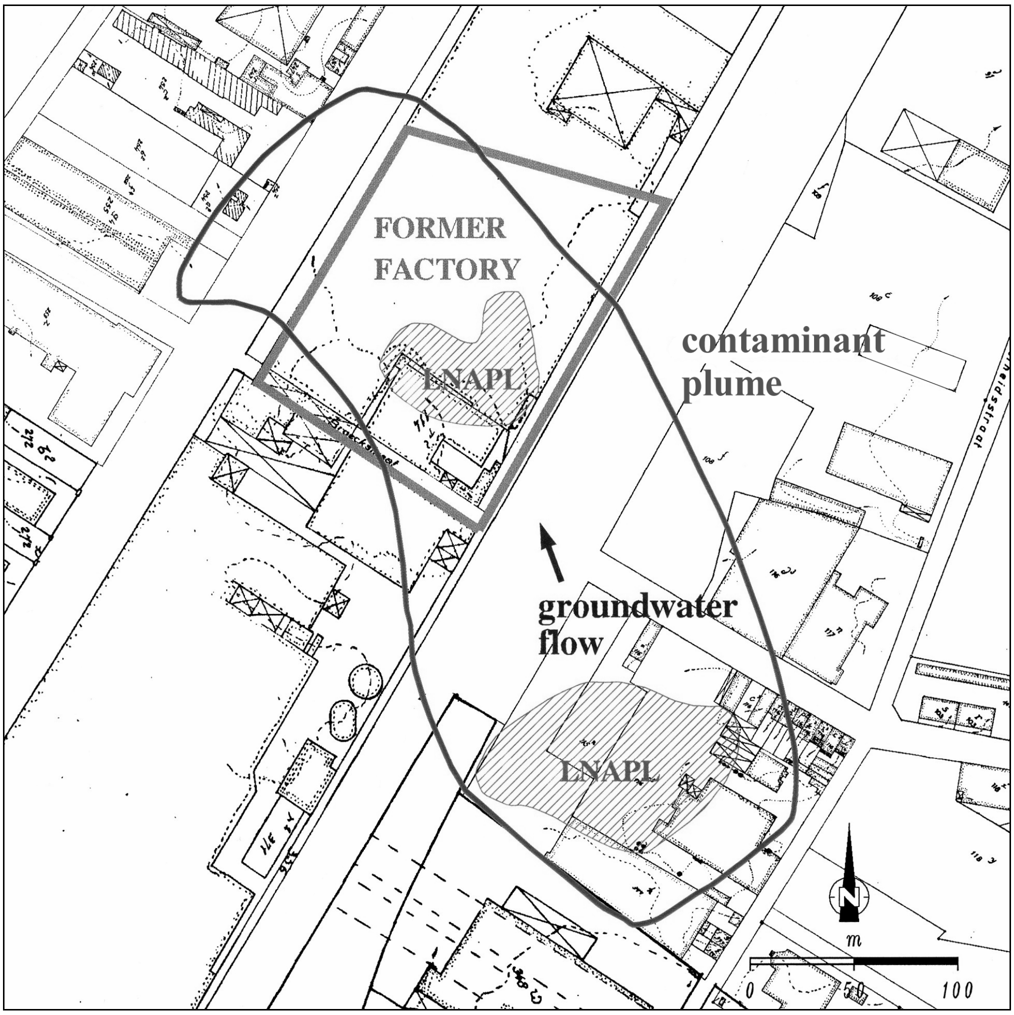

Fig. 1 Schematic view of a VOC contamination at and around a former paint and varnish factory

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# Evidences for *in situ* natural attenuation of monochlorobenzene in an anaerobic contaminated aquifer

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The Bitterfeld/Wolfen region in Germany comprises a contaminated area of about 25 km$^2$, corresponding to about 200 million m$^3$ contaminated groundwater. The area is contaminated as a result of the activities of the former organic industry, primarily with chlorinated aliphatics but also BTEX compounds, hexachlorocyclohexane, chlorobenzenes and many other contaminants. Monochlorobenzene (MCB) is a contaminant almost ubiquitously found throughout this area. MCB degradation has been observed and well studied under aerobic conditions, but under anaerobic conditions complete degradation of MCB has not been proven yet. We studied anaerobic degradation monochlorobenzene using a variety of tools.

Here, we provide evidence of the *in situ* biodegradation of MCB under anaerobic conditions. Laboratory microcosms were prepared anaerobically from groundwater, an *in situ* bioreactor approach was used to study the incorporation of MCB into biomass (phospholipid fatty acids; PLFA), the carbon stable isotope composition of MCB was analysed to study the *in situ* contaminant degradation.

A previous study showed that the stable isotope composition of the MCB along the flow path was enriched in $^{13}$C-MCB in the residual fraction of up to 4 δ units, comparing the centre of a plume relative to the fringe, suggesting in situ degradation of the compound (Kaschl et al., in press). Anaerobic laboratory microcosms were prepared from several groundwater sources in Bitterfeld to test for anaerobic MCB degradation. MCB concentrations decreased in several microcosms, but the activity could not be sustained or transferred yet.

*In situ* bioreactor systems (BACTRAP), were used to assess the *in situ* degradation potential of MCB. In this set-up, BIOSEP®-beads are loaded with a $^{13}$C enriched tracer substance. After several weeks to months incubation in a groundwater well, a biofilm forms on the surface of the beads. An analysis of the phospholipid fatty acid (PLFA) composition and the stable isotope composition of these fatty acids may be used to provide information on degradation and incorporation into biomass of the tested substance. BACTRAPs with $^{13}$C-labelled MCB as a tracer substance were used and incubated for several weeks in an anoxic portion of the MCB plume. The isotopic composition of the PLFA extracted from the biomass formed on the BACTRAP was analysed and provided evidence for incorporation of the $^{13}$C-label into biomass. The unsaturated fatty acids 16:1 and 18:1 showed a profound enrichment in $^{13}$C compared to saturated fatty acids 16:0 and 18:0. The relatively high content in $^{13}$C in these unsaturated fatty acids indicates degradation and incorporation of the carbon of MCB into phospholipid fatty acids and suggests the presence of a microbial population capable of complete MCB degradation. For the molecular survey of microbial communities involved in the degradation of MCB, DNA was isolated from bead materials and microcosms.

Potential degraders were assessed by the sequence analysis of clone libraries generated from PCR products amplified with universal 16S rDNA primers. Quantification of the detected community members will be carried out by FISH analysis.

Both, stable isotope composition analysis of MCB and the BACTRAP tracer study provided evidence for anaerobic degradation and incorporation of MCB-carbon into bacterial biomass, even though degradation rates in the field appear to be small. Further research should provide evidence for the *in situ* involved MCB degrading communities and the degradation pathway used.

**Reference**

Arno Kaschl, Carsten Vogt, Sylvia Uhlig, Ivonne Nijenhuis, Holger Weiss, Matthias Kästner and Hans H. Richnow, 2005, Isotopic fractionation indicates anaerobic monochlorobenzene biodegradation, Environmental Toxicology and Chemistry, *in press*

# Stable isotopes as expert witness in traffic accidents: assessing the likelihood between forensic samples of motor oils

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## 1 Introduction

Isotopic and molecular organic geochemistry based on bulk and compound specific $\delta^{13}C$ data (from EA/IRMS and GC/C/IRMS) and biomarker parameters (from GC/FID and GC/MSD), combined with the experience from the field of petroleum exploration and production geochemistry have played an important role in the development of forensic methodologies for the identification of oil spills in the marine environment (e.g., Kaplan et al., 1997; Philp et al., 2002). Here we explore a similar analytical approach for fingerprinting motor oil spills from traffic accidents.

In most traffic accidents involving a car crush, aliquots from motor oil spills can be recovered from the road or highway surface, and compared with the crankcase oil from the involved or suspected vehicles. The comparison of the chemical compositions of these forensic samples provides a scientific framework for the identification of the vehicles involved in the traffic accident, the reconstruction of the accident, and help the tracing of the driver/passengers of the vehicles. This is of prime importance for court decisions in traffic accidents. The results of this preliminary study show that a multivariate statistical treatment of the isotopic compositions of motor oil fractions, through calculation of likelihood ratios based on the MVN method (Aitken and Lucy, 2004), may be a way to assess links between motor oil spills and vehicles in cases of traffic accidents. The molecular characterizations of the oils provide additional information.

## 2 Methodology

### 2.1 Samples

In this preliminary case study, motor oil samples were obtained from the crankcase of 7 vehicles with gasoline engine and 3 vehicles with diesel engine, immediately after oil change (distance, $d$ = 0 km) and after a known driven distance ($d$ = x km) (Table 1). The first set of 10 samples ($d$ = 0 km), represent the oil-spill samples recovered from the road surface, and are called “recovered samples”. The samples at $d$ = x km, correspond to control oil samples taken from the crankcase of the involved or suspected vehicles, and are called “control samples”. A sample from motor oil purchased in a local gas station was analyzed as the “forensic” samples, and was used to test for eventual analytical shifts. All the samples were stored in 2 ml vials at +4°C until required for analyses.

### 2.2 Analyses

The oil samples were analyzed using procedures described previously (Spangenberg and Macko, 1998; Spangenberg and Frimmel, 2001). Aliquots of the oil samples were passed through an activated copper column to remove elemental sulfur. The sulfur-free oil samples were separated into three fractions (saturated, aromatic and the polar NOS compounds) using liquid chromatography. The bulk sulfur-free oils and the three oil fractions were analyzed for $\delta^{13}C$ by flash combustion on an elemental analyzer connected to an isotope ratio mass spectrometer (Finnigan MAT Delta S) that was operated in the continuous helium flow via a Conflo III split interface (EA-IRMS). Few samples had sufficient S and N compounds for isotopic analyses (results not discussed here for brevity). Three replicate isotopic analyses of each oil sample and fractions were performed. The reproducibility of the EA/IRMS $\delta^{13}C$ measurements is better than ±0.1‰ (1 SD).

### 2.3 Data treatment

A multivariate statistical analysis of the isotopic data, based on the principle of multivariate likelihood ratio was used to assess the links between the motor oil samples. This approach compares between-group variance with the within-group variance for multivariate normally distributed data (method MVN, see Aitken and Taroni, 2004 for detailed description; programs available at *http://www.blackwellpublishing.com/rss).*

In order to obtain an additional corroborative analysis, a chemical characterization of the saturated hydrocarbons was performed with an Agilent Technologies GC HP 6890 coupled to a HP 5973 quadrupole mass selective detector (MSD). Compound identifications were made by comparison with synthetic standards, GC retention times, interpretation of mass spectrometric fragmentation patterns and literature mass spectra.

## 3 Results and discussion

The $\delta^{13}C$ values of bulk "recovered" oil samples range from –26.81 to –32.49‰, with most of the samples around ~ –27 to –28 ‰ (Table 1). The variation of the $\delta^{13}C$ values of fraction within the “recovered” oil sample (bulk, saturated, aromatic, NSO) follows generally the conventional trend recognised in crude oil and bitumens (Stahl, 1978), increasing in the following order: $\delta^{13}C_{sat} < \delta^{13}C_{aro} < \delta^{13}C_{NOS}$, with $\delta^{13}C_{sat}$ up to 6.7‰ more negative than $\delta^{13}C_{NOS}$. This is not the case for all the “control” samples, with the difference $\delta^{13}C_{sat}$ - $\delta^{13}C_{NOS}$ between -0.94 to 0.91‰. The bulk, aromatic and polar (NOS) fractions of the "control" oil samples are depleted in $^{13}C$ by up to 2.59 ‰ compared to the "recovered" samples (Table 1, Fig. 1). The NOS fractions display the most important isotopic shift. This suggests preferential loss of $^{13}C$-enriched moieties, most probably from thermally more labile oil or additives fractions (e.g., preservatives, antioxidants). The saturated hydrocarbons of the "control" samples are enriched in $^{13}C$ by up to 1.24 ‰ compared to the "recovered" samples. This is the normal isotopic shift observed during cracking of hydrocarbons, which involve the release of $^{13}C$-depleted moieties (e.g., Spangenberg and Frimmel, 2001). The bulk and hydrocarbon fractions of the GP-4 oils are depleted in $^{13}C$ by ~5‰ compared to the other oils.

Table 1 Average (n = 3) values of C isotope compositions of bulk "recovered" oil and differences between isotopic composition of hydrocarbon fractions of "control" and "recovered" samples.

| Vehicle (engine)1) | Country2) | $\delta^{13}C_{bulk, R}$3) (‰, PDB) | Distance4) km (days) | $\Delta^{13}C_{bulk, C-R}$3) (‰) | $\Delta^{13}C_{sat, C-R}$ (‰) | $\Delta^{13}C_{aro, C-R}$ (‰) | $\Delta^{13}C_{NOS, C-R}$ (‰) |
|---|---|---|---|---|---|---|---|
| 1 (G) | CH | -27.12 | 2758 (58) | -0.39 | 1.14 | -1.07 | -1.82 |
| 2 (G) | CH | -27.99 | 2800 (60) | -0.41 | 1.24 | -0.57 | -2.59 |
| 3 (G) | FR | -26.81 | 286 (93) | -0.47 | 0.78 | -0.88 | na |
| 4 (G) | FR | -32.49 | 11139 (93) | -0.56 | 0.74 | -0.42 | na |
| 6 (G) | FR | -27.45 | 2669 (69) | -0.33 | 0.55 | -0.45 | -0.7 |
| 7 (G) | CH | -28.09 | 3325 (65) | -0.33 | 0.95 | -0.74 | -0.54 |
| 8 (D) | FR | -28.14 | 1703 (65) | -0.51 | 1.06 | -0.39 | 0.14 |
| 9 (D) | FR | -27.44 | 1308 (63) | -0.08 | 0.53 | 0.21 | -0.45 |
| 10 (D) | FR | -27.42 | 8859 (97) | 0.02 | 0.9 | -1.36 | -0.79 |
| 11 (G) | FR | -28.62 | 1000 (1) | -0.23 | 0.17 | -0.49 | -0.82 |

1)G = gasoline engine; D = diesel engine; 2)CH = Switzerland; FR = France; 3)R = recovered; C = control; 4)distance driven and days between "recovered" and "control" sample

The likelihood ratio approach was applied to compute the ratios of the probability of the comparison outcome between the "control" and the "recovered" samples based on the set of isotopic measurements given two competitive propositions: $H_p$ = the control and recovered oil samples come from the same crankcase, and $H_d$ = the control and recovered oil samples come from different crankcases. Briefly, there are three inter-related factors that determine the nature of the inference to be made: the number of replicate measurements, the within-source variation, and between-sources variation. The likelihood ratios (LR, probability of de $H_p$ vs. probability of $H_d$) were calculated from a measurements matrix composed from m = 11 cases (10 "recovered" and "control" oil pairs, and test sample), p = 5 variables ($\delta^{13}C_{bulk}$, $\delta^{13}C_{sat}$, $\delta^{13}C_{aro}$, $\delta^{13}C_{sat}/\delta^{13}C_{bulk}$ and $\delta^{13}C_{aro}/\delta^{13}C_{bulk}$), n = 3 replicates. Values of the LR > 1 supports hypothesis $H_p$: control and recovered oil come from the same crankcase, and values for LR < 1 support $H_d$: control and recovered oil come from different crankcases (Pierrini, 2005). The calculated likelihood ratios are given in Table 2.

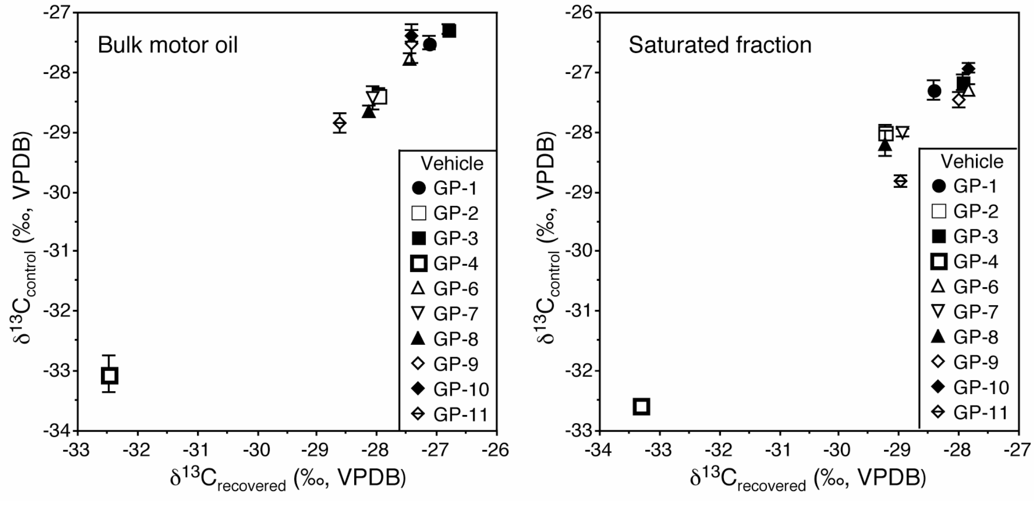

Fig. 1 Stable carbon isotope composition of the bulk and saturated fraction of recovered and control motor oil samples. Some error bars have been omitted for reasons of clarity.

Table 2 Values for the likelihood ratio

| Vehicle/ oil GP- | 1-con | 2-con | 3-con | 4-con | 5-con | 6-con | 7-con | 8-con | 9-con | 10-con | 11-con |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-rec | **232** | 0.0 | 0.0 | 0.0 | 0.2 | 107 | 0.0 | 0.0 | 19.4 | 300 | 0.0 |
| 2-rec | 0.0 | **622** | 0.0 | 0.0 | 0.0 | 0.0 | 1329 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3-rec | 1.4 | 0.0 | **67.4** | 0.0 | 62.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.2 | 0.0 |
| 4-rec | 0.0 | 0.0 | 0.0 | **3**$^{+12}$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5-"rec" | 4.1 | 0.0 | 892 | 0.0 | **1169** | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 6-rec | 129 | 0.0 | 0.0 | 0.0 | 0.0 | **807** | 0.0 | 0.0 | 46.6 | 122 | 0.0 |
| 7-rec | 0.0 | 2572 | 0.0 | 0.0 | 0.0 | 0.0 | **254** | 1.6 | 0.0 | 0.0 | 0.0 |
| 8-rec | 0.0 | 61 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | **231** | 0.0 | 0.0 | 0.0 |
| 9-rec | 234 | 0.0 | 0.1 | 0.0 | 0.7 | 202 | 0.0 | 0.0 | **1.2** | 49.9 | 0.0 |
| 10-rec | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5.5 | **4.2** | 0.0 |
| 11-rec | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | **27.3** |

Proposition $H_p$ is supported if LR is greater than 1. In all cases when recovered and control oil samples come from the crankcase of the same vehicle, the $H_p$ values are >1, there was no misleading evidence in favour of the defence, since $H_p$ is true (diagonal in Table 2). The LR between the test oil sample (GP-5) and the control sample GP-3 is 892, clearly supporting the hypothesis of a common source for both oils. This is an excellent result, because one of us (GP), for testing the analytical approach, took the test sample GP-5 from the same motor oil container used for the oil change in vehicle 3 (samples GP-3). As expected the isotopically very different oil GP-4, give large LR value for $H_p$ (Fig. 1, Table 2). For the hypothesis $H_d$ (control and recovered oil samples come from different bulk sources) the LR values are generally < 1. However, there are some LR values which are >1 (15 from 111), some very high, as 2572 for pair 7 - 2. These wrong "positive" tests would represent 13.5 % of misleading evidence for the court. For example, if we consider the motor oil pair 11, an expression of the likelihood ratio could be: It is 27 time more likely to get such isotopic ratios evidence (that is the expression of the analytical match) in case of recovered and control motor oil come from the same crankcase than recovered motor oil 11 - 11 come from one of the ninth other crankcases.

The distribution of the aliphatic hydrocarbons, in particular the biomarker hydrocarbons hopanes and steranes give further evidence for oil-oil correlation (Fig. 2). The molecular parameters (e.g., hydrocarbons concentration ratios) of the "recovered" samples compare favourably with the "control" samples, suggesting that little thermal maturation took place after a relatively short use of the vehicle engine. The occurrence of high unresolved complex mixture (UCM) in all oil samples makes the compound specific carbon isotope analysis impossible.

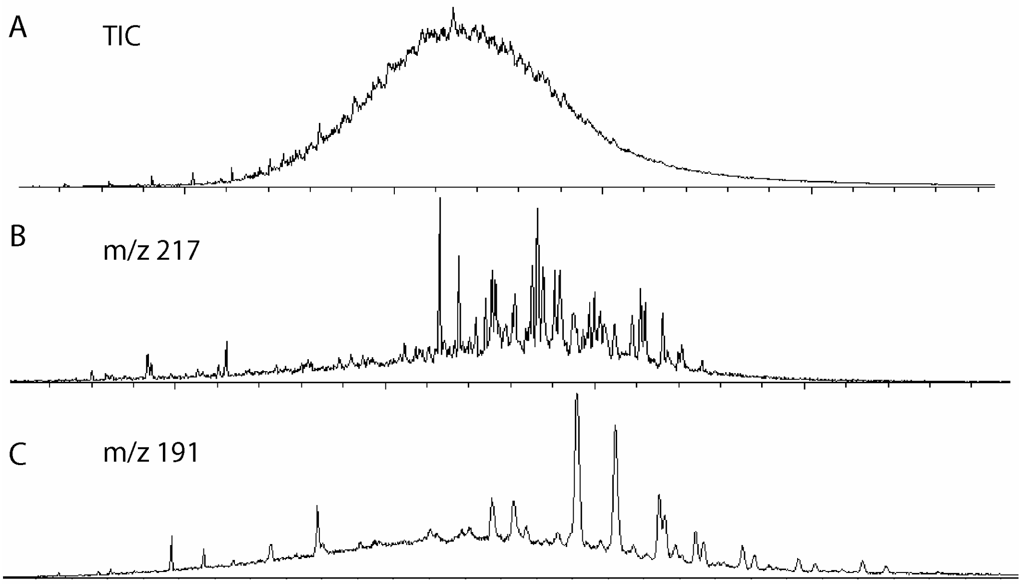

Fig. 2 Representative distribution of hydrocarbons in the saturated fraction of motor oil samples (sample GP-7 recovered). A. Total ion chromatograms (TIC). B. Distribution of the steranes (m/z 217). C. Distribution of the hopanes (m/z 191)

## 4 Conclusions

Stable isotopes and molecular characterization of motor oils can provide forensic evidence in case of traffic accidents. The crucial issue consist in the interpretation of the analytical results. The use of a likelihood ratio framework on a multivariate data set help to assess links between samples of motor oils, giving a fair and balanced evidence in the court. Further work is needed to validate the proposed approach, by using real forensic scenes covering as many different cases of traffic accidents as possible.

**Acknowledgements.** We thank Patrick Touron from the Institut de Recherche Criminelle de la Gendarmerie Nationale, and Torsten Vennemann from the Institute of Mineralogy and Geochemistry of the University of Lausanne for their interest and support regarding this project. This work was supported by the University of Lausanne and Swiss National Science Foundation grants to J.E. Spangenberg.

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# Isotopic investigation of dissolved and sedimentary sulfur compounds for assessing in-situ biodegradation of petroleum hydrocarbons in a sulfate rich urban aquifer

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Due to its contribution to the mineralization of organic contaminants to carbon dioxide and water, bacterial sulfate reduction (BSR) may be an important process for the long-term natural attenuation of contaminated aquifers. The preferential utilization of the lighter isotopes by bacteria usually results in the enrichment of the lighter isotope in the produced sulfide and of the heavier isotope in the remaining sulfate. For sulfur, the isotopic enrichment in the sulfate has been successfully used for the identification and quantification of BSR. However, only little is known about the behavior of oxygen isotopes in sulfate during sulfate reduction under the specific conditions of organic contamination. Therefore, part of the investigation was focused on the specification of possible fractionation parameters for oxygen in the residual sulfate. For assessing the potential and extent of anaerobic biodegradation, the sulfur isotopic composition of dissolved sulfate and sulfide as well as of sedimentary monosulfide, disulfide, and elemental sulfur was investigated. In order to recognize possible aerobic degradation, carbon isotope measurements of dissolved inorganic carbon were also conducted.

The contaminated Quaternary aquifer is situated within the city limits of Leipzig in a built-up area predominantly of residential and/or small business use. The contamination is directly related to the former operation of a gasoline station. Several spilling incidents during the last four decades, mostly due to corrosion and careless handling of the facilities, contributed to hydrocarbon contamination of the groundwater.

The Quaternary aquifer mainly consists of sand and gravel deposits from the Pleistocene Elster-glacial and has a thickness of 10-15 m. In the study area and beyond, the aquifer is completely concealed by buildings and pavement disabling a local groundwater recharge. Part of the source zone of the contaminants is situated below the groundwater table. Additionally, a floating organic phase is present. The prevailing dissolved contaminants in the groundwater are different BTEX compounds. The average composition of the BTEX is 30 % benzene, 20 % toluene, 10 % ethylbenzene, and 40 % p, o-xylene. Maximum BTEX concentrations are between 25.000 and 30.000 µg/L. While most sampling wells showed no pollution with MTBE, concentrations higher than 10.000 µg/L were measured in two sampling wells in the center of the contaminant plume.

A first indication of biodegradation of the organic contaminants is given by the $\delta^{13}C$ values of the dissolved inorganic carbon (DIC). During degradation, isotopically light $CO_2$ is formed depleting the DIC pool in $^{13}C$. Values of non-contaminated groundwater range between -17 and -18 ‰ (VPDB). Several sampling wells within the contaminant plume show $\delta^{13}C$ values of lower than -20 ‰. This clearly indicates a degradation of the hydrocarbons. However, a conclusion whether the degradation followed an aerobic or anaerobic pathway cannot be reached by considering the carbon isotope data only.

The isotopic composition of sulfur in the dissolved groundwater sulfate is shown in Fig. 1. The typical correlation between the fraction of the residual sulfate and the $\delta\,^{34}S\text{-}SO_4$ proves the occurrence of BSR.

The average isotopic enrichment factor for $^{34}$S was calculated from a logarithmic fit using a Rayleigh equation. The obtained enrichment factor for sulfur ($^{34}$ δ) of -25 ‰ is consistent with previously reported data for comparable environments.

In contrast to observations in other recent case studies, a simultaneous enrichment of $^{18}$O in the residual sulfate was detected (Fig. 1). Compared to the enrichment of $^{34}$S, the enrichment of $^{18}$O is less strong but still significant. The calculated isotopic enrichment factor for oxygen ($^{18}$ε) is -7 ‰.

The determined enrichment factor for sulfur was used for calculating the theoretical sulfur isotopic composition of coexisting dissolved sulfide. Despite the convincing logarithmic correlation between the fraction of the residual sulfate and δ$^{34}$S-$SO_4$, the measured δ$^{34}$S-$S^{2-}$ values do neither match the expected values for an accumulating product reservoi nor the values expected for an open system with $H_2S$-loss. Furthermore, no obvious local correlation seems to exist between dissolved and reduced sedimentary sulfur compounds. This gives rise to the assumption that bacterial sulfate reduction is not the sole sulfur transformation occurring in the investigated aquifer section. Rather, a very dynamic sulfur cycling is indicated. BSR, mainly occurring in local reduction cells, seems to interfere with the partly re-oxidation and/or bacterial disproportionation of reduced or intermediate sulfur compounds in sections of the flow path. The latter assumption is supported by the ubiquitous occurrence of elemental sulfur in the sediment matrix of the contaminated zone.

Nevertheless, our results show that BSR is the most important biodegradation process at the investigated site leading to a significant and sustainable reduction of the BTEX concentration in the outflow area.

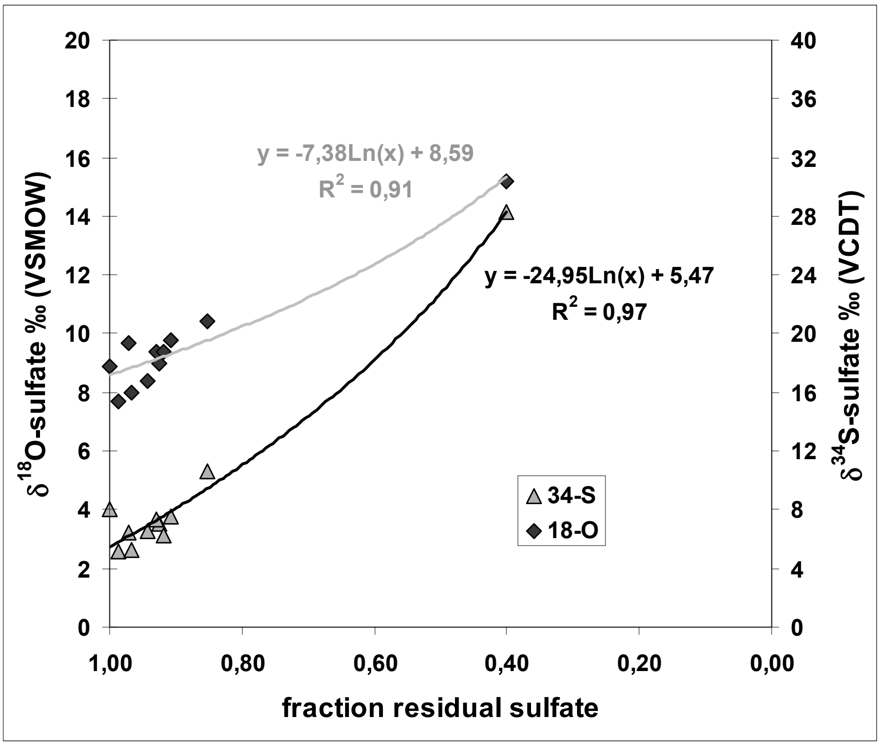

Fig. 1 Correlation between the remaining $SO_4$-fraction and the isotopic composition of $SO_4$ in groundwater samples from the study area

# Tracing the impact of river bank filtration on the transport of xenobiotica in urban groundwater by stable isotopes

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In many urban areas a growing demand for high quality water is counteracted by increasing degradation of the available water resources. Besides industrial contaminants the urban aquatic environment is increasingly polluted by low concentrated but potentially harmful xenobiotic compounds such as pharmaceuticals, fragrances, and plasticizers (Wiegel et al. 2004). Such xenobiotica and their metabolites reach the environment mainly by passing municipal sewage plants into surface water or by diffuse leakage from the urban sewer system into groundwater.

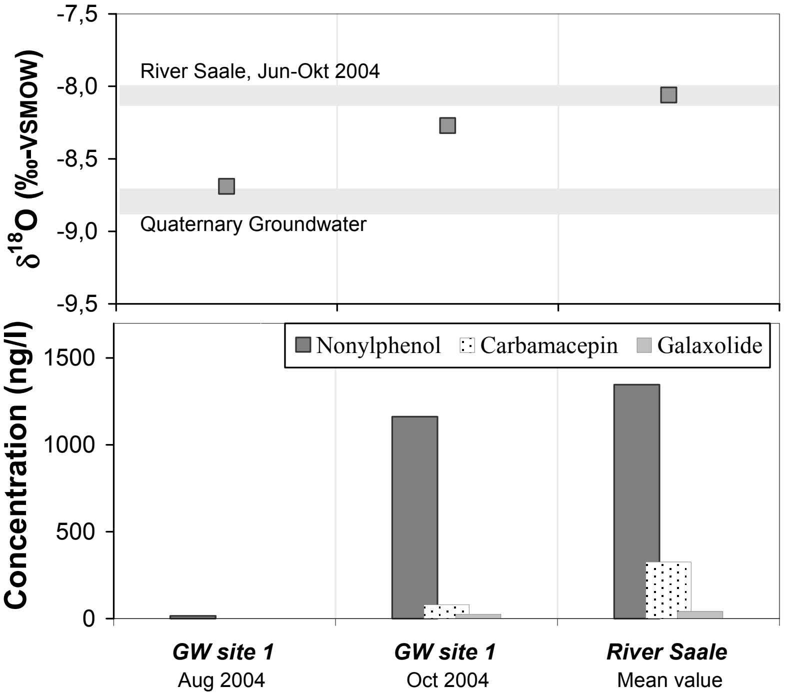

Fig. 1 $\delta^{18}O$ and concentration of selected xenobiotica in groundwater at site 1 from two different sampling dates. For comparison the mean values of the river Saale are given in the third column.

In the urban region of Halle/Saale, Germany, we used stable isotopes of water ($^{18}O$, $^{2}H$) and of dissolved inorganic species ($^{34}S$-$SO_4$, $^{15}N$-$NO_3$) to assess the exchange of river water with groundwater and its impact on the transport of selected xenobiotica. The main objective was to 1) quantify the fraction of xenobiotica in urban groundwater that results from infiltrating surface water and 2) to identify processes that are able to substantially attenuate xenobiotica in groundwater or the colmation layer of the river.

Surface water samples from the river Saale and groundwater samples from the main aquifers were taken during a flood event in February/March 2005 and prior to the flood.

The first results reveal significant differences in isotopic signatures between river water and groundwater, especially during flood events. These differences can be used to identify river water infiltration into the quaternary aquifer (Trettin et al. 1999; Herczeg et al. 2002). Depending on the hydraulic situation, $^{18}$O and $^{34}$S in accordance with hydraulic measurements suggest the dominance of river water at some of the groundwater sites. The intrusion of surface water clearly is accompanied by a sharp increase in xenobiotica concentration (Fig. 1). This gives evidence that a significant portion of xenobiotica present in the investigated groundwater results from river water intrusion.

At present, the influence of diffuse seepage from the sewer system is indicated by enriched $\delta^{15}$N values in only two of the investigated wells, corresponding with elevated concentrations of xenobiotica. Information on attenuation processes during infiltration of river water and transport in groundwater may be derived from comparing the ratios of conservative tracers (isotopes) with contaminants (xenobiotica). However, on basis of the preliminary results no clear trend is visible but comprehensive conclusions can be expected on completion of the data acquisition.

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# Effects of covering spoil piles on its water budget determined by environmental isotopes

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Since the beginning of the 20th century, salt mining activity in Germany heaped up several spoile piles of more than 20 Mio $m^3$ salt each (predominantly NaCl). Owing to missing protection of the ground basis, precipitation water which loaded up to saturation with dissolved salt, contaminates surface- and groundwater all the time. Recently techniques were applied covering the surface of the piles to reduce the flow-rate of precipitation water through the salt, but still without quantitative control over efficiency of this measure. Dye tracer experiments have been done, unfortunately without success, and the two-years lasting data record of conductivity, density, and pH remained doubtful.

Two spoile piles were investigated for comparison, one with a partial but increasing cover of material that clogs water percolation, and one without any cover. Brines of four outflows at the base of each were collected monthly over a period of more than half a year. The input was controlled via on-site precipitation samplers. Tritium together with O-18 content of these samples was analysed. The seasonality of tritium in precipitation was clearly reflected by the samples of the uncovered spoile pile, whereas for those of the covered one, very strong damping was observed. Anyhow, samples of the same pile but from different outflows exhibit individual pattern, indicating partly the grow-up history of the respective spoile pile.

Applying lumped parameter models to the data from the outflow brines, precipitation water is calculated to reside in the uncovered spoile pile only few months, but in the partly covered one some years. These results simply reflect the effect of pile cover. But because the mean residence times of the partly covered spoile pile are of the order of the covering process, the flow system within the pile might be still far from steady state conditions.

## Session 2

# Geochemistry & Water

# Isotope fingerprints in the earth sciences: a critical discussion

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An isotope fingerprint can be defined as an isotope composition that provides information about the origin, the formation and/or environment of a sample. The use of fingerprints in the earth sciences relies on assumptions such as the preservation of the original composition during geological history. Ideally, an isotope fingerprint is indicative of the origin of a particular sample. Examples of this type exist in the geological environment, but in many cases isotope values can be interpreted in more than one way and therefore additional information from other parameters is generally needed to support the proposed origin.

I will provide an overview of the different isotope fingerprints used in earth sciences and will discuss their strengths and weaknesses. Special attention will be given to biosignatures (isotope signatures left by life) and to different water types that move through the exogenic and endogenic cycle of the Earth. Principal water types are meteoric, ocean and juvenile water, all of which have a strictly defined H- and O-isotope composition. All other types of water can be considered as being derivatives or mixtures from one or more of the three reference waters.

The characteristic feature of biosignatures are kinetic isotope fractionations during biological activity that lead to isotopically depleted C-, S-, and to a lesser extent N- and Fe-isotope compounds relative to the starting material. Of special relevance in this connection are C- and S-isotope ratios as indicators of the earliest life on Earth. This is a controversial issue since the classic paper of Craig (1953). Carbon isotope ratios in the oldest rocks from Greenland that are 3.8 to 3.9 billion years old convince some investigators that life was present then, but isotopic evidence is ambigous. Similarly controversial is the emergence of bacterial sulfate reduction on Earth.

Isotope compositions (C,O,Sr) are used also as geological time markers. Isotope ratios may provide stratigraphic markers in sediments enabling correlations of sedimentary sections that are thousands of kilometers apart. Examples of this type are carbon isotope ratios that can be related to oceanic anoxic events and to the snowball earth hypothesis.

# Stable isotope ratio measurements using the Finnigan NEPTUNE multicollector ICPMS using high mass resolution

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Recently multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) has opened the door to study isotope ratios of almost every element with very high precision. The advantage of the ICP ion source is that it can ionize all elements with very high sensitivity. Samples can be introduced into the mass spectrometer from atmospheric pressure through nebulization of liquids or direct laser ablation of samples in the laser ablation chamber. The aerosol is transported by an Ar and/or He gas flow to the ICP source where it is effectively ionized and introduced into the mass analyzer through a differential pumping system. The variable multicollector detector array allows the user to adjust the detector positions along the focal plane of the mass spectrometer such that all isotopes of interest can be measured simultaneously. Eight moveable Faraday cups plus one fixed Faraday cup can be used for the measurement. If very small signals need to be measured miniaturized ion counters can be used instead. Up to eight ion counters can be installed simultaneously.

With this technique stable isotope fractionations of elements like Li, B, Mg, Si, S, Ca, Fe, Cu, Zn, … can be studied. The advantage of ICPMS over thermal ionization mass spectrometry (TIMS) is that the instrumental mass fractionation is much more stable over time. This is the key for high precision isotope ratio measurements in particular for stable isotope systems. However, since the ionization takes place in a hot argon plasma, molecular interferences of argon based molecules as well as other species like oxides or double charged species can show up in the mass spectrum and interfere with elemental isotope peaks. High mass resolution is needed to effectively discriminate against these interferences. The high resolution ion optics of the Finnigan NEPTUNE meet this requirement and expand the power of isotope ratio measurements even to elements where previously isobaric interferences were the limit.

In this paper the instrumental capabilities will be discussed and the attainable precision of this technique will be demonstrated in particular for stable isotope systems like Li, B, Si, Ca, Fe.

# The mineral isotope composition of two Precambrian carbonatite complexes from the Karelian – Kola region

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The isotope composition of carbonatites is used to constrain the composition of the subcontinental mantle and to discuss mantle heterogeneity in space and time. The high Sr and Nd concentrations of carbonatites are thought to provide their primary mantle isotope geochemistry against assimilation and later disturbance. Investigation of Precambrian carbonatites are especially useful for the discussion since when mantle heterogeneity started.

We carried out a combined investigation (microscopy using cathodoluminescence, trace element geochemistry, O-, C-, Sr-, Nd-, and Pb-isotopes on separated minerals) from two Precambrian carbonatite complexes from the Karelian – Kola region: a) the Siilinjärvi carbonatite complex, which is one of the oldest on Earth (about 2.6 Ga) and Tiksheozero (about 2.0 Ga).

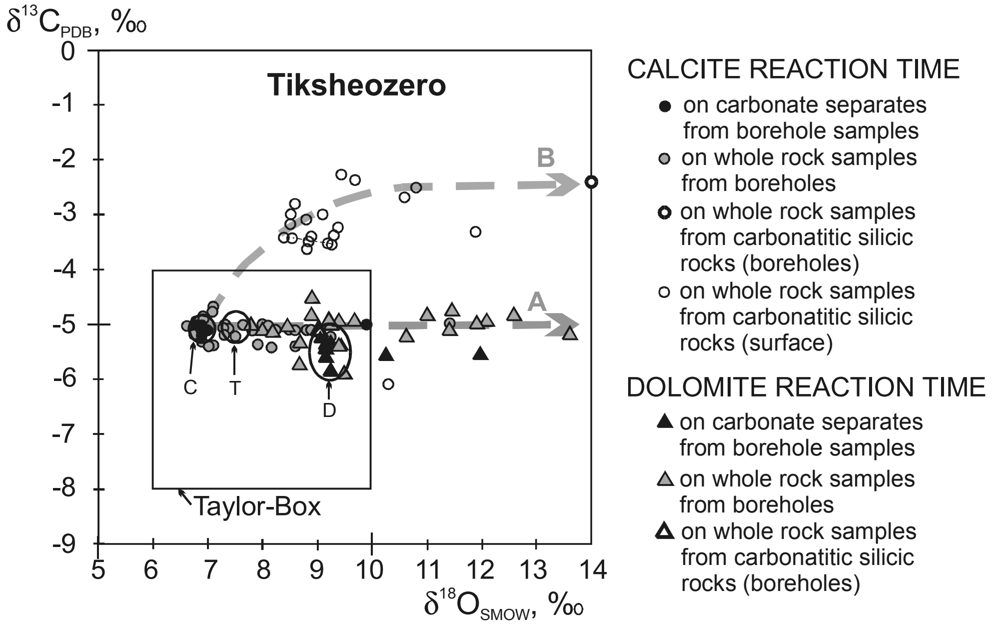
Microscopic investigations helped to distinguish several carbonate generations. A later carbonate generation was discovered by cathodoluminescence microscopy along grain boundaries. This carbonate contains lots of tiny fluid inclusion. Its formation is probably related to water release during ascent of the carbonatitic magma. The O- and C-isotope composition is very uniform only for the first carbonate generation, whereas the second generation (which recrystallised due to the water release) yields identical C- but higher O-isotope ratios. Carbonatitic silicic rocks with carbonate contents less than 50% often yield a distinct O- and C-isotope composition compared to carbonatites.

It seems possible, that the Sr concentration of apatites, carbonates and whole rocks can be slightly lowered due to the water release. No related obvious change of the Sr-isotope composition was observed. However, many of the samples taken at surface show clearly lower Sr-concentrations which are sometimes accompanied by higher Sr-isotope composition. Therefore, a change of the primary Sr-isotope composition of ancient carbonatites cannot be ruled out and is probably related to interaction with surface water.

The Nd-isotope composition shows less influence of interaction with post-magmatic fluids although in very few cases carbonates show a lower Nd-isotope composition. The Pb-isotope composition of most of our samples seem to be disturbed by post-magmatic processes.

Samples taken from boreholes reported a good estimate for the primary mantle isotope composition of the Tiksheozero complex, whereas a much higher degree of overprint disturbed most of the primary isotope ratios in the Siilinjärvi carbonatites.

Fig 1


Tiksheozero
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δ18OSMOW, ‰
B
A
C
T
D
Taylor-Box
CALCITE REACTION TIME
● on carbonate separates from borehole samples
● on whole rock samples from boreholes
○ on whole rock samples from carbonatitic silicic rocks (boreholes)
○ on whole rock samples from carbonatitic silicic rocks (surface)
DOLOMITE REACTION TIME
▲ on carbonate separates from borehole samples
▲ on whole rock samples from boreholes
△ on whole rock samples from carbonatitic silicic rocks (boreholes)

# Development of methods for recovery of water from fluid inclusions for stable isotope analysis

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## 1 Introduction

In most geological samples fluid inclusions are fairly small, ranging in size from *n* to *n*×100 µm. Even though unusually large individual inclusions have been studied (e.g., Genty *et al.*, 2002), those cases are exceptions. Recent attempts to study individual inclusions by opening them in a flow of He with a UV laser (Sharp *et al.*, 2001b) yielded useful results only for relatively large (>100 µm) inclusions of water and large and dense (>100 µm; $\geq 0.3$ g·cm$^{-3}$) inclusions of $CO_2$. Therefore, presently isotope compositions of fluid inclusions in most mineral samples have to be studied by bulk methods.

An obvious drawback of the bulk analysis is that any given amount of the sample could contain multiple populations of fluid inclusions, formed at different times sometimes by different processes. Fluids from these diverse sources are mixed in unknown proportions, thus making interpretations ambiguous. One application where the bulk character of analysis is of lesser concern is the studies of speleothems. These deposits form through addition of layers in which time-resolved populations of fluid inclusions could be isolated. Our work was primarily directed at the development of techniques for studying isotope compositions of water from speleothems.

## 2 Methods of water recovery

At present there are two basic methods for the recovery of water, and other volatiles, from fluid inclusions for isotopic analysis: thermal decrepitation and crushing. Thermal decrepitation involves heating of a sample to 750-900$^{o}$C. This method is known to produce significant depletion of hydrogen isotope in the recovered water (20-30 ‰; Goede *et al.*, 1990; Matthews *et al.*, 2000). Since the depletion factors reported for different case studies vary substantially, the method must be locally calibrated, which is not always feasible. The reasons for the depletion are not well understood. High temperatures of decrepitation may lead to reactions between gas species, as well as to cracking of organic molecules and hydrocarbons that could be present in inclusions and/or in the matrix of the sample. In some analytical protocols (e.g., those employing re-oxidation of $H_2$ formed during heating; McGarry *et al.*, 2004), hydrogen produced by cracking could be analyzed along with the hydrogen of inclusion water thus affecting the analyses. In addition, strong heating of calcite results in production of large amounts of $CO_2$, which makes determination of $\delta^{18}O$ values impossible.

