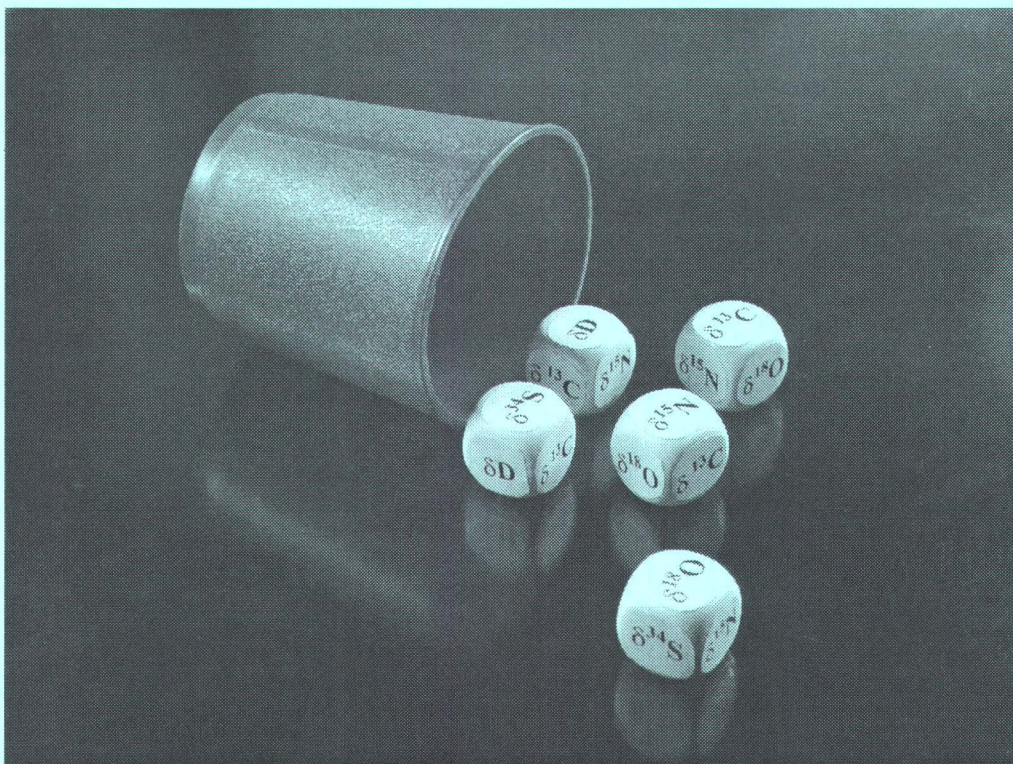


# 4<sup>th</sup> Austrian Workshop on Stable Isotopes in Environmental and Earth Sciences

Graz, 22-23<sup>rd</sup> November 2002



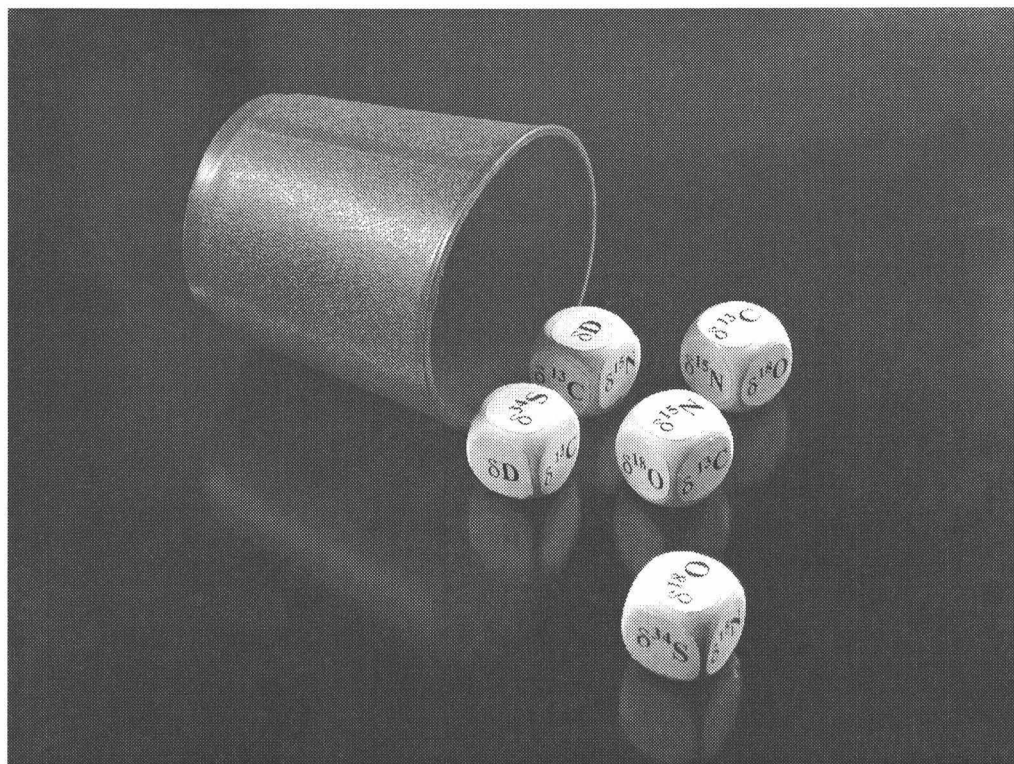
**Berichte  
des Institutes für Geologie und Paläontologie  
der Karl-Franzens-Universität Graz**