Earlier attempts at crushing under vacuum also encountered isotopic depletions due to incomplete recovery of water adsorbed onto the freshly crushed mineral surface. The technique developed by Dennis et al. (2001) employing crushing under vacuum at 150oC (the temperature is low enough not to induce cracking of hydrocarbons or water) seems to overcome this problem. It was shown to quantitatively remove adsorbed water, so that the results did not show any isotope depletion.

The overall low recovery of water, however, appears to be the weak point of the crushing technique: McGarry et al. (2004) reported that the recovery in crushing was substantially lower as compared to decrepitation. Crushing required ca. 1.0 g of speleothemic calcite to obtain useful MS signal (Dennis et al., 2001), whereas thermal decrepitation allowed work with the 0.15-0.20 g-samples (Matthews et al., 2000). To provide results that could be usefully interpreted, the size of the sample should be kept at a minimum. The fragment of speleothemic calcite of 0.5 g could contain hundreds if not thousands annual growth layers. In order to increase temporal resolution of the analyses, the efficacy of gas recovery must be brought as close to unity as possible.

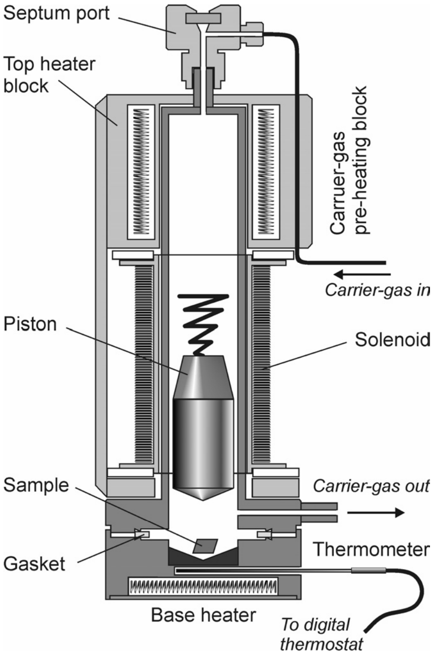

Fig. 1 Schema of the crusher for fluid inclusion studies

In our work, crushing was selected as the method of choice for water recovery from fluid inclusions. Our attempts were aimed at maximizing the recovery, which included two separate tasks: (1) the improvement of the efficacy of crushing, and (2) the improvement of the efficacy of desorption. Another goal was to make the system user-friendly, portable, and easily adaptable to existing standard analytical configurations.

## 2.1 Crusher design

The starting point of our design was the crushing cell described in Dennis *et al*. (2001), which employs electromagnet that lifts and drops a piston, hanging on a spring just clear of the sample in an evacuated tube. The new version of the crusher is shown in Fig. 1.

## 2.2 Efficacy of crushing

In new crusher electromagnet is used in a dynamic impulse mode. It generates short impulses of the strong magnetic field, which accelerate the piston upward. A stainless steel spring mounted on the upward-facing side of the piston provides for the rebound from the top of the piston tube. The piston then accelerates downward and crushes the sample. Impulses are repeated at ca. 1 Hz. The piston and the anvil plate are made of hardened steel. The base of the piston is machined as a $120^{o}$-cone and the anvil plate is shaped accordingly. This creates a shear component in the impact on the mineral grains, which improves crushing.

The efficacy of crushing in this system is controlled by many factors including: the energy of the magnetic impulse; the mass of the piston; the initial position of the piston relative to magnet; the elasticity of the rebound spring; the length of the piston tube, and the pneumatic resistance. These parameters have been optimized experimentally.

With this crusher we were able to obtain useful signal from speleothem samples as little as 0.3-0.4 g and from hydrothermal calcite of 0.1 g (*ca.* 0.3-0.5 µl of water).

### 2.3 Efficiency of gas removal and desorption

Crushing occurs in the flow of carrier-gas (He), which significantly enhances the efficacy of evacuation of water from the crusher, as compared to vacuum systems. The crusher has a built-in resistance heater at its base, near the sample. The magnet support hosts another heater for the top part of the piston tube, as well as heat exchanger for pre-heating of the incoming carrier-gas. The working temperature during the crushing is maintained at 150$^{o}$C, so that the water is in gaseous state. This facilitates its entrainment in the carrier-gas flow and minimizes adsorption.

The direction of the carrier-gas flow is toward the sample, which minimizes the diffusion of volatiles released inside the crusher. At the carrier-gas flow rate of 40-50 $cm^3 \cdot min^{-1}$, linear velocities of gas inside piston tube are *ca.* 1-2 $mm \cdot s^{-1}$, and the exchange rate for the total crusher volume is about 1 $min^{-1}$. The water is completely evacuated from crusher after 10-15 min of flushing (*cf.* 1.5 hrs in vacuum; Dennis *et al.*, 2001).

### 2.4 User-friendliness and versatility

One important parameter variations of which could affect the quality of analyses is the working temperature in the crusher. In our design the temperature near the base of the anvil plate is measured by a resistance thermometer PT100, and is maintained within ±2oC of the set value by a digital thermostat.

To provide an option of the express calibration, a removable septum port could be mounted at the top of the piston tube. This allows for direct injection of the µl-amounts of standard water with the syringe into the crusher (the latter may contain crushed anhydrous calcite). In addition, the method of calibration involving crushing of glass capillaries containing standard water along with the anhydrous Iceland spar (as described in Dennis et al., 2001) can also be used.

The inlet and outlet carrier-gas ports are equipped with standard Swagelok fittings for the 1/16" o.d. stainless steel tubing. The crusher is designed to operate in the continuous gas-flow mode, which means that it can easily be integrated into the on-line IRMS analytical schemes, such as the "glassy carbon reduction" method described by Sharp et al. (2001a) and recently successfully used by Vonhof et al. (2005). In addition, it is designed to hold "static" vacuum down to n·10-7 bar; therefore it could also be used in vacuum configuration. Yet another option is the dual gas flow-vacuum scheme for the off-line water recovery, which is described below.

In this communication we emphasize the use of the crusher for stable isotope analyses of water from speleothems. Besides, the crusher could be used to recover fluid inclusion volatiles for analyses by gas chromatography and quadrupole mass spectrometry. High efficiency of gas recovery and operation at relatively low temperatures preventing gas reactions and cracking of organic matter make this crusher an attractive add-in for these applications.

## 3 Gas flow-vacuum water recovery system

Although recent successes in application of techniques for rapid on-line analysis of tiny amounts of water are encouraging (Sharp *et al.*, 2001a; Vonhof *et al.*, 2005), there will be a continued need for collection of water or other volatiles released from fluid inclusions in vacuum-tight vessels or sealed glass ampoules for subsequent chemical reactions and off-line analyses. Mass spectrometric analysis of gas mixtures released from inclusions may also require some gas manipulations (e.g., cryogenic purification; oxidation of $CH_4$ to $CO_2$ and $H_2O$; etc.), which should be carried in the off-line mode.

In view of that, we developed a dual gas flow-vacuum extraction system, which is used in conjunction with the crusher described above (Fig. 2). The sample is crushed in the flow of a carrier-gas, after which the water is collected in the cryogenic (liquid $N_2$) U-trap. Once the gas recovery is complete, the carrier-gas flow is shut off and the vacuum branch is engaged. When the line is evacuated, the water sample can be transferred from U-trap into the glass ampoules containing reagents (e.g., Zn, $CoF_3$, or $BrF_5$). The ampoules can subsequently be flame-sealed. The system allows for the splitting of the incoming carrier-gas flow into two parallel branches, so that two aliquots could be obtained from the same crushing run.

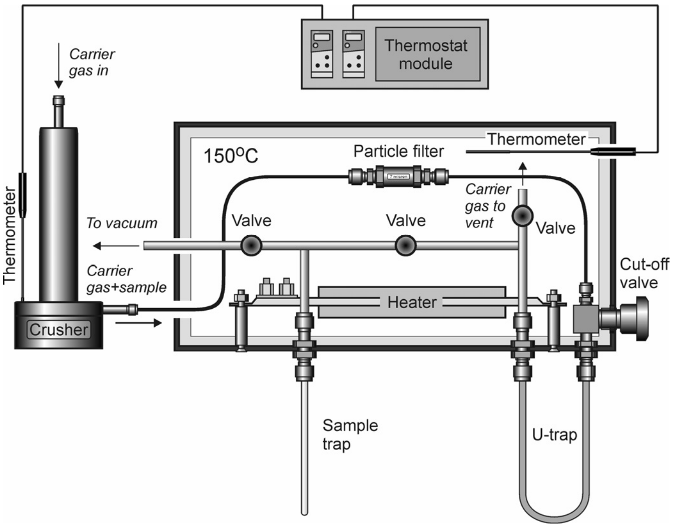

Fig. 2 Schema of the gas flow-vacuum recovery system to be used with fluid inclusion crusher. Electromagnetic part of the crusher and energy supply wiring are not shown for simplicity

All components of this system are mounted within compact insulated box which is heated by a resistance heater. The temperature (up to 160°C) is controlled by a digital thermostat. Crusher is connected to the system in such a way that the transfer tubing does not contain any "cold" parts. This assembly represents a stand-alone unit, which could be connected, through vacuum port, to an outlet of the existing vacuum line in the isotope laboratory.

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# Determination of δD and $\delta^{18}$O in brackish and saline natural waters. Part I: The question of distillation of water samples prior to isotopic analysis

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## 1 Introduction

There are several papers in the literature concerning directly the problems of determination of isotopic composition of water in concentrated aqueous salt solutions. The occurrence of the so-called isotope salt effect has been recognized while standard procedures of determination of isotopic composition of water are applied (Taube 1954; Sofer and Gat 1972, 1975; Horita 1989; Horita and Gat 1988; Koehler et al. 1991).

This part of the paper focuses on the experimental and procedural aspects of determination of isotopic composition of brackish and saline waters. Prior to begin the measurements of isotopic composition of a few tenths of samples of oil-associated waters, we would like to be sure about the quantitative and qualitative range of the potential influence of the salinity on the measured δ values while applying standard procedures of determination of isotopic composition of water. On chosen part of the water samples with different salinity (10,9 g/l – 48,9 g/l) we did detailed experimental study and the results are presented in this paper. The main objective of the study was to check experimentally whether the application of the vacuum distillation process - time-consuming and rather inconvenient, is indispensable or not, in order to avoid potential measurable influence of diluted salts on the δ values and obtainment of precise and reliable measurements. Moreover, two standard methods of hydrogen isotope determination, namely, water reduction on zinc and on chromium, were compared in the light of their sensitivity on the influence of salinity.

## 2 Characteristic of Waters and Techniques Applied

10 samples of natural brackish and saline waters were taken to isotopic analyses. The general chemical characteristic of waters is presented in Table 1.

For the comparison the Dead Sea water was also used, where the isotope salt effect undoubtedly occur while standard procedures of determination of its isotopic composition are applied. The waters considered come from oil-wells, but they were not additionally purified except glass-microfiber syringe filters to remove oil droplets or solid contaminants. However, the smell of hydrocarbons remained in the solution.

The oxygen isotope ratio of brackish and saline waters has been determined by means of $CO_2$ gas equilibration with water (Epstein and Mayeda 1953; Roether 1970) using continuous flow system. Equilibration time was 5 h with shaking and buffering of samples to the pH in the range 6,0 – 6,5. The hydrogen isotope ratio of waters has been determined by conventional procedures of quantitative decomposition of water by hot metal to hydrogen gas. Two off-line techniques were applied: (1) decomposition of water by hot chromium (Muhle et al. 1981), and (2) decomposition of water by hot zinc (Coleman et al. 1982). These two techniques were compared in relation to their reliability and potential sensitivity on salinity.

The vacuum distillation of waters considered has been done in the simplest manner. The precipitates were heated up to 250 °C by about 15 - 20 min.

Table 1 Chemical characteristic of waters taken to isotopic analyses

| No | $Na^{+}$ | $K^{+}$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^{-}$ | $HCO_3^{-}$ | $SO_4^{2-}$ | $Br^{-}$ | $I^{-}$ | TDS | hydrogeochemical class |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mg/l | | | | | | | | | | |
| 1 | 3549,6 | 37,1 | 13,0 | 16,0 | 3184,0 | 4059,4 | 2,0 | 39,7 | 10,6 | 10916,9 | Cl-$HCO_3$-Na |
| 2 | 4465,6 | 11,0 | 4,0 | 15,0 | 5559,6 | 2327,1 | 4,0 | 63,1 | 33,7 | 12484,7 | Cl-Na |
| 3 | 3903,2 | 23,9 | 22,1 | 33,5 | 2713,9 | 6167,7 | 4,0 | 7,7 | 3,3 | 12915,2 | $HCO_3$-Cl-Na |
| 4 | 5310,4 | 54,0 | 29,0 | 10,0 | 6164,6 | 3306,1 | 272,0 | 106,0 | 14,2 | 15276,2 | Cl-$HCO_3$-Na |
| 5 | 5900,4 | 27,0 | 40,0 | 23,0 | 8485,1 | 1366,1 | 4,0 | 29,6 | 11,1 | 15893,3 | Cl-Na |
| 6 | 6379,8 | 36,0 | 55,0 | 52,8 | 7994,0 | 3738,3 | 1,0 | 28,4 | 9,9 | 18310,2 | Cl-$HCO_3$-Na |
| 7 | 7252,4 | 30,0 | 6,0 | 6,0 | 9360,0 | 3166,9 | 112,0 | 61,3 | 17,7 | 20117,7 | Cl-Na |
| 8 | 7588,6 | 138,0 | 40,0 | 9,0 | 10258,8 | 2757,2 | 154,0 | 66,2 | 16,5 | 21038,7 | Cl-Na |
| 9 | 9633,1 | 32,0 | 113,0 | 135,0 | 12397,9 | 5123,7 | 4,0 | 298,0 | 27,2 | 27778,8 | C-Na |
| 10 | 17927,9 | 6,2 | 93,0 | 140,1 | 24956,4 | 5622,4 | 8,0 | 145,0 | 10,8 | 48918,2 | Cl-Na |
| DS[*] | 40100,0 | 7650,0 | 17200,0 | 44000,0 | 224000,0 | | | 5300,0 | | 338250,0 | Cl-Na |

[*] DS – Dead Sea water; average chemical composition after Dead Sea Research Centre, Israel

## 3 Results and Discussion

The results of all isotopic measurements are presented in Table 2.

Table 2 Results of the determination of isotopic composition of brackish and saline waters considered in this study. DS – Dead Sea water. For more explanations see the text.

| Sample | $\delta^{18}O$ vs VSMOW [ ‰ ] | | | | | | δD vs VSMOW [ ‰ ] chromium method | | | | | | δD vs VSMOW [ ‰ ] zinc method | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | original water | | | distilled water | | | original water | | | distilled water | | | original water | | | distilled water | | |
| | x | x/n | σ | x | x/n | σ | x | x/n | σ | x | x/n | σ | x | x/n | σ | x | x/n | σ |
| 1 | (3)[***] | 1,13 | 0,035 | 1,12 | | | (5) | -17,6 | 2,320 | (2) | -15,7 | 0,177 | (7) | -17,0 | 1,991 | (7) | -17,6 | 1,319 |
| 2 | (3) | 2,85 | 0,040 | 2,74 | | | (4) | -14,5 | 1,845 | (2) | -14,8 | 0,134 | (5) | -12,8 | 1,086 | (3) | -13,3 | 1,234 |
| 3 | (3) | -5,21 | 0,083 | -5,12 | | | (4) | -48,1 | 0,961 | (3) | -45,6 | 0,670 | (4) | -47,8 | 1,132 | (3) | -46,8 | 0,613 |
| 4 | (3) | 4,77 | 0,185 | 4,64 | | | (4) | -23,6 | 1,842 | (3) | -25,0 | 0,467 | (4) | -22,3 | 1,224 | (3) | -23,0 | 0,509 |
| 5 | (3) | -1,34 | 0,031 | -1,20 | | | (5) | -32,9 | 2,657 | (3) | -30,7 | 0,511 | (5) | -33,2 | 2,283 | (3) | -32,7 | 0,499 |
| 6 | (3) | 1,29 | 0,195 | 1,12 | | | (4) | -30,1 | 1,939 | (3) | -28,8 | 0,883 | (3) | -30,2 | 1,241 | (2) | -29,7 | 0,792 |
| 7 | (3) | 4,56 | 0,100 | 4,51 | | | (4) | -21,5 | 1,292 | (3) | -18,7 | 0,950 | (4) | -21,6 | 1,613 | (3) | -19,9 | 0,674 |
| 8 | (3) | 5,18 | 0,067 | 5,21 | | | (3) | -21,2 | 1,080 | (3) | -20,4 | 1,406 | (3) | -21,4 | 1,453 | (5) | -22,7 | 1,019 |
| 9 | (3) | 4,16 | 0,049 | 4,07 | | | (4) | -19,5 | 2,255 | (3) | -18,4 | 0,404 | (4) | -18,5 | 0,687 | (5) | -19,1 | 1,023 |
| 10 | (3) | 2,31 | 0,051 | 2,32 | | | (5) | -14,2 | 1,077 | (2) | -14,3 | 0,898 | (4) | -13,8 | 1,072 | (6) | -14,1 | 0,816 |
| DS | -3,34[a] | | | 5,14 | | | 3,68<br>4,05<br>2,50 | 3,41 | 0,810 | 6,62<br>6,21<br>6,30 | 6,51 | 0,182 | 5,4<br>6,1<br>6,5<br>6,9<br>7,2<br>6,4 | 6,4 | 0,631 | 5,0<br>4,6<br>6,0<br>5,1<br>5,7<br>5,4 | 5,3 | 0,534 |
| | 4,19[b]<br>4,07[b]<br>4,36[b]<br>4,19[b] | 4,20 | 0,119 | | | | | | | | | | | | | | | |

[***] - figures in brackets show the number of measurements made; particular measurements could not be presented due to the limited space

x – single measurement; x/n – arithmetic mean value; σ - standard deviation;

[a] – value after 5 h equilibration;

[b] – values after 23,5 - 27 h of equilibration

### 3.1 Measurements of $\delta^{18}O$

Obtained precision of measurements of δ values did not exceed 0,2 ‰; moreover, in many samples were closed to normal for this Laboratory precision of measurements in fresh water, namely 0,05 ‰. One time only distilled waters have been measured, as no difference greater than 0,2 ‰ were observed between mean $\delta^{18}O$ value for mineralized waters and single measurement for distilled one (tab. 2). It means that for all brackish and saline waters taken to the experiment measured $^{18}O/^{16}O$ activity ratio can be considered as equal to $^{18}O/^{16}O$ concentration ratio or at maximum, the difference between these values is much less then the precision of measurements obtained. On that base, we found that for brackish and saline waters with this range and type of salinity no additional processes of water desalination (distillation) have to be applied in order to obtain reliable and precise measurements of its oxygen isotopic composition. To realize how the potential isotope salt effect could alter and complicate the measurements, the Dead Sea water was taken to analysis (Tab. 1). After standard time of equilibration the obtained value of $\delta^{18}O$ for this brine was far from equilibrium (Tab. 2). After 23,5 h of equilibration the quite stable value appear around 4,20 ‰. The activity $\delta^{18}O$ differ significantly from the concentration $\delta^{18}O$ represented by the measured $^{18}O/^{16}O$ ratio of distilled Dead Sea water (Tab. 2). The difference between these two δ values is the clear evidence of the isotope salt effect. To study the oxygen and hydrogen composition of water the concentration $\delta^{18}O$ is needed rather than activity. In relation to brines the problem arise, because it is doubtful if all water can be recovered from the brine during distillation. It is expected that our $\delta^{18}O$ value obtained for distilled Dead Sea water is also affected by this kind of fractionation and do not reflect realistic concentration value. Calculated analytical $\Delta\delta^{18}O$ activity correction after Sofer and Gat (1972) for all brackish and saline waters considered are placed far below the precision of measurements. For the average composition of the seawater the correction is about 0,057 ‰ (Sofer and Gat 1972) which is on the border of precision of measurements. Contrary the Dead Sea water: calculated $\Delta\delta^{18}O$ equals about 2,18 ‰. Finally, corrected $\delta^{18}O$ concentration for the Dead Sea water equals 6,38 ‰ vs VSMOW. This value is higher than $\delta^{18}O$ concentration measured in our study. It might suggest that the water was not completely recovered from the brine during distillation and heating precipitates, and considerable fractionation of isotopes occur. It means that the simple distillation of mineralized waters have limited application.

### 3.2 Measurements of δD

All samples have been measured applying two conventional techniques of hydrogen isotope determination in water. Both are off-line and give concentration D/H ratio. The normal precision of δD measurements is 1 ‰ for both techniques obtained on the long term standard deviation of laboratory standard water. There are significant difference between these two techniques in relation to the way how the water is introduce to the reduction on hot metal. Generally, in chromium off-line technique the water was heated in the injection port by a heat gun ($T \approx 100 - 150^{o}C$) and then distilled water flowed through the reduction oven. In zinc off-line technique the water was introduced into the reaction vessel together with metal, evacuated, sealed and then putted into the oven in the temperature of the reaction.

As can be seen on table 2, all samples of original water have been measured several times because the results scattered with standard deviation usually much higher than 1 ‰. This can be observed in both techniques. There has not been found any regular quantitative relationship between the salinity or chemical composition of brackish and saline water and the standard deviation of measurements. Distilled waters have been measured at least two times. Almost in all cases the standard deviation of measurements was much better for distilled water than for saline one.

It means that the distillation of water improve significantly the quality of the measurements. The difference between the mean values of δD for original and distilled waters usually are within the range of 1 – 1,5 $^{o}/_{oo}$. No regular relationship between the magnitude of this difference and salinity has been found. The magnitude of this difference is usually a little bit higher for chromium technique which may be due to the way of water introduction on hot metal which, additionally, suggests that this technique is more sensitive on the salinity. Finally, it can be stated that for this range and type of salinity its quantitative influence on the obtained values of δD is rather negligible. However, we suggest application of vacuum distillation if precise measurements are required. Despite of the accuracy of the measurements, the reproducibility of the Dead Sea brine seems to be better than many samples of brackish and saline waters considered. However, the significant difference between mean values of δD for original and distilled water can be observed with application of chromium technique. The difference is surely caused by the way how water is introduced to the reduction. It seems that temperature of the heat gun and/or the time of heating of the original brine in the injection port is too small to recover all the water from the precipitate and considerable isotopic fractionation occur. Such phenomenon did not occur in zinc method, where this difference is within the range of precision of measurements. Moreover, in relation to zinc method the value of δD obtained for original brine seems o be more reliable because the distilled water might be altered by the isotopic fractionation during incomplete distillation of water from the brine – as the distillation process was performed in much lower temperature then the reduction of the brine (about 500 °C). It suggests, that only direct introduction of water to reduction on hot metal may reduce the isotope salt effect unless the distillation step of water will be carried on in high enough temperature or with application of additional chemical desalination.

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# Isotopic evidences for a new type of groundwater in the Kinneret basin, Israel

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## 1 Abstract

Different types of unspecified waters continuously enter Lake Tiberias, which surrounded by the shoulders of the Jordan-Dead Sea Graben to the east and west and the elevated Korazim block to the north. The amount of dissolved solutes in the waters ranges from some hundred to several tenthousands TDS (mg/l). Different types of saline water emerge around the lake in clusters and are assumed to enter the lake also through off-shore sources. The isotopic composition of waters, emerging in Tabgha cluster next to the lakes shore, indicates a recharge area different from the known catchment. The highest elevation of Tabgha catchment is in the Upper Galilee with around 900 m msl. None of the groundwaters in that area of replenishment show as light stable isotope composition as Tabgha springs on the lakeshore. This gives the evidence for a groundwater from the much higher elevated Mt. Hermon with the necessary depleted isotopic signature in recharge. Such a component was sampled in the some 1000 m depth Shamir well ($\delta^{18}O$: -7.1 ‰, $\delta D$: -34.8 ‰) in the northern Hula valley. It is therefore assumed that, fresh or maybe brackish groundwater with similar light ($\delta^{18}O$: -7.1 ‰ and $\delta D$: -34.8 ‰) or even lighter signatures flow from Mt. Hermon through the deep underground of the Hula and through the Korazim block into the Kinneret valley. It emerges in the Tabgha springs and most probably also in off-shore sources in Lake Tiberias. The evidence of such an isotopically depleted component in the groundwaters of Tabgha springs gives the first time the option to prove, that the Korazim block is permeable for groundwater from the north and it is therefore also able to reach the Kinneret basin and the lake via this way.

## 2 Introduction

Lake Tiberias is situated in the north of Israel, in one of the pull-apart basins of the Jordan-Dead Sea Rift Valley, which is part of the large Syrian-East African Riftsystem. Its 2,700 km$^2$ drainage basin includes the Galilee Mountains to the E-NE, the Hula Valley and the Mount Hermon Massif to the north and the Golan Heights to the NE (Fig. 1). The surface and subsurface drainage of the direct and indirect watershed is always towards the Graben and with -210 m msl represents Lake Tiberias the local erosion base. The Hermon, about 2,800 m tall, is the highest peak in the area and earns similar to the Galilee and the Golan about 650-700 mm precipitation a year. Towards the lake, the tectonically basin of the Hula Valley follows. The elevated and highly fractured Korazim Block (Belitzky, 2002) separates both, the Hula- and the Kinneret basin.

Deep reaching fault systems occur along the margins of the graben *sensu stricto* and are concentrated at the rim of the graben system. In particular, the western margin of the Kinneret basin is separated by NW-SE-faults in the morphotectonic blocks of Tiberias, Tel Rakkat and Tabgha.

In each of these blocks a specific cluster of springs occurs, where saline waters emerge. The clusters are independent from each other and show their own hydraulic and hydrochemical behaviour. Saline waters are known from all over the Kinneret basin. They emerge as springs, mostly bounded to areas of dense fault-systems. The tectonic features are the reasons for the three spring clusters on the western shore of the lake: Hammey Tiberias, Fuliya and Tabgha. Sources of saline waters are bound to the proximal parts of the Graben *sensu stricto*, that's why no saline groundwaters are observable more than some kilometres away from the main faults of the graben.

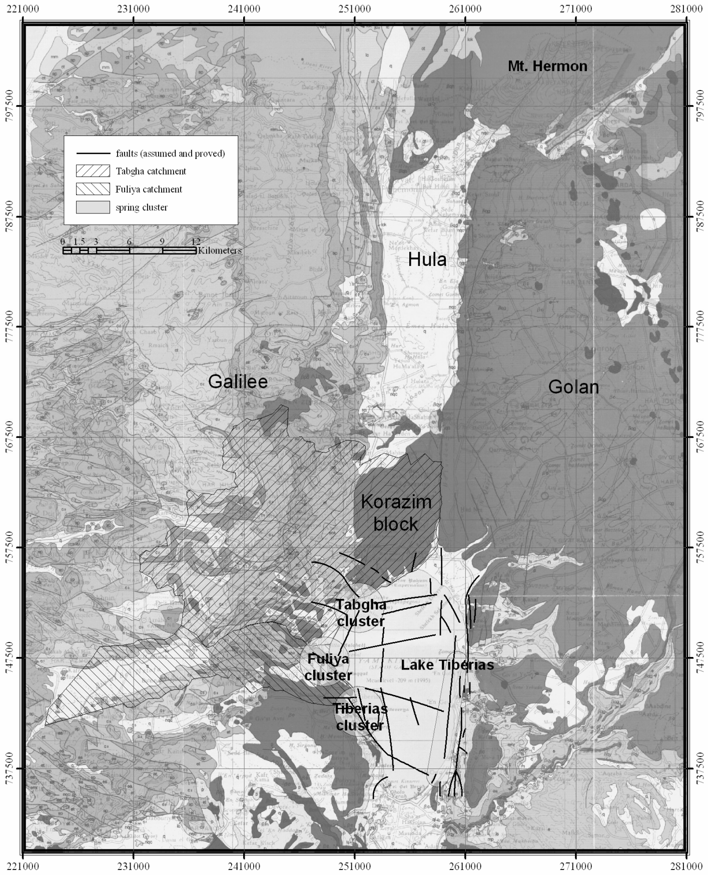

Fig. 1 Geological map of Lake Tiberias and adjoining territories of the direct and indirect watershed

The lake itself, as the largest surface freshwater reservoir in the Levant is continuously endangered by saline waters, which enter the lakes water body off- and onshore. The sources and their mechanisms are investigated since decades but still under debate.

Beside several hydrogeological surveys (Nishri et al., 1999, Dror et al., 1999; Gvirtzman et al., 1997; Rimmer et al., 1999; Abbo et al., 2003), mass- and volume balances give a rough estimation about the hydraulic systems of the Kinneret basin and it is most suggested, that all three western clusters are most responsible for the salinisation of the lake, but the intensity is dependent on seasons and amount of recharge in the catchments (Siebert et al., 2005).

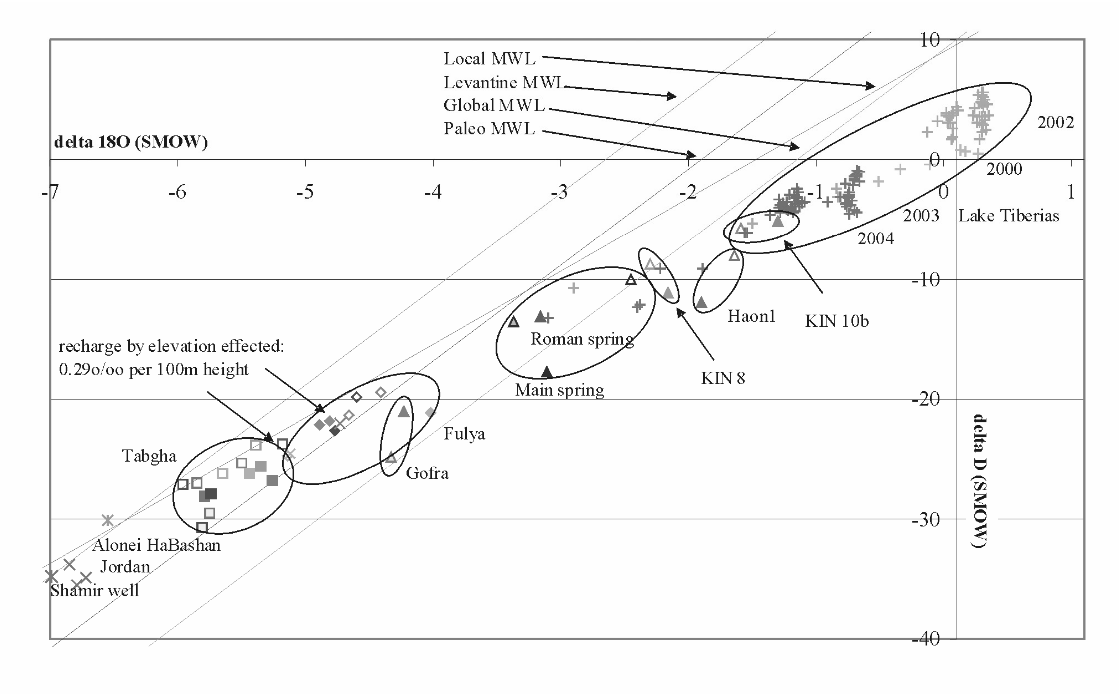

Fig. 2 Cross-plot of stable isotopes d D vs. d 18O – SMOW-normalised nn the basis of 52 data pairs (IAEA) of precipitation from station Har Kna'an in the Upper Galilee (New Israel Grid: 247E; 764N; 934 m msl) the Local Meteoric Waterline $\delta D=6.1*\delta 18O+9.5$ is calculated, which is in excellent correlation to the one given by Bergelson et al. (1999). The slope of the LMWL is much smaller than of the Global- ($\delta D=8*\delta 18O+10$) or Levantine MWL ($\delta D=8*\delta 18O+22$). (squares: Tabgha, diamonds: Fuliya, triangles: thermo-saline waters, crosses: lake water, lying crosses: rivers and distal recharge)

## 3 Results and Discussion

In the cross plots of $\delta^{18}O$ vs. $\delta D$ all water samples from the study area plot between the Levantine Meteoric Water Line (LMWL) (Dansgaard, 1964) and Global (GMWL) (Craig, 1961), except the thermo-saline waters of wells KIN 8, KIN 10b, Ha'On, Tiberias Hot springs and Lake Tiberias (Fig. 2). All isotopic data of groundwaters from the limestones plot on a straight line sub-parallel to the LMWL.

The isotopically lightest waters always originate from the elevated recharge areas in eastern Galilee, Golan and Hermon massif and are independent of the lithology of the aquifer. The thermosaline waters show the heaviest $\delta^{18}O$ and $\delta D$ values. All waters of the spring clusters are mixtures between isotopically light fresh recharge and of isotopically heavy brines from the Lower Aquifer (Fig. 3). At similar salinity, waters of the Tabgha area are isotopically lighter than those from Fuliya and Gofra area because of (1) the different altitudes of the corresponding recharge areas (Poage & Chamberlain, 2001) and (2) mixing with isotopically depleted water from the (northern) Hula Valley which flows through permeable strata and faults in Korazim block (Belitzki, 2002). The absence of isotopically very light water, flowing from the west towards Tabgha (wells Huqoq, Kalanit and Hazon) evidences, that the very light isotopic values in waters from En Sheva or KIN 7 are caused by contributions from the north via the Korazim block.

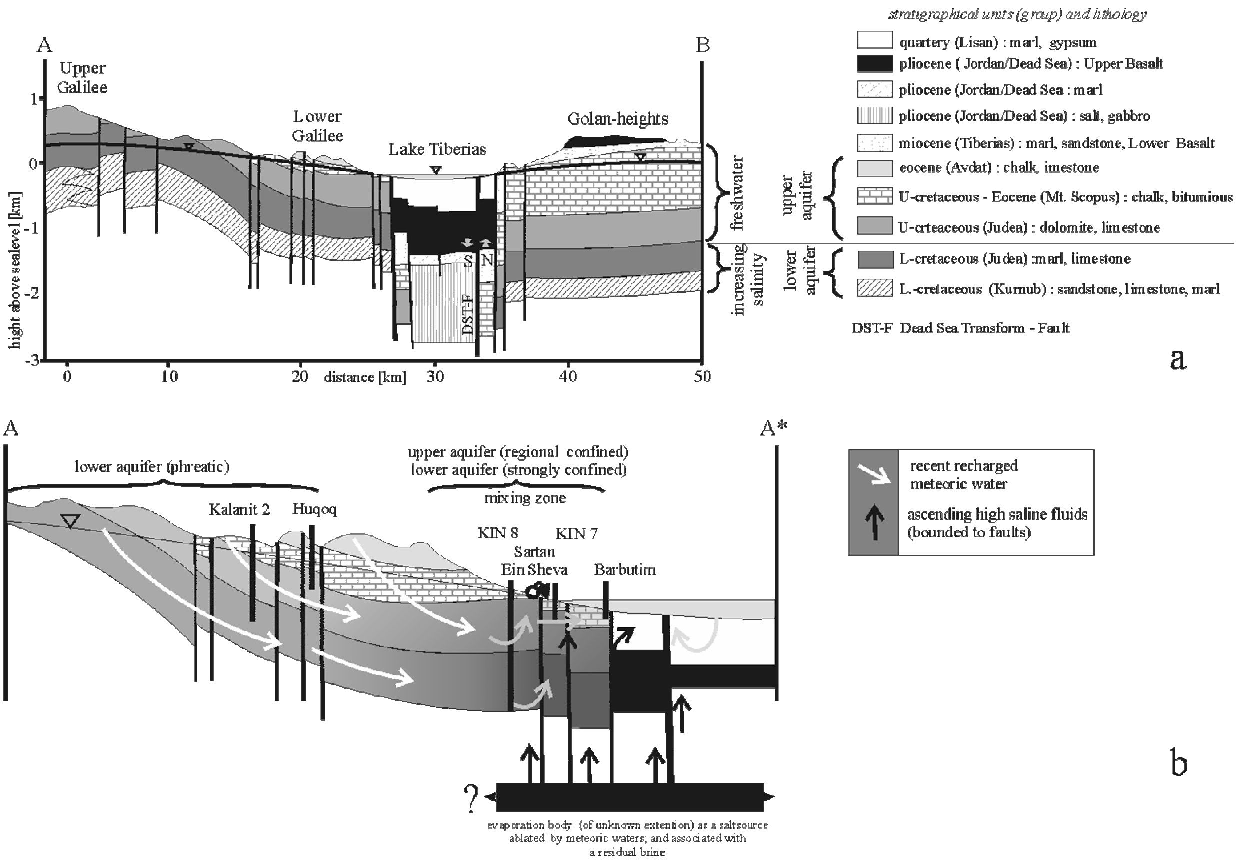

Fig. 3 a) cross-sections through the rift at Lake Tiberias;
b) schematic section through western margin at Tabgha with wells and springs of Tabgha cluster

Such isotopically depleted groundwater is only known from the Shamir well, some 50 km to the north of Lake Tiberias in the Hula Valley. En Sheva shows $\delta^{18}O$ of -5.8 ‰ and δD of -28.1 ‰. Such low values are unknown from recharge water in the west, which is not less than $\delta^{18}O$ of -5.59 ‰ and δD of -23.05 ‰ (Bergelson et al., 1999). At Fuliya the isotope compositions of waters from the wells Hitin 3 and Hitin 4 correspond with that of springs at the lakeshore. Most saline waters show heavy isotope values, no matter what cluster they belong to. In these waters heavy isotope composition is correlated with salinity.

Therefore it is unambiguous; the observed light isotopic compositions of groundwaters from Tabgha could only be the result from recharge from higher elevations like the Mt. Hermon area and proves the first time the hydraulic transmissivity of the so called Korazim block.

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# Geochemical and isotopic investigations of a fractured rock aquifer including embedded lakes

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## 1 Introduction

Hydrochemical and hydrogeological investigations of lakes embedded in fractured rocks give information about flow paths of a heterogeneous aquifer system. In this study, three neighbouring quarries resulted from porphyry mining and filled by rising groundwater, as well as surrounding groundwater observation wells are investigated for main components and isotopes of water and nitrate. The aim of the study is to characterise the hydrogeological situation and to verify the existence of hydraulic connections between the three quarry lakes.

## 2 Study area

The quarry lakes of the hill „Kautzenberg“ are situated near the town Löbejün, about 15 km north of the city Halle (Fig. 1). Rhyolite for construction industry has been mined in this area for a long time. At the hill “Kautzenberg”, it started in the 18th century. The lake “OSB” is located near the top of the hill, whereas lake “USB” lies on the slope. The lakes are used for recreation activities (e.g. swimming, diving and climbing).

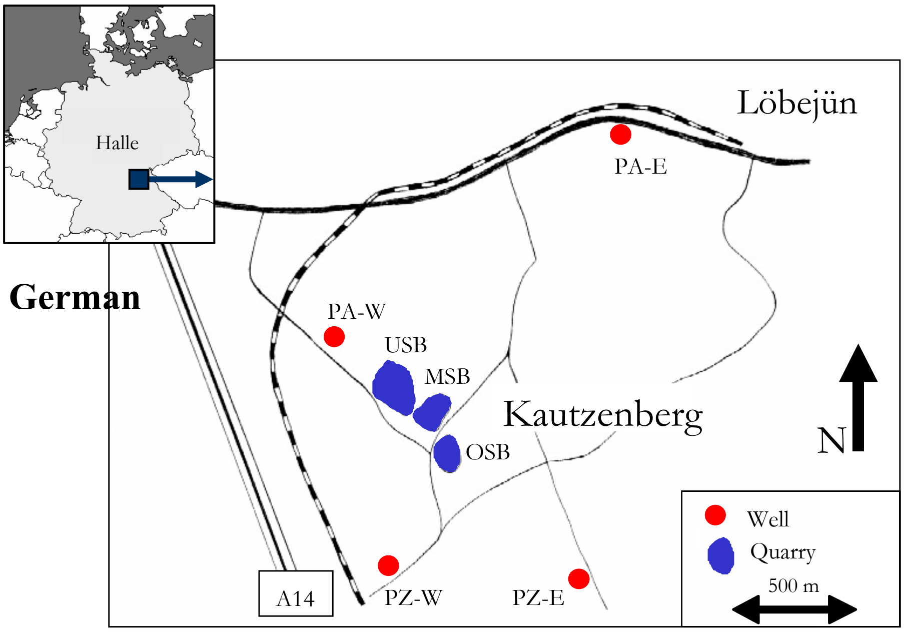

Fig. 1 Study area - lakes on the hill “Kautzenberg” near the little town “Löbejün”

The groundwater in the rhyolite flows on individual fractures and fracture networks. The main fractures are arranged north-south as well as east-west. A minor fracture system is found in the northwest-southeast direction. The tectonic characteristics are different for the lake “USB” on the slope. The minor fracture system is more dominant here than in the other lakes (Schwab, 1965). The general groundwater flow direction as is from south to north. A watershed is situated in the south of the study area. According to the tectonical situation, it is probable that the groundwater flow direction is changing from north to northwest between lake “MSB” and lake “USB”. The water column of the lakes is well mixed. The maximum depth of the lakes ranges between 10 and 17 m.

## 3 Chemical and isotopic data

Surface water of all three lakes, water column profiles of the pit lake “USB” and surrounding groundwater observation wells were analysed for main components, trace elements and isotopes. The main results of the sampling campaign in March 2004 are shown in Table 1.

Table 1: Chemical and isotopic data of the investigated water samples

| | **Lake** | | | **Groundwater observation well** | | | |
|---|---|---|---|---|---|---|---|
| | **USB** | **MSB** | **OSB** | **PZ-W** | **PZ-E** | **PA-W** | **PA-E** |
| pH | 7.2 | 7.6 | 7.4 | 7.3 | 7.0 | 6.9 | 6.6 |
| Conductivity (mS/cm) | 0.92 | 0.75 | 1.02 | 1.75 | 1.10 | 1.64 | 1.37 |
| Ca (mg/l) | 134 | 98.4 | 160 | 294 | 162 | 296 | 205 |
| Mg | 26.5 | 17.8 | 28.1 | 78.0 | 37.3 | 50.5 | 50.5 |
| K | 5.34 | 8.01 | 6.83 | 1.91 | 2.16 | 2.67 | 1.84 |
| Na | 26.7 | 27.8 | 24.6 | 27.4 | 18.2 | 56.7 | 34.9 |
| Si | 0.75 | 1.70 | 0.75 | 4.70 | 4.70 | 4.90 | 6.40 |
| Fe | 0.04 | 0.05 | 0.03 | 0.09 | 0.06 | 0.06 | 0.07 |
| Al | 0.09 | 0.04 | 0.04 | 0.06 | 0.05 | 0.12 | 0.09 |
| $SO_4$ (mg/l) | 337 | 211 | 398 | 635 | 295 | 588 | 543 |
| $HCO_3$ | 92.5 | 101 | 80.8 | 274 | 156 | 294 | 156 |
| $NO_3$ | 4.34 | 36.4 | 4.88 | 126 | 72.3 | 117 | 59.0 |
| Cl | 53.8 | 40.7 | 75.8 | 142 | 57.5 | 61.7 | 70.6 |
| DOC (mg/l) | 1.81 | 1.35 | 2.50 | 3.29 | 3.10 | 5.82 | 2.53 |
| $\delta^{18}O$ $H_2O$ (‰ SMOW) | -1.87 | -6.05 | -1.88 | -9.17 | -8.94 | -8.67 | -9.22 |
| $\delta^{2}H$ $H_2O$ (‰ SMOW) | -27.6 | -49.6 | -28.2 | -65.5 | -63.4 | -63.0 | -65.7 |
| $\delta^{15}N$ $NO_3$ (‰ air) | 5.1 | 5.7 | 5.3 | 4.3 | 5.1 | 5.4 | 5.1 |
| $\delta^{18}O$ $NO_3$ (‰ air) | 9.7 | 11.8 | 1.5 | 1.6 | 3.9 | 1.7 | 8.1 |

## 4 Discussion

The chemical data for the lakes “OSB” and “USB” are nearly identical. The water of lake “MSB” is influenced by the added groundwater due to anthropogenic influences and has higher a nitrate concentration and lower $\delta^{18}O$- and $\delta^{2}H$-values than the other lakes.

Lake and groundwater differ in chemical and isotopic data. Due to the use of fertilizer, the nitrate concentrations of the groundwater are higher than 50 mg/l. The contents of Si, $NO_3$, $SO_4$ and DOC decrease in the lake water as a result of microbiological processes. Si concentrations of the groundwater (~ 5 mg/l) exceed the amounts measured in the lakes (~ 0.8 mg/l). These differences between lake and groundwater are caused by an uptake of silica by diatoms. The high K concentrations in the lake water could be explained by an input fertilizer or anthropogenic urine (Erdinger et al., 1997).

The isotope ratios $^{18}O/^{16}O$ and $^{2}H/H$ of all lakes are influenced by evaporation whereas the groundwater isotopes reflect the isotopic composition of the precipitation. Compared to other German lakes, the evaporation rate in the study area (evaporation – precipitation ~ 250 mm/a) is quite high and leads to relatively heavy $\delta^{18}O$- and $\delta^{2}H$-values in the investigated lake waters. Therefore, the isotopically enriched lake water can be used as a tracer in the outflow of the lakes. The observation well "PA-W" shows the only significant change in these isotope ratios. The calculated lake water amount for this well is about 7 % (Bozau et al., in review). The isotopic values of the well "PZ-E" are normally the same as measured in the wells "PZ-W" and "PA-E". There is no explanation for the lower isotopic values measured in March 2004.

Although, the nitrate concentrations of all lakes are lower than in the surrounding groundwater, an enrichment of $\delta^{15}N$-values in the lake water due to microbiological activities was not observed (Fig. 2). The $\delta^{15}N$-values of all studied water samples vary between 4 and 6‰. There is also no continuous behaviour of the measured $\delta^{18}O$-values in nitrate (Fig. 3).

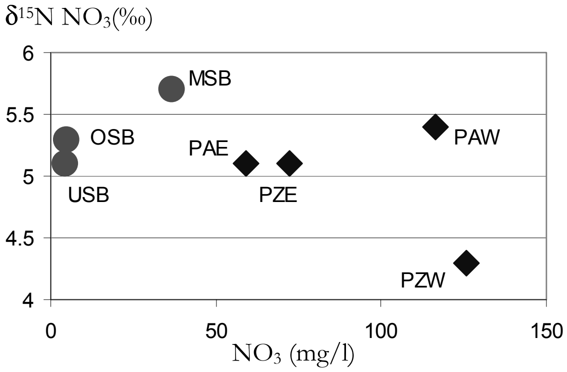

Fig. 2 Relationship between nitrate and $\delta^{15}N$-values in the lakes and wells

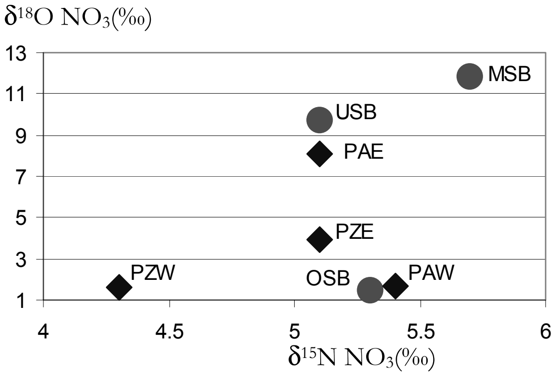

Fig. 3 $\delta^{15}N$- and $\delta^{18}O$-values in nitrate of the lakes and wells

The $\delta^{15}N$- and $\delta^{18}O$-values of nitrate are considered as a powerful tool for identifying denitrification processes in groundwater (e.g. Fukada et al., 2003; Teranes & Bernasconi, 2000). The data of our study area show that the isotopic composition of nitrate does not support the theory of a microbial nitrate reduction within groundwater-lake interaction.

Furthermore, the studied elements and isotopes cannot serve as natural tracers to get information about flow paths in the study area. To find hydraulic connections between the lakes a tracer test seems to be necessary.

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# High spatial resolution sulfur isotope analysis of sulfide minerals from the Kupferschiefer deposits of Lubin area, SW Poland

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## 1 Introduction

The Kupferschiefer copper deposits of the Lubin area (Fore-Sudetic monocline, SW Poland) are among the largest in Europe and have great economic importance. They are strata-bound in Zechstein sediments (Oszczepalski and Rydzewski, 1991). Ore mineralization occurs not only in the black shale horizon but also irregularly in sandstones below the shale and in dolomites and limestones above the shale layer. Ore minerals are usually tiny, dispersed grains of a few micrometers in size, but sometimes occur as small veinlets, nests, or massive forms. Over 100 ore minerals are present but only a few have economic importance. Chalcocite is the prevailing copper mineral. Chalcopyrite, bornite, digenite and covellite also occur in in large quantities (Mayer and Piestrzyński, 1986).

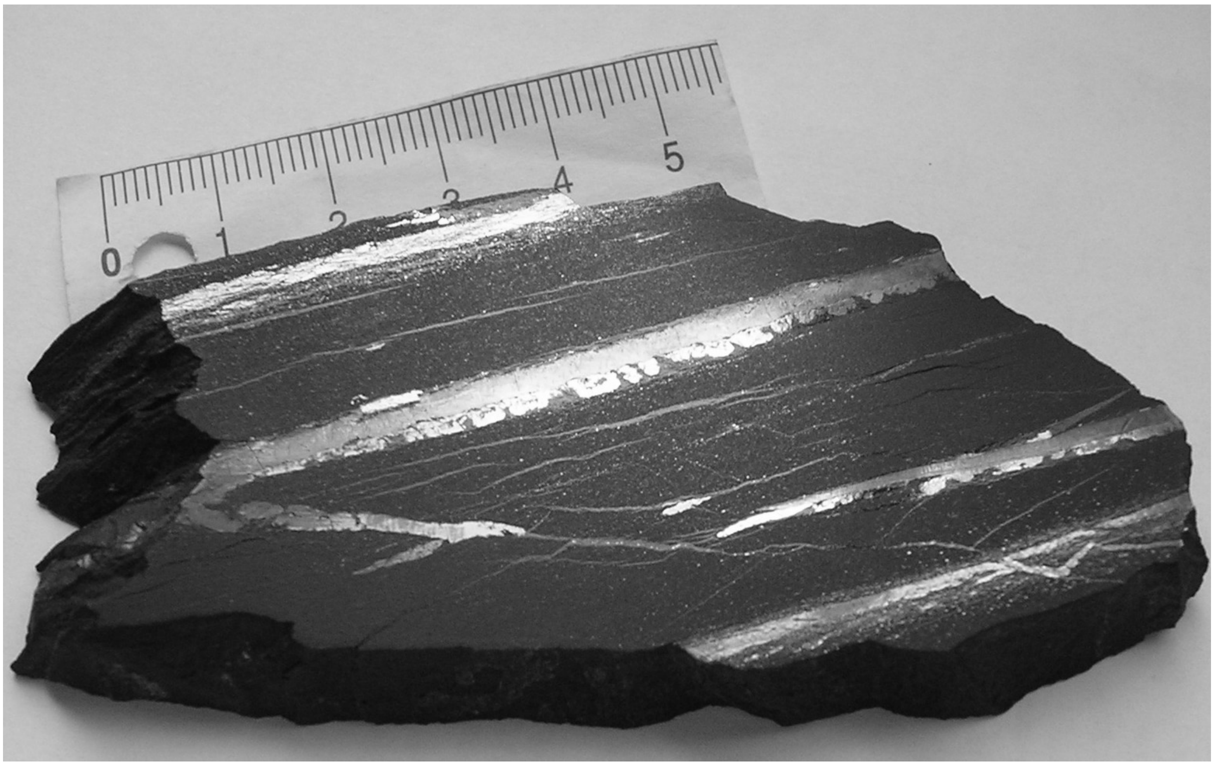

Fig. 1 Slice of black shale cut by various sulfide veins

Kupferschiefer deposits were formed as a result of complex, multistadial processes details of which are still under discussion. Although some sulfides may have formed during the deposition of Zechstein sediments under euxenic conditions, there is evidence that the main mineralization stage was post-sedimentation or even post-diagenetic. The economic copper sulfide concentrations were formed after mixing of reduced, $H_2S$-containing solutions generated in the black shale environment with hot, oxygenated, metal-rich solutions coming from the basement. These solutions mixed and reacted along the lithological boundaries of shale strata acting as a geochemical barrier. After the deposition of the main sulfide, extensive redeposition of sulfides took place which led to formation of epigenetic veins and massive ore concentration.

For this study, a slice of the black shale rock cut by various sulfide veins of different generations taken from the Lubin mine (Fig.1) was investigated by isotope ratio mass spectrometry (IRMS) coupled with a laser microprobe at the University of Calgary.

## 2 Analytical techniques

High precision spatially resolved analyses of $\delta^{34}S$ in sulfides were carried out, similar to those described by Kelley and Fallick (1990). The sample was placed in a small chamber with a window in its lid and $O_2$ admitted to a pressure of ca. 250 Torr. (Fig. 2). The laser beam ( Nd-YAG at fundamental frequency in a pulsed mode) passed though the window and was focused on a selected site using a supplementary aiming laser and a video camera. This results in intense heating of a small area at the surface, where the sulfide is evaporated and reacted with the $O_2$. The $SO_2$ product was purified cryogenically in a small vacuum line adjacent to a dual inlet IRMS. The size of the craters produced by the laser was determined by the amount of $SO_2$ required for analysis (Fig. 3). The reproducibility of $\delta^{34}S$ analysis was about 0.06 per mill. A correction was made for isotope fractionation due to incomplete conversion of sulfide to $SO_2$.

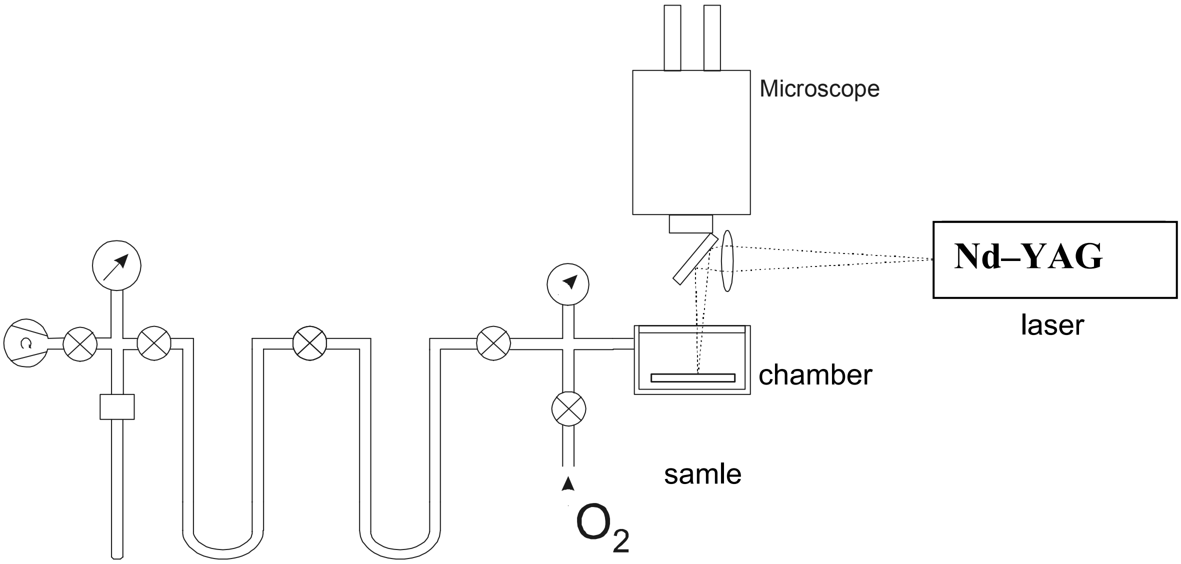

Fig. 2 Schematic diagram of laser extraction-purification line

## 3 Results

Strongly negative $\delta^{34}S$ values obtained for all analyses are in great concordance with commonly accepted provenience of the sulfide arising from the bacterial reduction of sulfate (*see* Sawłowicz, 1989; Jowett *et al.*, 1991). The laser probe method realized $\delta^{34}S$ values of copper sulfide minerals on a millimeter scale. Hence we were able to demonstrate significant variations in sulfur isotopes composition across individual veinlets and along some veinlets.

A nearly monomineralic chalcopyrite veinlet in the upper part of the black shale revealed a homogeneous sulfur isotope composition with a $\delta^{34}S$ value of –24.75 per mill. . This result is close to that obtained (-23.95 per mill) nearby for the whole veinlet and tiny dispersed grains of chalcopyrite using conventional isotope analyses with a VG PRISM mass spectrometer. Dispersed sulfides (mostly chalcopyrite with some chalcocite and bornite) below the chalcopyrite veinlet were found to have a $\delta^{34}S$ value of –21.84 per millusing the PRISM. Significant variations were found in the isotopic compositions of sulfides forming a 5 mm thick veinlet in the central part of black shale specimen. This veinlet is composed of laminae of chalcopyrite (upper part of the veinlet), bornite (middle part) and chalcocite (bottom part). Chalcopyrite contains the heaviest sulfur with $\delta^{34}S$ values from –19.24 to –19.01 per mill. Bornite shows markedly more negative values (-25.42 to –27.70 per mill), whilst chalcocite in this veinlet has the lightest sulfur with $\delta^{34}S$ values from -27.27 to –28.13 per mill.

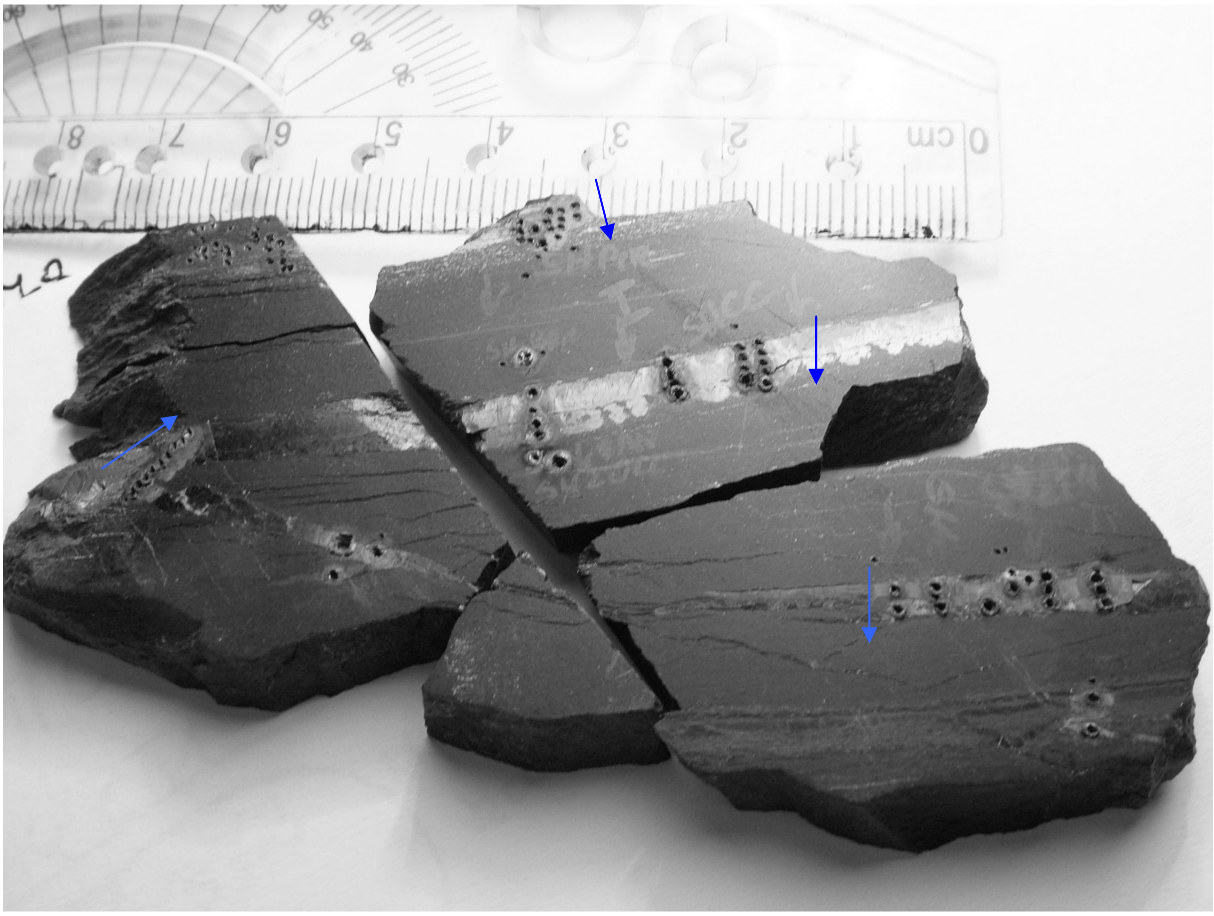

Fig. 3 Pieces of the original sample after laser extraction. The arrows indicate direction of successive extractions.

Another lower veinlet consists of bornite and chalcocite laminae similar to that described above. Bornite in this veinlet, like chalcocite, has a slightly higher $\delta^{34}S$ value (-24.75 per mill) like chalcocite. But in the chalcocite lamina, the interior is isotopically lighter (-27.14 per mill) than the edge (-24.15 per mill). A similar trend was observed in a swelling sulfides nest formed at the cross-over of two diagonal veinlets on the left margin of the specimen. A traverse of 9 extractions was taken from this elongated nest which is composed mainly of chalcocite. The values of $\delta^{34}S$ vary there from –21.93 to –29.43 per mill, and are distributed along the profile as shown in Table 1.

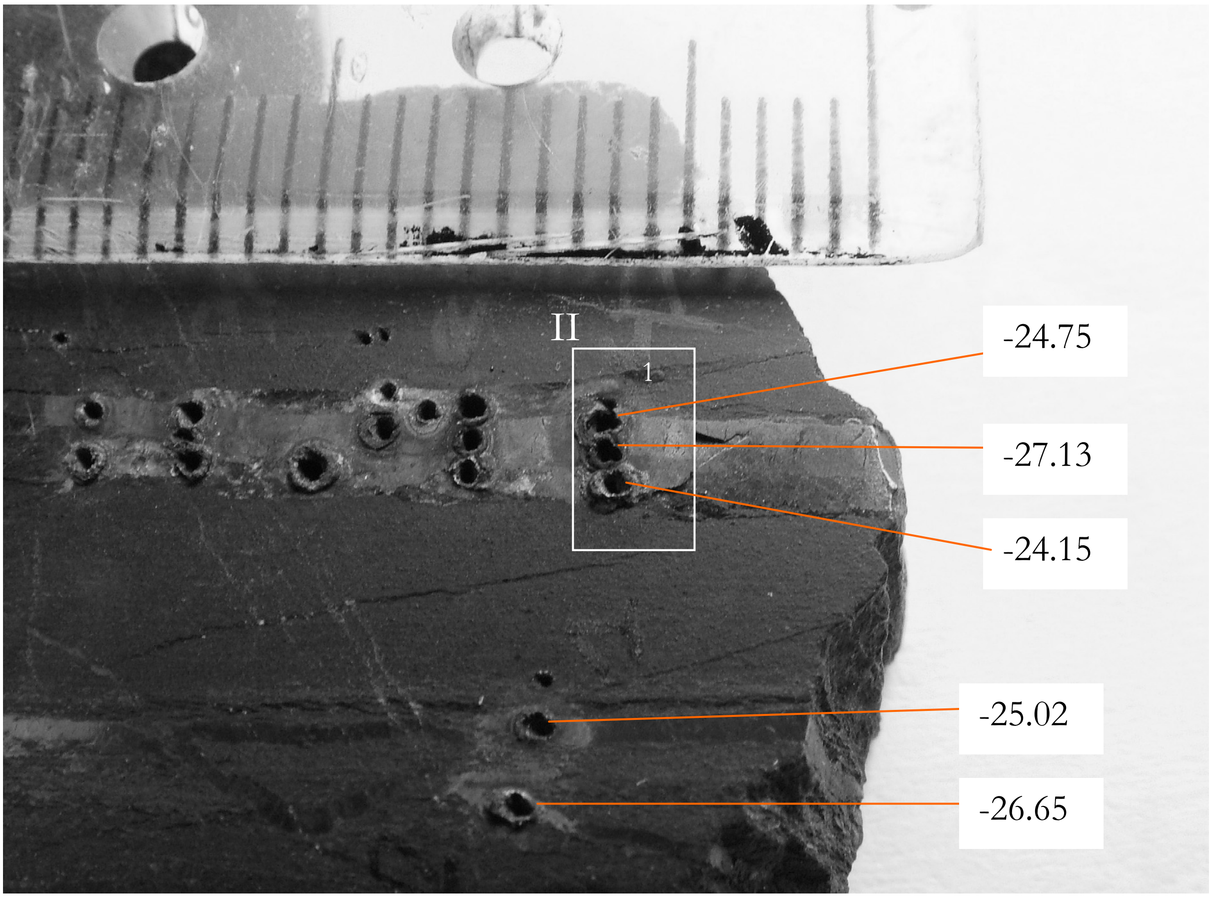

Fig. 4 Vein of chalcocite and bornite with measured delta values

Irregular, thin chalcocite veinlets in the lower part of specimen also contain light sulfur, with $\delta^{34}S$ values of -25.02 and –26.65 per mill.

These detailed analyses have shown that copper sulfides forming epigenetic veinlets in the black shale have variable sulfur isotope composition even over mm distances, this must reflect changes in their crystallization conditions.

Table 1 The isotope profile of chalcocite nest

| spot no. | $\delta^{34}S$, ‰ |
|---|---|
| 1 | -25.76 |
| 2 | -26.55 |
| 3 | -26.92 |
| 4 | -27.63 |
| 5 | -27.00 |
| 6 | -28.76 |
| 7 | -29.43 |
| 8 | -26.70 |
| 9 | -21.93 |

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# Stable isotope composition of daily and monthly precipitation in Zagreb

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In the frame of the IAEA Research Contract *Tritium and stable isotope distribution in the atmosphere at the coastal region of Croatia* we determined isotope composition of monthly precipitation ($^3$H activity, $\delta^2$H, $\delta^{18}$O) during the three-year period (2001-2003) at six stations (4 maritime and 2 continental) in Croatia (Horvatinčić et al, 2005). The aim was to determine natural variations of radioactive isotope $^3$H, as well as distribution of stable isotopes in precipitation over a relatively small area with different climatic and geographical characteristics. In this investigation we also included the stable isotope measurements of daily precipitation collected at one of the continental station, Zagreb, for the period October 1, 2002 to April 1, 2003. These isotopic data of individual precipitation can give us more information of individual mass trajectories, e.g., more information on the source of the atmospheric moisture during particular events.

Daily air temperature and amount of daily precipitation for sampling period are presented in Fig. 1. The samples were collected in the colder period of the year (autumn-winter) with maximum temperature of 16.5°C (23 Oct 2002) and minimum of -6.1°C (10 Jan 2003). Mean temperature of the whole 6-month period is 6°C, and for the first 3-month (October-December) period and the second 3-month peroiod (Januar-March) temperatures are 7.6°C and 2.4°C, respectively. The mean annual temperature for the long term period (1961-1990) in Zagreb was 11.4°C (Krajcar Bronić et al, 1998). Most of precipitation in sampling period was in the form of rain, but in December, January and February also snow was collected (Fig. 1).

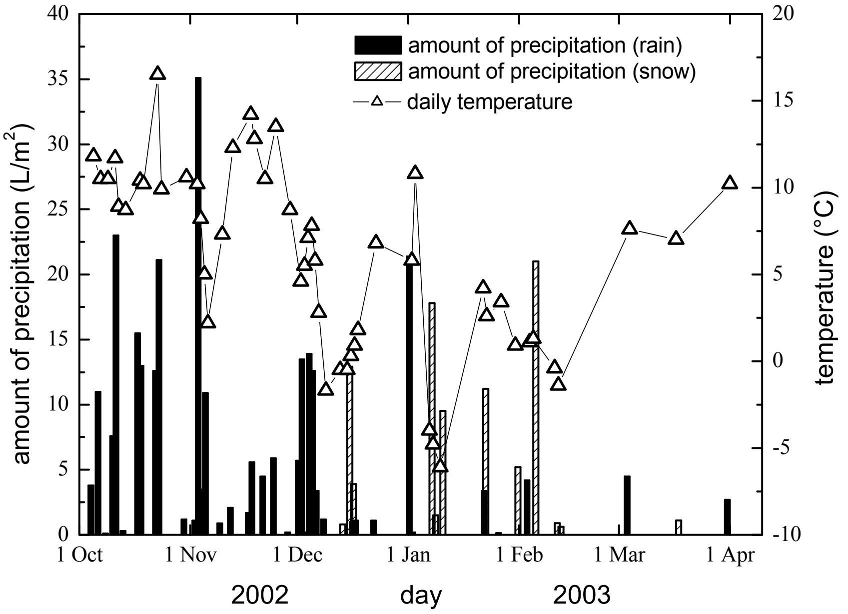

Fig. 1 Daily air temperature and amount of daily precipitation for sampling period, October 2002 – March 2003

$\delta^2H$ and $\delta^{18}O$ of daily precipitation, as well as temperature in the sampling period, are shown in Fig. 2. Good correlation between stable isotope composition and temperature is obvious. The higher values are measured in the period October-December. $\delta^{18}O$ vs temperature correlation (Fig. 3) for daily precipitation showed that $\delta^{18}O$ vs temperature slope for this period was 0.65‰/°C for the mean temperature of 6°C, while the slope for long-term measurements of monthly precipitation in Zagreb is 0.33‰/°C (Krajcar Bronić et al, 1998). The slope calculated for the first 3-month period is lower (0.52‰/°C), and the slope for the second 3-month period is higher (0.80‰/°C) than the slope for the whole 6-month period. This is in accordance with the observed dependence of the slope $\delta^{18}O$ vs temperature for the continental and maritime stations of Croatia (Horvatinčić et al, 2005) – the higher the mean temperature, the lower the slope.

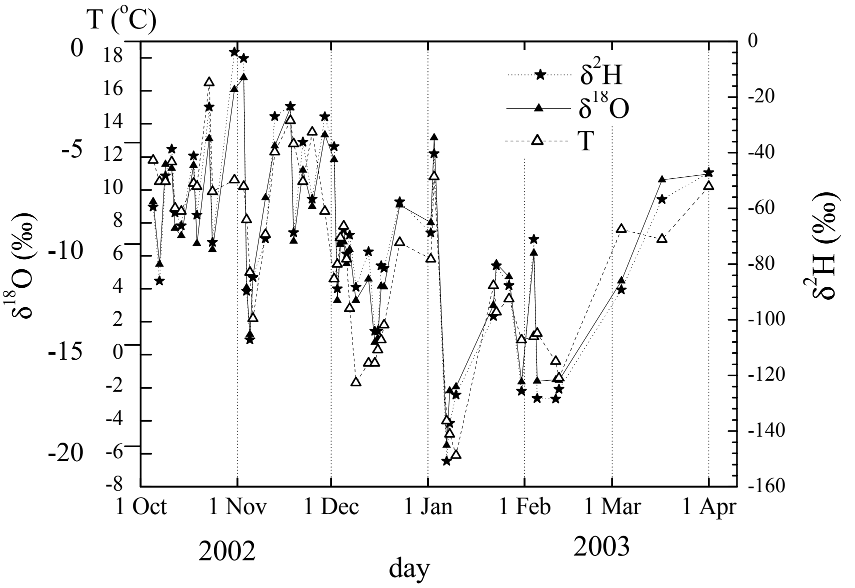

Fig. 2 Comparison of daily air temperatures and stable isotope (*δ*$^{18}$O and *δ*$^2$H) composition of daily precipitation in Zagreb for period October 2002 – March 2003

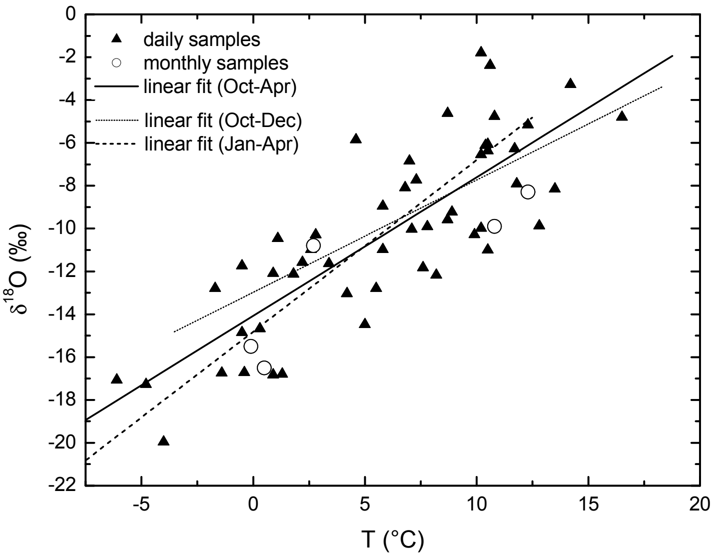

Fig. 3 Temperature dependence of $\delta^{18}O$ values for the sampling period. $\delta^{18}O$ of monthly composite samples are shown for comparison.

The correlation between $\delta^{18}O$ and $\delta^{2}H$ obtained for daily samples collected in the 6-month period (Fig. 4) is $\delta^{2}H = (7.9\pm0.2)\ \delta^{18}O + (7.5\pm2.0)$, and it fits well to the Global Meteoric Water Line (GMWL is $\delta^{2}H = 8\ \delta^{18}O + 10$), as well as to the long-term LMWL (Local Meteoric Water Line) for Zagreb, $\delta^{2}H = (7.7\pm0.1)\ \delta^{18}O + (4.5\pm0.8)$ (Horvatinčić et al, 2005). We also measured $\delta^{2}H$ and $\delta^{18}O$ values of monthly precipitation for the same period as daily precipitation and the values are compared at Fig. 4. The MWL for monthly precipitation [$\delta^{2}H = (7.9\pm0.3)\ \delta^{18}O + (11.3\pm3.9)$] has the same slope but higher intercept compared with the MWL for daily samples, but it lies inside measurement error. The MWL slope for the 6-month period is higher than for the long-term LMWL slope. The reason is that MWLs were calculated on the basis of autumn-winter sampling with less expressed evaporation, while LMWL is calculated for all seasons.

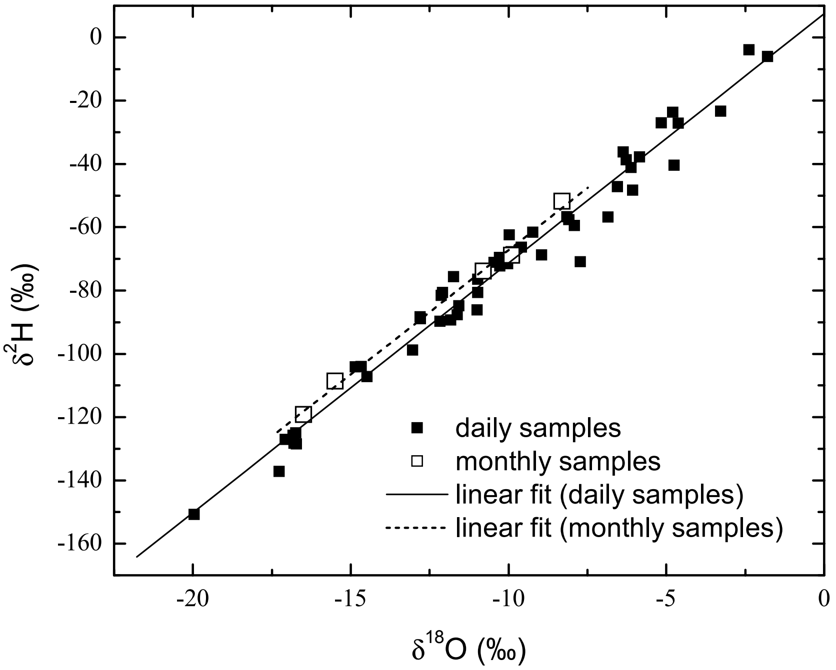

Fig. 4 Correlation between $\delta^{18}O$ and $\delta^{2}H$ for daily and monthly samples collected in the period October 2002 – March 2003

Deuterium excess of daily precipitation (Fig. 5) does not show any particular correlation with temperature or amount of precipitation. Additionally, we tried to correlate the stable isotope composition with the type of weather (e.g., cyclone, anticyclone, etc.) but no correlation was observed. However, the average value of d-excess for the first three-month period (October-December) is 10.2‰ and is higher than the d-excess for winter months (January-March) 5.5‰. These values can indicate that in the Zagreb area (north Croatia) in autumn period the influence of air masses from the Mediterranean area prevails, and in the winter the Atlantic air mass circulation is more significant.

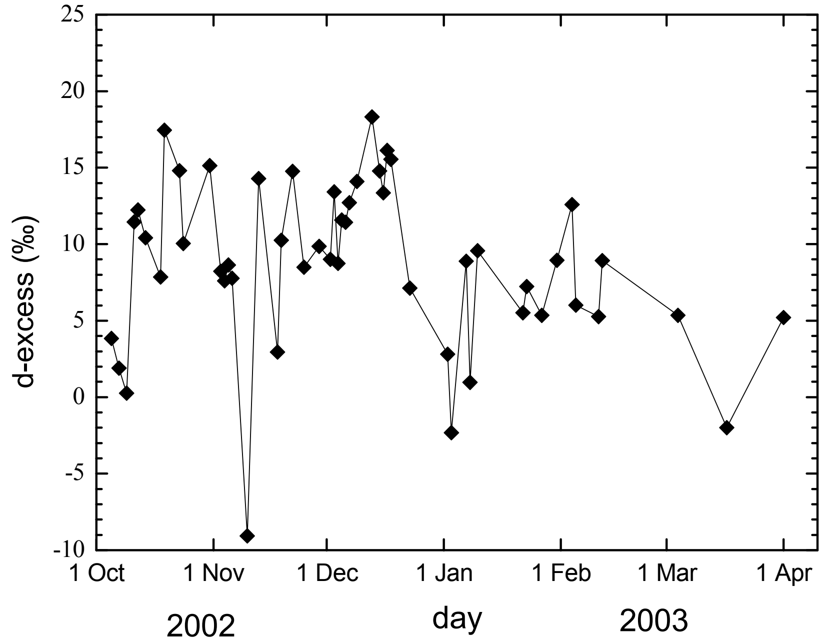

Fig. 5 Deuterium excess of daily precipitation in Zagreb for period October 2002 – March 2003.

Beside stable isotope composition we measured also tritium activity of precipitation from the 6-month period, but only for monthly precipitation. The tritium activity was in the range of 4.5 to 9.9 TU, with the lowest value in March, and the highest in December. All these tritium activities are typical for the winter time period.

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# Geochemical investigations of the dissolved gases in the Boom Clay pore water

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## 1 Introduction

The Oligocene Boom Clay (northern Belgium) has been studied for over twenty-five years as a potential host rock for the final disposal of high-level and medium-level radioactive waste. To assess the safety of the Boom Clay as a geological barrier, a good understanding of its geochemistry is essential as it reveals the stability of the host rock and influences the migration of radionuclides.

The HADES URF (High Activity Disposal Experimental Site, Underground Research Facility) located at 223 m depth in the Boom Clay layer at Mol (Belgium) is one of the few research facilities world-wide where experiments can be conducted concerning the disposal of radioactive waste.

The plastic Boom Clay is characterized by a 19-24 % water content. A recent study focuses on the geochemistry of the Boom Clay pore water (De Craen *et al.* 2004. To support and better understand the pore water geochemistry, an accurate (*in situ*) determination of the partial pressures of the dissolved gases is needed.

A good methodology to measure representative *in situ* $pCO_2$ values, is to use a set up in which the experimental boundaries are imposed and controlled by the Boom Clay formation itself. Under normal Boom Clay physicochemical conditions there is no gas phase present in the Boom Clay pore water. This is because all volatile and gaseous species, thus also carbon dioxide, are below their saturation limit. They are only present as dissolved components of the Boom Clay pore water.

## 2 Principle

The main idea of the new $pCO_2$ measurement technique is to bring Boom Clay pore water in contact with an artificial, chemically non reactive, inert gas (Ar) phase. As a consequence of this contact the dissolved carbon dioxide starts to transfer into the gaseous phase. At equilibrium the distribution of the carbon dioxide between the gas and the liquid phase is proportionally related and defined by the Henry's law constant.

## 3 Experimental set-up

Boom Clay pore water is circulated around, so that the gas phase becomes equilibrated with the *in situ* Boom Clay conditions. The contact and geochemical equilibration of the circulating water with the Boom Clay is ensured by the pores of the piezometric-filterscreen. In this close circuit the real Boom Clay pore water flows, in which a large volume of static inert gas is present that can be sampled in portions large enough to be measured without creating major pressure disturbances (disequilibrium conditions).
To make this new technique work under *in situ* conditions the following experimental set-up has been designed and constructed (Fig. 1):

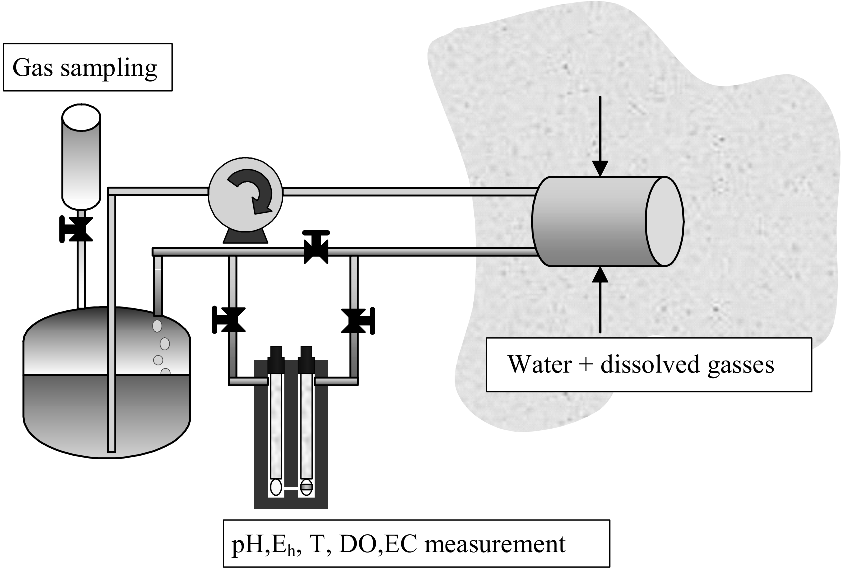

Fig. 1 Schematic representation of the experimental set-up used for $pCO_2$ measurement

The experiment is called **PEGASUS**, an acronym that stands for "**P**artial pressure **E**volution of dissolved **GAS**ses in real **U**nderground **S**ituations" and is in operation since July 2004.
The expectations for PEGASUS are that an *in situ* representative $pCO_2$ value will be obtained. The latter is a pre-requisite for detailed geochemical modelling. An additional benefit of the set-up is that it offers the possibility to simultaneously measure other geochemical parameters such as pH, Eh, temperature, conductivity, dissolved oxygen, alkalinity, salinity and isotopic compositions of the gases. These features can and will be used to gain better insight into the geochemistry of the Boom Clay.

## 4 Results

Before the gas sampling we left the opened gas sampler ampoule for one week attached to the PEGASUS set-up in order to avoid any isotopic fractionation during the sampling. Gas composition measurements were conducted at three different laboratories (SCK•CEN Waste and Disposal Department, SCK•CEN LHMA, IRMM) with different mass spectrometers (Quadrupole MS, Finnigan MAT 271). These measurements confirmed, that gases dissolved in the Boom Clay porewater contain $CH_4$, $CO_2$, $N_2$, $H_2O$, $O_2$ beside the artificially introduced argon. We found that the $CH_4$ concentration is the highest whereas the $CO_2$ is present in rather low concentrations in the PEGASUS gas sample.

The main potential source of methane and $CO_2$ is bacterial degradation of organic matter. Typically anoxic bacteria may be naturally present in the Boom Clay. The presence of three distinct families of bacteria (methane forming, sulfate-reducing, and thiosulfate-reducing) has been revealed by bacteriological analyses of the Boom Clay slurries. Experimental work regarding gas generation and migration in the Boom Clay has been carried out (Ortiz *et al.* 2002).

Besides the gas composition measurements we determined the stable isotopic composition of the $CO_2$ gas at the IRMM Laboratory using a Finnigan MAT 271 mass spectrometer. The measured $\delta^{13}C$ (PDB) = - 6,365 ‰ value suggests a mixed origin for the $CO_2$. Possible sources of the $CO_2$ are: equilibrium with carbonate minerals (fossils and carbonate conretions), decomposition of organic matter, bacterial activity.

Stable isotope geochemistry might help us in unravelling several processes related to the origin and possible evolution of the dissolved $CO_2$. The petrography and stable isotope geochemistry of septarian carbonate concretions occuring in different levels of the Boom Clay is well known (De Craen 1998). The $\delta^{13}C$ values (-17.5 to -20.5 ‰) of the concretionary carbonate show that bacterial sulphate-reduction processes were dominant during their early - diagenetic formation.

For further interpretations ongoing stable isotopic measurements of dissolved $CH_4$, solid and dissolved organic matter is needed.

**Acknowledgement**
This work is undertaken in close co-operation with, and with the financial support of NIRAS/ONDRAF, coordinating the National Belgian Radioactive Waste Management Program. A special thanks to the Ministerie van de Vlaamse Gemeenschap, Department Onderwijs and the Hungarian Scholarship Board for their financial support for a fellowship of the first author.

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# The water isotopes use for determination of water origin in karstic areas: case study

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The Movile Cave, located in the South-eastern part of Romania, is one of the caves that have received the most attention during the last years from the scientific community because it is the site of a groundwater ecosystem that is rich in hydrogen sulphide and carbon dioxide, poor in oxygen, and also contain significant amounts of methane, it is a peculiar, practically unique environment, the cave ecosystem completely driven by chemosynthesis.

Scientists dispute origin of the water in this unusual cave: some researchers sustain the paleo-origin of water; other researchers sustain the origin from Danube River. Our studies suggest that the origin of groundwater from cave area is from recent precipitation. Using the water isotopes the determination of the origin of groundwater in cave area was made in six steps: 1) the analyse of the $\delta^2H$ - $\delta^{18}O$ covariance, 2) the correlation of the $\delta^2H$ - ΔDens average values, 3) the □$^2H$ - time correlation, 4) the mixing lines, 5) the spatial variation of the $\delta\,^2H$ average values, and 6) the tritium determination.

For the correct identification of the water origin in cave, the study of the isotopic composition of the groundwater and their relationship with the isotopic composition of the present-day precipitations was made. The comparison of the $\delta^2H$ and $\delta^{18}O$ values for the groundwater with those of the precipitations on a regional scale shows the connection between the groundwater and the meteoric input signal. Comparing the $\delta^2H$ and $\delta^{18}O$ values from precipitation fallen over SE Europe from data base for the nearest GNIP's stations (located at low altitude) with our results, the isotopic analyses for the most groundwater samples have the values lower than the precipitation fallen over study area. Shallow bores (Sarmatian formations) tap water with $\delta^{18}O$ average values of –11.2 ± 0.7‰ with about –1.0‰ lower than precipitation, and the deeper wells (Eocene-Cretaceous-Jurassic formations) tap water with lower $\delta^{18}O$ values (-12.5±0.5‰), with about –2.5‰ lower than the δ values found in present-day rainfall. The $^2\delta$ average values from groundwater are lower than that expected from present-day rainfall, being depleted in deuterium by ~ 15 ‰ in comparison to present precipitation in the SE Europe. The dexcess defined as $d = \delta\,^2H - 8 * \delta^{18}O$, places the isotope composition of the groundwater samples relative to that of the Global Meteoric Water Line (GMWL, for which d=10‰). The range of values of the dexcess parameter is from d = 5.36‰ to d = 12.20‰, the average values of the dexcess parameters of the measurements of the groundwater samples are of 7.1‰ for springs, 9.1‰ for Sarmatian wells and 10.8‰ for deep wells (Mesozoic limestone). Compared to the range of dexcess values from the present-day rainfall in SE Europe, the samples have the same dexcess values that than found in the present-day rainfall.

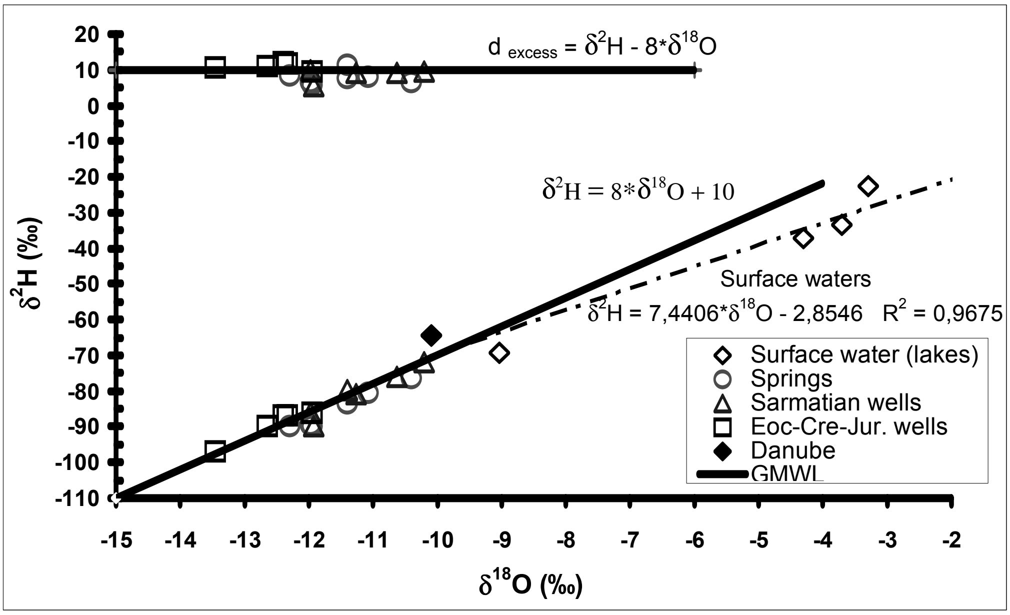

Fig. 1 The $\delta^2H$ - $\delta^{18}O$ convariance

The groundwater samples can be seen to be distributed along the GMWL (Craig line) and was much lighter (more negative) than surface water (Fig.1). The isotopic composition of water from springs and Sarmatian wells plots along a GMWL and from deeper wells plots about 2 per mil above, and closely parallel to the meteoric water line. In general, the MWLs for groundwater have ranges of the slopes that are similar or slightly higher to those of the GMWL. In contrast, surface water from Danube and the lakes from the parts of the southern Dobrogea plots below the GMWL and the slope is bellow 8 as a result of the evaporation in humid atmosphere (~90%), the lakes being located near the sea coast. The first conclusion was that the water from Movile Cave is the meteoric water as origin, the most probably from precipitation from SE Europe fallen over high altitude, which shifts the δ values to more negative values due to the temperature differences between the lowland and highland.

The distribution of the samples in the diagram $\delta^2H$ – ΔDens of mean values point out the three types of water from isotopic point of view: 1) waters that have low deuterium content $\delta^2H < -88‰$, 2) samples with deuterium content of about mean value $\delta^2H \approx -85‰$, and 3) waters with higher deuterium content $\delta^2H > -80‰$. The mesothermal, sulphidic and fresh waters from the study area are significantly depleted in heavy isotopes, these values are not typical for the groundwater and surface water from the low land of the Dodrogea district, which present the $\delta^2H$ values of about -75‰. These values suggest that the groundwater has been recharged at a much higher altitude than that of the emergence. Most probably, the water from the cave area comes from the Balkan Plateau.

The seasonal variation of the deuterium content of precipitation input is reproduced, after damping and delay. The deuterium concentration is lower in summer that in winter (similar results were recorded by Flora and Longinelli, 1989, for karstic springs along the Adriatic coast, near Trieste). This six-month shift of the isotopic composition suggests a long way of water movement (Fig. 2). Most probably, the water from the cave area comes from the Balkan Plateau.

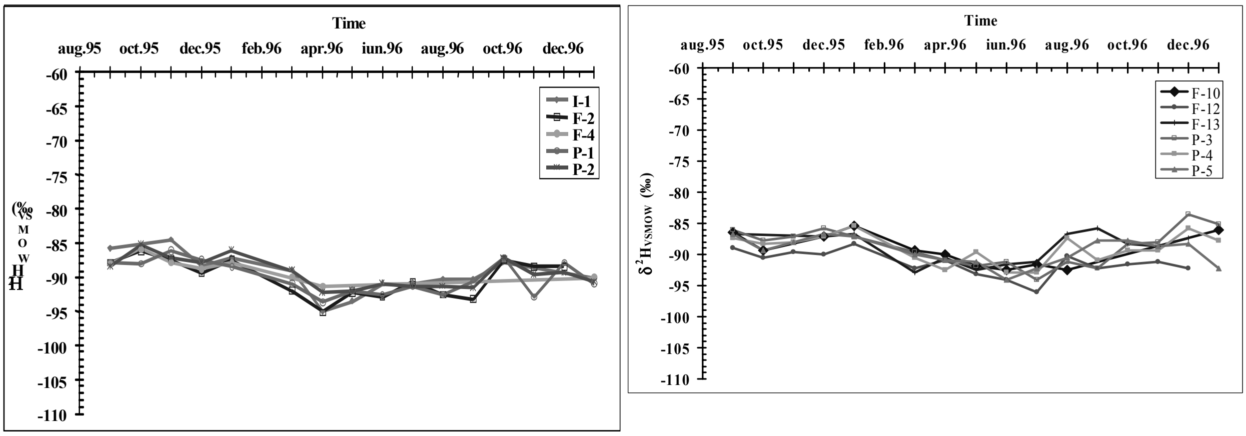

Fig. 2 The variation of the $\delta^2$H values in time

The diagram of the mixing lines suggests that the water from cave belong to a mixing water system. One end member is the isotopically light water and another end member is the isotopically enriched water. In the spatial variation of the deuterium mean content the closed lines delineated the area with the water movement by vertical and the open lines by horizontal. The vertical movement is: 1) for the aquifer caught in Mesozoic limestone that has isotopically light water, 2) for the springs and wells on the Kara Oban site, which have isotopically light water, too, 3) for the samples of Sarmatian aquifer from the south-western part of study area, which present a higher deuterium content and 4) for the Movile Cave that have a mixing water.

Tritium content of the groundwater presents the six-month shift of the isotopic composition as the deuterium content has shown, suggesting a long way of water movement, too. The values seem to indicate that groundwater from the Movile Cave is a mix of submodern (prior to 1950s) and modern groundwaters (<5 to 10 years) in different rates. The conclusions are the following:

1) The origin of the water from the Movile Cave is meteoric, from the modern and submodern precipitation fallen over a higher altitude than that of their emergence.
2) Most probably, the water from the cave area comes from the Balkan Plateau.
3) The cave is a buffer system between the confined aquifer from depth and the unconfined aquifer from the Sarmatian deposits. The connection between them is of double U shape ( ⊔⊔ ), having the cave in the middle branch.

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# Concentration and separation of uranium and thorium from sediment in north Algerian Sahara using organophosphorus extractant and ions exchange resin

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In order to be quantified in an environmental sample, isotopes of thorium and uranium, alpha emitters, must be extracted from the matrix then separated between them before being measured individually.

In this presentaion, we describe a method to quantitatively isolate the uranium and thorium from sediments samples and obtaining electrodeposits suitable for high resolution alpha spectrometry.

After dissolution of the sediment sample in hydrochloridric medium, the uranium and thorium contained in sediment sample are concentrated by coprecipitation with H3PO4 in ammoniacal medium. The precipitate is then dissolved in dilute nitric acid.

The uranium is passed through a TrU-Spec column constituted of octyl(phenyl)-N,N-diisobutyl-carbamoyl-methylphophine oxide (CMPO) dissolved in tributyl phophate (TBP) supported on inert substrate (Amberlite XAD-7). The uranium is stripped from the column with dilute ammonium bioxalate.

The thorium is passed through a column of ions exchange resin [Bio rad AG1-X2]. The thorium is stripped from the column with HCl 8M.

The uranium and thorium are electrodeposited on stainless steel disks and counted on an alpha spectrometer.

# Session 3

# Ecology

# Global application of stable hydrogen isotopes to wildlife forensics

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Crucial to understanding the ecology of migratory animals is the ability to link geographical regions used by individuals; including breeding, wintering, and intermediate stopover sites. Conventional forensic approaches used to track animal movements have long relied on extrinsic markers, such as banding, and the subsequent recovery of the same marked individuals. This approach has generally been a failure for most small or non-game animals. The more recent use of chemical intrinsic markers, such as the naturally occurring stable isotopes in animal tissues, offers an alternative and greatly improved approach. Stable hydrogen isotopes, in particular, have been successfully used for nearly a decade in wildlife forensics as means of determining the origins and movement of various migratory animals.

The hydrogen isotope content of precipitation ($\delta D_p$) varies both widely and systematically across earth's continents as a result of hydrological processes and climate. The resulting patterns in rainfall thereby providing a powerful geographical label that is translated through soil water to plant matter and into dietary components and tissues of trophic level organisms. As a result, the hydrogen isotope contents of locally grown tissues (i.e. feathers, hair, nails) are potentially ideal tracers of geographical origin for migratory organisms that temporally move and feed between distinct isotopic biomes.

The hydrogen isotope method has demonstrated excellent forensic potential where 1) sufficient spatial variations of precipitation isotopes exist, and 2) strong mechanistic relationships link mean precipitation and the hydrogen isotope ratios in the biological tissues or species of interest. Currently, GIS-based global precipitation isotope maps reveal the greatest potential for applying hydrogen isotope forensics to wildlife movements exist in mid- to high-latitude continental regions, where the strongest spatial isotope gradients exist. In many cases, these large-scale hydrological isotope gradients fortuitously coincide with the migratory endpoints or overlie the pathways for many long distance migrant species. As a result, $\delta D$ in animal tissue and $\delta Dp$ in rainfall relationships provide a significant predictive power to link habitat use both in North America and Europe and several other continents.

New scientific approaches frequently shed new light on previously intractable problems. At the same time, further investigation and testing of these new techniques eventually reveals some drawbacks or limitations. In this presentation we will cover the development of hydrogen isotopes as forensic tool in ecological research, as well as point out were our current deficiencies exist. Specific successful case studies are used to demonstrate:

- Avian migration linkages and dispersal – songbirds in North America,
- Insect migration – the monarch butterfly phenomenon,
- Game bird “hunter take” conservation research issues,
- Multi-isotope multivariate source assignments of waterfowl,
- Altitudinal migration of hummingbirds.

Finally, an ongoing problem of using hydrogen isotopes in wildlife forensic research is the fact that a proportion of tissue hydrogen exchanges H with ambient moisture, and this exchangeable H cannot be eliminated using procedures such as nitration. The result is that tissue hydrogen isotope assays are not comparable among isotope laboratories around the globe. We proposed a new “comparative equilibration” approach using standardized reference tissue types analyzed with like samples. An inter-lab comparison reveals that the use of comparative equilibration yields results within +/-3 permil for various tissue types different among labs, and so this approach will be very useful for standardizing hydrogen isotope measurements in future global wildlife forensic studies.

# Nitrogen isotope ratios as indicator of organic production

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The confirmation that food is produced by organic (in Germany: ecological) agriculture neccessitates not only a good bookkeeping but also the possibility to control the authenticity by independent methods. Two reasons call for such a physical method: The increasing prices for organic food and the loss of trust the consumers as a result of adulterations or frauds. To increase the acceptance of organic food the consumer must trust the label. Even the big discounters start more and more into this segment.

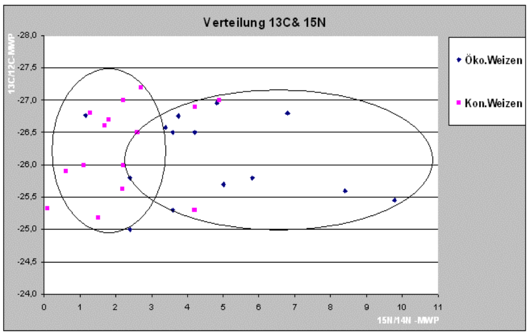
The chemical composition cannot serve as an indicator, for no significant differences between both classes of products have been found. Thus, physical methods should be applied to confirm or reject the hallmark. Stable isotopes are used to trace back materials to their geographical origin. Carbon isotopes are mainly a memory of the carbon dioxide fixation, modified by the ecological conditions especially of the water regime of the plant. the isotopic composition of sulphur and nitrogen depends mainly on the fertilisation. Unfortunately phosphorus cannot be applied for there is only one stable isotope. Sulphur is a good indicator for fertilisation and for environmental monitoring of pollution but plays a minor role in the plant biomass.

At the other site nitrogen has an intensive turnover between the reduced and oxidized form, where losses occur resulting in an isotopic fractionation. Therefore most nitrogen in the soil pool is enriched up to values of at least +5 ‰ or higher. In systems where the nitrogen cycle is isolated from fresh supplies as in deserts the values rise up to + 15 ‰ or in closed nutrient chains as in the sea plankton even up to + 22 ‰. The isotope ratios of fertilizer nitrogen depend on the production procedure. Mineral fertilizer made by the Haber-Bosch procedure (i.e. the formation of ammonia from air nitrogen) shows δ-values around +2 ‰, fertilizer of natural origin values higher than + 5 ‰ (guano, manure). Unfortunately the symbiotic microorganisms of legumes fix air nitrogen without any remarkable isotopic enrichment.

Both influences must be taken into account measuring the nitrogen isotopic ratio of biomass. The increase of the δ-values can be counteracted by the growth of nitrogen fixing plants and masked by the fertilization with liquid manure. The effect can be seen in Figure 1 comparing conventionally and organically produced wheat from different regions of Germany. The $^{15}N/^{14}N$- data overlap between both groups but most of them are far enough to allow a differentiation. From the data one may confirm other observations that $^{15}N/^{14}N$.values above +5 ‰ are an indicator for organic farming, but for lower values one cannot reject the hallmark organic. As expected the $^{13}C/^{12}C$-data show no significant tendency.

Another set of data, unfortunately comparing conventionally produced wheat with organically produced barley, confirms the result of the limit proposed above (Figure 2). From our experience we expect only minor influences of the two different species on the nitrogen isotope ratio. The samples were also collected across the main area of Germany. The histogram points to another problem. Most of the farmers have changed to organic farming only some years ago. Thus, the soil will not be in a new equilibrium.

A comparison of nitrogen fertilisation and harvest loss with the whole nitrogen pool of the soil results e.g. in long turnover rates of up to more than 100 years for nitrogen (own results in the vineyards of Neustadt/Wineroute) or more than 30 years for carbon (Ewiger Roggenbau Halle/Saale). This means that many soils which are cultivated organically cannot stay in a new equilibrium.



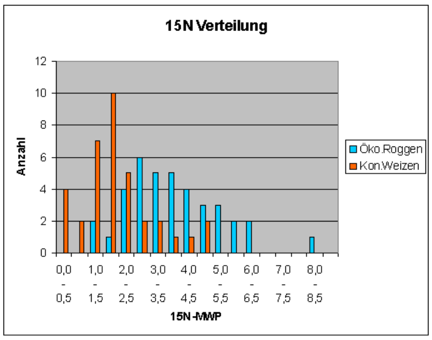


Fig 1 (left) $^{15}N/^{14}N$ and $^{13}C/^{12}C$-data of organically (ecological, ökologisch)(light bars) and conventionally(dark bars) produced wheat

Fig 2 (right) Histograms of organically produced barley (ecological, ökologisch) (light bars) and conventionally produced wheat (dark bars), samples from various regions of Germany

Otherwise comparing a farm which is run with mineral fertilizer to a farm with intensive growth of nitrogen-fixing alfalfa (Figure 3) both differ in their $^{15}N/^{14}N$-ratio, the organic farming results in higher δN-values.

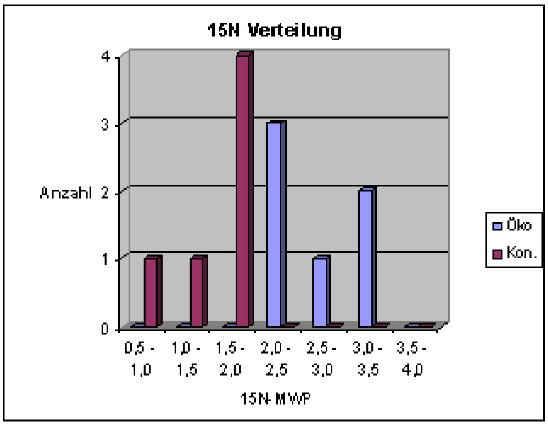


Fig. 3 Comparison of wheat from two different farms in the area between Cologne and Aachen, one working organically (light bars), the other strict ecologically (dark bars), using alfala as nitrogen source intensively

At the moment the natural variation of stable isotopes of nitrogen is one tool to confirm partly the origin of a sample from organic farming if the $^{15}N/^{14}N$-value is above + 5 ‰. But intensive growth of plants fixing air nitrogen as alfalfa may disturb the applicability as well as the use of manure in conventional farming resulting in enriched δN-values.

At the other hand this variability which depends on the geological situation, the history of the soil fertilisation , the species of plants grown and the deposition or emission of atmospheric nitrogen compounds may be used to differentiate between various batches. Cereal mills ask for an intsrument to test whether a certain batch really originates from the field under contract. To enhance the selectivity at least four stable isotope ratios are used to assign successfully a sample of wheat to batches from different fields. This is a tool to prevent the addition of material from other batches. The higher prices of organic food could encourage farmers to “dilute” their product with cheaper material. Presently the big discounters start up with organic corners, but have no real guarantee for the origin announced.

This method has also been applied to trace back the origin of samples during the contamination of wheat with nitrofen. Another application is the control of the egg production comparing the feed and the eggs to ensure that the feeding is in accordance to the contracts between producer and trader. Organic farming allows only a limited amount of maize in the feed. This portion can be easily detected as an increasing $^{13}C/^{12}C$-ratio.

The legal base for the food and feed control are the EU regulation 178/2002 (traceability) and the new German LFGB (food and feed law book) which. In the presentation actual cases will be included for the whole market changes quickly and new problems and solutions will appear and will be solved permanently. The global world market will supply us with an increasing amount and variety of products all year round. On the contrary more and more consumers trust in the products out of their own region only.

# Effects of clear cutting and soil preparation on natural $^{15}$N abundance and N concentration in the needle and soil of two boreal conifer tree species

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This study concerns on the impacts of site preparation methods on the interspecific variations of N concentrations and 15N-fractionation in needles and soils of two conifer tree species; Scot pine (*Pinus sylvestris*, L.) and Norway spruce (*Picea abies*, (L.) Karst); three methods of site preparation were i) mound (broken O/E/B horizons piled over undisturbed ground), ii). deep (exposed C-horizon) and iii). shallow (exposed E/B horizon). Our study has found significant differences among, closed forest, clear-cut control and clear-cut site after site treatments in term of their needle and soil N concentrations and $\delta^{15}$N natural abundances. These differences have partly been also explained by the natural abundance of $\delta^{15}$N. For instance, this study has demonstrated that the pattern of natural $^{15}$N abundance in the needle and soil reflects the interspecific variations in forest N cycling as well as the effects of clear cutting and site preparation methods. Foliar $\delta^{15}$N reflected both the N cycling and their soil N sources in our study. For example, the pine tree species at both closed forest (FO) and clear-cut control sites (CO), having higher N concentrations than the spruce, had strongly depleted foliar $\delta^{15}$N natural abundance; the depleted $^{15}$N in the foliage was assumed to be caused during the mycorrhizal fractionation of $^{15}$N during its transfer from mycorrhiza to plant body. Furthermore, foliar $\delta^{15}$N also indicated the different N sources; we speculate that the proportion of mycorrhizal N-uptake by the pine might have been greater than that by the spruce. On the contrary, for the clear-cut treatment site (TP), both tree species did not vary significantly in their N concentrations and this supports our above mentioned hypothesis, because mycorrhizal occurrences in the disturbed soils of the TP site should be very low, causing only a less mycorrhizal tree root infection and most of the N uptake should be directly from soil. We assumed from our isotopic studies that the mycorrhizal N-uptake is very prominent at the N-limited site. Other factors undoubtedly influence isotopic signatures and N concentrations in plants, but under the generally N-limited conditions prevalent in our site, the role of mycorrhizal fungi appears to be very important. The natural abundances of $\delta^{15}$N in needles and soils of the forests ecosystems studies also proved to be a useful indicator of N cycle under the different site preparations methods. The highly $^{15}$N-enriched needles and soils of the different treatment plots (except mound treatment plots) of TP site compared to the FO and CO sites, indicated that the main source of N uptake by trees at this site seems to be mainly directly from soil.

The relative $^{15}$N enrichment of the vegetation to soil gradients at the CO site reflected its impacts on the N dynamics. The more $^{15}$N-enriched needle and uppermost soil organic layer at the clear cut site than that found at the natural forest site indicated the increased level of nitrification in the clear-cut site soil; the higher values of $\delta^{15}$N in the surface soil might have been caused by the plant uptake of more $^{15}$N-enriched $NH_4^+$, resulting from the increase in nitrification after clear cutting.

# Carbon isotopes distribution along pine needles *(Pinus nigra)*

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## 1 Introduction

Stable isotope analyses of $^{13}C/^{12}C$ ratio in recent plant can help to better understand mechanisms of assimilation and dynamics of the plant growth and it is a standard method to distinguish between $C_4$ and $C_3$ plants ( O'Leary 1995, Leavitt and Long 1986, Farquhar et al. 1989, Schleser 1991).

The objective of this study was to determine $\delta^{13}C$ distribution of single needles in pine trees. The mechanisms of carbon isotope fractionation in the atmospheric $CO_2$-plant system is crucial step to calibrate the isotopic tool for paleoenvironmental reconstructions.We show spatial carbon isotope variations in black pine needles, collected from trees at the coast of south-western Croatia island and southern Spain. Needles were segmented into the base, middle and the top and each segment was analyzed separately. Although our data are similar to those on stable carbon isotope variations in single tree foliage obtained by other authors, our results refer to segmented needles.

## 2 Materials and methods

Needles samples from single stands of pine *Pinus nigra* Arnold from Croatia (Žirje Island; **N** 44˚00', E 17˚30', 40 m altitude a.s.l.) and southern Spain (Benalmadena near Malaga; N 36˚58', W 4˚58', 200 m altitude a.s.l.) were collected on 22nd of May 2001 and on 5th of October 2003, respectively. Young needles (about 2-3 and 7 months old) and old needles (1 and 2 years old) have been selected for carbon isotope analyses. The needles were cut perpendicularly to the longer axis into three segments: the base, middle and the top (Tab. 1a and 1b). Needles Zr1.3 and Zr1.4 from Croatia (Tab. 1b) were segmented into halves (two parts only) thus the results are not well comparable to all the other needles always cut into three parts.

About 1-3 mg of each sample was combusted with CuO wire in a sealed quartz tube, under vacuum at 900°C. The obtained $CO_2$ gas was cryogenically purified using liquid nitrogen and dry-ice ethanol mixture. The $CO_2$ was admitted to Finnigan-Mat Delta E mass spectrometer for isotopic ratio analyses. The obtained results are shown as δ value relative to the PDB standard. The analytic precision was 0.05 ‰ whereas reproductibility was ca. 0.5 ‰.

## 3 Results

The $\delta^{13}C$ value in needles from Croatia and Spain varied from –28.25‰ to –24.43‰ and from –27.58‰ to –25.27‰, respectively (Tab. 1a, 1b and Fig. 1). The difference in $\delta\ ^{13}C$ values between the base $\delta\ ^{13}C_b$ and the top $\delta\ ^{13}C_t$ of a single needle ($\Delta^{13}C_{b-t}$) varied from 0.02 ‰ (Spain, B 2.3, Tab.1, young needle) to 2.32 ‰, (Croatia, Zr 2.3, Tab. 2, old needle).

The average $\Delta^{13}C_{b\text{-}t}$ values of all needles varied from 0.78 ‰ and 1.73 ‰ in Spain and Croatia, respectively (Tab.1a and 1b).

The $\Delta^{13}C_{b\text{-}t}$ value in young needles from Croatia varied from 1.85 to 2.05‰, with an average 1.95 ‰, while $\Delta^{13}C_{b\text{-}t}$ in older needles varied from 1.16‰ to 2.32‰, with an average of 1.51 ‰ (Tab.1b.). Therefore, in general, older needles show higher $\Delta^{13}C_{b\text{-}t}$ values than younger ones (Tab.1b.).

Table 1: $\delta\ ^{13}C$ values in needles a) from Spain (B – Benalmadena) ca. 7moths old needles; b) from Croatia (Zr – Žirje) Zr 1.1 to Zr 1.4 are up to 3 months old needles, Zr 2.1 to Zr 2.4 - more than a year old

**t** - top; **m** - middle; **b** – base; **X** – not relevant; **n.a.**-not analyzed ( Zr 1.3 and Zr 1.4 were cut into two parts)

a)

| **Spain** | **Isotopic composition** | | | **whole needle** | **difference (‰)** |
|---|---|---|---|---|---|
| **Sample name** | **$\delta\ ^{13}C_t$** | **$\delta\ ^{13}C_m$** | **$\delta\ ^{13}C_b$** | **average** | **$\Delta^{13}C\ _{b\text{-}t}$** |
| B 1.1 | -27.58 | -26.57 | -25.78 | **-26.64** | **1.80** |
| B 1.2 | -27.21 | -26.38 | -26.56 | **-26.72** | **0.65** |
| B 1.3 | -26.17 | -25.89 | -25.86 | **-25.97** | **0.31** |
| B 1.4 | -26.94 | -26.48 | -26.41 | **-26.72** | **0.53** |
| average | -26.97 | -26.33 | -26.15 | **-26.51** | **0.82** |
| | | | | | |
| B 2.1 | -26.88 | -26.03 | -25.27 | **-26.49** | **1.61** |
| B 2.2 | -26.85 | -25.70 | -26.04 | **-26.20** | **0.81** |
| B 2.3 | -25.83 | -26.23 | -25.81 | **-26.06** | **0.02** |
| B 2.4 | -26.62 | -26.41 | -26.13 | **-26.20** | **0.49** |
| average | -26.55 | -26.09 | -25.81 | **-26.23** | **0.73** |
| **average of all** | **-26.62** | **-26.13** | **-25.87** | X | **0.78** |

b)

| **Croatia** | **Isotopic composition** | | | **whole needle** | **difference (‰)** |
|---|---|---|---|---|---|
| **Sample name** | **$\delta\ ^{13}C_t$** | **$\delta\ ^{13}C_m$** | **$\delta\ ^{13}C_b$** | **average** | **$\Delta^{13}C_{b\text{-}t}$** |
| Zr 1.1 | -26.65 | -26.52 | -24.80 | **-25.99** | **1.85** |
| Zr 1.2 | -26.48 | -26.13 | -24.43 | **-25.68** | **2.05** |
| Zr 1.3 | -26.26 | n.a. | -26.02 | **-26.14** | **0.24** |
| Zr 1.4 | -25.99 | n.a. | -25.06 | **-25.53** | **0.93** |
| average | -26.35 | -26.33 | -25.08 | **-25.83** | **1.95*** |
| | | | | | |
| Zr 2.1 | -28.25 | -27.53 | -26.97 | **-27.58** | **1.28** |
| Zr 2.2 | -27.76 | -26.05 | -26.60 | **-26.80** | **1.16** |
| Zr 2.3 | -27.53 | -26.97 | -25.21 | **-26.57** | **2.32** |
| Zr 2.4 | -26.99 | -27.08 | -25.70 | **-26.59** | **1.29** |
| average | -27.63 | -26.91 | -26.12 | **-26.89** | **1.51** |
| **average of all** | **26.56** | **-26.47** | **-25.25** | X | **1.73*** |

***** - the average value do not represent samples Zr 1.3 and Zr 1.4.

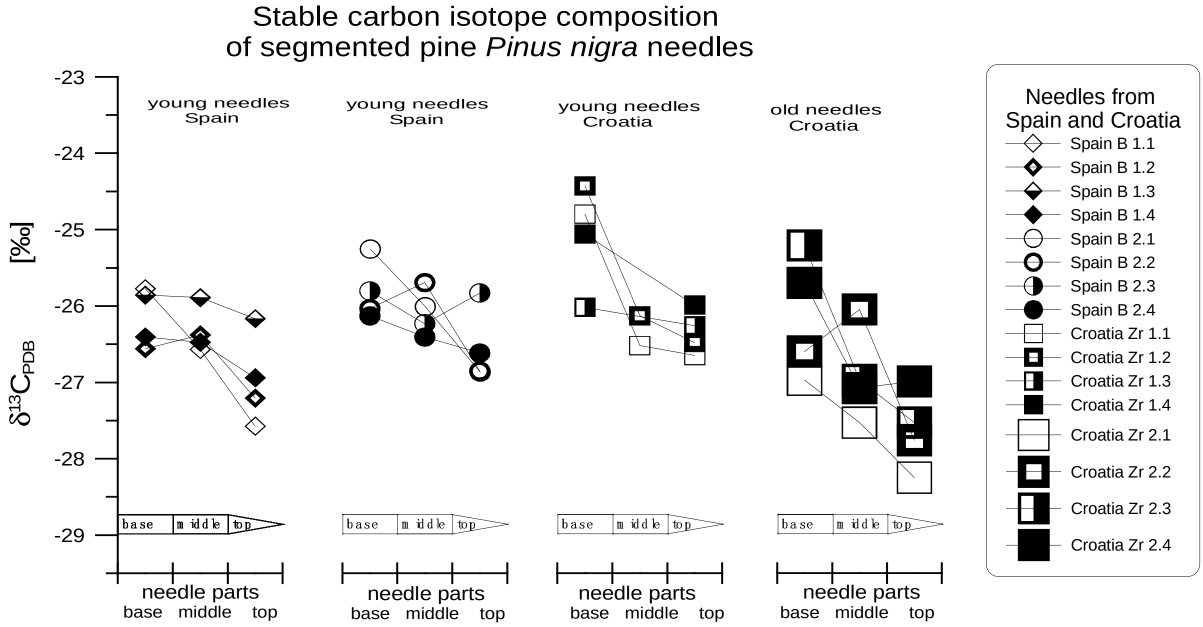

Fig. 1 Stable carbon isotope distribution along the needles of *Pinus nigra*

# 4 Discussion

## 4.1 Whole needles – growing conditions and age classes

As atmospheric carbon dioxide is the only source of carbon for plants, $\delta^{13}C$ in plants is controlled by its $\delta^{13}C$ and isotope fractionation during assimilation. Atmospheric $\delta^{13}C(CO_2)$, due to buffering by the global ocean, is stable in a short term scale. Carbon isotope fractionation between atmospheric $CO_2$ and assimilates is the combined result of an enzymatic carbon isotope fixation effect, which is about −27 ‰, and a diffusion isotope effect that results in a –4.4 ‰ isotope fractionation. The overall difference between the isotopically lightest ($\delta^{13}C$ = -28.25 ‰) and isotopically heaviest ($\delta^{13}C$ = –24.43 ‰) parts of different needles of the same tree from Croatia reached $\Delta^{13}C$ = 4.22 ‰ (with an average 1.73 ‰), while in Spain regardless he age of needles, the $\Delta^{13}C$ value was up to 2.31 ‰ (with an average 0.78 ‰) and $\delta^{13}C$ varied form –27.58‰ to –25.27 ‰. We suggest that variation in humidity and isotopic exchange of atmospheric $CO_2$ with oceanic DIC (Dissolved Inorganic Carbon) was the main reason of the difference in the $\Delta^{13}C_{b-t}$ between the Croatian and Spanish needles.

The younger needle is, the higher $^{13}C/^{12}C$ isotope ratios are observed. Possibly, differences in dynamics of photosynthesis and in the structure of photosynthetic organs cause this trend. Young needles have lower contents of compounds responsible for carbon fixation as compared to the older ones. We postulate that efficient assimilation by less developed stomatae of younger needles results in an enhanced kinetic isotope effect, which leads to the higher $\delta^{13}C$ value.

## 4.2 Segmented needles

The base part of a needle is always enriched in $^{13}C$-isotope as compared to the top, and the middle part of the same needle shows usually a middle range of $\delta^{13}C$ value in the same needle.

This can be caused by the mechanism of needle growth - as base shows intercostal growth (Hejnowicz 2002) it can be suggested that needles grow at the base, and this part of the needle is the youngest, whilst the top of the needle is the oldest one.

$\delta^{13}$C gradient occurs along all the needles analyzed, regardless the age (2-3-months, 7 months old needles and in the older ones, 1 or 2-year-old needles), season or tree location, because needles collected at the beginning of vegetation season (May) show the same trend in $\delta\ ^{13}$C value as needles sampled at its end (October). Therefore, the $\delta^{13}$C trend can not be the result of seasonal variation in $\delta^{13}$C value of atmospheric $CO_2$ showing small increase during vegetation period and a reverse trend during winter. The older parts of needles (spring growth) should show lower $\delta^{13}$C value as compared to the younger (summer and autumn growth). This corresponds to our results, but in the coastal area this effect should be smaller due to dominating role of the oceanic DIC. However the Croatian needles show largest $\Delta^{13}C_{b-t}$ values, while they should be expected to be small due to the buffering role of the ocean. Differences in carbon isotope composition between the base and the top ($\Delta^{13}C_{b-t}$ ) are slightly smaller in younger needles (0.78‰ in Spain) than in the older ones (1.51‰ in Croatia). This can be due to a short time of growth, when the atmospheric $\delta^{13}$C was steady Those results may suggest that temperature variations or other seasonal variations do not control the intraneedle carbon isotope distribution, and carbon isotopes are not retranslocated after fixation into the structure when needle is not growing anymore. Moreover, the smaller $\delta^{13}$C gradient along the needles from Spain results probably from smaller variation of air humidity and $\delta^{13}$C of assimilated $CO_2$ at the growing site.

It is well known that chemical composition of primary and secondary products contained in the needle tissue varies with time and age of needles. The primary products in $C_3$ plants are usually isotopically heavier in carbon, than the secondary ones, e.g. carbohydrates (such as sucrose or starch) are enriched in $\delta^{13}$C comparing to cellulose and especially lignin and lipids, which are isotopically the lightest. Likewise, storage tissues (e.g. roots and seeds) are isotopically heavier than remaining tissue (Farquhar et al., 1989; Gleixner et al.,1993; O'Leary,1995). The young base of needle might contain some primary or storage products. During the growth the needles use a storage material (e.g. starch) hence $^{12}$C isotopes are preferably incorporated into the new tissue, while the remaining storage material is enriched in $^{13}$C isotope. Consequently, the older parts of needles are $^{13}$C-depleted as compared to the younger part at the base which are found to be $^{13}$C-enriched.

## 5 Conclusions

1. Needles grow at the base, so this part of the needle is the youngest. Consequently, the top of the needle is the oldest one. Base of a needle is always $^{13}$C-enriched with respect to the top of the needle. Middle of the needle shows usually medium isotope values.

2. Intraneedle spatial inhomogeneity occurs in all the needles analyzed, regardless the age class and season - needles collected at the beginning of vegetation season (May) show the same trend in $\delta^{13}$C value as needles sampled at its end (October).

3. The seasonal temperature variation was negligible for the discovered $\delta^{13}$C distribution trend.

4. Carbon isotopes are not retranslocated after fixation into the structure of the needle.

5. Remarkably high $\Delta\,^{13}C_{b-t}$ values, and regular pattern, are dominantly caused by isotopic and chemical composition of primary and secondary products contained in the growing part of a needle and kinetic isotope fractionation during decomposition of storage materials at the base.

6. Smaller $\delta^{13}C$ gradient along the needles from Spain results probably from smaller temporal variation in the air humidity and $\delta^{13}C$ of assimilated $CO_2$ at the growing site.

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# Potential of natural fouling communities for assimilation of fish farm derived particulate nitrogen: a case study in Gulf of Aqaba (Red Sea)

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Offshore fish farms release large amounts of soluble and insoluble inorganic and organic waste into the sea. In contrast to the negative effects that aquaculture often has on the sediments and benthos below and adjacent to the fish cages, diverse communities of sessile, and often cryptic, fouling organisms appear to thrive on ropes, buoys, nets, etc., associated with fish farms. Marine organisms are systematically enriched in $^{15}$N with respect to their food, therefore the nitrogen stable isotopic composition ($\delta^{15}$N) of tissues provides a powerful tool for determination of sources of nutrition and trophic relationships among animals (Schwarcz, 1991, Yoshii et al., 1999). The objective of the present study was to trace and quantify the flow of nitrogen from the fish cages to the natural fouling communities associated with artificial hard substrates deployed in the vicinity of fish cages, and thus to evaluate their potential for removal of farm-derived particulate nitrogen waste.

The Ardag fish farm is located at Eilat in the northern end of the oligotrophic Gulf of Aqaba (Fig. 1). The annual production during the study period (2001 – 2003) was approx. 1400 t gilthead sea bream (*Sparus aurata*). The “fish farm” and “reference” experimental sites were located 10 and 300 m W of the farm, respectively. At each study site, four floating plastic arrays were moored to the seafloor in June 2001. Each array consisted of 8 mesh cylinders (black NETLON Str7011 net, 25 mm square mesh) 50 cm high, 25 cm diameter, secured on a horizontal frame at 8 m depth. The total surface area available for settlement on each mesh cylinder was 0.5 m$^2$. The mesh cylinder arrays were oriented perpendicular to the predominant current direction, to maximise their exposure to suspended particles transported by the currents.

Samples of particulate organic matter (POM) and organisms associated with hard substrates were collected at the fish farm site and at a reference site. These were used to differentiate between the uptake of nitrogen released from the fish farm and from natural nitrogen sources. Samples of fish food and faces (fish farm particulate effluents) were also analysed to characterise the particulate waste deriving from the farm. These data enabled us to determine the relative contribution of various forms of POM (fish farm effluent versus natural seston) to the diet of the organisms associated with the hard substrates. In this study we have focused only on the incorporation of POM by the associated organisms and have not addressed uptake of dissolved organic matter or dissolved inorganic nutrients.

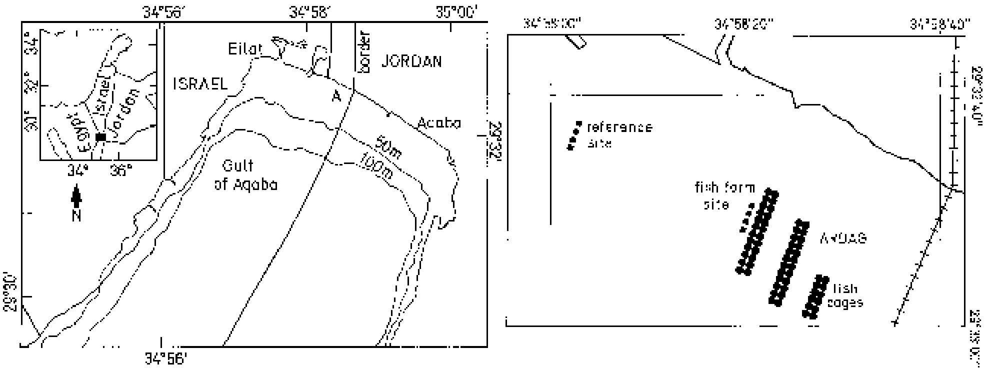

Fig. 1 Location map of the Ardag fish farm and the reference site

Samples of fish food were taken from the Ardag fish farm in June 2001and April 2002. Faecal material was collected by stripping fish (300 to 400 g body mass) after acclimating to the tested feed for 5 days. Fish were fed in the evening and stripped 8 - 9 h later. In addition, POM was collected seasonally by means of sediment traps deployed at 8 m depth for 24 h at the farm site and for 48 h at the reference site in order to obtain enough material for isotope analysis. Sediment trap samples were filtered onto 47 mm GF/C glass fibre filters (Whatman), rinsed with deionised water to eliminate salts and oven-dried overnight at 50°C. Conspicuous fouling organisms were removed from the plastic mesh cylinders bimonthly at both study sites. The organisms were briefly rinsed with deionised water, dried at 50°C to constant weight and processed for isotope analyses. Composite samples, consisting of entire fouling communities, were also removed from randomly selected mesh cylinders (one per array) by thoroughly scraping off all associated biomass. Composite samples of at least three individual organisms, or sections of colonies of small organisms (e.g. bryozoans) were pulverised and homogenised for isotope and elemental analyses. It is noteworthy that the composite samples contained many cryptic (non-conspicuous) fouling organisms that were not included in the individual organism sampling.

Nitrogen concentrations of individual fouling organisms and entire communities were determined using a Vario EL-III CHN elemental analyser. Nitrogen stable isotope composition ($\delta^{15}N$) was determined using a continuous flow isotope ratio mass spectrometer Europa 20-20 with ANCA SL preparation module (PDZ Europa Ltd., U.K.). Standard deviation of the measurement determined on multiple analyses of working standards was generally ≤ 0.2‰, while standard deviation of the samples was generally ≤ 0.3‰. To validate the differences in abundance (in terms of % total dry mass) of organisms and their $\delta^{15}N$ values at both sites, we applied the T-test for independent samples by group (Statistica 6.0 data analysis software system, StatSoft Inc.).

To estimate the retention of farm-derived N in biofouling community, organisms belonging to related taxa were pooled for the purpose of calculation. POM – organism pairs at the reference site were used to estimate enrichment (ε) of organisms in $^{15}N$ with respect to their food, expressed in a manner similar to that used by Wada et al. (1991, 1993) as

$$\delta^{15}N_{\mathrm{organism}} = \delta^{15}N_{\mathrm{food}} + \varepsilon.$$

Assuming that the isotopic separation between food and organisms was the same for the same species at the fish farm and at the reference sites, the fraction of N in organisms' diet deriving from the fish farm POM was estimated using a simple linear mixing model (Schwarcz, 1991, Phillips, 2001):

$$\delta^{15}N_{food} = \delta^{15}N_{organism} - \varepsilon = B \times \delta^{15}N_{POM-B} + F \times \delta^{15}N_{POM-F}, \text{ and } B + F = 1,$$

where B and F are the fractions of background and farm-derived POM, respectively, and $\delta^{15}N_{POM-B}$ and $\delta^{15}N_{POM-F}$ are their nitrogen isotopic compositions. The standard deviations and confidence limits (95%) of the food source estimates were calculated following Phillips and Gregg (2001). In this calculation, only the N isotopic composition of organisms and their potential food were considered (N concentrations in background and farm-derived POM may not be the same, but were not determined here). Therefore the results obtained represent only the fraction of organisms' nitrogen deriving from the consumption of farm-derived seston.

The two study sites differed with respect to total abundance of organisms associated with the mesh cylinders, where the dry weight of total fouling communities at the fish farm site exceeded that at the reference site from 3 to 12 fold. Although the biomass on the mesh cylinders increased steadily, the community structure at both sites did not change with time at a statistically significant level. Several species of algae, sponge, coelenterates, bivalves, bryozoans, polychaetes and tunicates were determined. Statistically significant differences between fish farm and reference sites ($p<0.05$) were observed only in the relative abundance of algae 7, 9 and 11 months after deployment (MAD), sponges at 3 MAD and polychaetes at 9 MAD. In most cases, an enrichment in $^{15}N$ in conspicuous organisms collected at the fish farm as compared to those from the reference site was observed (statistically significant at $p<0.05$), in average by up to 1.6‰. The difference in $\delta^{15}N$ of sponges at the two sites (up to 2‰) is noteworthy since sponges comprised a considerable fraction of the fouling biomass on cylinders at the fish farm site. The exceptions to this were: a) "algae" that had significantly different values only in October 2002 and b) bivalves and bryozoans ($p=0.10$ and $p=0.06$, respectively). Temporal variations in nitrogen isotopic composition were observed for all sampled species, and ranged from 1‰ for algae to 4.6‰ for serpulide polychaetes.

Total community biomass (dry weight of composite samples) ranged from 1074±127 g $m^{-2}$ (June 2002) to 1437±272 g $m^{-2}$ (February 2003). In the last 3 months of observation, the mean biomass of entire communities constantly decreased. The N concentration in composite samples ranged from 1.8 (April 2002) to 2.2 wt.% (March 2003), with a mean value of 2.0 ± 0.7 wt.%. The comparative isotopic composition analysis indicated an enrichment of 2.1‰ in $^{15}N$ at the fish farm site. The composite community samples that were removed from the cylinders differed from samples of individual (conspicuous) organisms in that the composite samples also included many cryptic, unidentified and microscopic organisms. The composite community samples exhibited the same pattern of $^{15}N$ – enrichment at the fish farm relative to the reference site. Moreover, the $\delta^{15}N$ values of entire biofouling communities were consistently higher than the weighted sum of $\delta^{15}N$ values of conspicuous macro-organisms; most probably due to the fact that both the macro- and the smaller organisms take up and incorporate farm-derived N (Bode et al., 2003). We found that the $\delta^{15}N$ values of the fouling communities on the mesh cylinders plateaued when community biomass stopped increasing. This is a noteworthy observation, since the organisms continue to process the same $^{15}N$-enriched fish farm effluents and should have, in theory, increased $\delta^{15}N$ values. On the basis of that finding we hypothesise that the POM ingested by the deteriorating fouling community serves mainly for metabolic purposes. From the $^{15}N$ enrichment of composite fouling communities at the fish farm site we conclude that the entire community is more efficient in retaining farm-derived nitrogen than the sum of individual conspicuous species. It appears that farm-derived POM represents a substantial part of the diet of many suspension feeders associated with the mesh cylinders deployed adjacent to fish cages.

The retention capacity of fouling communities, estimated from individual, conspicuous species data, increased with time both in terms of absolute (g N $m^{-2}$ mesh) and relative (g $kg^{-1}$ dry weight) amount of farm-derived N, reaching values of 5.6±1.5 g N $m^{-2}$ or 3.3±1.1 g N $kg^{-1}$ dry weight. Nitrogen uptake, based on data from composite communities (conspicuous and cryptic organisms), ranged from 5.4 – 17.0 g $kg^{-1}$ farm-derived N. There was also a temporal increase in community N retention rates, from 0.12 g $m^{-2}month^{-1}$ 2 MAD to 0.6 $m^{-2}month^{-1}$ 9 MAD, suggesting that older communities may be more efficient at capturing fish farm effluents than younger ones, but only until these reach a steady state. Moreover, filtering efficiency appears to be greater in mixed as opposed to mono-specific biofouling communities. Nevertheless, the results show that for capturing the amount of particulate N, which is annually released from a fish farm producing similar amount of sea bream as Ardag (Lupatsch and Kissil, 1998), would require between 250.000 and 600,000 $m^2$ of mesh cylinders of the same design. At present, the scale of such massive structures around fish farms seems impractical, but there are other alternatives available to increase the sustainability of net-cage aquaculture. If we assume that the net removal of fish farm effluents is a positive action, removal of <100% of the farm effluents is also a beneficial activity and we may approach more practical and acceptable scales of biofiltration systems.

This study has demonstrated that stable isotopes of nitrogen are an effective tool to both trace and quantify the flow of N from fish farms or other point sources to the surrounding living communities of suspension feeders. It is possible that a similar approach may be applied to enable us to follow and quantify the flux of dissolved nutrients released from other point sources to the surrounding marine ecosystem. This would be especially interesting in the case of aquaculture effluents since most of the nitrogen is released to the surrounding waters as ammonia.

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# $CO_2$ concentration and $\delta^{13}C$ through time in sets of monthly air samples from downtown Parma and from the Parma and Taro river valleys, Italy

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Discrete monthly air samples have been collected from September 2004 in the town of Parma, along North-South and East-West runs (16 samples altogether) by means of four litre Pyrex flasks. The Pyrex flasks were carefully evacuated to $10^{-3}$ mm Hg, opened at the fixed sites between about 11.00 and 12.00 a.m., and closed after air collection by means of high vacuum greasless stopcocks. The atmospheric $CO_2$ samples were separated from other air gases in the laboratory by means of a vacuum line by very slow pumping (about 7 ml/min) through a Swagelock micro-valve and a liquid nitrogen cooled spiral trap. After pumping down the flask to about $10^{-3}$ mm Hg, the trap was isolated and heated to about -80°C by means of an ethyl alcohol-liquid nitrogen slash. The evolving $CO_2$ was collected in a sample tube and measured by means of a Finnigan Delta S mass spectrometer for its $^{13}C/^{12}C$ ratios. The accuracy of the procedure was tested by means of a number of air samples collected and treated in the same way. The standard deviation for carbon isotope measurements ranges between ± 0.02 and ± 0.04 per mil ($1\sigma$ ). No correction was made for the $N_2O$ effect since this correction would be meaningless when compared to the expected isotopic differences. The $CO_2$ concentrations were calculated on the basis of the intensity in the mass spectrometer of the $^{12}C^{16}O_2^+$ ion beam of each sample after calibration with artificial air samples whose $CO_2$ concentration was determined at the Monte Cimone Observatory, Sestola, Modena, Italy by comparison with primary standards normally used at the Observatory. Aim of this study is the semi-quantitative evaluation of the contribution of domestic heating to the atmospheric $CO_2$ pollution in downtown Parma by comparing fall and spring values with winter values. The monthly measurements will continue until May 2005. The results obtained up to now suggest that the contribution of domestic heating is quite small, the main source of polluting $CO_2$ being essentially the heavy car traffic. In fact, the different sites monitored in downtown Parma show, during winter, changes of the $CO_2$ concentration and isotopic composition, when compared to the fall values, ranging roughly between -10 and +15 %.

During the same time interval, sets of discrete air samples have been collected along North-South runs from the town of Parma to the Apennine ridge following the river Parma and the river Taro valleys and measured according to the same technique. The results obtained up to now show occasional jumps of the $CO_2$ concentration and $\delta^{13}C$ values towards higher and lower values respectively. These sudden changes are difficult to understand and to reconcile with environmental and/or meteorological conditions. Most of the results do not undergo large variations remaining fairly homogeneous during the first months of this study.

# Carbon isotope discrimination affected by atmospheric pollutants

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## 1 Introduction

Trees are interactive monitors of the environment. They preserve information about climate and other environmental conditions in annually resolution based on tree rings. In this regard stable isotopes are a useful tool to extract this information from tree rings. Photosynthesis converts $CO_2$ of the atmosphere and water of the soil to carbohydrates. The stable isotope ratios in wood cellulose are influenced by physiological process and conditioned by the ratios occurring in the matter uptaken. Stable carbon isotopes record the balance between stomatal conductance and photosynthetic rate. $^{18}O/^{16}O$ ratios reflect leaf transpiration, controlled dominantly by vapour pressure deficit. Since the beginning of the Industrialisation (ca. AD 1800) pollutants and additional carbon dioxide come from anthropogenic sources. Some authors (Feng, 1998, Francey 1999, Arneth 2002) investigated the effects of additional carbon but only few the contribution of phytotoxic gases (Savard 2004, Saurer 2004). Here we present a study of the influence of various local environmental variation and air pollutants to the $\delta^{13}C$ and $\delta^{18}O$ values under equal climate conditions on recent pine trees.

## 2 Sampling sites

For our comparative investigation we chose a region in Lusatia characterised by inner dunes. The sites of the studied trees follow a gradient from moist on the bottom to dry on the top of the dunes. Lusatia is a mining area producing lignite for large-scale power plants. These power plants emitted large amounts of airborne pollutants particularly dust and sulphur dioxide.

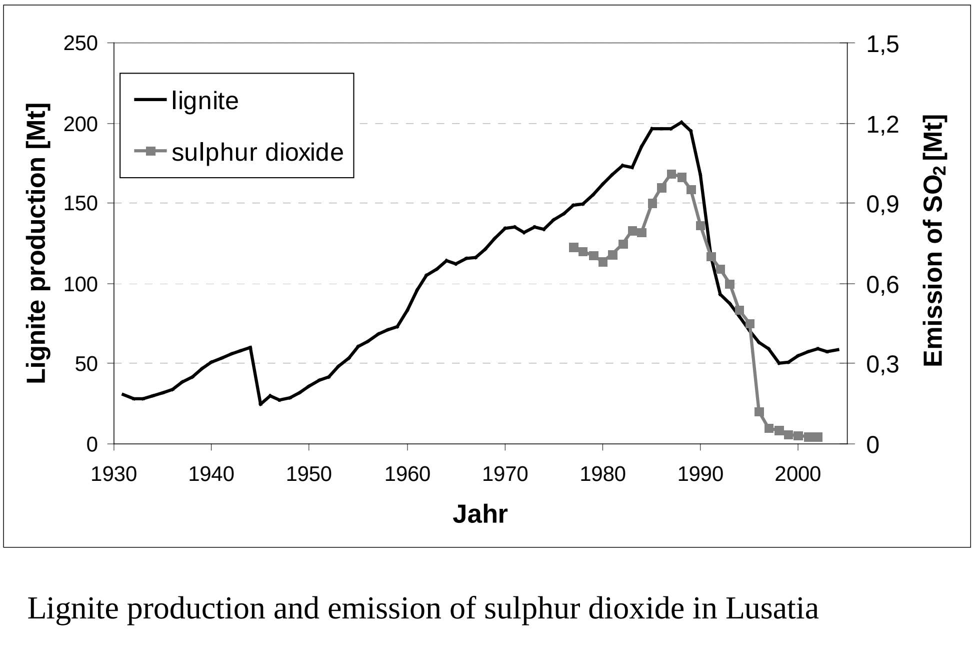

Fig. 1 Lignite production and emission of sulphur dioxide in Lusatia

The reported emission of $SO_2$ increased from 730 kt to 1010 kt from 1975 until 1989. Through the political collapse of the GDR the lignite-fired power plant pool in Eastern German is currently undergoing an extensive modernization process. Old plants were shut down. The efficiency and environmental compatibility of those power plants were substantially improved by retrofit equipment. Total immission where reduced from annual average value ca 100 $\mu g/m^3$ in 1988 under 8 $\mu g/m^3$ in 1998.

For large scale comparison and as a reference we sampled cores from pine trees at a location near Jena in Thuringia. Here the pine grows on a south-exposed limestone slope under very dry conditions. Jena is situated 250 km west of Lusatia in contrary average wind direction. Only the city causes direct anthropogenic impact on the reference site.

On each site of both transect, 15 to 20 dominant Scots pines were sampled by taking two cores per tree. After cross dating and measuring the ring width, we chose two pine trees from the upper and the middle site and three trees from the lower site for the isotope analysis. At the location near Jena we sampled cores from 45 Scots pines and two pines were chosen for isotope measurement.

The samples were cut and annual ring separated in the laboratory using scalpel. Cellulose was prepared according to the method proposed by Gray and Song (1984).

The obtained $\delta$-cellulose (insoluble in 17 % NaOH solution) was dried at 50°C and homogenized. Aliquots of ca. 250 $\mu g$ were weighed into silver capsules. $\delta\ ^{13}C$ and $\delta^{18}O$ were determined with HEKAtech pyrolysis reactor connected to IRMS-DELTA plus XL (ThermoFinnigan) (Knoeller, 2005).

## 3 Material and methods

On each site of both transect, 15 to 20 dominant Scots pines were sampled by taking two cores per tree. After cross dating and measuring the ring width, we chose two pine trees from the upper and the middle site and three trees from the lower site for the isotope analysis. At the location near Jena we sampled cores from 45 Scots pines and two pines were chosen for isotope measurement.

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## 4 Results and discussion

In order to compare individual curves a transformation of the time-series into indexed curves is necessary. Long-term trends are thus removed from the individual curves by division of a Gaussian-weighted running average. The results show that the annual variations of the $\delta^{18}O$ signature are similar for both - moist and dry sites in Lusatia as well as Lusatia and Jena. We interpret this similarity as a large scale climate effect.

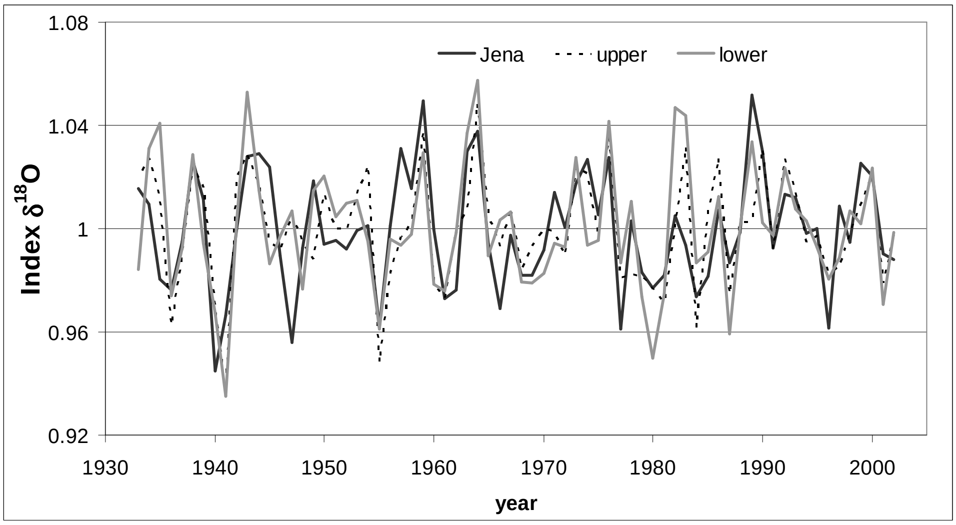

Fig. 2 Indexed $\delta^{18}$O-value for lower and upper test site near Rietschen (Lusatia) compared to reference site of Jena

On the other hand the carbon isotope ratio is strongly influenced by airborne pollutants. The $\delta^{13}$C shift to heavier values is opposite to common findings. Normally, the addition of anthropogenic $CO_2$ causes a trend to more negative values. The discrimination decrease step by step about 3.5 ‰ compared to time before 1920. The first step was after the Second World War and the foundation of the GDR. The next was 1964 to be associated with commissioning of power plants Lübbenau and Vetschau. The last step is in the 1970’s when power plant Boxberg start-up.

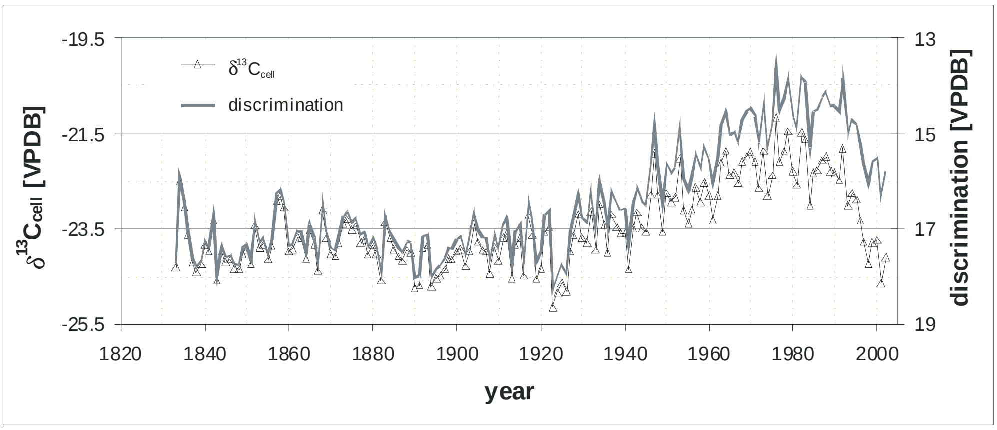

Fig. 3 Carbon isotope results obtained for two old trees selected at the upper site (black, triangular) and calculated discrimination with theoretical values if changes in isotope ratios of atmospheric $CO_2$ (grew)

This effect can be explained with additional carbon isotope fractionation after the photosynthetic $CO_2$ assimilation. Trees are sensitive to $SO_2$ pollution. More precisely, they have a physiological response, for example higher respiratory rate. Respiration tends to lower discrimination.

In general, on sites with better soil moisture availability lower isotope ratios of carbon are apparent. But the year to year variation is similar for all investigated sites. On the other hand the correlation between climate data and the isotope signal of carbon is disturbed by air pollution in East Germany.

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# Turnover of soil organic carbon – The microbial perspective

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Soils are important terrestrial carbon pools as they contain ≈ 1550 Giga tons of organic bound carbon which is more carbon as hold in land plants and the atmosphere together. Soil organic carbon, also known as soil organic matter (SOM), is a dynamic carbon reservoir, because of the permanent carbon exchange between soils and the atmosphere (Schlesinger, 1997). Depending on land use and soil management they may act as sources and sinks of organic carbon. Thus they play a central role in the global carbon cycle. The soil microbial biomass is the key to major biogeochemical cycles including the carbon cycle because degradation and turnover of organic carbon in soils are mainly driven by the activity of soil microorganisms (Paul & Clark, 1996).

In this work we have used soil samples from long term experiments that have undergone a vegetation change from C3 to C4 plants to investigate the turnover of organic carbon processed by the microbial biomass. Through different $^{13}$C isotope fractionation in C3 and C4 photosynthetic pathways C3 and C4 plants hold different $^{13}$C signatures of ≈-27 ‰ (C3) and ≈ -12 ‰ (C4) which results in different natural labelled SOM. By analyzing $\delta^{13}$C-values of the new SOM with C4 input and SOM of the C3 reference site with C3 input it is possible to calculate turnover times of organic carbon by the remaining C3-SOM in C4 cultivated soils {Balesdent, 1996 #394. Also compound specific turnover can be calculated when $\delta^{13}$C-values of individual compounds are used (Gleixner *et al.*, 2002).

As a first experiment we have applied Py-GC/MS-IRMS analysis to C3- and C4-SOM where SOM is pyrolyzed and volatile pyrolysis products are transferred to a GC-column connected to an ion trap mass spectrometer for compound identification and to an isotope ratio mass spectrometer for $^{13}$C isotope measurements. Identified pyrolysis products had various origins. On the one hand they represent plant input to the soil with lignin and polysaccharide derived structures as *2-methylphenol* or *3-furaldehyde*, but also pyrolysis products derived from microbial biomass like *1H-Pyrrol* or *ethylbenzene* could be identified (Table 1).

Table 1: Turnover times of pyrolysis products derived from different sources corresponding to plant and microbial origin

| Pyrolysis produkt | derived from | origin | Turnover time [years] |
|---|---|---|---|
| 3-furaldehyde | polysaccharides | plants | 187 |
| 2-furaldehyde | polysaccharides | plants | 180 |
| 2,4-pentadienal | polysaccharides | plants | 88 |
| 5-methyl-2-furaldehyde | polysaccharides | plants | 109 |
| 1-H-pyrrol | chitin / protein | microbial biomass | 184 |
| toluene | protein / polyphenol | microbial biomass | 136 |
| ethylbenzene | protein / lignin | microbial biomass | 274 |
| benzene | polyphenol | microbial biomass | 81 |

The occurring pyrolysis products are in good agreement with results published by Gleixner et al. (2002). Calculated turnover times are very high, for microbial but also for plant derived compounds (Table 1). This was rather unexpected as microorganisms are short lived and a residence time of hundreds of years in the soil environment is very unlikely because microbial remains are rapidly degraded after cell death (White *et al.*, 1979). However, this result may indicate possible recycling of organic carbon in soils and thus high turnover times of microbial carbon would be indicative for microbial used carbon sources. During this mechanism microbial remains would be consistently reused over long periods of time.

As this theory needs evidences more specific biomarkers characterizing microbial biomass have to be analyzed for their turnover time. Here we have chosen to analyze phospholipid fatty acids (PLFA) as they exclusively represent biomarkers for living and thus active microbial biomass (Zelles, 1999). Therefore we extracted phospholipids from fresh soil samples taken from C3 and C4 cultivated soils and after derivatization we obtained phospholipid fatty acids that were analyzed as their methyl esters for $\delta^{13}$C-values using GC/MS-IRMS.

$\delta^{13}$C-values of PLFA are clearly labelled by the input of C3 and C4 vegetation. However differences between $\delta^{13}$C-values of PLFA from C3 and C4 cultivated soils vary about 5 to 18 ‰ (Fig. 1). This indicates that several carbon sources like plant debris and SOM-carbon must be used by soil microorganisms (Fig. 2).

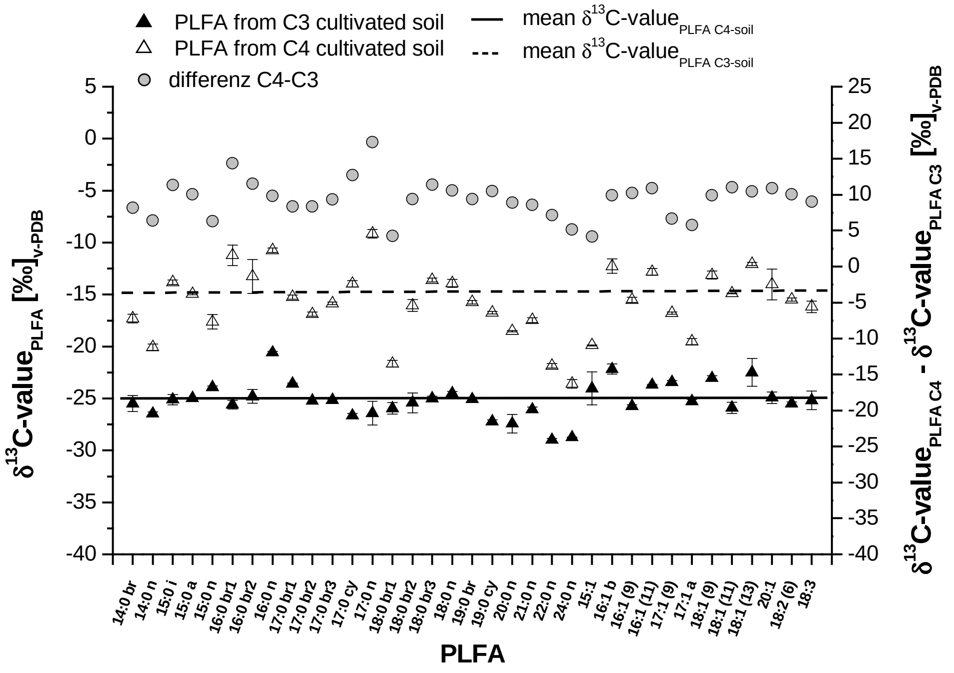

Fig. 1 $\delta^{13}$C-values of PLFA extracted from C3 and C4 cultivated soils. Isotopic differences of $\delta^{13}$C-values of PLFA obtained from both soils are shown by the grey circles; numbers correspond to the right Y-axis

PLFA extracted from C4 cultivated soil whose $\delta^{13}$C-values are near the isotopic signature of C4 plant material (about -12 ‰) show high differences to $\delta^{13}$C-values of PLFA from C3 cultivated soil whereas PLFA whose $\delta^{13}$C-value is near the isotopic signature of C4-SOM (about -24 ‰) show relative low differences. This clearly demonstrates plant material and SOM as microbial carbon sources in soil.

Figure 2 shows the relationship between δ$^{13}$C-values of PLFA from C4 cultivated soil and the isotopic difference to the PLFA from C3 cultivated soil (Fig. 2). It clearly demonstrates that C4-SOM partly still holds the isotopic signature of the former C3 vegetation which reveals slow labelling by the new vegetation and therefore low turnover of soil organic carbon (Gleixner *et al.*, 2005). As the vegetation change was performed 39 years before soil sampling and the C3 signature is still present there must be stabilization processes occurring in soils. As the δ$^{13}$C-values of PLFA show the microbial substrate utilization of plant but also SOM derived carbon recycling of organic carbon by microorganisms as proposed by high turnover times of microbial derived pyrolysis products becomes very likely.

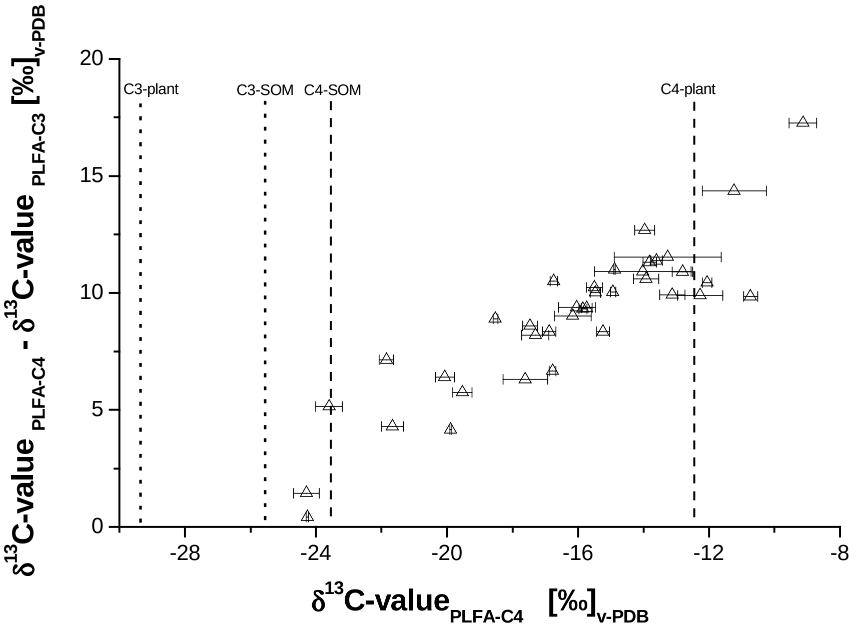

Fig. 2 δ$^{13}$C-values of PLFA from the C4 cultivated soil are plotted against their isotopic differences between C3 and C4. Additionally bulk δ$^{13}$C-values of C4 plants, C4 SOM, C3 plants and C3 SOM are shown

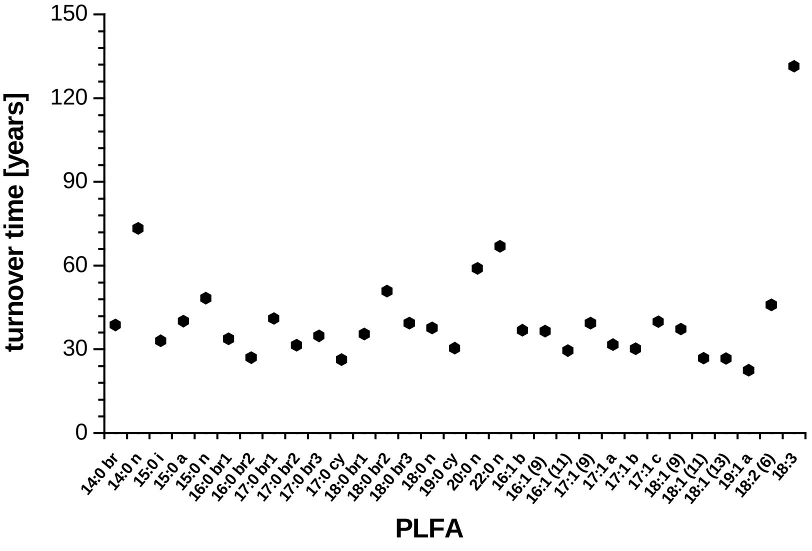

Fig. 3 Turnover times of microbial carbon calculated by $^{13}$C-values of phospholipid fatty acids extracted from naturally C3 and C4 labelled soils

Calculated turnover times of microbial carbon analyzed as PLFA show that organic carbon may be retained within the microbial biomass for about 40 years (Fig. 3). As PLFA are parts of microbial cell membranes that are easy degradable this is an evidence of biological carbon recycling in soils. The discrepancy between turnover times of microbial carbon obtained by pyrolysis products (more than 100 years) and PLFA (≈ 40 years) is probably due to different microbial marker compounds detected by the two techniques.

We conclude that the observed high turnover times of pyrolysis products and PLFA do not show the times these organic molecules remain in soils but clearly demonstrate the residence time of microbial used carbon. Thereby microbial remains and plant debris are rapidly degraded by soil microorganisms and organic carbon will be available for the synthesis of new biomolecules over long periods of time. As shown by calculated turnover times this mechanism may be maintained for several hundreds of years.

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# C and O isotope working standards from $C_3$ and $C_4$ photosynthates

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## 1 Introduction

The C and O isotope ($\delta^{13}C$, $\delta^{18}O$) compositions of bulk fossil and modern photosynthetic products (photosynthates) are commonly analyzed as part of bio-(geo)chemical research, including paleoclimate, environment, animal and plant physiology, pharmaceutical, forensic, flavor, and food authentication. The standardization and validation of the C isotope analyses of organic material is assessed with commercially available international reference material (IRM) with certified $\delta^{13}C$ values (e.g., USGS-24 graphite, NBS-22 oil, IAEA-PEF1 polyethylene foil). This is not the case for the analysis of O isotopic composition of organic compounds. The validation of the measurement of $\delta^{18}O$ values for organic matter by on-line high temperature pyrolysis is hampered by the lack of organic IRM with certified $\delta^{18}O$ values. Calibration and standardization of the pyrolytic procedure is usually performed using available inorganic $\delta^{18}O$-IRM, such as carbonates and water (e.g., VSMOW, GISP, SLAP, NBS-19 limestone, NBS-20 calcite, NBS-127 barium sulfate). However, suitable standards for oxygen isotope analysis of organic matter are lacking (e.g., Kornexl et al., 1999). Here we describe the preparation of organic working standards for carbon and oxygen isotope ($\delta^{13}C$, $\delta^{18}O$) analysis in biological material. The organic standards are compared with international standards and other calibration material.

## 2 Choice of working standards

Generally, analytical deficiencies (e.g., low pyrolysis yields, variable peak-background relations, bad reproducibility and accuracy) can be eliminated by using an optimized procedure for both reference material and samples, and an appropriate normalization with calibration material of chemical and physical characteristics (almost) identical to those of the samples. Working standards should: 1) cover a broad range of δ-values, 2) have a high chemical stability, and low hygroscopicity, 3) a composition similar to the analytes, 4) be safe and easy to handle, 5) available in significant quantities, and 6) of low cost.

The carbon isotope compositions of most organic material in the biosphere are linked to the processes of photosynthetic $CO_2$ fixation. The most important atmospheric $CO_2$-fixing reactions are the $C_3$ and $C_4$ pathways (e.g., O'Leary, 1993). $C_3$ plants (plants adapted to temperate ecosystems, including most vegetables, fruit and wheat) use the Calvin cycle for $CO_2$ fixation, and the $\delta^{13}C$values fall into the range –34 to –22 ‰. The $C_4$ plants use the Hatch-Slack cycle, and have lower isotopic fractionation compared to $C_3$ plants. $C_4$ plants are plants adapted to hot, arid environments, comprising most plants in the tropics, including millet, maize, sugar cane and savanna grasses, and are relatively enriched in $^{13}C$ (–16 to –9 ‰). The mechanism controlling fractionation of oxygen isotopes in biosynthetic processes are not well understood compared with carbon and hydrogen isotopes (e.g., Hayes, 2001).

The $\delta^{18}$O values of photosynthates are largely controlled by the environmental climatic conditions during their formation (e.g., Lajtha and Marshall, 1994). Water in terrestrial $C_3$ and $C_4$ plants is more enriched in $^{18}$O than local ground water, and an isotopic fractionation of ~27‰ for $^{18}$O occurs during cellulose synthesis (Sternberg, 1989).

Carbohydrates, with a general molecular formula $CH_2O$, are the most abundant organic molecules in the biosphere. They are photosynthates of carbon, hydrogen, and oxygen, including, for example, the monosaccharide sucrose (table sugar), the polysaccharides starch, and cellulose. Cellulose is plant fiber, a fibrous chain of D-glucose constituting the major structural material in all plants. Wood is largely cellulose while paper is almost pure cellulose. Thus, potential organic working standards covering a broad $\delta^{13}$C and $\delta^{18}$O range would be $C_3$ and $C_4$ carbohydrates (cellulose or sugars) from distinct geographic origin.

## 3 Methodology

### 3.1 Samples

The $C_3$ samples include toilet paper, laboratory roll paper, XEROX laser-copier-inkjet paper, and white sugar from local sources. The $C_4$ samples include Egyptian papyrus (*Cyperus papyrus*), leaves from maize (Ivory Coast), and sugarcane (Brazil). 11 samples from different toilet paper were obtained from local supermarkets. All toilet papers were non-colored, non-perfumed, and produced from 100 % recycled paper. The maize leaves were thoroughly washed with deionized water and cut into small strips. Papyrus was obtained from the edges of a souvenir from Egypt. These apparently certified and paint-free peaces were thoroughly washed with distilled dichloromethane, ethanol, and deionized water. All samples were dried (70°C, 48 h), cooled to ambient temperature in a dessicator, and stored in tight glass vials with screw-cap or in PE-bags.

### 3.2 Analytical methods

The C isotope composition was measured by flash combustion on an elemental analyzer (Carlo Erba 1108 EA) connected to a ThermoQuest/Finnigan Delta S isotope ratio mass spectrometer via a ConFlo III split interface (EA-IRMS). The calibration and standardization of the $\delta^{13}$C values were performed with the UNIL laboratory standards (glycine, working values $\delta^{13}$C = –26.1 ‰; urea, $\delta^{13}$C = –43.1 ‰; pyridine, $\delta^{13}$C = –29.0 ‰), and the AQCS reference material IAEA-CH-3 cellulose ($\delta^{13}$C = –24.9 ‰) and IAEA-CH-6 sucrose ($\delta^{13}$C = –10.4 ‰). The accuracy of the $\delta^{13}$C analyses was checked by analyses of the AQCS reference materials: USGS-24 graphite ($\delta^{13}$C = –15.9‰), NBS-22 oil ($\delta^{13}$C = –29.7 ‰), and IAEA-PEF1 polyethylene foil ($\delta^{13}$C = –31.8 ‰. The oxygen isotopic composition ($\delta^{18}$O) was measured with a ThermoQuest/Finnigan high temperature conversion elemental analyzer (TC/EA) coupled to a Delta Plus XL isotope ratio mass spectrometer. The pyrolysis reactor was operated at 1250°C. The $\delta^{13}$C and the $\delta^{18}$O values are reported relative to VPDB and VSMOW, respectively. The calibration and reproducibility of the TC/EA/IRMS measurements was assessed by replicate analyses of the laboratory standard benzoic acid (working values $\delta^{18}$O = 26.0 ‰), IAEA-CH-3 cellulose (working values $\delta^{18}$O = 32.6 ± 0.3 ‰), and IAEA-CH-6 sucrose (working values $\delta^{18}$O = 36.4 ± 0.6‰, Kornexl et al., 1999). Recently, A. Z. Csank (ISOGEOCHEM posting from 14.02.2005) reported $\delta^{18}$O value for IAEA-CH-3 cellulose in the range +32.2 to +32.9 ‰. The reproducibility of the EA/IRMS and TC/EA/IRMS measurements, assessed by replicate analyses of the laboratory standards glycine, urea, and benzoic acid are better than ±0.1 ‰ for $\delta^{13}$C and ±0.3 ‰ for $\delta^{18}$O (1 s).

## 4 Results and discussion

All the samples were analyzed for the stable C isotope composition (Table 1). The $\delta^{13}C$ values of the toilet papers (TP) and the roll paper have a narrow range typical of $C_3$ photosynthates (–25.5 to –24.1 ‰). In a first stage the toilet papers were checked for homogeneity by replicate (n ~ 5) analysis of the carbon isotope composition (Table 1). The XEROX paper is enriched in $^{13}C$ by ~2 ‰ compared to the toilet papers. This isotopic difference may reflect different paper sources and different production procedures (bleaching with e.g. chlorine, chlorine dioxyde, oxygen, ozone, or hydrogen peroxyde). Toilet paper sourced from 100 % recycled paper is generally (not exclusively) chlorine-free, and bleached with oxygen. XEROX has specific sourcing policy, and its paper come from companies committed to a set of environmental, health and safety requirements (www.xerox.com/ environment). The $\delta^{13}C$ values for the 11 toilet paper samples range from –24.43 to –26.04 ‰, with reproducibilities between 0.14 and 0.92 ‰. The inter- and intra-sample variabilities, for a similar paper source of Swiss toilet paper, most probably reflect differences in the papermaking procedures, particularly bleaching chemicals. The color of the TP samples varying from white to yellowish and grayish, reflect differences in the bleaching procedures. The $\delta^{13}C$ values of two samples (TP1 and TP2) from the same toilet paper purchased in different supermarkets differ in 0.61 ‰. This difference is smaller than the reproducibility of the $\delta^{13}C$ measurements for these samples (~ ±0.9), and is explained by the compositional heterogeneity of this toilet paper. TP-5 ("soft deluxe cashmere" 4 layers toilet paper) and XEROX paper appear to be the most homogeneous material, with a $\delta^{13}C$ = –24.93 ± 0.14 ‰ (n = 12) and –22.27 ± 0.17 ‰ (n = 13), respectively. The reproducibility was better than ±0.2 ‰ (1 s) for the $\delta^{13}C$ values of the TP-5, XEROX paper, white sugar and the $C_4$ samples (papyrus paper, maize and sugar cane). This is better than the ±0.27 and ±0.43 obtained for the IAEA carbohydrate standards CH-3 and CH-6 measured within the runs. These samples were submitted to oxygen isotope analysis (Table 1, Fig. 1). The toilet paper, XEROX-paper, white sugar, and maize leaves reproduced well for $\delta^{13}C$ (better than ± 0.25), similar to that measured for IAEA-CH-3 (±0.27) and IAEA-CH-6 (±0.43). The raw cane sugar is very hygroscopic, and the $\delta^{18}O$ values vary strongly with residence time of the sample in the silver capsule during weighing of the other samples and in the auto-sampler before analysis. Four analyses were performed directly after weighing, which reproducing to ±0.34 for the $\delta^{18}O$ values (Table 1). The Egyptian papyrus paper has a $\delta^{18}O$ of –32.02 ± 0.50 ‰ (n = 9).

## 5 Conclusions

The C and O isotope composition of white toilet paper, XEROX laser-copier-inkjet paper, white table sugar, maize leaves, and papyrus studied here, are in the ranges of $\delta^{13}C$ from –26.5 to –10.3 ‰, and $\delta^{18}O$ range 25.7 to 32.6 ‰, typical for $C_3$ and $C_4$ biological material. These three materials cover a broad δ-range (4.2 ‰ for $\delta^{18}O$ and 4.3 ‰ for $\delta^{13}C$) compared to the commercially available carbohydrate standards. Toilet paper, XEROX paper, and table sugar is used by many, and is most often considered valuable when it is not there in time of need.

Table 1: Average and standard deviation (1 s) values of C and O isotope compositions of the photosynthate samples

| Sample | Description/Origin[1] | $\delta^{13}C$ (‰, VPDB) | $\delta^{18}O$ (‰, VSMOW) |
|---|---|---|---|
| TP-1 | TP M budget 3 layers | –25.43 (0.88, n = 5) | - |
| TP-2 | TP M budget, 3 layers | –26.04 (0.83, n = 4) | - |
| TP-3 | TP M budget, 2 layers | –25.35 (0.92, n = 4) | - |
| TP-4 | TP M deluxe sensitive, 4 layers[1] | –24.45 (0.67, n = 4) | - |
| TP-5 | TP M soft deluxe cashmere, 4 layers[1] | –24.93 (0.14, n = 12) | 29.81 (0.20, n = 9) |
| TP-6 | TP M soft, 3 layers[1] | –24.89 (0.18, n = 4) | - |
| TP-7 | TP M budget, 2 layers | –24.43 (0.30, n = 4) | - |
| TP-8 | TP COOP classic, 3 layers | –25.50 (0.59, n = 3) | - |
| TP-9 | TP COOP-nouveau classic, 3 layers[1] | –24.96 (0.23, n = 4) | - |
| TP-10 | TP M soft, 3 layers, 100% fibers | –24.81 (0.19, n = 4) | - |
| TP-11 | TP DANKE 3 layers | –24.59 (0.39, n = 4) | - |
| Lab. roll paper | UNIL-IMG laboratories, 2 layers | –24.12 (0.19, n = 4) | - |
| XEROX | XEROX business A4 copier paper | –22.27 (0.17, n = 13) | 25.66 (0.25, n = 9) |
| white sugar | table sugar, M | –26.54 (0.14, n = 12) | 29.71 (0.21, n = 10) |
| papyrus | papyrus paper, Egypt | –10.27 (0.16, n = 13) | 32.02 (0.50, n = 9) |
| maize leaf | maize, bio-farm, Ivory Coast | –11.67 (0.20, n = 14) | 28.42 (0.22, n = 11) |
| cane sugar | raw cane sugar, bio-farm, Brazil | –11.61 (0.17, n = 11) | 32.58 (0.34, n = 4)[2] |

Abbreviations:

TP = toilet paper
M = Migros supermarket
n = number of replicate analysis
- = not analyzed
[1] label state: "bleached with oxygen"
[2] cane sugar is strongly hygroscopic

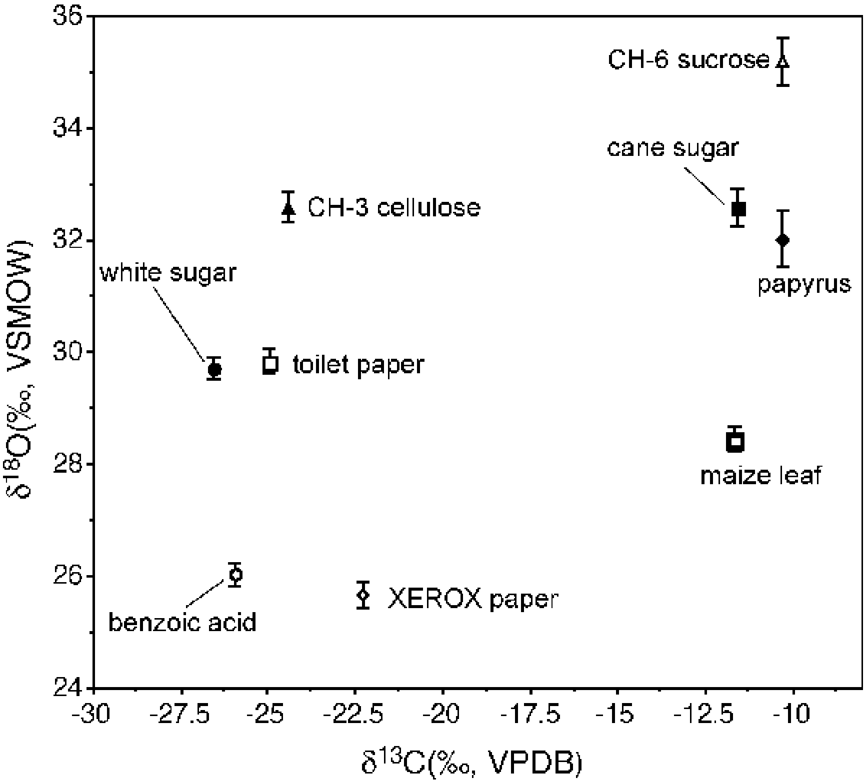

Fig. 1 $\delta^{13}C$ vs. $\delta^{18}O$ plot of the studied $C_3$ and $C_4$ photosynthate samples

**Acknowledgements**

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# Use of $^{15}N$ tracer technique to understand chronic responses of *Daphnia magna* after short-term expose to the pyrethroid insecticide fenvalerate

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The present study aims to understand the causes of the chronic responses of *D. magna* after exposure to a 24 h-pulse of the pyrethroid fenvalerate. Previous studies reported that zooplankton species exposed to a short-term contamination of fenvalerate face feeding reduction. Thus, it was hypothesized that less energy is available to growth retarding the age at which reproductive size is reached. To test this hypothesis, feeding activity after exposure was investigated by tracing alternatively *D magna* neonates or the microalga *Desmodesmus subspicatus* with the stable isotope $^{15}N$. The exposure to fenvalerate concentrations > 0.3 µg/l resulted in smaller individuals with no changes in $^{15}N$ abundance [atom-%] in their bodies.

This clearly indicated a reduction in the feeding activity that resulted in growth retardation. The Daphnia reproduction test showed that the age at first reproduction was also delayed at concentrations > 0.3 µg/l, and that resulted in a reduction of the reproductive output and the population growth rate. Since *D. magna* need to growth before to reproduce, it was possible to conclude that the reduction in the feeding activity retarded somatic growth and delayed the age at first reproduction.

# Anthropogenic lakes – negligible sources for climate relevant gases?

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## 1 Introduction

Recent atmospheric measurements indicate that concentration of greenhouse gases are increasing. Besides other gases methane represents an atmospheric trace gas. Main sources are believed to be flooded rice fields, ruminant enteric digestion, and natural wetlands followed by landfills, biomass burning, natural gas leakages, lakes, oceans, and others. (Khalil and Shearer, 2000). Research has concentrated more or less on the major sources, although there is still uncertainty in the estimates of emission rates from individual sources in particular under different geographic and climatologic conditions. In the same way less is known about the minor sources, particularly the smaller of the minor sources.

On the important conferences on climate change the industrial sources of greenhouse gases and their reduction are traditionally standing in the focus of interest. The importance of aquatic ecosystems is underestimated or misconceived.

Due to the building of reservoirs for use of water power or water level regulation of rivers as well as the flooding of mining pits after extraction of copious raw materials the number of lakes is ever growing.

Only in Germany the lake portion on landscape will increase by more than new 500 anthropogenic lakes as a consequence of open cast lignite mining. More than 100 lakes will have surfaces of more than 50 ha (Fig. 1)

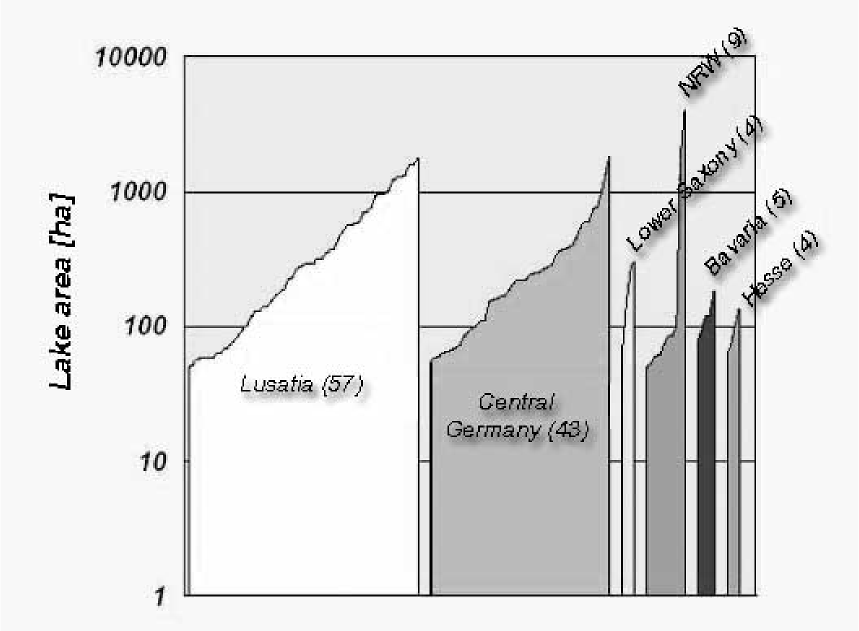

Fig. 1 Area distribution of mining lakes (Nixdorf et al. 2002)

In consequence of the used mining technology there is a great morphological and lake type variety within the mining lakes including small littoral as far as large deep lakes (Junge et al. 2005). The latter are often characterised by meromictic behaviour. Besides simple shaped basins there are more complex morphological structures that show dimictic behaviour.

Thermal stratification is a common feature of lakes. In some extent a chemical stratification can be observed, too. Due to the stratification some parts of the water body of a lake are partly or completely excluded from circulating and exchange processes (Monimolimnion). Such water layers are often sinks for organic and inorganic substances. Due to a insufficiency or absence of oxygen (anoxic conditions) organic substances are decomposed reductively. One end member represents methane.

Examples for methane formation in natural lakes with input of organic substances or high eutrophication level in Germany are e.g. Lake Stechlinsee (Mecklenburg, Hemmann et al., 1994), Lake Constance (South Germany, Faber et al., 1996), Lake Plußsee (Schleswig-Holstein, Nüsslein et al., 2000).

The aim of our study was to get information about methane formation in younger anthropogenic lakes.

## 2 Methods and results

The gas samples were obtained by means of a gas hood or by degassing of water samples. The chemical composition was determined gas chromatographically. For some components also the isotope ratios were determined by isotope ratio mass spectrometry.

The following case studies are examples of anthropogenic lakes situated in Central Germany. They represent different lake types (closed and open water basins) of various ages (<10 a up to 50 years) and various water depths (< 10 up to ~50 metres).

Case study 1: mining lake „GK“

used for industrial waste, gas hood, gas bubbles from 1 m depth

| Chemical composition | | Isotopic composition |
|---|---|---|
| $CH_4$ | 0.3 Vol.-% | $\delta^{13}C$ –62.1 ‰ |
| $CO_2$ | 12.2 Vol.-% | $\delta^{13}C$ –23.6 ‰ |
| $Ar/O_2$ | 3.0 Vol.-% | |
| $N_2$ | 84.5 Vol.-% | $\delta^{15}N$ -0.5 ‰ |

Case study 2: mining lake „VO“

used for industrial waste, pneumatic degassing of water from ~9 m depth

| Chemical composition | | Isotopic composition |
|---|---|---|
| $CH_4$ | 23.3 Vol.-% | $\delta^{13}C$ –43.3 ‰ |
| $CO_2$ | 7.5 Vol.-% | $\delta\ ^{13}C$ –21.7 ‰ |
| $Ar/O_2$ | 1.1 Vol.-% | |
| $N_2$ | 68.1 Vol.-% | $\delta^{15}N$ -1.2 ‰ |

Case study 3a: Mining lake „HU“
recreation and bathing lake, pneumatic degassing of water from 27-29 m depth (significantly increased electrical conductivity)

| Chemical composition | | Isotopic composition |
|---|---|---|
| $CH_4$ | ca. 15 Vol.-% | $\delta^{13}$C –45.9 ‰ |
| $CO_2$ | ca. 25 Vol.-% | $\delta^{13}$C –19.0 ‰ |
| $Ar/O_2$ | ca. 10 Vol.-% | |
| $N_2$ | ca. 50 Vol.-% | $\delta^{15}$N -0.1 ‰ |

Case study 3b: Mining lake „HU“
recreation and bathing lake, gas hood, gas bubbles from ~0.4 m depth near the shore

| Chemical composition | | Isotopic composition | |
|---|---|---|---|
| $CH_4$ | ca. 20 - 70 Vol.-% | $\delta^{13}$C | -88 to -73 ‰ |
| $CO_2$ | ca. 10 - 20 Vol.-% | $\delta^{13}$C | -25 to -23 ‰ |
| $Ar/O_2$ | traces | | |
| $N_2$ | ca. 70 - 10 Vol.-% | $\delta^{15}$N | ~ -0,1 ‰ |

volume of dissolved gases: 60 - 170 ml/l

Case study 4: Mining lake "GO"
newly flooded lake, vacuum degassing of water from 45 m depth
(weak increased electrical conductivity)

| Chemical composition | | Isotopic composition |
|---|---|---|
| $CH_4$ | 0.4 Vol.-% | $\delta^{13}$C –90.8 ‰ |
| $CO_2$ | 74.3 Vol.-% | $\delta^{13}$C –16.4 ‰ |
| $Ar/O_2$ | traces | |
| $N_2$ | 25.3 Vol.-% | |

volume of dissolved gases: 68 ml/l

Case study 5: Mulde reservoir
recreation lake, gas hood, gas bubbles, water depth ~ 20 m

| Chemical composition | | | Isotopic composition | | |
|---|---|---|---|---|---|
| Sampling point | SP1 | SP2 | | SP 1 | SP 2 |
| $CH_4$ | 67.5 | 84.8 Vol.-% | $\delta^{13}$C | -53.5 | -52.2 ‰ |
| $CO_2$ | n.d. | 6.0 Vol.-% | | | |
| $Ar/O_2$ | 4.2 | 1.8 Vol.-% | | | |
| $N_2$ | 28.3 | 7.4 Vol.-% | | | |

## 3 Discussion and conclusions

Case studies 1 and 2 represent lakes that used for dumping of industrial wastes rich in organic materials. These may be broken down by micro organisms and under anoxic conditions ultimately result in methane.

Case study 3a and 3b refers to a lake used for recreation purposes. The water is of good quality. The morphology of this lake is characterised by an deep trough-like structure filled with saline water forming a monimolimnion. Pumping this water to the surface great amounts of gas are released. Here and there in the shallow water near the shore sometimes could noticed gas bubbles. They contained also methane.

Case study 4 refers to a single basin within a larger lake system. About 2 m over the bottom a slightly raised electrical conductivity could be measured. After pumping water from this layer to the surface it did not degas spontaneously. Using vacuum degassing small amounts of methane could be released. A gas chromatographic analysis of the extractable organic substances showed an increased content of fatty acids. These may be metabolites of higher organic substances.

A main source - besides organic wastes in special cases (1 and 2) - of such metabolites and precursor substances for methane are believed to be lignite. All the investigated mining lakes have a common feature, they have direct contact to coal seams. Therefore a direct interaction is possible. There were also mining pits, with already for mining exposed lignite seams, flooded. That means, there is a huge reservoir of carbon compounds available for bio-chemical destruction.

Case study 5 represents also an former mining pit where the Mulde river is passing through. For many years during the stagnation periods gas bubbles could be watched on the lake surface. The chemical investigation of these bubbles offered again fractions of methane.

In all investigated samples the isotopic composition of methane indicates its biogenic genesis.
These preliminary results show that also relatively young anthropogenic lakes can emit greenhouse gases like carbon dioxide and methane in high concentrations. They are mainly formed from organic substances under shortage or absence of oxygen. It is known that the magnitude of gas formation depends on several factors, but a carbon source has to be. In some case studies could be shown, that the formation of methane is not restricted on lakes with high contents of organic carbon but also proceeds in lakes poor in nutrients. Here obviously lignite seams are the main sources for carbon. Benefiting for these processes are temporarily or permanently stable water layers. Great depths and salt contents offer good conditions for it. With the involvement of former mining pits into river systems they may be get sediment traps - also for suspended organic matter – and so an additional carbon source is available.

The results show, that anthropogenic lakes are sources for greenhouse gases. For quantifying the processes further integrated research is necessary.

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# Effects of environmental factors on $\delta^{13}C$ of lichens

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The previously studies (Conti and Ceccetti, 2001) have summarized the effects of pollutants on lichens. The stable isotope abundance of carbon in a species of lichens has been investigated in a study relating $\delta^{13}C$ values with know levels of selected pollutants as $SO_2$, $NO_2$, and $O_3$ (Batts et all, 2004). To establish a correlation between any pollutant factors and $\delta^{13}C$ in lichens, it is necessary to understanding the effect of the factors in the natural environment that have been shown to affect the growth characteristics of lichens and influence their survival.

This study was designed to determine the extent to which the carbon isotope ratio in four species of lichens was influenced by such features of the natural environmental as humidity, rainfall, and temperature.

The lichens chosen for this study was species Cladonia fimbriata (L1), Hypogymnia physodes (L2), Peltigera canina (L3), and Pseudovernia furfuracea (L4). Samples were kindly donated by the herbarium of the Botanical Garden of the Babes Bolyai University of Cluj Napoca. The lichen species were collected in 1978, 1989, 1994, and 2003 in three different mountains from Romania at altitude of about 1300 m. These sampling sites were selected because they are at great distance of any anthropogenic pollution. At the time of sampling, field data (temperature, relative humidity, and average monthly precipitation) were recorded.

$\delta^{13}C$ in whole lichen specimens were determined using standard mass spectrometric techniques with a precision of ± 0.3 ‰.

The range of $\delta^{13}C$ measured for these lichens in 56 samples was –26.93 ‰ to –19.06 ‰. The mean value was –23.38 ‰. The $^{13}C$ content of the lichen in natural setting is dictated by effects associated with the assimilation of carbon, metabolism and biosynthesis, and the ultimate cellular carbon budget.

We have found a weak but negative correlation between $\delta^{13}C$ and relative humidity (Fig. 1), and a positive correlation between $\delta^{13}C$ and average monthly precipitation at the studied sites (Fig. 2). This correlation was found for all the studied lichen species L1, L2, L3, and L4. Fig.1 and Fig. 2 refers to only one species, noted L1. Effect of rising humidity on $\delta^{13}C$ is the opposite of that of increasing rainfall.

The moisture is an important factor influencing the $\delta^{13}C$ in the lichen. Photosynthesis in lichens takes place only in light after the lichen thallus has been wetted by air-born moisture or through direct exposure to liquid water. The conclusion is that under humid condition, $^{12}C$ enriched components accumulated, reducing the $\delta^{13}C$ value. This result is shown for L1 species (Fig. 1) where with increasing humidity, $\delta^{13}C$ values decreasing.

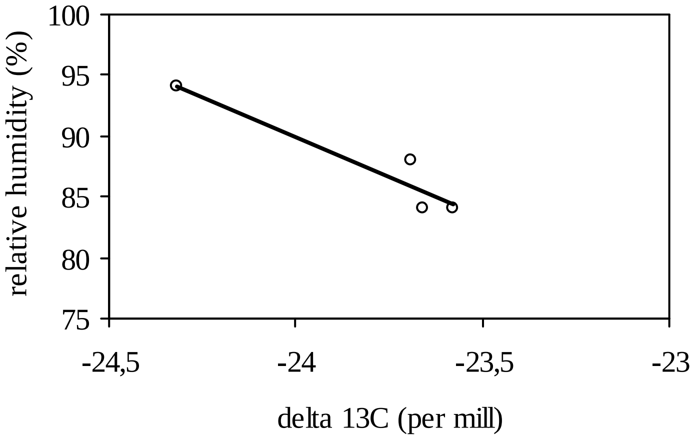

Fig. 1 The relationship between $\delta^{13}C$ (‰) and relative humidity (%) for Cladonia fimbriata

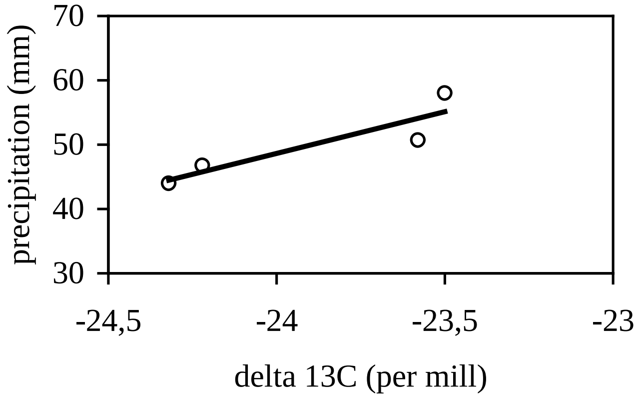

Fig. 2 The relationship between $\delta\ ^{13}C$ (‰) and average monthly precipitation (mm) for Cladonia fimbriata

Lichens have no specialized mechanism for water uptake and no way of maintaining a water balance. In lichens, saturation levels of water are thought to lead to increased resistance to $CO_2$ transport into the lichen, with a subsequent of reduction in discrimination, that is an increase of $\delta^{13}C$ ‰ in lichen. With increasing water content of the lichen thallus, $\delta^{13}C$ values rise until the rate of diffusion of $CO_2$ into the thallus becomes rate limiting. This result is shown for L1 species in Fig.2: with increasing of the monthly precipitation, $\delta^{13}C$ values increasing, too. Simply stated the more liquid water there is in the lichen environment, the higher (less negative) the $\delta^{13}C$ value.

Each point in Fig. 1 and Fig. 2 represent the average of measurements for six samples of L1 species, collected in the same site and the same date.

The result of this study was found that of natural factors humidity tended to decrease the value of $\delta^{13}C$, and the precipitation to which the lichens were exposed tended to increase $\delta^{13}C$ value. The effects were minor of the order of 1 ‰ for all species, excepting L3 species where the effect was +3 ‰. From their opposite effects, the natural parameters could be assumed to cancel out.

We submit that this result is important to the field of environmental monitoring of pollutants. The outcome of a monitoring study would be only interpretable where the effect of natural environmental factors on a species of lichen were either negligible or systematic.

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# Online measurement of $N_2$-fluxes from soil cores by using the zeolite KÖSTROLITH SX6® coupled to a GC-ConFlow-IRMS

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Investigations of transformation and transport processes of gaseous N-compounds (NO, $N_2O$, $N_2$) concerning the soil/atmosphere N-cycle have been conducted since several decades. One of the main challenges remained is the examination of $N_2$-fluxes from soils. Since $N_2$, as the final product of biotic N-transformation (denitrification) in soils, is the major gas building the earth atmosphere (78,08 Vol.%) measurements of $N_2$-fluxes from soils are rather difficult. Basically three different approaches have been developed: (a) use of N-isotopes (stable $^{15}N$ or radioactive $^{13}N$) to mark soil $N_2$ (Wolf and Russow, 2000;Bergsma et al., 2001), (b) application of $C_2H_2$ to inhibit $N_2$-formation in soils (Koops et al., 1997;Khalil et al., 2004), and (c) creation of an artificial soil atmosphere with Helium as a substitute for $N_2$ (Scholefield and Hawkins, 1997;Butterbach-Bahl et al., 2002). All previously conducted measurements using one of the mentioned approaches are necessarily designed as closed-systems. Thus, flux calculation rest up on a concentration gradient of $N_2$ over time. Consequentially periodic interruptions of the flux measurement were inevitable. Our novel approach, based on work by Sich and Russow (1999), allows the measurement of $N_2$-fluxes within an open-system on laboratory basis. Hence, $N_2$ released from a soil sample (soil core) can be measured continuously for a long time period without any destructive interventions and at high sampling frequency.

The main objective of this study was to develop an open measurement system capable of measuring $N_2$-fluxes from soils based on the principle of enrichment technique (Sich and Russow, 1999;Bergsma et al., 2001) and common $^{15}N$ isotopic analysis. For that purpose we tried to use the molecular sieve KÖSTROLITH SX6® (Chemiewerk Bad Köstritz), since it is adsorbing $N_2$-gas with high efficiency. SX6® is a synthetic crystalline aluminosilicate with a regular micropore structure (faujasite type, 0.9 nm). Originally it was developed as a highly efficient absorbent for the non-cryogenic oxygen enrichment using pressure(vacuum) swing adsorption (PSA/VPSA) technique.

For measuring $N_2$-fluxes from soil samples we use incubation vessels designed for soil cores (250 $cm^3$). A carrier gas passes the surface of the implemented soil core at a constant low flow rate (10 to 15 ml $min^{-1}$). After a transient period the incubation system reaches equilibrium. Afterwards it is assumed that the current $N_2$ gas concentration within the downstreaming carrier gas is independent from the flow rate, but only controlled by biotic and abiotic factors of the soil system. Thus, capturing $N_2$ from the downstreaming carrier gas for a short period of time (amount $N_2$ per time unit) would allow calculation of the current inherent $N_2$-flux rate of the system. Since impurities from ambient air are inevitable $^{15}N$ labeling is necessary for a distinct differentiation between soil $N_2$ and atmospheric $N_2$. Using both the molecular sieve KÖSTROLITH SX6® for $N_2$ adsorption and a GC-ConFlow IRMS System for $^{15}N$ isotopic analysis we are able to measure $N_2$-fluxes within an open soil system.

Our novel approach is so far the first method for measuring online $N_2$-fluxes from soil samples within an open-system.

Since an open system allows long time measurements without any destructive interventions different studies concerning $N_2$-fluxes are conceivable, also beyond soil sciences. Because of the simplicity of this approach scientists well equipped for analysis of $^{15}$N gas species should be able to use it without having significant costs.

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# Deuterium content in plants with short lifetime: preliminary results

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The stable isotope composition of the hydrogen in the plants water is strongly influenced by the environmental conditions and is dependent on physiological performances. The water in the cycle precipitation-soil-plants-atmosphere presents the isotopic composition variable due to the inter-annual changes in rainfall, temperature and humidity. The deuterium content of the water of the plant leaves with short time (legumes) may identify the contribution of the ecosystem components to the exchange fluxes with the atmosphere. Soil water and leaf water are the sources of the evapotranspiration (ET) that transfer large quantities of water and energy between the land surface and the atmosphere. The deuterium content of the leaves water increases during plants growing from greenhouses (closed system for water cycle), the watering being reasonably constant during the growing period. This may be an indicator of trends in ET, but most probably is the plant aging.

The deuterium content of leaves water is not yet well understood and can involve 1) hydrogen isotope effects associated with leaf water enrichment due to the ET and equilibration with humidity of atmosphere, 2) the ability to use the hydrogen in photosynthetic and respiration processes and/or 3) the exchange of hydrogen isotopes during the transport of carbohydrates (such as sucrose) from leaves to developing xylem in shoots and 4) the isotopic fractionation associated with biochemical synthesis. The differences in isotopic discrimination between these processes need to be better characterized.

## Session 4

# Sedimentology

# Authigenic sulfur phases as recorders for black shale-triggered anaerobic oxidation of methane: Results from ODP Leg 207

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Sediments are carriers of proxy signals for present and past microbial activity. The presented study deals with diagenetic processes in the deep biogeochemical sulfur-carbon-metal cycles of sediments recovered from Demerara Rise (Leg 207). We try to identify those reactions that may take part in the formation, alteration, or modification of proxy signals by means of inorganic and stable isotope geochemical pore water and solid phase investigations. The project focuses on the potential of the isotopic composition of sulfur-bearing authigenic minerals to reflect the history of biogeochemical reactions in deeply buried sedimentary sequences as well as early diagenetic reactions during black shale formation. Euxinic conditions during black shale formation are shown by the high ratios of reactive to total iron. Are authigenic sulfides useful paleo-proxies? Are deeply buried black shales acting as a bioreactor for driving ongoing diagenesis by a deep biosphere via methane as substrate? Associated with the reactions in the coupled carbon-iron-sulfur cycles is the development of authigenic barite enrichments. These serve as indicators for the evolution of dissolved sulfate-barium diffusion fronts in association with methane fluxes derived from deeply buried TOC-rich strata. Especially, we extract informations about metabolic processes from the covariation of S and O isotopes preserved in authigenic barites. From stable isotope analyses we deduce that extremely heavy authigenic pyrite and barite above the black shale sequence reflect different sulfate/sulfide pore water gradients caused by temporarily changing methane fluxes from underlying black shales. Isotopically heavy sulfur-bearing minerals seem to be indicative for anaerobic methane oxidation. Pyrites found within the black shales show a wide range of sulfur isotopic compositions essentially reflecting early diagenetic signals, that are within the range found at other Cretaceous black shale settings.

# Microbially-derived methane in coalbed gases: compound-specific carbon-isotopic study of coalbed gases from the Illinois Basin, USA

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The overall coalbed methane (CBM) potential in the Illinois Basin has been underestimated due to the low rank of coals and their correspondingly low thermogenic gas potential. Our recent compositional and isotopic data suggest that, in addition to thermogenic gas, these coals contain a significant contribution of microbially-generated methane (Fig. 1). Coal beds of high volatile bituminous rank ($R_o$ 0.54 to 0.75%) occur at depths from 100 to 350m. Several drill sites in the SE Illinois Basin provided gas samples from five Pennsylvanian-age coal beds. We determined (i) $^{13}C/^{12}C$ ratios in hydrocarbons $C_1$ (i.e. $CH_4$), $C_2$, $C_3$, *i*-$C_4$, *n*-$C_4$ and in $CO_2$ and (ii) D/H ratios in $C_1$.

Since our coals are at or above the threshold for thermogenic gas generation ($R_o \sim 0.55\%$), the gases are usually of mixed thermogenic and microbial origin, with the biogenic component being formed by a microbial $CO_2$ reduction pathway. For example, gas from 100m-deep Springfield coal from southwest Indiana with $R_o$ of 0.56% contains 98% $C_1$ and only traces of higher alkanes, whereas the age-corresponding more mature coal in western Kentucky at a depth of 350m and $R_o$ of 0.75% yields gas with 5.6% $C_2$ and 1.3% $C_3$. These Indiana and Kentucky coalbed gases also differ isotopically in terms of $\delta^{13}C_{CH4} = -63.1‰$ and -49.5, and $\delta^{13}C_{CO2} = 2.8‰$ and -20.6‰, respectively (Fig. 2).

The contribution of microbially-generated methane ranges from 0 to 100% (Fig. 1), as inferred from a carbon isotopic composition of $C_1 - C_4$ hydrocarbons (Katz 2002). For example, in the lower-rank Springfield coal in Indiana and eastern Illinois, the contribution of biogenic methane ranges from 57% to 100%, whereas it is negligible in the highest-rank Springfield coal in western Kentucky. Based on the temperature-dependence of $\Delta\delta^{13}C$ in microbially-controlled $CH_4$-$CO_2$ systems, we arrived at temperature estimates for bacterial methane formation via $CO_2$-reduction in lower-rank coals. The predicted temperatures for our sampled coalbeds are in close agreement with the measured coalbed reservoir temperatures when microbially-generated methane is the predominant gas component.

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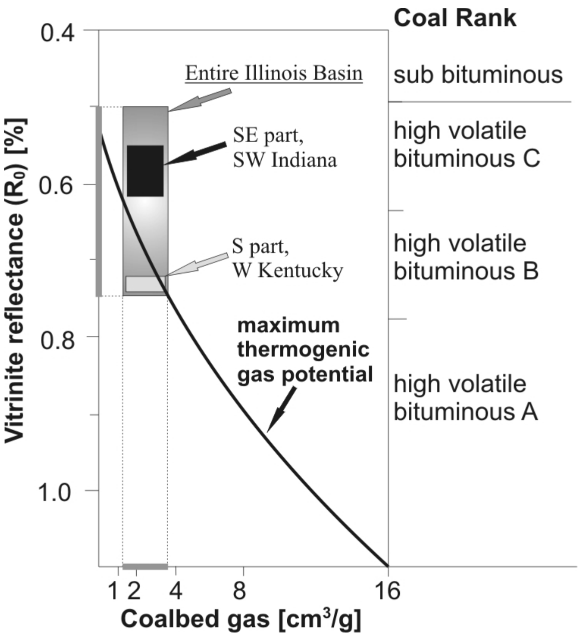

Fig. 1 Range of vitrinite reflectance ($R_0$) of Illinois Basin coals versus coalbed gas content. The black curve (Meissner 1986) outlines the maximum amount of thermogenic gas that can be generated from coal at a specific maturity. Position of the black rectangle clearly suggests that in SE-part of Illinois Basin, besides thermogenic gas, there has to be another important source of coalbed gas, whereas in S-part of the basin coalbed gas is almost purely thermogenic.

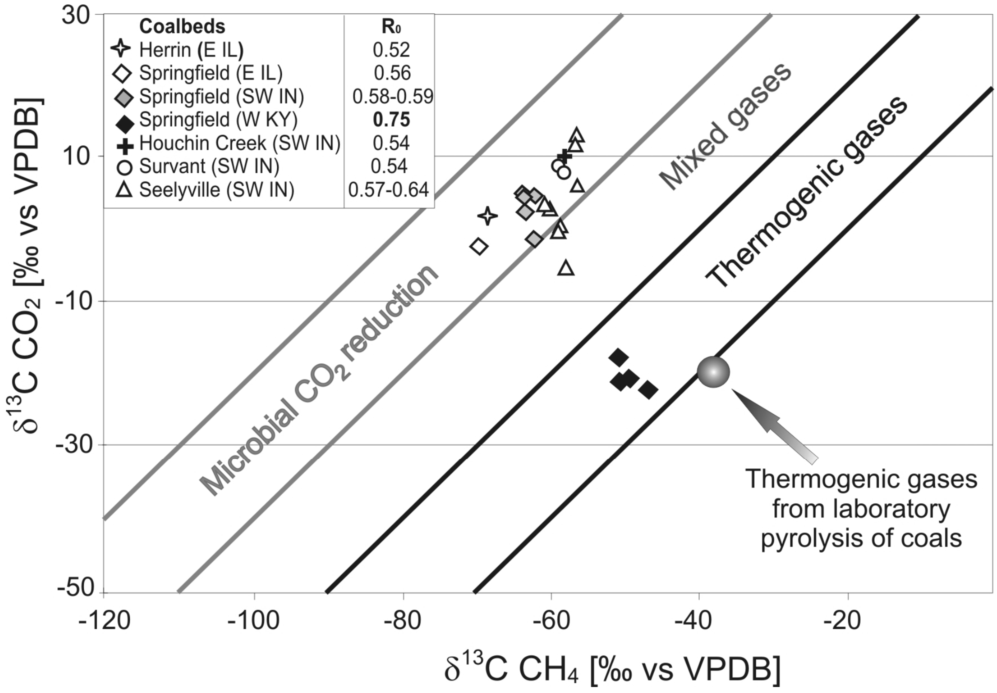

Fig. 2 Carbon isotopic signatures of methane and $CO_2$ in coalbed gases from the Illinois Basin. Coalbeds in the legend in stratigraphic sequence. Genetic ranges of gases and pyrolysis data after Smith and Pallasser 1996.

# Early diagenesis of sulphur in recent estuarine sediments (Authie Bay, N France)

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Bacterial sulphate reduction in the organic rich marine and estuarine sediments is often accompanied by large S stable isotope fractionation (up to 70‰) due to kinetic isotope effects. S isotope fractionation also occurs in the oxidative part of the sulphur cycle, however, culture studies showed that it does not exceed 2‰ during oxidation of reduced S compounds, and 20‰ during disproportionation of elemental S into $S^{2-}$ and $SO_4^{2-}$. (Fry et al. 1985, Böttcher et al. 2001, 2001a). Isotopic compositions of sulphur in the sedimentary organosulphur and pyrite pools suggest, that they can be formed simultaneously in competitive processes, where $Fe^{2+}$ (or metals in general) seems to be more efficient in trapping reduced S, or subsequently. The enrichment of organic matter with sulphur during earliest stages of diagenesis has been amply documented in marine sediments, while the importance of such reactions in freshwater environments is not very much appreciated. Considering the importance of bacterial sulphate reduction in the overall process of the decomposition of sedimentary organic matter, and the affinity of both sulphide and organosulphur compounds for binding metals in organic-rich aquatic sediments, great attention has been paid to the studies of early diagenesis of S in marine and freshwater sediments.

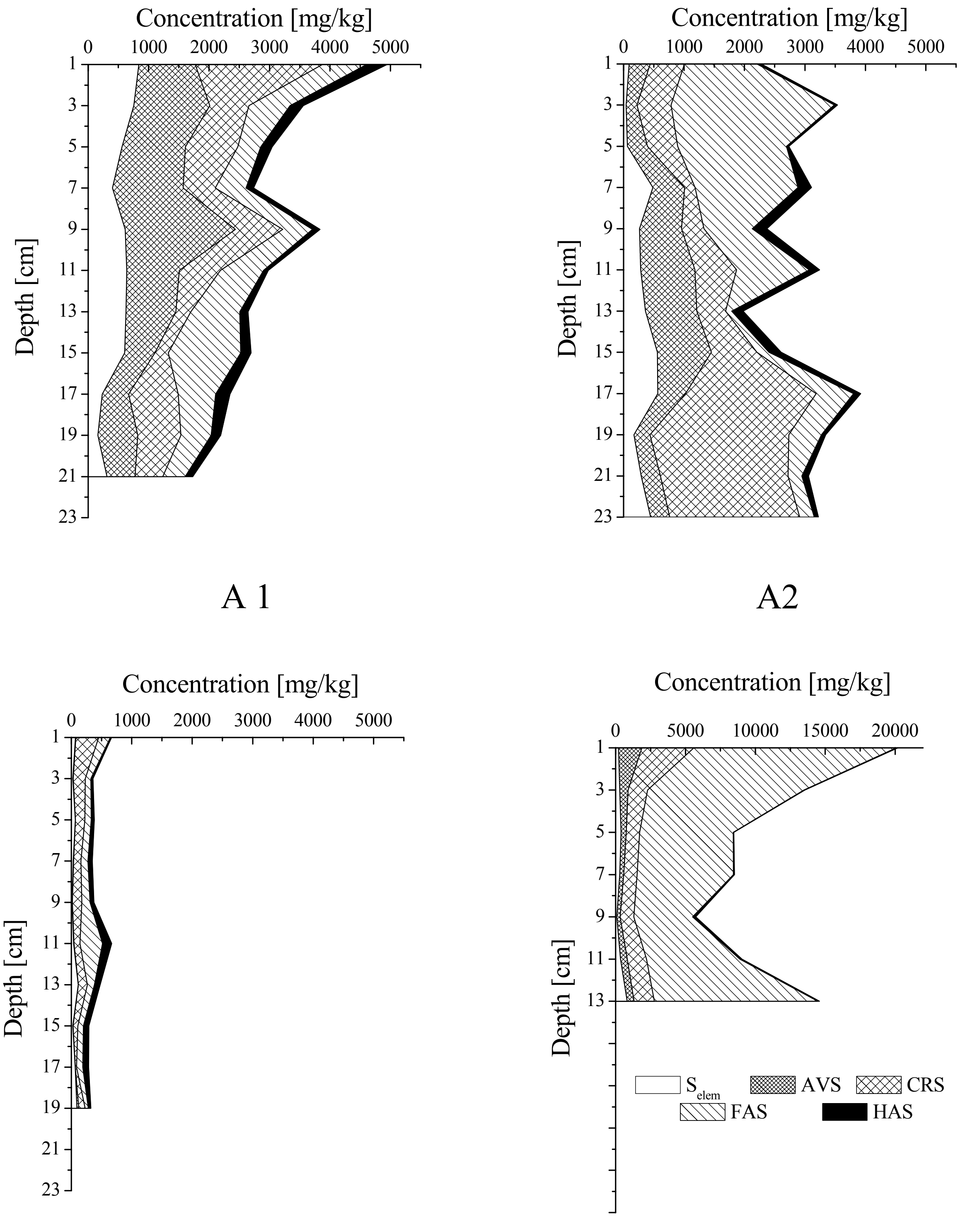
The aim of our study was to investigate the distribution of sulphur species in the sediment of the Authie River estuary (Authie Bay, N France) at three different characterised by increasing marine influence. Formation pathway and timing of incorporation of S into fulvic and humic acids were estimated based on stable isotope composition of sedimentary S species. The freshwater site of Authie Bay, poor in sedimentary organic matter, was compared to an organic-rich fluvial sediment of the Rupel River (Belgium) in order to evaluate the influence of organic matter on S speciation and formation sequence of S species in the freshwater sediment.

The river Authie (in total 95 km long) flows into the Channel at the city of Berck (N France); the estuary is situated on the border between Somme and Pas-de-Calais Departments. The river is considered as relatively pristine, although it is affected by a series of water mills with small dams (up to 2 m high) for different uses, such as power plants or aquaculture. The Rupel River receives a large amount of organic matter inputs through the River Zenne, which transports untreated urban and some industrial waste waters from the city of Brussels. The sampling sites in the Authie estuary were located (1) in the lower estuary at the entrance into the Channel with salinity 31 (Site A1 – Authie Aval), (2) about 1,5 km upstream the site A1, where the environment is still saline, however, the organic matter originates predominantly from terrestrial sources (site A2) and (3) at Pont-a-cailloux, about 5 km upstream the site A1, where no marine influence could be observed (A3). The sampling site on the Rupel River was located near the town of Willebroek N of Brussels. Authie and Rupel are both tidal rivers, with tidal heights of about 5m.

Sediment samples were collected manually on intertidal flats at low tide, using 10 cm i.d. Plexiglas tubes and immediately sealed using rubber stoppers. Redox potential (Eh) and pH were determined on site by inserting the electrodes into the core through 1 cm side openings in the tube, covered with plastic adhesive tape. Sediment cores were extruded and cut into 2 cm thick segments in a $N_2$ filled glove bag immediately after coring. Sediment segments were packed into plastic bags, sealed and stored frozen (-24°C) till further processing. Following parameters were determined: concentrations and stable isotope compositions of sedimentary organic carbon and nitrogen, the degree of Fe pyritisation, concentrations and stable isotope compositions of dissolved sulphate and sulphide, as well as sedimentary S species: acid volatile sulphides (AVS, mainly consisting of FeS), Cr-reducible sulphide (CRS, consisting of pyrite and elemental S), elemental S ($S^0$), and S bound to fulvic (FAS) and humic (HAS) acids. AVS and CRS were extracted using sequential extraction procedure developed by Canfield et al. (1986), modified by Billon et al. (2001). Dissolved sulphate and sulphide, as well as elemental sulphur were extracted following the procedure described by Hennecke et al. (1997), while HAS and FAS were extracted using the procedure described by Brüchert and Pratt (1996). As the CRS comprises pyrite, as well as the elemental S, the contribution of the $S^0$ was subtracted from the CRS concentration determined by the sequential extraction. Stable isotope compositions of S species, extracted in the form of $Ag_2S$, CdS or $BaSO_4$, were determined using a Europa 20-20 continuous-flow mass spectrometer with ANCA SL preparation module for solid and liquid samples (EA-IRMS).

Distribution of S species in the sediment cores from all 4 sampling sites is shown in Fig. 1. Both total S concentrations, as well as distribution of S species varied with depth at all 4 sites. Dissolved sulphate was the most $^{34}$S-enriched species (up to +70‰ at site A2) , except in the Rupel River sediment, where the most enriched species was FAS (up to +10‰); the most $^{34}$S-depleted species was pyrite at all four sites (-23 to +10‰). The isotope separation between pyrite and other reduced inorganic S species (AVS and $S^0$) varied between -2 and 24‰, changing with depth and from site to site. Small separation between AVS, $S^0$ and pyrite at site A1 below 10 cm indicates that here the pyrite may be formed by direct reaction of FeS and $S^0$. Large separation, such as in the upper parts of the sediment column and at freshwater sites (A3 and Rupel River), show that it is rather a result of secondary recycling of sedimentary sulphides (Brüchert, 1998).

FAS and HAS formation seem to be independent on the availability of the reactive Fe. Enrichment of HAS and FAS with $^{34}$S with respect to sulphides, and their formation above the AVS and CRS, indicate the presence of considerable amount of biosynthetic S in the organic S pool. $\delta^{34}$S of HAS and FAS are generally not correlated with their concentration and lie between those of dissolved sulphate and sulphides, confirming the assumption that dissolved sulphide was not directly bond to the organic substrate. Using a simple mixing equation for determination of sources of S in the organic matter (Brüchert, 1998), it was estimated that around 70% of organosulphurs are of biosynthetic origin, while the rest is diagenetic. The $\delta^{34}$S of fluxes of added diagenetic S to the organic substrates were estimated using the procedure similar to those described by Sayles and Curry (1988) for C fluxes and was between –12 and + 8%, i.e. values that are lower than those of dissolved sulphate. This indicates that the sulphur incorporated into the organic matter was subject to sulphate reduction and most probably also of recycling of reduced S in the sediment.



A 1

A2

A 3

Rupel

Fig. 1 Distribution of sedimentary S species in the sediment cores from Authie Bay and Rupel River

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# Sulfur and oxygen isotopes of Lower Miocene nonmarine evaporites in the Upper Silesian Coal Basin

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In the Carpathian Foredeep Basin that is filled with synorogenic flysch and molasse sediments, mainly deltaic and turbiditic siliciclastic deposits of Miocene age, evaporites of Early and Middle Miocene age occur (Fig. 1). In the Polish part of the Foredeep, the evaporites are Middle Miocene (Badenian) in age. In the Ukrainian and Romanian parts of the Carpathian Foredeep in addition to the Badenian, the most important phases of evaporite deposition are related to Karpatian and Eggenburgian (Wójtowicz *et al.*, 2003).

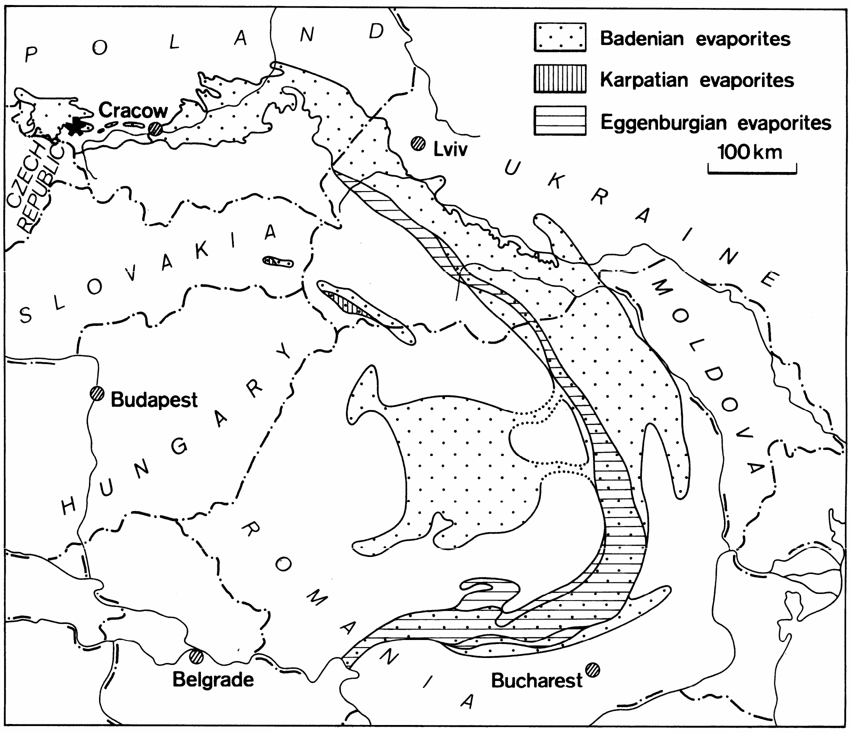

Fig. 1 Location of study area with respect to occurrence of Miocene evaporites in the Carpathian Foredeep.

In Upper Silesia segment of the Carpathian Foreland Basin, in the W-E elongated Zawada Basin located between Rybnik and Oświęcim (Fig. 2), anhydrite-bearing deposits were recorded approximately 250 m below the Badenian evaporites and some 25 m below the Lower Badenian Skawina Formation in two boreholes: Zawada I and Woszczyce IG1 (Jura, 2001).

The anhydrite-bearing deposits in the latter borehole (Fig. 3) are underlain by a series (77.7 m thick) of mostly mudstones and claystones except for the lower part of the series dominated by sandstones; at the base of this series breccia (1.6 m thick) occurs that overlies the Roet deposits; Roet deposits in turn are overlying Upper Carboniferous deposits. In the basal breccia Eggenburgian foraminifers occur, and in the top portion of the lower part of the series Late Ottnangian pollen assemblage was recently found (Peryt *et al.*, in press). As above the anhydrite-bearing series Karpatian foraminifers occur (Odrzywolska-Bieńkowa, 1986), and because evaporites need a climate aridization to be formed, it was concluded that the anhydrite-bearing series represents the Karpatian (Peryt *et al.*, in press) when a regional climate aridization during Karpatian time period occurred in the entire Carpathian region.

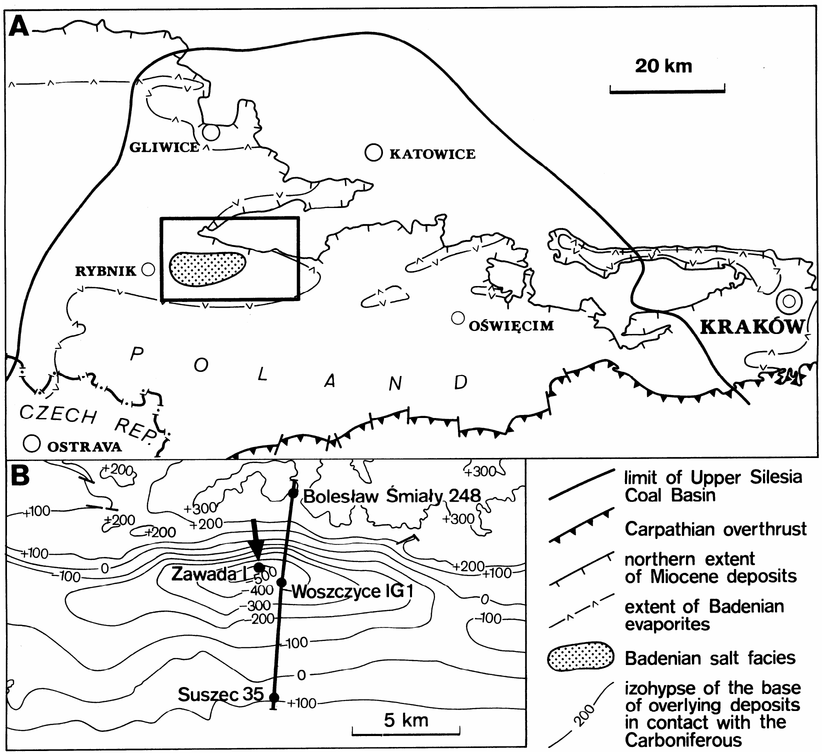

Fig. 2 A - location of Miocene deposits in Upper Silesia, B – map of the top of the Carboniferous deposits showing the location of Zawada I and Woszczyce IG1 boreholes

The anhydrite in the anhydrite-bearing complex occurs as an admixture in dolomitic claystones and siltstones. The anhydrite content is 20 – 55%. The most common mode of occurrence of the anhydrite are millimetric (rarely up to 4 cm) crystals arranged parallel to the bedding. The anhydrite is replacing gypsum that formed displacive lenticular crystals within claystones. The gypsum was replaced by the anhydrite during burial and locally there occurs the secondary gypsum.

Sulfate for the isotope analyses were extracted from pulverized core specimens by leaching with distilled water at room temperature and subsequent precipitating as $BaSO_4$, from which $SO_2$ or $CO_2$ were quantitatively extracted for sulfur and oxygen isotope analyses.

These both analyses were performed on dual inlet and triple collector IRMS with precision of 0.06‰. The results of the isotope analyses are shown in Fig. 3.

In order to explain the origin of the mother brine, from which evaporitic sulfates were precipitated, the evaluated delta values of the mother brine (the measured delta values reduced by respective corrections on isotope fractionation during crystallization, cf. Claypool *et al.* 1980) are plotted in Fig. 4. Additionally the isotope data are plotted there for recent air-borne sulfate ion (A. Trembaczowski 1989, Ph.D. Thesis at UMCS, Lublin). The atmospheric sulfate ion has the same variation range for $\delta^{34}S$ as evaluated for the mother brine sulfate. Also the highest values of $\delta^{18}O$ of atmospheric $SO_4^=$ which were formed in summer are in excellent agreement with those of mother solution. Therefore, we have inferred that the mother sulfate was formed in the atmosphere during extensive fires of coal deposits which were surrounding the Zawada valley. If we assume that the investigated sulfates were precipitated in a lake then the observed delta-profiles may by explained by the reservoir effect.

The upward trend of $\delta^{18}O$ value may by due to enrichment of the remaining sulfate in heavy isotope, whilst the lowering of delta may indicate a major inputs of newly formed sulfate. Note that isotope effect during crystallization is larger for $^{18}O/^{16}O$ than for $^{34}S/^{32}S$ (3.5‰ and 1.65‰, respectively).

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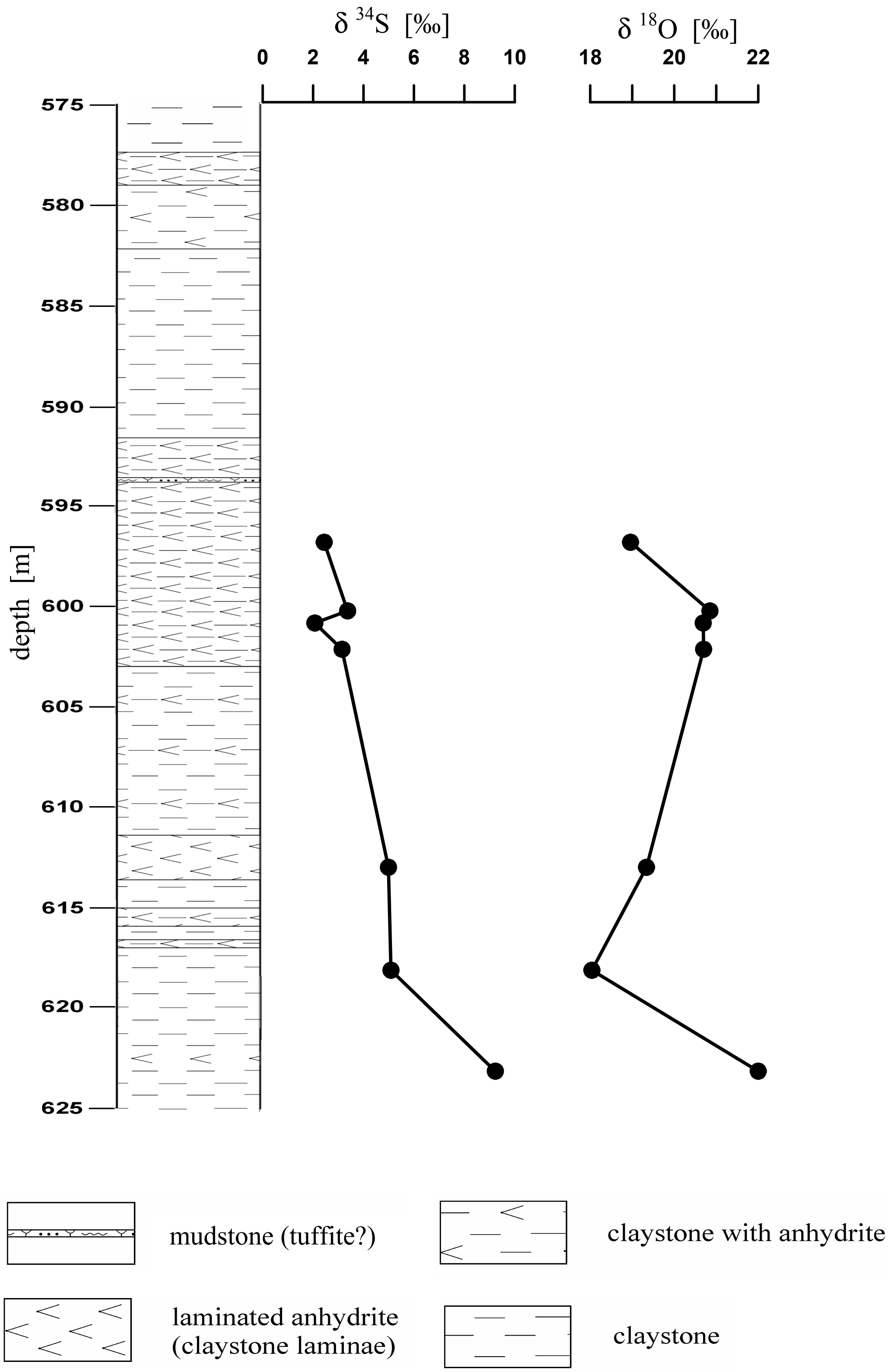

Fig. 3 Litologic section and isotope profiles of evaporitic sulfates in Woszczyce IG1 borehole

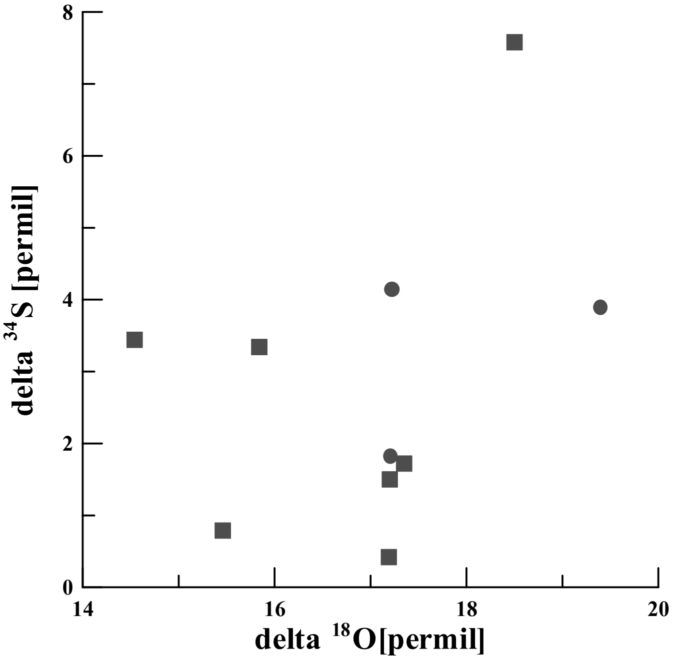

Fig. 4 A comparison of the isotope compositions of the mother solution (squares) and sulfate formed in recent summer precipitation (circles)

# Ordovician and Silurian carbon isotope trend: a state of art report based on the East Baltic data

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Isotopic methods have gained an eminent position in palaeoclimatology, palaeoceanology and stratigraphy also in the early Palaeozoic. Despite good progress achieved in isotope palaeoclimatology and palaeoceanology, different environmental interpretations are still under debate or uncertain. More likely, success in carbon isotope stratigraphy will be achieved depending mainly on how complete and detailed a standard trend used as a basis for comparisons is. Of course, correct correlation of sections and biostratigraphic dating of samples are crucial for obtaining reliable results. Despite different complications we believe that the general pattern of carbon isotope changes can well serve as a stratigraphic, and with some caution, also as a palaeoclimatologic tool for Ordovician and Silurian time.

Isotope studies embracing the southwestern sector of the Baltica continent, including the present East Baltic (Estonia, Latvia and Lithuania), Gotland, Scania and the Oslo region, but also the Anglo-Welsh area, i.e. the part of Avalonia which joined Baltica in the late Ordovician, commenced roughly 20 years ago (Brenchley et al. 1994; Wenzel and Joachimski 1996). The data presently available from the East Baltic allow us to discuss a more or less continuous curve of $\delta^{13}C$ values beginning with the post-Hunnebergian Ordovician until the Silurian–Devonian boundary beds (~58 my).

Carbon isotopes were determined by the whole-rock method that allows sampling an entire section at more or less regular intervals not depending on the occurrence of bioclasts. In selecting the sampling interval the stratigraphic context (lithology, unit thickness and boundaries) was considered. The quality of the carbon isotope data based on whole-rock analyses has been discussed in several papers. Brenchley et al. (2003) investigated in detail the reliability of isotope signals in the Late Ordovician rocks of Estonia and noted that major changes in isotope values reflect primary composition. The comparison of the Baltic latest Ordovician and Silurian whole-rock (Kaljo et al. 1998, 2000) and brachiopod shell isotope data (Heath et al. 1998) shows only slight difference in $\delta^{13}C$ values but great similarity of the corresponding curves. Study of diagenetically unaltered brachiopods in the lower Silurian of Gotland (Munnecke et al. 2003) shows that positive $\delta^{13}C$ shifts are correlated with high confidence with East Baltic whole-rock data.

Until very recently most of the Ordovician carbon isotope publications were devoted to the study of the Hirnantian, less of the middle Caradoc and the Cambrian–Ordovician boundary interval. The last year was highlighted by a burst of new data, among them the first report of the middle Ordovician carbon isotope data published by Ainsaar et al. (2004). Understandably, this progress could not be considered in the “big biodiversification book”, where the Ordovician $\delta^{13}C$ trend is shown in a very general way (Shields and Veizer 2004). But, considering also the results of the last few years, a nearly complete and more detailed trend for the Ordovician could be compiled based on the data from Baltica and Laurentia, with supplementary data from elsewhere.

Here we show the first step in compiling an as complete as possible $\delta^{13}C$ curve for the post-Hunnebergian Ordovician based on a data set from Baltoscandia.

Carbon isotope changes during post-Hunnebergian Ordovician time (~30 my) were investigated using whole-rock samples. As the corresponding sequence of rocks is stratigraphically nearly complete in Baltoscandia, an attempt was made to use it to elaborate the general pattern of carbon isotope changes in most of the Ordovician. Complications caused by several local hiatuses, condensed sections and facies changes were mitigated by the study of overlapping sections.

The following positive carbon isotope events were observed (Kaljo et al. 2004; Martma 2005):

(1) the mid-Darriwilian excursion (peak $\delta^{13}C$ value 1.9‰) in the Aseri Stage;
(2) the mid-Caradoc excursion (2.2‰) in the uppermost part of the Keila Stage;
(3) the first late Caradoc excursion (2.3‰) in the lower part of the Rakvere Stage;
(4) the second late Caradoc excursion (2.4‰) in the upper part of the Nabala Stage;
(5) the early Ashgill excursion (2.5‰) in the lowermost part of the Pirgu Stage;
(6) the mid-Ashgill excursion (2.0‰) in the upper part of the Pirgu Stage;
(7) the widely known large Hirnantian excursion (in Estonia the peak value reaches 6.7‰) in the Porkuni Stage.

The late Ordovician Hirnantian excursion (Brenchley et al. 2003) is usually linked to a major glacial event, even if some carbon cycling mechanisms are not completely understood. The environmental causes suggested for the earlier minor shifts range from global climatic and glacial events to very local changes in basin regime and sea level.

The following positive carbon isotope excursions have been established in the East Baltic Silurian (dating in terms of graptolite zonation according to Kaljo et al. 1998; Kaljo and Martma 2000; Kaljo et al. 2003):

(1) the early Aeronian excursion (3.7‰) in the *D. triangulatus* Biozone;
(2) the early Sheinwoodian excursion (5.2‰), with the peak in the *M. riccartonensis* Biozone or slightly above it;
(3) the middle Homerian excursion (4.6‰ ), main peak in the *M. ludensis* Biozone, with one or two smaller shifts below the main shift;
(4) the middle Ludfordian excursion (8.2‰), the most prominent one in the Phanerozoic. The last excursion has been correlated with the *N. kozlowskii* Biozone, but conodonts provide a direct dating – the last occurrences of *Polygnathoides siluricus* below the main shift and the appearance of *Ozarkodina wimani* and *O. crispa* above the excursion (Martma et al. 2005).

Most of isotope shifts occur close to levels of biodiversity changes, as shown by the most widely recognized Oandu crisis in the Caradoc, Hirnantian mass extinction and the Wenlock Ireviken event.

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# Variations of $\delta^{13}C_{TOC}$ values of clastic sediments from Thuringia related to biogeochemical carbon cycle

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The photosynthetic carbon fixation must be a very ancient achievement in the evolution of life on Earth (Schidlowski and Aharon, 1992). The uptake of inorganic carbon into the biomass leads to a marked enrichment of $^{12}C$ in the generated organic substance (Welte et al., 1972). The $\delta^{13}C_{TOC}$ variation of the global biomass is approximately between –20 and –30 ‰. The photosynthetic isotope effect is a function of $CO_2$ concentration, the growth rates and the temperature (Rau et al., 1992; Kump and Arthur, 1999). Therefore, the isotope ratio of the deposited organic carbon depends on the $^{13}C$ of source $CO_2$ in the surface layer and on the preservation conditions during the deposition. The productivity in the surface water is controlled by the nutrient supply. Nutrients are abundant when ocean waters are well mixed and upwelling brings nutrients to the surface water layers. Such well-mixed oceans existed during cold climate phases. In earth's history several changes of warm and cool modes were recognized (Frakes et al., 1992). Measurements on ice cores have confirmed for the late Pleistocene that the $CO_2$ concentration in the atmosphere was lower during ice ages (Sigman and Boyle, 2000) whereby the processes that are responsible for the observed $CO_2$ variations are not completely understood up to now. The isotope composition of sediment-TOC may give hints to biogeochemical processes in relation to predominant climate conditions, different depositional processes as well as tectonics (Hayes, 2004).

In Thuringia, Central Germany, a sedimentary sequence is exposed from the Neoproterozoic up to the Triassic. The degree of metamorphism is low so that fossils and the primary sediment textures have been preserved. This region of Schwarzburg Anticline (SWA) is acknowledged as target section by the German Stratigraphic Commission (Menning, 2002). We have analysed the TOC contents and the $\delta^{13}C$ values of more than 650 samples from this profile. The isotope studies were carried out on mineralogically and geochemically well characterized rocks. On this way the facies and preservation conditions during the sedimentation may be evaluated. The TOC contents range from 0.03 to 24 wt.% and the $\delta^{13}C$ values from –35.0 to –20.2 ‰. All Neoproterozoic samples are characterized by $\delta^{13}C$ values < –30‰. A sharp rise of the $\delta^{13}C$ values (–27.3 ± 0.6‰) was found about 25 m below the basis of the Goldisthal Formation. Maaß et al. (1986) were the first who described the $\delta^{13}C$ depletion of Neoproterozoic sediments. This isotopic shift between Neoproterozoic and Paleozoic was found world-wide in marine sediments (e.g. Magaritz et al., 1991; Aharon and Liew, 1992; Kaufman et al., 1993; Kaufman and Knoll, 1995). This shift appears to have been initiated by glaciations and mixing of nutrient-rich anoxic waters into the photic zone (Martin, 1995). Thuringia, the part of the micro continent Armorica, drifted during the late Ordovician northwards.

This decay was connected with a trend for the long-time increase of the sea-level (Legget et al., 1981). Therefore, the preservation conditions of organic matter were going better during the post-Ordovician time. The Silurian is marked by low sediment thickness but extremely high TOC contents. The Silurian samples indicate excellent preservation conditions by the highest V/Rb ratios with $^{13}C$ values always < –28 ‰. The sedimentation took place under strictly anoxic marine environmental conditions. Martin (1996) speculated that Cambro-to-Devonian seas were characterized by a secular trend of increasing nutrient levels.

Independent of that, the $\delta^{13}C_{TOC}$ values are a little bit more enriched in $^{13}C$ in the Uppermost Devonian. In the Carboniferous, the samples represent the transition from marine to continental deposition conditions. The uppermost Carboniferous samples were deposited under continental conditions and have more enriched $\delta^{13}C$ values (> –22.2 ‰). These more enriched $\delta^{13}C$ values were found up to Upper Permian (Zechstein –21.5 ± 0.9 ‰). During the Triassic age the $\delta^{13}C$ value were clearly depleted compared to the Permian/Upper Carboniferous. The rare gray claystone intercalations in the red Lower Triassic sediments show a mean value of -25.8 ± 0.8 ‰, whereas Muschelkalk and Lower Keuper have $\delta^{13}C_{TOC}$ values of about -27.5 ‰. The $\delta^{13}C$ values of Middle and Upper Keuper are -24.5 ± 1.1 ‰ and -25.5 ± 0.1‰, respectively. The variations of $\delta^{13}C_{TOC}$ values will be discussed compared to the global trend (Hayes et al., 1999) and in relation to regional tectonic and paleogeographic conditions.

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# Basin-Scale changes in Upper Cretaceous paleosols: paleoenvironmental implication for the Maastricht deposits, South Carpathians

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The main objectives of the this study are to characterize the Maastrichtian facies and palaeosols from Haţeg basin, Romania, in order to get information about the conditions that controlled their formation. For this purpose, field observation regarding the geometry of the deposits and their internal structures as well as mineralogical, geochemical analyses have been carried out from samples collected along representative profiles.

The south-western South Carpathians represent a nappe pile, which is mainly composed of pre-Alpine basement nappes separated by the ophiolitic Severin unit. Within the Haţeg basin the Upper Cretaceous sequences were divided into sedimentary groups, separated by local unconformities. Two different continental formations of Maastrichtian to Lower Palaeogen age are known: the Densuş-Ciula and the Sânpetru Formations, both representing molasse type deposits. The Late Cretaceous basin subsidence correlates with the stacking of the Getic nappe on the top of the Danubian realm, as well as uplift of the surrounding areas and orogenic collapse (Bojar et al., 1998; Willingshofer et al., 2001). The basin is bordered to the northwest of the Pui locality, as well as to the south by faults crosscutting the Maastrichtian strata. Burial of the Maastrichtian strata by younger deposits was limited to a few hundred meters.

The *Densuş Ciula Formation* crops out in the north-western part of the basin and it is divided into three sub-formations, with a total thickness of nearly 4 km (Anastasiu and Csobuka, 1989). The Lower Densuş Ciula Sub-formation contains volcano-sedimentary sequences interlayered with lacustrine marls, which lie discordantly on uppermost Campanian flysch deposits (Grigorescu and Melinte, 2001). The Middle Densuş Ciula Sub-formation with a total thickness of 2 km, is represented by matrix-supported conglomerates, cross bedded sandstones and massive red, brown and green-grey mudstones. These mudstones contain fossil dinosaur eggs, bones, teeth, multituberculate remains, molluscs shells and plants (Grigorescu et al., 1999; Grigorescu et al., 1994). The Maastrichtian age is indicated by fresh water gastropod assemblages including *Bauxia bulimoides, Gastrobulimus munieri, Rognacia abreviata, Ajkaia cf. gregaria,* and palynological assemblages, with *Pseudopapilopollis praesubhercynicus* (Antonescu et al., 1983; Pana et al., 2002). The dinosaur assemblage includes *Magyarosaurus dacus, Zalmoxes robustus, Zalmoxes shqiperorum, Telmatosaurus transsylvanicus, Euronychodon* (Grigorescu and Csiki, 2002). The probably Palaeogene sediments of the Upper Densuş-Ciula Sub-formation are devoid of volcanoclastic material, as well as of dinosaur remains.

The *Sânpetru Formation* crops out mainly along Râul Mare and Sibişel valleys. Preliminary magnetostratigraphy for the Sânpetru Formation, upstream the point called La Scoaba, corresponding the location 6 in our study, suggests that the sedimentation, with two short interval of normal polarity, started at the end of chron C32n (probably < 72 Ma) (Panaiotu and Panaiotu, 2002). All the other palaeomagnetic sites distributed upstream, for more than 4 km, until the upper limit of this formation, have only reversed polarity and the corresponding time interval is probably chron 31r, between 68.7 – 71.0 Ma. The mean palaeolatitude of Haţeg Basin during this period is best estimated from palaeomagnetic results obtained from contemporaneous magmatic activity: 27° N ± 5° (Panaiotu, 1998). The Sânpetru Formation is almost devoid of coarse volcanoclastic sediments; dinosaur bones are frequently found here either including: *Magyarosaurus dacus*, *Zalmoxes robustus*, *Zalmoxes shqiperorum*, *Telmatosaurus transsylvanicus, Struthiosaurus transsylvanicus, Euronychodon* and dromaeosaurids (Grigorescu and Csiki, 2002). Mammal remains were found within this formation as well (Grigorescu et al., 1985; Smith et al., 2002).

In this study, granulometry, bulk and clay mineralogy from 11 samples from Tuştea, Bărbat Valley and Sibişel were analyzed. A total of 113 carbonate concretions were cut and only calcite drilled from the central part of the concretion was used for stable isotopic analysis. Dinosaur eggshell fragments were cleaned in ultrasonic bath and sampled using a 0.5 mm drill.

Tuştea quarry, situated near to the northern border of the basin, is characterized by the presence of well drained, soils with smectite as the main clay component. FTIR analysis of the less than 2µm smectite fraction shows that the mineral is a montmorillonite As the most prominent pedogenic feature is the presence of the calcic horizon the soils can be classified as calcisols (Mack et al., 1993). Along the profile, the carbonates show a narrow range of isotopic compositions, with $\delta^{18}O$ isotopic values between 24.1 and 25.0 ‰ (SMOW) and $\delta^{13}C$ between 8.1 to -8.9 ‰ (PDB).

The profile along Bărbat Valley shows preponderantly calcisols, with the main clay mineral smectite. Illite and chlorite are subordinately found. The oxygen isotopic compositions of calcretes are ~0.5 ‰ lighter than those from Tuştea. The soils are interpreted as being formed under more humid conditions and they are similar with those situated at the bottom of the sequence developed along Sibişel Valley. The abundant smectite from Tustea and Barbat Valley sediments as well the presence of good developed soils reflects palaeoenvironment conditions predominantly controlled by climate (Bojar et al. 2005, in press).

Preliminary magnetostratigraphic data along Sibişel valley section, indicate that sedimentation started at the end of chron C32n. All other palaeomagnetic sites distributed upstream, until the upper limit of this formation, have only reversed polarity and the corresponding time interval is probably chron C31r. Along this valley, the sequence shows a general coarsening upward trend. The palaeosol type change from calcisols to vertisols dominated sequences. The soils are moderate to weakly developed. The mineralogical composition of the clay fraction change as well from smectite- to illite and chlorite-dominated. These features points toward unstable tectonic condition and higher uplift rates of the surrounding area within chron C31r. Toward the top of the sequence, the oxygen and carbon isotopic composition of calcretes become 1 and ~2 ‰ lighter, respectively. These changes indicate transition from rather semi arid toward more humid and possible cooler conditions and correlate with the worldwide trend for chron 31r (Barrera et al., 1997).

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# Carbon, oxygen, and hydrogen isotope fractionation during experimental formation of pirssonite

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The mineral pirssonite ($Na_2Ca[CO_3]_2{*}2H_2O$) occurs in oil shales and sediments of evaporated lacustrine lakes as the Green River formation (Milton & Fahey, 1960) and Searkes lake (Smith 1979). The stable isotopes of carbon, oxygen and hydrogen are extremely usefull in deducing carbonate formation conditions and may preserve informations about the paleoenvironment. For a correct interpretation of natural isotopic signals, however, a carefull experimental calibration is fundamental. Less work has been done on hydrated carbonate minerals, so far. The present study is an extension of previous work, where stable carbon isotope fractionation during pirssonite formation was studies experimentally at 60 and 90°C (Böttcher, 1994).

In the present study, stable carbon, oxygen and hydrogen isotope fractionation was investigated during experimental formation of pirssonite at 86±3°C. Pirssonite was formed via the transformation (dissolution-precipitation) of anhydrous calcium carbonate (natural aragonite, synthetic calcite) or natural gaylussite in aqueous sodium carbonate solution. This approach is similar to the one described by Bury & Redd (1930).

The newly formed solid was enriched in $^{13}C$ and 18O compared to the dissolved carbonate ion (essentially the carbonate ion and the sodium carbonate ion pair), and in 18O compared to water. Deuterium, on the other hand, was depleted in the hydrate molecules of the pirssonite lattice compared to the aqueous solution.

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# Carbon isotope fractionation of methane and $CO_2$ during coalbed gas desorption from coal, Illinois Basin, USA

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Canister desorption of coalbed gas from coal is a standard technique used for assessment of the coalbed methane abundance in coal. In this study we show that there are considerable changes in composition of the gas and in carbon stable isotopic signatures of gas species over the duration of desorption. The changes imply that there are diffusivity and/or adsorbance differences between gases and between isotopically heavier versus lighter molecules of the same gas species. It is an important issue when a representative gas sample for isotopic and compositional analysis needs to be collected.

The offline and GC/MS online analyses have been performed on the coalbed gas samples from Springfield and Seelyville coal beds of Pennsylvanian age from the SE Illinois Basin, SW Indiana, USA. The results suggest that methane desorbs faster than $CO_2$ and there can be a 2-fold increase of $CO_2$ content over the time of desorption (Fig. 1). At the end of a 90-day desorption process, the $\delta^{13}C$ values of $CH_4$ and $CO_2$ had increased by 1-2‰ and 9‰, respectively (Figs. 1 and 2). Based on the incrementally collected and individually measured gas volumes, we used mass balances to calculate the composition, $\delta^{13}C$ ($CH_4$), and $\delta^{13}C$ ($CO_2$) values of the entire desorbed gas. We concluded that, at a desorption temperature of 15 to 20ºC, the fraction of gas that desorbs after removal of the first half of the theoretically available gas best represents the overall compositional and isotopic average. Half of the available gas had desorbed from our coal samples between the 5th and 12th day of desorption, for coal cores with a length of ~30cm and a diameter of ~7.6cm. The maximum yield of coalbed gas ranged from 1 to 4$cm^3$ gas per gram coal and can be predicted via extrapolation from the incremental gas yields over the first five days of desorption.

Carbon stable isotope results obtained via on-line and off-line methods express similar patterns of fractionation in methane during desorption from coal, although with a 0.25‰ offset (Fig. 2). The systematic $\Delta\delta^{13}C$ offset is likely due to the fact that a tank of $CO_2$ in helium was used for calibration in online GC/MS work, rather than an organic reference material that passed through the same analytical train as the $CH_4$ analytes.

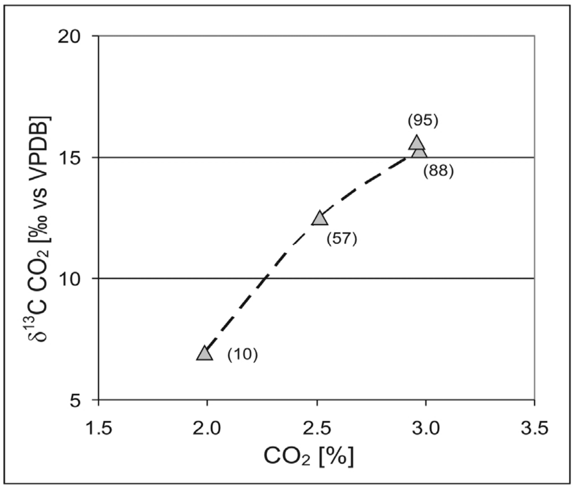

Fig. 1 Changes of $\delta^{13}C(CO_2)$ and $CO_2$ content in sequentially collected coalbed gas samples during canister desorption from Seelyville coal, SE Illinois Basin. Numbers in brackets specify the calculated $CO_2$ already desorbed at the time of gas sampling [% of total $CO_2$].

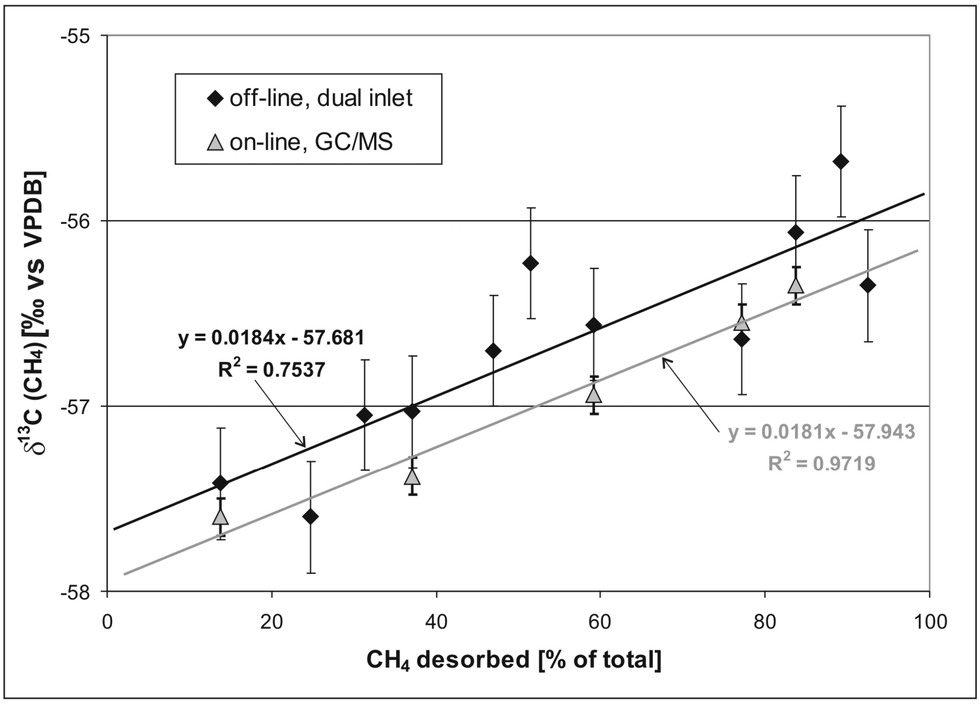

Fig. 2 Carbon isotopic drift of methane desorbing from the same coal as in figure 1.

# Carbon istopic preliminary studies on paleoenvironmental variations recorded in the Lower Carboniferous deposits from the Bardzkie Mountains (Sudetes, SW Poland)

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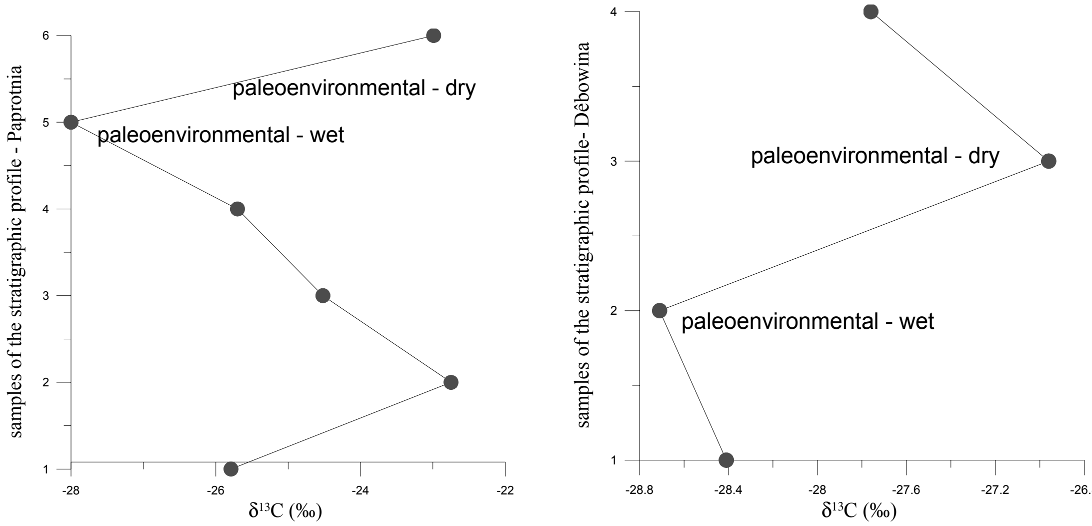
The Bardzkie Mts. Structure is a unit of the complex tectonostratigraphic system of West Sudetes Mts. This unit in general is compsed of sedimentary and slightly metamorphosed rocks of Late Ordovician to earliest Late Carboniferous. (Haydukiewicz, 1986; Wajsprych, 1986, 1995) . Two main successions: an allochthonous, completely exotic succession assigned to the Upper Ordovician-Devonian and an autochtonous Famenian-Lower Carboniferous platform succession have been described and all the borders of this unit are clearly of tectonic origin (Wajsprych (1986, 1995).

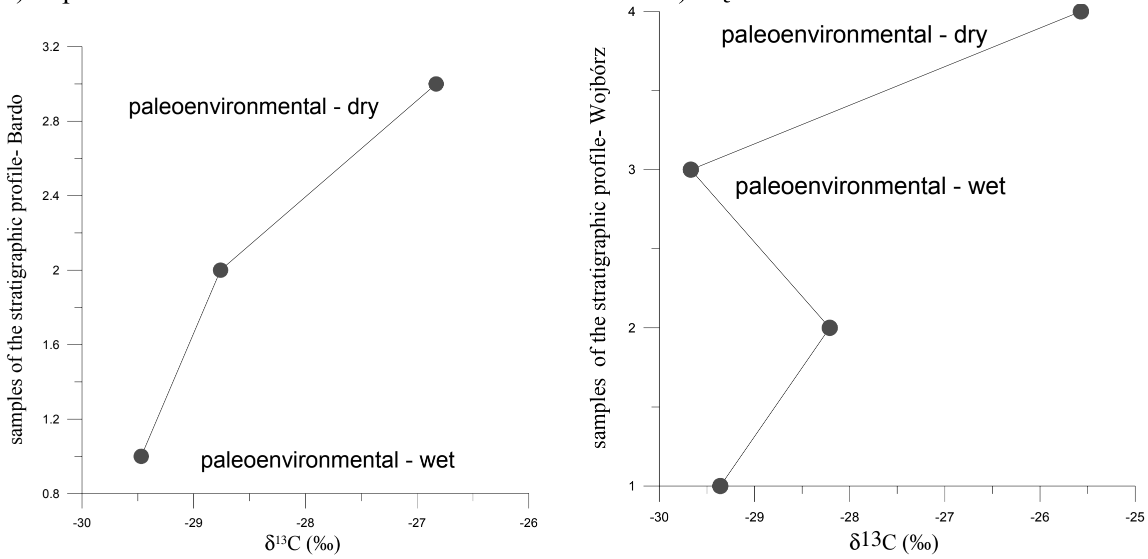
The analyzed samples were collected from outcrops adjacent to Nowa Wieś, Dzikowiec, Wojbórz, Jarota, Bardo, Srebrna Góra and Paprotnia villages. They represents the autochtonous platform finegrained rocks as mudstone shales and silt-silica shales, and shows rich and diverse palynological assemblages suitable for stratigraphic, paleonvironmental and isotopic studies.

Majority of Carboniferous miospore taxa are very important indicators for paleo-environmental reconstructions due to variable ecological preferences shown by different plant groups (Phillips and Peppers 1984, DiMichele et al. 1985, Phillips et al. 1985, DiMichele and Phillips 1994). Howevere, not only the composition of the entire palynological material but also the preservation level of miospores and is important for paleoenvironmental analysis. There were five plants groups: arborescent lycopsids, herbaceous lycopsids, conifers, ferns, and seeds ferns. In each individual sample they were noted in at variable ratios. For each of examined samples a composition diagram of plant association was constructed for preliminary paleoenvironmental reconstructions. However, there are also certain groups of miospores which botanic belonging is unknown. This made our plaeoenvironmental reconstructions more difficult.

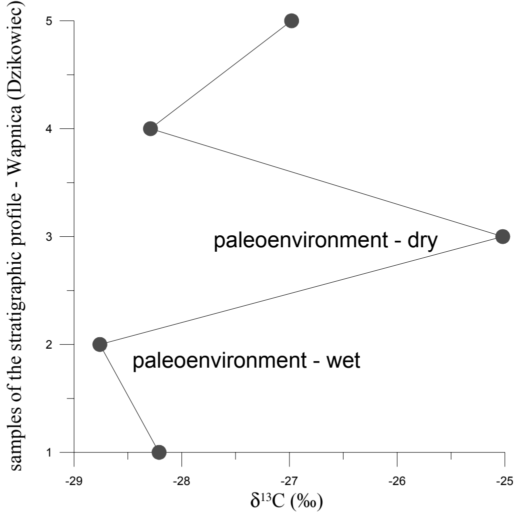
Generally, in the studied samples dominate miospores produced by arborescent plants, such as sphenopsids and ferns. They were accompanied by smaller quantities of herbaceous plants. The content of specific miospores from Paprotnia, Wapnica and Nowa Wieś indicates domination of sphenopsids and ferns. Seed ferns, arborescent lycopsids and herbaceous lycopsids occur in smaller content in palynologic material of the samples studied. Sphenopsids and calamites occured on lake margins, near streams, and in planar parts of the mires, while another group of ferns grew mainly on lowlands and partly on uplands where. However, all these plants required less moisture than mires-forming plants especially lycopsids (Phillips and Peppers 1984; Moore 1987; DiMichele and Phillips 1994). It is shown that $\delta^{13}C$ in recent trees and δ34S values in peat-forming plants, are strongly controlled by wet atmospheric precipitation or water availability (e.g. Jędrysek et al 2003, Jędrysek and Skrzypek 2005).



a) Paprotnia b) Dębowina



c) Bardo d) Wojbórz



e) Wapnica

Fig. 1 Carbon isotope variations in Lower Carboniferous plants remains form Bardzkie terrestrial sedimentary series

Preliminary $\delta^{13}C$ and $\delta^{18}O$ studies have been carried out in the Bardzkie Mts. but they concerned carbonaceous concretions from Paprotnia sedimentary series (claystones and muddy claystone, the pseudobiohermal level build up with a bush-like colony of the *Rugosa* corals and mudstone and sandy-mudstone containing high concentrations of fauna remains, (Wajsprych and Jędrysek 1994). In the present study the greatest problem of the $\delta^{13}C$ isotopic analysis of miospores was preparation and extraction of these miospores from the sedimentary non-organic matrix and non-miosphore organic (plants) remains. We have not succeded with separation of miosphres and threfore the entire organic (plants) remains have been analyzed for $^{13}C/^{12}C$ isotope ratios. The obtained δ13C values range from -29,47 ‰ to -25,25 ‰ ( Fig.1.) The δ13C value of fossil plants' remains studied, are in the range of living C3 plants in which δ13C values vary between –35,0 ‰ and –21,0 ‰ (e.g. Ehleringer 1991). These plants are characteristic for moderate climate. The obtained results proved dominant contents of C3 organic matter of terrestrial origin. The results of isotopic study correspond with the results of palynologic study that lower carboniferous paleoflorar assemblages grew in a moderate climate. From miosphores population ratios and trends in $\delta^{13}C$ comparative analysis (Fig 1 a-e) it can be concluded that carboniferous plants grown in wet conditions show low $\delta^{13}C$ values and dry climates results in increasing trends in $\delta^{13}C$ values in plants.

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## Session 5

# Paleoclimatology

# Stable isotopes as proxies for the reconstruction of past climates

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During the past decades much energy has been spent on the derivation of surrogate environmental and climatic data. In view of the current discussion on how strong mankind is interfering with climate, its history is of utmost importance and has been investigated by various methods, using many climate archives of very different origin. Methods such as floral or pollen analysis, screening of historical notes, exploration of tree ring width and high precision Sr/Ca ratios in corals and other marine carbonates etc. have widely been employed. However, in many cases stable isotope research provides a better approach for the investigation of past climates. In this respect efforts for climate reconstruction basically center on systems which comprise lake and ocean sediments, ice cores, tree rings and corals. They frequently allow reconstructions on interannual and multidecadal to centennial time scales, which is rather important for climate modelling. Two different types of archives will be looked at, namely tree-rings and lacustrine sediments.

Trees render the highest time resolution thus far possible to achieve. In some cases they even allow the reconstruction of seasonal events. To date transfer functions are generated from modern data sets relating $\delta^{13}C$ and $\delta^{18}O$ values from cellulose of tree rings to climate quantities. The corresponding regression models reveal partly strong correlations with relative humidity, temperature or precipitation amounts. However, no general rule can be given as to which relation is valid – decisive is the location of the trees. Examples will be given to demonstrate the potential inherent in isotope-climate reconstruction. Recently it could be shown that isotope investigations are also feasible using tropical trees which do not necessarily show rings. Intra-annually resolved data will be given which enable the recognition of global phenomena such as el Niño events.

The most commonly used source of palaeothermometric information namely calcareous microfossils are abundant in many marine and lacustrine sediments. Thus, they are used in numerous studies for climate reconstruction by measuring the corresponding $\delta^{18}O$ and $\delta^{13}C$ values. However, in numerous areas of palaeoclimatic interest biogenic carbonates are sparse or absent from the floor sediments. In most of these areas oxygen isotopes from biogenic silica of diatoms and sponges are a potentially powerful alternative. Nevertheless, they have rarely been used primarily for two reasons: firstly because of uncertainties in the temperature relationship of the oxygen isotope fractionation between biogenic silica and water and secondly due to substantial difficulties in its oxygen isotope analysis. These problems have recently been overcome by high temperature carbon reduction of biogenic opaline silica and secondly by measuring the corresponding isotopes with regard to changes in the temperature of lacustrine surface waters. Examples of climate reconstruction will be shown using oxygen isotopes of both biogenic carbonates and biogenic silica as climate proxies.

# A stable isotope record of an ice core from Akademii Nauk ice cap, Severnaya Zemlya, Russian Arctic

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In the Eurasian Arctic, the archipelago of Severnaya Zemlya is the easternmost one which is covered by considerable ice caps. This gives the opportunity to get regional paleo-climate information from ice core records. In 1986/87 the first ice core was drilled on Akademii Nauk ice cap, the northernmost one on Severnaya Zemlya (Savatyugin and Zagorodnov (1988), Klement'yev et al. (1991). This core was analyzed with relatively low data resolution. A chronology was published by Klement'yev et al. (1988 and 1991) and Kotlyakov et al. (1990). These authors claimed a Late Pleistocene bottom age for this core. From 1999 to 2001 a new 724 m long ice core was drilled on Akademii Nauk to proof the maximum resolution possible to be obtained and to check the time-scale published so far for this glacier (Savatyugin et al. (2001), Fritzsche et al. (2002)). This project was carried out in co-operation between the Alfred Wegener Institute (AWI), Germany, the Arctic and Antarctic Research Institute (AARI) St. Petersburg and the Mining Institute St. Petersburg, Russia. The knowledge of annual layer thickness is the basis for the chronology of the core. One of the main problems is that infiltration processes caused by melting and even rain during summer time will smooth or destroy seasonal signals. The variation of stable isotopes of water ($\delta D$ and $\delta^{18}O$) is the most common tool to reconstruct the annual layer thickness also in areas with percolation as Pohjola et al. (2002) have demonstrated but sometimes oscillations in D-excess values better resolve the annual variation (Stichler et al. (1979)). We used D-excess and $\delta^{18}O$ for determination of layer thickness.

A recent mean accumulation rate of about 460 $kgm^{-2}a^{-1}$ was found at the drilling site close to the summit of Akademii Nauk using horizons with increased $^{137}Cs$ radioactivity as time markers. Pinglot et al. (2003) have found two such peaks coursed by nuclear weapon tests in the beginning of 1960s and by the accident of Chernobyl nuclear power station in 1986. Zagorodnov et al. (1990) reported the same value of 460 $kgm^{-2}a^{-1}$ as mean accumulation rate of two years of observation (1986/87) in the area of station "Mir" at summit on the Akademii Nauk ice cap. The data of electrical conductivity, $\delta^{18}O$ and melting content are published by Fritzsche et al. (2005) in high resolution for the upper 136 m of the new drilled ice core. These data cover about 275 years following the preliminary dating basing on counting of annual variations of D-excess and $\delta^{18}O$ supported by peaks in the electrical conductivity signal, assumed to be produced by historical volcano eruptions. The highest peak in electrical conductivity was found in a depth of 25.79-25.94 m connected with huge increased nss $SO_4^{-2}$ content observed by ion chromatographic analyses of the dissolvable constituents. This indicates that this horizon was influenced by a volcano event most likely the eruption of Bezimyanny in 1956. Weiler et al. (2005) confirmed the recent mean accumulation rate by core chemistry studies.

The annual layer thickness is decreasing with depth because of thinning under the pressure of the upper layering ice. An annual layer thickness of approx. 11 cm could be observed close to the bottom using stable isotope variations. We have calculated a basal age of approx. 2500 years for the Akademii Nauk ice cap interpolating the annual layer thickness between the upper part of the core studied in detail and the range close to the bottom were data are available in high resolution. Counting of electrical conductivity cycles results in a bottom age of 2650 years. In this calculation we assume that annual layers were never eroded by melting. This age and the annual layer thickness we found can be explained only giving up an equilibration assumption for the Akademii Nauk ice cap at least for the past. That means we assume that the glacier was growing up to its today's altitude from an initial stage almost at sea level. This has to be considered for paleo-climate interpretation of $\delta^{18}O$ data.

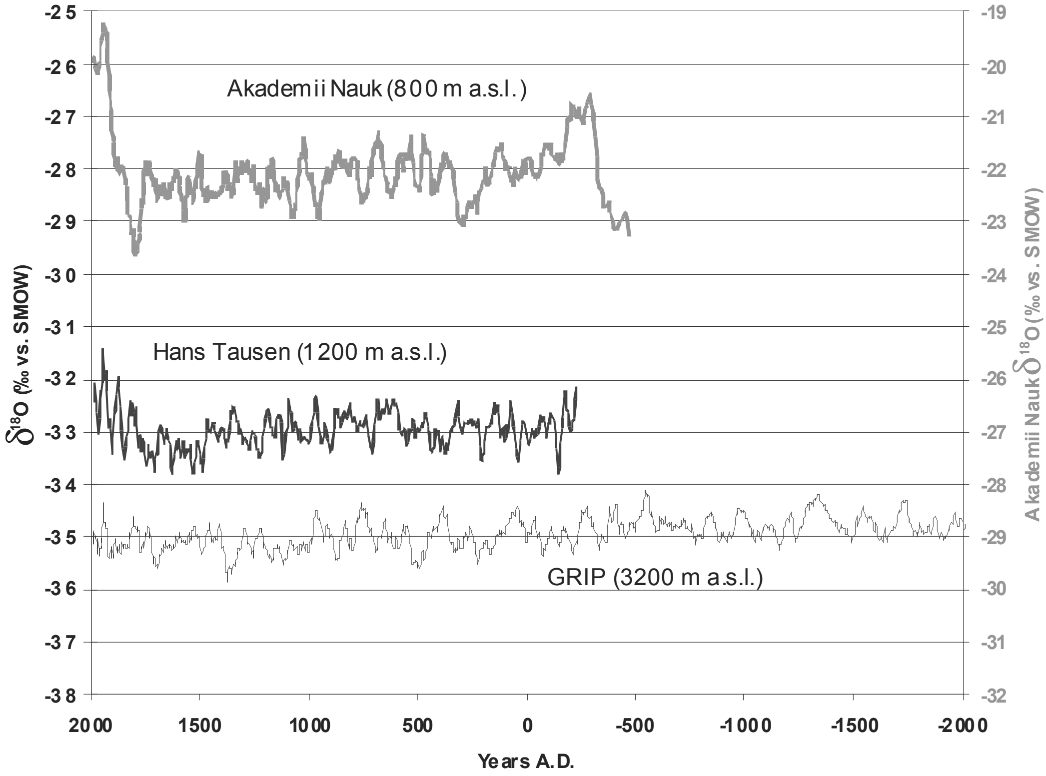

Fig. 1 Comparison between $\delta^{18}O$ records from Academii Nauk ice cap (30 years running mean), Hans Tausen ice cap (North Greenland) and GRIP (summit of Central Greenland). For Akademii Nauk the data are corrected assuming an altitude effect coursed by a growing of the ice cap

The oxygen isotope data of the Akademii Nauk ice core drilled in 1999/2001 are shown in Fig. 1 using our preliminary chronology. The $\delta^{18}O$ values had been corrected assuming a continuous growing of the ice cap and an altitude effect of 4‰/100m. The data show the trend of temperature of the last 2500 years on Akademii Nauk ice cap. They are indicating a relatively warm period about 2300 … 2400 years BP followed by a relatively long lasting colder time span with minima at about 300 AD and 1800. The little ice age couldn't be found as a characteristically drop down in temperature but a dramatically warming was observed since app. 1800. Kotlyakov et al. (2004) found this warming for the same period in surface temperatures reconstructed from temperature depth profile of the drill on Akademii Nauk in 1986/87. Since 1875 the warming is documented in meteorological data for the whole Eurasian Arctic.

Similarities like this warming were found in $\delta^{18}O$ values from Hans Tausen ice cap (North Greenland) and Akademii Nauk (Fig. 1) which could not be observed in the record from Central Greenland (GRIP). It makes clear that summit of the Greenland ice cap has special climate conditions which not necessarily reflect climate changes in the maritime Arctic at least in Late Holocene. Such changes seem to be stronger in lower altitude and smaller size of the ice cap.

The drilling project was funded by the German Ministry of Education and Research (03PL027A/3).

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# Stable isotope investigations on tree-ring cellulose of Late Glacial pine chronology of Reichwalde (Lusatia). Effects caused by destruction of fossil woods

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The isotope data of Late Glacial fossil pine forest founded under the peat deposition at Reichwalde opencast mine show some anomalies, non-explainable by dating failures or climate influences. There was assumed, that the investigated celluloses were not pure enough, because until now unknown coloured inclusions were found in some samples, probably disturbing the measurement especially of $\delta^{18}O$ values. The chemical nature and the influence of these inclusions were checked to obtain a possibility to eliminate them with an additional preparation step. The common cellulose preparation method had to be adapted to the very specific late glacial wood material from Reichwalde due to more degraded structures in this material. The methodically investigations provided results about diversification of cellulose structure and isotope ratios ($\delta^{13}C$, $\delta^{18}O$) during the single preparation steps solvent extraction, bleaching with sodium chlorite and separation of $\alpha$-cellulose with sodium hydroxide. These preparation procedure was amended by means of an additional flush with hydrochloric acid.

# Effect of river regulation on the isotopic characteristics of river water and molluscs

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Variations in the isotopic compositions ($\delta^{13}C$ & $\delta^{18}O$) of carbonate shells of molluscs from lacustrine and fluvial sedimentary profiles are often used for paleoenvironment reconstructions. The variations are interpreted as a result of changes in the environmental conditions, or more often as reflections of climate change. The isotopic compositions of present day molluscs are regarded to be representative of the present day climate and environment. Anthropogenic effects are usually not taken into account, or if they are considered, then human impacts of only the 20th century are discussed.

Two big rivers dominate in the Carpathian Basin, the Danube and the Tisza, which caused a lot of sufferings by flood events for the people living along these river courses and flood area. Solving this problem both rivers were regulated in the 19th century.

The scale of regulation of the Tisza River was outstanding, while that of the Danube was moderate. Accordingly, a significant shift has been observed in the stable carbon and oxygen isotope composition of the pieces of three Unio species living in the today Tisza River (1997-2001) comparing with those lived in the riverbed before the regulation of the river (Fig. 1). The shift in the oxygen isotope composition reflects the change in the $\delta^{18}O$ value of the river water. The Tisza River was highly meandering with tranquil water flow passing through a relatively long distance before the regulation. The slow flow allowed a significantly higher level of evaporation resulting in higher $\delta^{18}O$ value of the water (see Fig. 1). When the river was not regulated, in every springtime or early summer, it flooded a huge area, where practically there was no main course of the river. So the effect of evaporation on the isotopic composition of the water was not homogeneous, which is reflected well by the spread of $\delta^{18}O$ values of the subfossil Unionidae shells (Fig. 1).

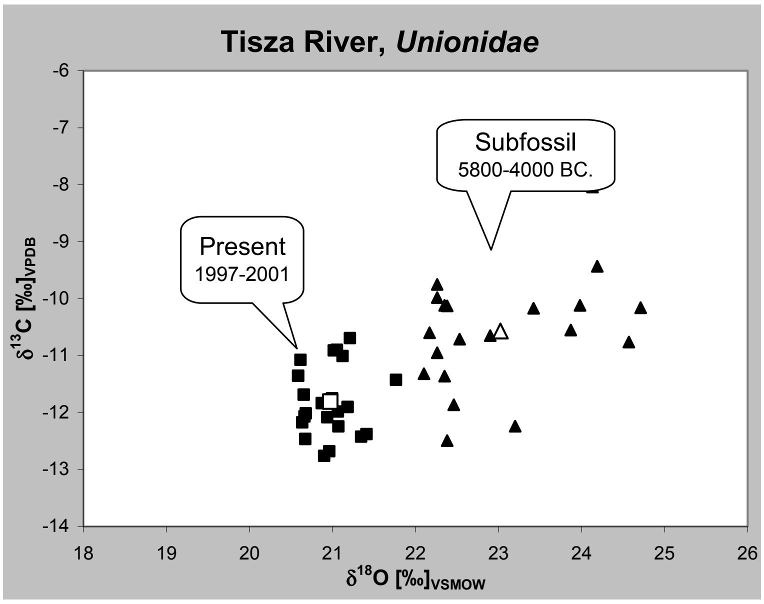

Fig. 1 The stable carbon vs. oxygen isotope composition of present day and subfossil molluscs from the Tisza River. Open symbols represent the average values.

Rodriguez et al. (2001) reported positive shift in the $\delta^{18}O$ value of bivalve mollusc *Mulinia coloradoensis* caused by diversion of Colorado River water. Quite a reversal process happened than in the case of Tisza. The diversion of river water increased the rate of evaporation because of the lowered discharge rate, and the increase in the relative surface of water. As a result the $\delta^{18}O$ value of carbonate shell of mollusc *Mulinia coloradoensis* became positive. The regulation of Tisza decreased the rate of evaporation because of the canalization of the river.

Beside the shift in $\delta^{18}O$ value, the stable carbon isotope composition changed as well in the Tisza River. It is an indication that the isotopic character of the carbon cycle in the river of slow flow differs from that of rapid flow, although the flow of present day Tisza is not really rapid since being a lowland river on the studied course. Talbot (1990) interpreted the covariance between the $\delta^{13}C$ and $\delta^{18}O$ values of primary lacustrine carbonate as a feature of closed basins. When a closed lake is getting ahead on its evolution pathway the $\delta^{13}C$ and $\delta^{18}O$ values of carbonate precipitate is becoming more and more positive. Something similar feature can be observed regarding the quick flow – slow flow – flood area – lake series. Control samples from the Lake Balaton confirm this observation.

Since the regulation of the Danube River was relatively small, this shift in the stable isotope composition of Unionidae shells from the Danube is not so significant (Fig. 2), moreover, there is no shift in the $\delta^{13}C$ value.

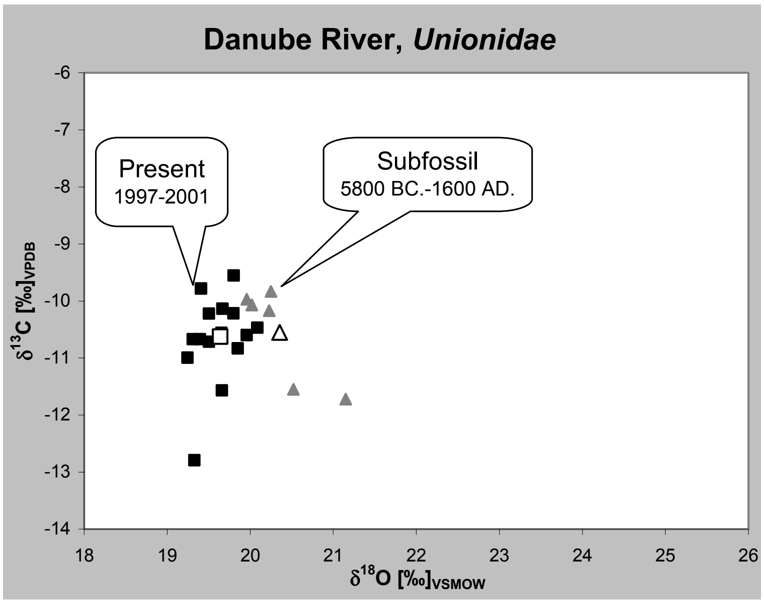

Fig. 2 The stable carbon vs. oxygen isotope composition of present day and subfossil molluscs from the Danube River. Open symbols represent the average values.

A significant difference can be observed between the $\delta^{18}O$ values of the Unionidae shells of the Tisza and Danube Rivers, which is caused by the different origin of river waters. During spring and summer a considerable amount of Danube water originates from the high elevations Alps as a snow melt, while in the Eastern Carpathians (catchment area of Tisza) snow melts during the springtime, so the water of Tisza River in summertime originates mainly from precipitation fallen at that time.

This study is the first to show the effect of riverbed regulation on the isotopic characteristics of the river water and river bed.

## Acknowledgements

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# Stable isotope study on the carbonate phases of the Basaharc loess-paleosol profile (Hungary)

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Loess and intercalated paleosols have been studied for many decades in Hungary, however, less is known about the forms of secondary carbonate components and their stable isotope characteristics.

Loess-paleosol sequences can record paleoenvironmental changes occurred during Pleistocene. Isotopic signatures of paleosol carbonates are commonly used to infer past ecologic and climatic conditions and shifts in the soil record. The study of paleosol carbonates, involving micromorphological investigation accompanied by stable isotope analysis (e.g. Pustovoytov & Terhorst, 2004), also enables the reconstruction of pedogenesis.

The former brickyard of Basaharc is located in the valley of the Danube at the northern end of the Transdanubian Range. The 20 to 25 m thick loess-paleosol sequence overlies the alluvium of the second terrace of the Danube, formed on Miocene andesite agglomerates (Pécsi & Hahn, 1987). Basaharc is the type section of three paleosol layers: the Basaharc Lower (BA) paleosol and the Basaharc Double (BD) paleosol, all of them are forest steppe soils (Pécsi & Hahn, 1987). The section also contains a fossil soil layer called Mende Upper (MF), which is the youngest one among the paleosols at Basaharc.

All the paleosol layers and the loess between them contains considerable amount of carbonate. Primary carbonate derived from carbonate rocks by eolian transport is essentially composed of calcite and dolomite grains, while secondary carbonate (calcite) formed during pedogenesis is usually present in various forms. Secondary carbonate precipitates can be large scale forms, e.g. nodules of variable size and impregnations in the soil matrix. Discrete small scale secondary carbonate precipitates less than a few millimetres in size are calcified root cells and hypocoatings in and around root channels and calcite filaments in pores and cavities. These small scale carbonate accumulations are also known from other European loess-paleosol sequences and their formation is related directly or indirectly to biological activity during pedogenesis (Becze-Deák et al., 1997).

Preliminary stable C and O isotope investigation was carried out on carbonate accumulations collected from each paleosol layer. Secondary carbonate rich samples from the B and C horizons of the paleosols were analysed, but microscopic and X-ray diffraction analyses indicated that samples also contained more or less primary carbonate. The presence of primary carbonate is problematic, since it is usually derives from Mesozoic marine carbonates (Manze et al., 1974), therefore it can shift the isotope composition of bulk samples toward higher values.

$\delta^{13}C$ values of carbonate accumulations range from -8.1 to -10.3‰ and their oxygen isotope composition is between -6.8 and -9.3‰ vs. V-PDB (Fig. 1). Data are close to the endmember isotope values typical for pedogenic carbonates formed in soil covered with C3 type paleovegetation. $\delta^{13}C$ and $\delta^{18}O$ values indicate moderate climatic conditions and different from those characteristic for periglacial environments.

Samples from the different paleosol layers do not show significant differences in isotope composition. One sample from the Mende Upper paleosol has higher C isotope value; however, the value possibly doesn't indicate any change in the paleoenvironment conditions since the sample contains the highest amount of primary carbonate among all. Beside pedogenic carbonate (s.s., that is formed in vadose environment) two carbonate accumulations formed under phreatic conditions were also analysed from the Basaharc Lower paleosol. The isotope composition of phreatic carbonate seems not to differ from that of the vadose carbonate.

Further (isotope) studies on soil carbonate, especially on small scale carbonate accumulations are planned with the exclusion of primary carbonate phases.

This study is supported by the Hungarian Research Fund (OTKA D 48631).

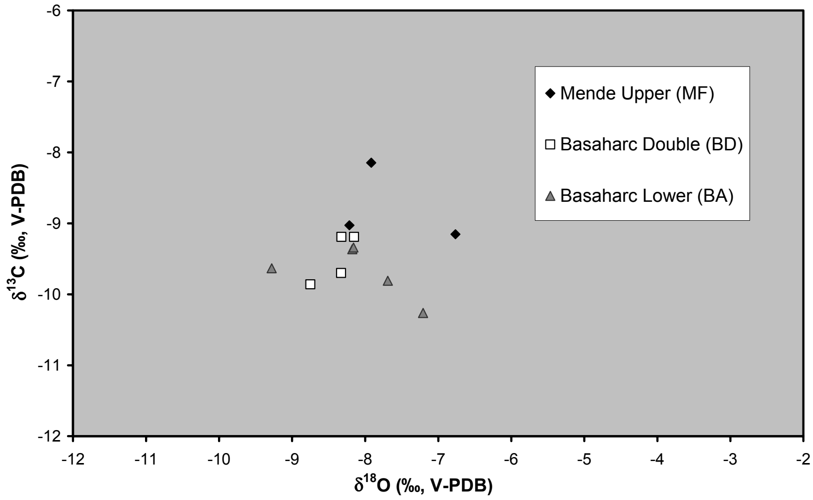

Fig. 1 Stable C and O isotope composition (in ‰ relative to V-PDB) of carbonate accumulations collected from the different fossil soil layers of the Basaharc loess-paleosol profile.

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# Geochemical and isotopic variations in recent freshwater carbonates in Krka river, Croatia; Implication for climate reconstruction

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Environmental and climatic changes are potentially recorded in recent terrestrial carbonates, such as speleothems or tufas. Stromatolite-like crusts have been the subject of great interest since they contain mm-size laminae, which are considered to represent annual climatic records. The origin of the light and dark layers has been attributed to seasonal variations in microbial assemblages and their activities, water chemistry and carbonate precipitation rates (Janssen et al., 1999, Matsuoka et al., 2001, Kano et al., 2003). Nevertheless, although several studies have demonstrated that tufas contain valuable climatic and environmental records, they received surprisingly little attention, most probably due to the non-equilibrium conditions of precipitation of fluvial carbonates.

In the Krka River, tufas occur in a multiple series of cascades over the entire length of the stream from spring to the estuary, where the climate changes from continental to Mediterranean. While no stromatolites from Krka river bed were found so far, a stromatolite-like crust occurred on the ceiling of the concrete the tunnel diverting river water to the hydroelectric power plant Jaruga close to Skradinski buk (Fig. 1). Since the age of the crust is exactly known, it could provide a valuable isotopic and geochemical record that could be potentially used for high-resolution environmental reconstruction. The aim of the study was to compare the isotopic and geochemical records of the laminar crust so as to evaluate their potential for climate and environmental reconstruction.

Water samples were taken seasonally from November 2000 to August 2002 at the top of the main cascades, except at site 2 (Miljacka), where the waterfall is not accessible; here the samples were taken at the power plant. Bulk tufa samples were collected from the riverbed at the main waterfalls. Laminar incrustations were found at Jaruga power plant close to site 4. They were formed on a concrete substrate from water spray, showing typical dark and light coloured laminae with an average thickness of about 1.5 mm. The tunnel was constructed in 1937 and cleaned in summer 2000, so the age of the sample and its growth rate are known.
The river water was analysed for $\delta^{18}O$, $Ca^{2+}$ and $Mg^{2+}$ concentrations, while in carbonates the $\delta^{18}O$ and $\delta^{13}C$ were determined. In the laminar crust, also the $Ca^{2+}$, $Mg^{2+}$, $Sr^{2+}$ and $Ba^{2+}$ concentration profiles were determined using ICP-OES method.

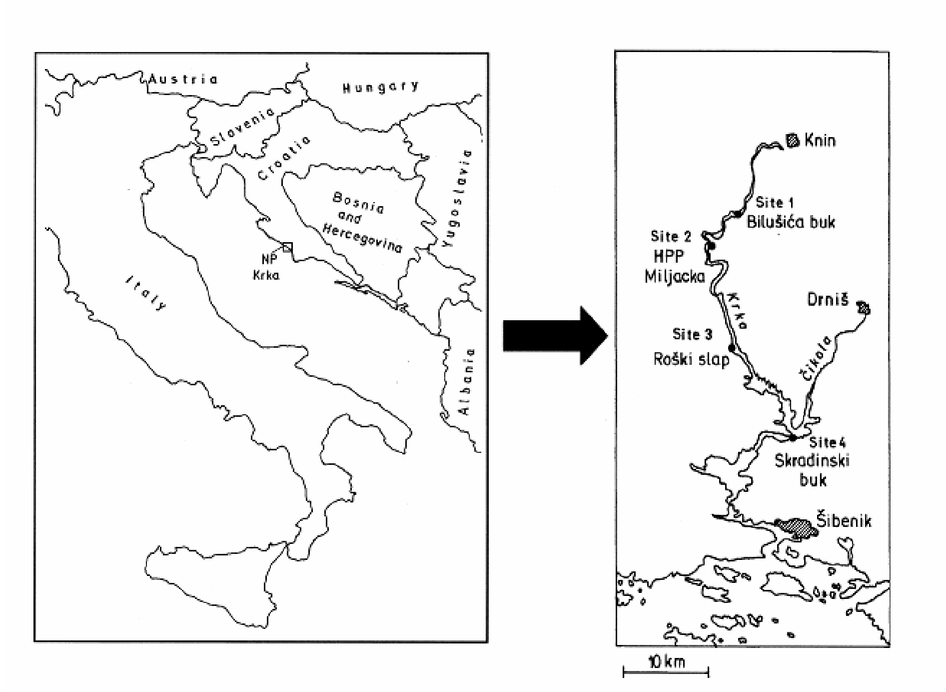

Fig. 1 Location map of the sampling sites on the Krka River

Results of the isotope analyses of water and bulk tufa collected at the main cascades have been discussed elsewhere (Lojen et al., 2004). Briefly, it was found that the calculated temperature of carbonate precipitation (Craig, 1965) matches the measured values only at sites where water temperature is low and relatively stable throughout the year. The higher the temperature, the bigger was the difference between the calculated and measured values; no difference between measured and calculated values occurred around 10.6°C. (Fig. 2).

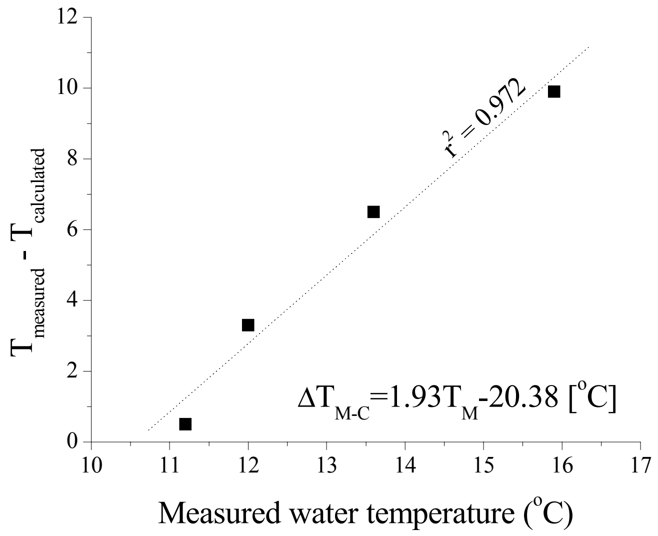

Fig. 2 Measured and calculated temperature values

C and O isotope record of the laminar crust also showed similar discrepancy as bulk tufa samples; the calculated temperature of precipitation of laminae was much lower than reasonably expected. Ihlenfeld et al. (2003) found that beside $\delta^{18}$O and $\delta^{13}$C records, the Ca/Mg and Sr/Ba ratios of laminar carbonates represent a reliable tool for reconstruction of crystallisation temperature and geochemical conditions of fluvial carbonate formation. It was found that Ca, Mg, Sr and Ba concentration profiles show similar variations, i.e. coin-ciding minima and maxima, reflected also in C and O isotope records. Considering the range of Mg/Ca ratio of water (0.17-0.24), the partition coefficient of Mg between water and precipitate ($D_{Mg}$) remains unaffected (Howson et al., 1987), i.e. variations of both $Mg^{2+}$ concentration and $\delta^{18}$O of the precipitate are dominated by temperature fluctuations and not by changing water chemistry. The $D_{Mg}$, defined as a ratio between Mg/Ca ratios of precipitate and water, had a value around 0.033, which is typical for freshwater environments (Howson et al., 1987). The temperature dependence of Mg/Ca ratio of water was calculated from the data obtained during 2 years of river observation and was $T[°C] = 200 \times (Mg/Ca)_{water} - 18$. Assuming that the $D_{Mg}$ remained unchanged in the same river system through 60 years of precipitation, the temperature of tufa precipitation could be calculated from Mg concentrations in the laminar crust. The calculation of precipitation temperature from $\delta^{18}$O record (Craig, 1965) gave too low values, while Mg record gave temperatures close to the values measured in the last few years of observation. Nevertheless, the fluctuations (10-35°C) of Mg-temperature curve seem to be too large.

Assuming that the discrepancy between the calculated and measured value of the precipitates from the river bed and the laminar crust should follow the same rule, then the $\delta^{18}$O-derived temperature record might be corrected using the linear function derived from the Fig. 2. Corrected temperatures, derived from the $\delta^{18}$O curve, reasonably resemble the measured values during last few years (cf. Fig. 3). Since the precipitation rate during summer periods is larger than during the winter, the average calculated T of precipitation for the last decade (about 22°C, laminae 60-70) are reasonable. Nevertheless, precipitation temperatures during the first decade of precipitation (after 1937, when the tunnel was constructed), should be in average by 6° lower than nowadays. No temperature record for this period is available, however, such a big difference in mean summer temperature seems to be too large. The reasons can be manifold. Although one cannot expect equilibrium conditions of calcite precipitation from the spraying water, the conditions at the beginning of crust formation, which grew on very alkaline concrete substrate, were even less in equilibrium than nowadays when the crust thickness reached about 8 cm and the crust surface has no contact with the substrate. From the differences in grain size and structure between older and younger parts of the crust, it becomes evident, that the recrystallisation of the crust occurred during last decades, especially in older part. However, it is not possible to estimate whether the recrystallisation influenced (and if so, to which extent) the $\delta^{18}$O values of laminae. Finally, the differences in $\delta^{13}$C of organic matter of the crust between older and younger parts (about 2‰) indicate that either the sources of $CO_2$, or hydrological conditions, or the colonising community must have changed in last 6 decades.

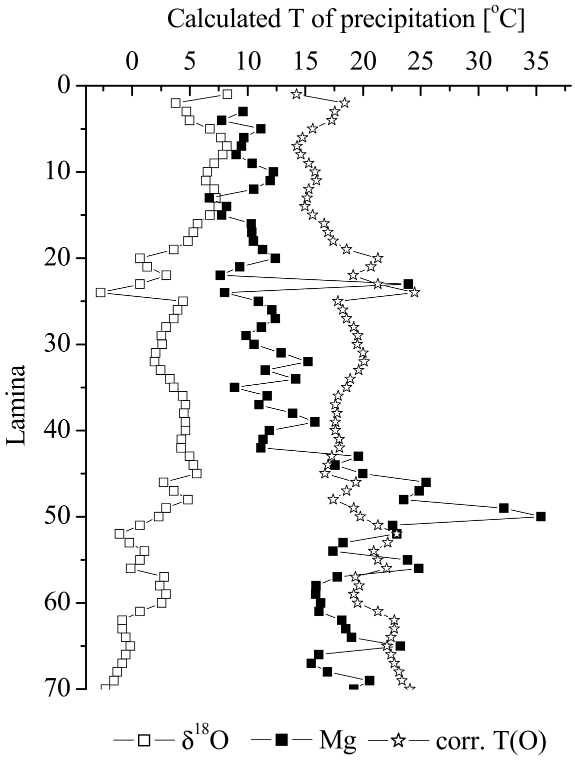

Fig. 3 Calculated temperatures of precipitation of laminar crust at the Jaruga power plant

In conclusion, both oxygen isotope, as well as geochemical records in the laminar crust to a certain extent reflect the temperature and other environmental conditions during the period of precipitation. However, the exact estimation of the precipitation temperature is not yet possible.

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# Environmental isotope studies in Croatia

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## 1 Introduction

In Radiocarbon and Tritium Laboratory of the Rudjer Bošković Institute in Zagreb, Croatia, isotopes are applied in various types of studies: environmental, geochronological, arhaeological, hydrological, etc. Radiocarbon ($^{14}C$) and tritium ($^{3}H$) data measured in the Laboratory are often combined with the stable isotope ($^{2}H$, $^{13}C$, $^{18}O$) data. In this paper we would like to present an overview of the most important results of environmental isotope studies performed in our Laboratory. Most of our studies have been performed in the karst area of Dinaric Mountains, and specifically at the Plitvice Lakes National Park system, about 150 km south from Zagreb.

## 2 Isotope composition ($^{2}H$, $^{18}O$, $^{3}H$) of precipitation

Monthly samples of precipitation have been collected at two stations in the continental regions of Croatia and Slovenia, namely at Zagreb and Ljubljana, respectively. The stations are included in the GNIP network (Global Network of Isotopes in Precipitation) and have long-term isotopic records, since 1976 and 1981, respectively (IAEA 2005, Krajcar Bronić et al. 1998). In the period 2000 – 2003 the network was extended to six additional meteorological stations along the Adriatic coast (Krajcar Bronić et al. 2004, Horvatinčić et al. 2005).

The largest seasonal variations were observed at both continental stations (~13‰), and they can be attributed to the largest temperature variations at these stations. The differences between minimal and maximal values decrease in a south-east direction. The corelation between $\delta^{2}H$ and $\delta^{18}O$ is good for all stations, and both slope and intercept of the regression line decrease in the south-east direction. Annual weighted mean d-excess values vary between 9‰ in Zagreb and 14‰ in Dubrovnik. Good corelation between mean monthly air temperature and monthly $\delta^{18}O$ was obtained for all stations. The highest slope was obtained for the high-altitude station Zavižan (0.37‰ /°C), followed by ~0.3‰ /°C for the continental stations. The the slope was the smallest for the south-Adriatic stations having the highest mean annual temperatures.

Tritium activity in monthly precipitation at all sampling stations for the observation period 2001 – 2003 shows seasonal variations that are more pronounced at the continental and north-Adriatic stations. The $^{3}H$ activity in precipitation decreases along the Adriatic coast from north-west to south-east. Since the mean temperature increases in the same direction, the decrease of $^{3}H$ activity may be due to the influence of increased sea-water evaporation.

## 3 $^{14}C$ in the atmosphere

Atmospheric $CO^{2}$ has been collected on a monthly basis in Zagreb and Plitvice since 1984 and 2003, respectively. Seasonal variations in $\Delta^{14}C$ have been observed at both locations.

The mean annual $^{14}C$ activities in Zagreb were decreasing after the maximum in 1960-ties and approached the natural pre-bomb activities (Krajcar Bronić et al. 1998). During the last 3 years the mean $^{14}C$ activity $\Delta^{14}C$ remains about 30‰.

The atmospheric $^{14}C$ activity in the region for period 1950 – 1985 was reconstructed by measuring $^{14}C$ activities of individual tree rings from the spruce tree grown at the Plitvice Lakes area (Kozak et al. 1989). A good agreement with the general atmospheric $^{14}C$ curve of the Northern Hemisphere was observed.

## 4 Isotopes ($^2H$, $^{18}O$, $^3H$) in karst springs

Stable isotope composition of several karst springs in the Plitvice Lakes area was determined seasonally in period 1983 – 1985 (Horvatinčić et al. 1986) and again in 2003 – 2004, and it was compared with the stable isotope composition of precipitation. Annual variations in precipitation (~13‰) are much higher than those in karst springs (<1‰). The springs are also characterized by a very constant temperature and chemical compositions, and all these facts suggest a thorough mixing of water in the karst aquifers. Tritium activities in spring waters were also measured on monthly bases for several years, and the mean residence time was determined by applying the exponential model. The MRT is very short, ranging between 1 and 4 years on the average (Krajcar Bronić et al. 1986). However, extreme meteorological conditions may change the MRT calculated by the exponential model. After extremely dry summer and fall of 1983, the older water with higher tritium content appeared at the springs and MRT was longer, between 4 and 8 years. After abundant winter precipitation, very low tritium activities (not much different from the winter precipitation) were measured in spring 1984.

## 5 Isotope composition ($^{13}C$, $^{14}C$) of dissolved inorganic carbon (DIC)

Carbon isotope composition ($^{13}C$, $^{14}C$ activity) of dissolved inorganic carbon (DIC) in water in the Plitvice Lakes system was measured in the period 1984 – 2002 at several locations along the water course of the Korana River. The mean values of $\delta^{13}C$ for DIC increase from –12.7‰ in springs to -9‰ in the surface waters (Fig. 1). The increase in $\delta^{13}C$ for DIC along the water flow is the combined result of $CO_2$ degassing and carbon isotope exchange between atmospheric $CO_2$ and DIC in the water (Srdoč et al. 1986a).

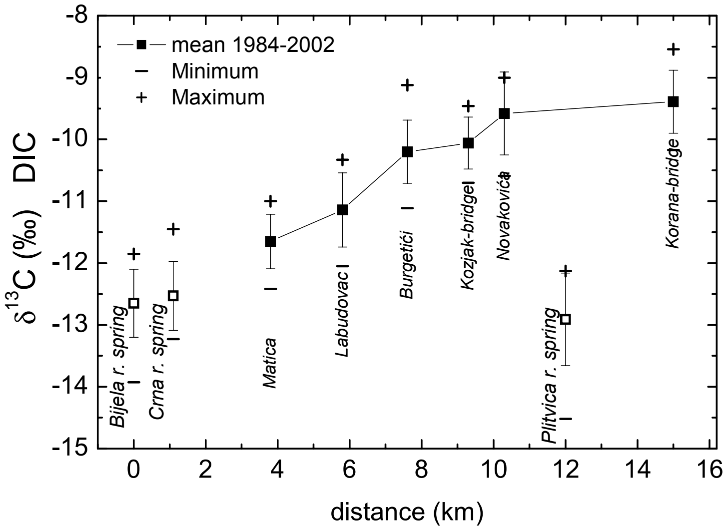

Fig. 1 $\delta^{13}C$ in DIC in spring and surface waters of the Plitvice Lakes system

## 6 Isotope composition of carbonate sediments

Various types of secondary carbonates (lake sediments, tufa, speleothem) precipitate from karst waters as the results of the same chemical process, but under different prevailing environmental conditions.

$\delta^{13}$C and $\delta^{18}$O of tufa from Holocene and Pleistocene (as determined by the $^{14}$C dating) from the Plitvice Lakes system (having continental climate) and from the Krka River system (having Mediterranean type of climate) are compared in Fig. 2. The range of $\delta^{13}$C values is the same for all samples, from -10‰ to -6‰. There is no statistical difference between the □$^{13}$C values either between the tufa from the same location but different time periods or between the tufa from different locations and the same period. This indicates that conditions for tufa precipitation were similar during each period and for both areas (Horvatinčić et al. 2003). The $\delta^{18}$O of tufa ranges from -11‰ to -6‰, and two groups are noticeable. The Holocene and Pleistocene data sets from the Plitvice and Krka areas are the same only for the same location, while they are not the same for the same period and different locations, because of different type of climate. The $\delta^{18}$O signature of tufa from Krka River is on average 1.7‰ (old tufa) and 1.8‰ (Holocene) higher than $\delta^{18}$O of tufa from the Plitvice Lakes. The difference may be explained by a different $\delta^{18}$O composition in waters from which tufa is formed and/or different mean yearly temperatures. Both of these factors are indicative for the different climate of the regions and both give rise to more negative $\delta^{18}$O values at Plitvice Lakes.

Mean $\delta^{13}$C values for the lake sediments taken from the 12 m long sediment cores from two lakes at the Plitvice Lakes area [(-8.6±0.1)‰ and (-8.9±0.2)‰ for Lake Kozjak and Lake Prošće, respectively] are similar to the mean $\delta^{13}$C for tufa from Plitvice Lakes, (-8.3±1.0)‰, but show much smaller fluctuations. There is also practically no difference in $\delta^{18}$O values between tufa (-9.6±0.3)‰ and lake sediments: (-9.9±0.3)‰ in Lake Prošće and (-9.3±0.2)‰ in Lake Kozjak. All of these values indicate stable climatic conditions for the region during last 6000-7000 years, which is the $^{14}$C age of Holocene tufa and lake sediment in this region (Srdoč et al. 1986b).

The $\delta^{13}$C of DIC in water and the $\delta^{13}$C of lake sediments can be compared. The $\delta^{13}$C of DIC in Lake Prošće is ~(-11)‰, and that of DIC in Lake Kozjak ~(-10)‰. The mean annual temperatures are 10.9°C and 10.6°C, respectively. Thus, the difference $\delta_{sedim}$-$\delta_{DIC}$ is 2‰ and 1.4‰ for Lakes Prošće and Kozjak, respectively, and it is in accordance with the equilibrium fractionation factor (ε~1.5‰ at 10°C). We can conclude therefore that sediment precipitation occurs under carbon isotope equilibrium.

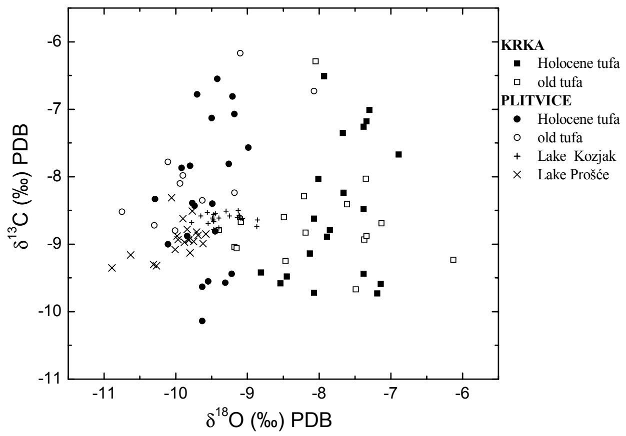

Fig. 2 Stable isotope composition of tufa and lake sediments

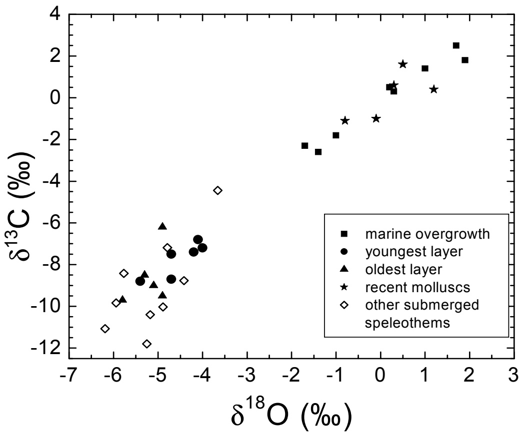

Fig. 3 $\delta^{13}C$ and $\delta^{18}O$ in submerged speleothems, marine overgrowth and recent molluscs

Isotope analyses, including $\delta^{13}C$, $\delta^{18}O$ and $^{14}C$ age, of tufa, lake sediments and speleo-thems in the Dinaric Karst, confirm that these deposits record environmental and climatic information. While speleothem is a good indicator of global climate and palaeoclimatic changes, tufa is a more sensitive indicator of palaeoenvironmental changes.

Isotope analyses of several speleothems from three submerged caves (depths of -38.5 m to -17 m) along the Eastern Adriatic coast were applied in an attempt of reconstruction of the late Pleistocene–Holocene sea-level rise along the Croatian cost. The marine biogenic overgrowth layer and the youngest and the oldest parts of the speleothems were dated by the $^{14}C$ method and their $\delta^{13}C$ and $\delta^{18}O$ were also measured. The start of overgrowth (i.e., the time of flooding by seawater) was determined to be 10,185 cal BP at -36 m, 9160 cal BP at -34 m, and 7920 cal BP at -23 m (Surić et al. 2005). Our results partially match the sea-level curves reconstructed for adjacent areas, Tyrrhenian Coast and French Mediterranean Coast. The stable isotope composition of the marine overgrowth is in the same range as that of recent molluscs from the Eastern Adriatic Sea (Fig. 3), and can be clearly distinguished from the stable isotope composition of the speleothem layers, which in turn is typical for the terrestrial speleothems in the karst region of Croatia with the prevailing Mediterranean type of climate.

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# Holocene isotopic shift of atmospheric sulfur – a case history from Hungary

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As one of the candidates for developing a depository for low and medium activity vaste of the Paks nuclear power plant, the Üveghuta granite (SW-Hungary), covered by thick loess, has been subjected to a detailed study of groundwater flow and water-rock interactions. This work resulted in a better understanding of hydrogeochemistry of the site. Here results concerning bacterial sulfate reduction and secular change of isotopy of atmospheric sulfur are reported.
The groundwater level is within the uppermost wheathered zone of the granite (Fig. 1). On the basis of numerous $^{14}$C measurements, fracture-filling water of the upper 400 metres of the granite was infiltrated during the last 30 thousands years. Waters having $\delta^{18}$O lower and higher than –11.4 ‰ are considered as of Holocene and latest Pleistocene ages, respectively.

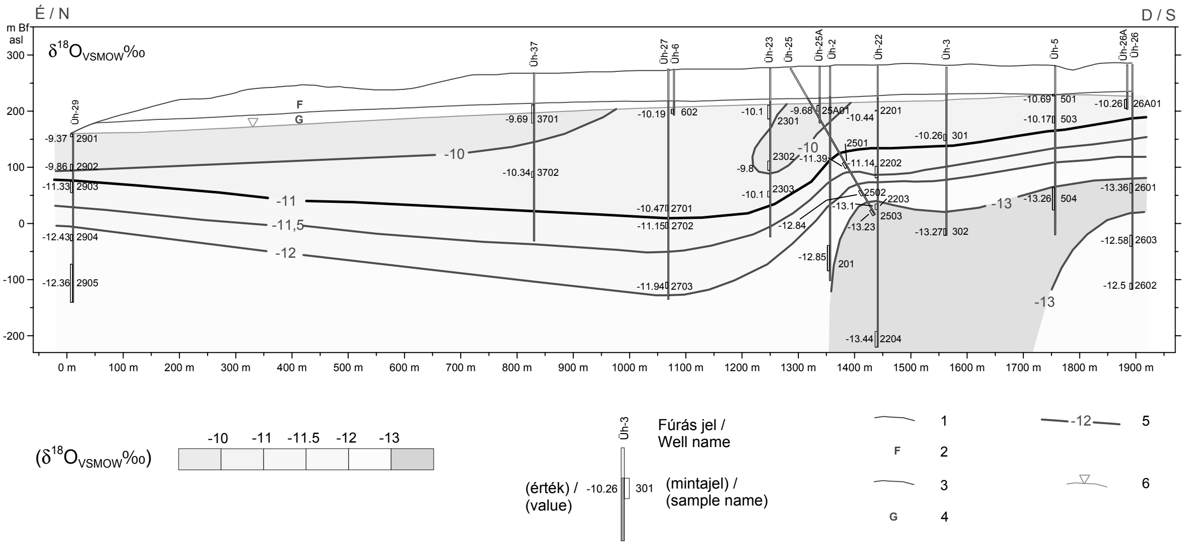

Fig. 1 Geological section of the Üveghuta granite G groundwater level F granite surface

Most Holocene waters contain nitrate in amounts higher than 4 mg/l, while earliest Holocene and Pleistocene waters are practically free of it (Fig. 1). With decreasing $\delta^{18}$O sulfate content decreases and its range becomes narrower (Fig. 1). Sulfate $\delta^{34}$S varies between –2 to 18‰ in Holocene waters, while its range is much broader in the Pleistocene ones reaching values as high as 45‰ (Fig. 1). Nitrate and sulfate patterns together with isotopy of sulfur show that (i) nitrate reduction took place already in earliest Holocene waters and (ii) sulfate reduction is advancing as age of infiltration of nitrate-free waters increases.

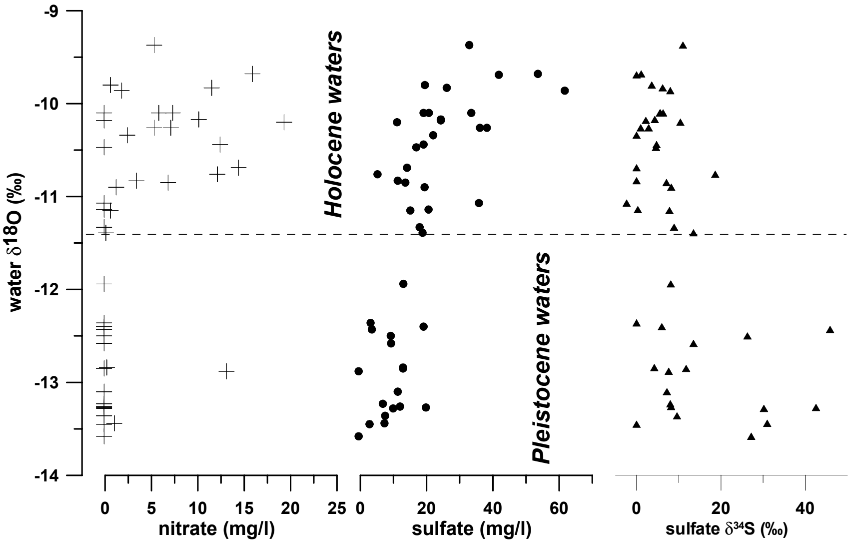

Fig. 2 Variation of nitrate and sulfate concentrations and sulfate $\delta^{34}S$ in fonction of $\delta^{18}O$

Assuming that in nitrate–free Holocene waters 10% of the sulfate is already reduced by bacteria and this process was accompanied by a 30‰ S-isotope fractionation, $\delta^{34}S$ of the original sulfate has been calculated. Results of this conservative calculation suggest that sulfur dissolved as sulfate in infiltrating waters has been enriched in $^{34}S$ up to at least 7‰ since the beginning of Holocene (Fig. 3). Since infiltrating waters were not able to dissolve significant amount of sulfur from the loess, the observed S-isotope shift is believed to represent a similar coeval change occurred in isotopic composition of atmospheric sulfur in the Carpathian realm.

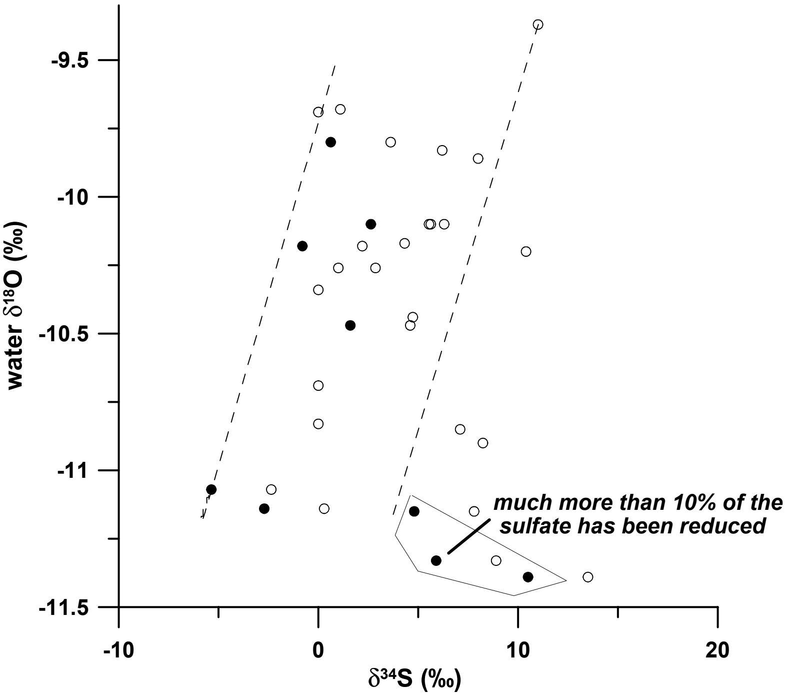
*much more than 10% of the sulfate has been reduced*

Fig. 3 Variation of original sulfate $\delta^{34}S$ in fonction of $\delta^{18}O$ ● corrected values

# The Eemian and Early Weichselian limnic sequence Ples: Reconstruction of paleoenvironmental change by using stable isotope methods and geochemistry

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The limnic profile Ples (N 57° 27``, E 41° 32``) is situated in the Upper Volga Region in Russia and comprises the period from the Late Saalian Glacial, the Eemian Interglacial and the first part of Early Weichselian up to the Brørup Interstadial (Grichuk & Grichuk 1959). The lithological composition of this carbonate free profile is mainly determined by clastic sediments (silt and clay) in cool periods and organic rich muds and peat during warm stages. The whole profile is about 8,5 m thick and exposed in a deep natural gully close to the Volga River.

Our results (fig. 1) allow us to trace changes in $CO_{2(aq)}$ and nutrient availability during lake development. In general, high contents of organic carbon and nitrogen are correlated significantly with relatively low $\delta^{13}C_{org}$-values (r=-0,47; n=141) and low $\delta^{15}N$-values (r=-0,66; n=141) respectively.

Periods with warm climate are associated with more negative $\delta^{13}C_{org}$ values. This is the opposite of what is expected, because an increase in lake productivity would shift the $\delta^{13}C_{org}$-values of autochthonous organic matter towards more positive values (e.g. McKenzie 1985). Probable associated mechanisms for the observed patterns of $\delta^{13}C_{org}$ are: (1) changes in the concentration of atmospheric $CO_2$, (2) influx of $^{13}C$ depleted $CO_{2(aq)}$ generated by decay of soil organic matter preferred in warmer periods and (3) recycling of respire, “light” $CO_{2(aq)}$ from the hypolimnion. An interesting feature is the prominent shift of $\delta^{13}C_{org}$ values at the Saalian/Eemian transition of about 4 ‰. This decrease towards lighter values is typical for glacial/interglacial transitions and has been found in many other limnic and marine sites (Hammarlund 1993; Prokopenko & Williams 2004; Watanabe et al. 2004). Similar as Hori and Meyers (1992) for Weichselian/Holocene transition, we interpret this as a reaction to the rise of atmospheric $CO_2$ from 180 ppm in glacial times to 280 ppm in the Eemian Interglacial (Petit et al. 1999).

Similar to $\delta^{13}C_{org}$, the $\delta^{15}N$ values are systematically lighter in periods with warmer climate. Probably this can be attributed to a rise in precipitation with low nitrogen isotope values (mean value -5 ‰; Moore 1974; Freyer 1978) during the Glacial-Interglacial-transition. In times of enhanced nitrate availability there is a maximum isotopic fractionation and this leads to more negative nitrogen isotope values in the organic matter (Fogel & Cifuentes 1993).

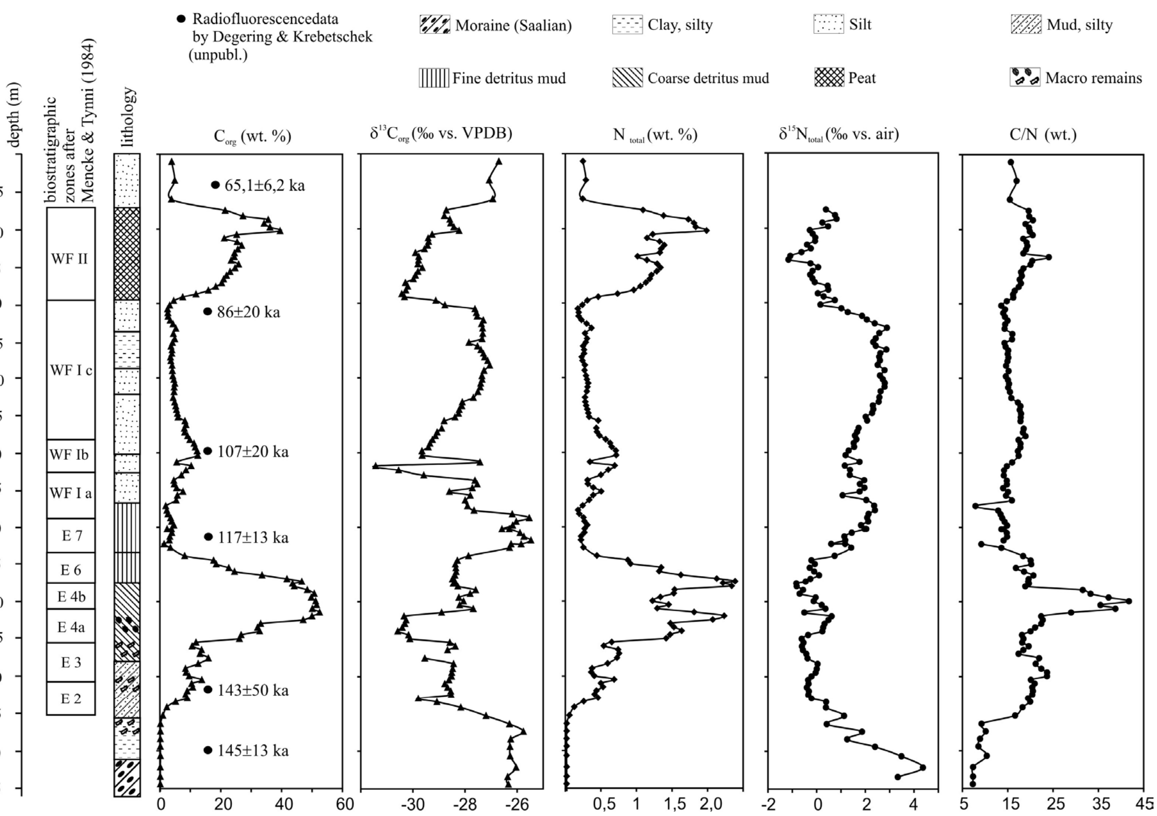

Fig. 1 Results of stable isotope and geochemical investigations in the profile Ples

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