**Band 6**

**Graz, November 2002**

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## **Preface**

The Karl-Franzens University and the Joanneum Research Centre are proud to host the 4<sup>th</sup> Austrian Work Shop on Stable Isotopes in Graz. The joint organisation of this workshop with members of an environmentally oriented research group (Joanneum Graz) and a group involved in geological sciences (University Graz) documents the value of Stable Isotope studies within a very wide spectrum of interests. Indeed, there is no other technique which covers such a wide range of disciplines including environmental sciences, geological sciences, biological sciences, medicine, technical applications... In addition, the evolution of new techniques and facilities to improve and refine the analytics of Stable Isotopes is in a steadily accelerating progress. We are proud to present contributions during this workshop that cover methodological, technical and scientific aspects of Stable Isotope research. Furthermore this meeting intends to help the highly diverse Stable Isotope Community growing together.

Ana-Voica Bojar, Albrecht Leis, Harald Fritz  
Graz, November 2002

## Contents

<i>Automatic, sensitive determination of the <math>^{15}\text{N}</math> abundance of inorganic N compounds in aqueous samples using the SPINMAS measuring system</i>	
Apelt, B., Götz, A. & Russow, R. ....	4
<i>Factors controlling the performance of IRMS System</i>	
Bergs, S.M.M. ....	4
<i>Temperature effects on delta <math>^{13}\text{C}</math> of soil-respired <math>\text{CO}_2</math>: an incubation study with arctic soils</i>	
Biasi, C., Wanek, W., Rusalimova, O., Meyer, H., Ranefeld, C., Barsukov, P. & Richter, A. ....	5
<i>Climatic record in Maastrichtian continental deposits of Southern Carpathians</i>	
Bojar, A.-V., Grigorescu, G., & Csiki, Z. ....	6
<i>Middle Miocene seasonal temperature changes in the Styria Basin, Austria, as recorded by the isotopic composition of Pectinide and Brachiopod shells</i>	
Bojar, A.-V., Hiden, H., Fenninger, A. & Neubauer, F. ....	7
<i>Recharge area of mineral springs in Jezersko area (N. Slovenia)</i>	
Brencic, M. ....	8
<i>Stable isotope ratios and the evolution of acidulous solutions</i>	
Dietzel, M. & Kirchhoff, T. ....	10
<i>High temperature pyrolysis a new field for stable isotope analysis</i>	
Gehre, M. ....	11
<i><math>\delta^{15}\text{N}</math> in soil profiles of differently managed temperature forest stands</i>	
Hertenberger, G., Wanek, W. & Berger, T.W. ....	12
<i>Untersuchungen der Sauerstoffisotopie von Conodonten aus dem Oberkarbon</i>	
Horacek, M., Joachimiski, M.M. & Buggisch, W. ....	14
<i>Hydrogeochemical and isotope study of the upper part of the Kupa river drainage area</i>	
Kapelj, S., Biondic, B., Markovic, T. & Biondic, R. ....	15
<i>Water and anion transport conversion in highly heterogenous, recultivated open mining fields with very different carbon levels and pH values: multitrace lysimeter studies</i>	
Knappe, S., Russow, R., Rupp, H., Richter, W. & Meissner, R. ..	17
<i>Stable isotope analyses on Miocene molluscs from the East Alpine region: A proxy for paleoenvironmental reconstructions</i>	
Latal, C., Piller, W.E., Harzhauser, M., & Mandic, O. ....	18

<i>Use of <math>\delta^{15}\text{N}</math> and <math>\delta^{18}\text{O}</math> isotope ratios to identify sources of nitrate in the unsaturated zone</i>	
Leis, A. ....	19
<i>Geology, stable isotope and fluid inclusion studies of the serpentinised Kenticha ophiolites, South Eastern Ethiopia</i>	
Mogessie, A., Bojar, A.-V., Kaindl, R., Belete, K.H. & Solomon, T. ....	21
<i>The Austrian Network for Isotopes in Precipitation (ANIP)</i>	
Papesch, W. & Kralik, M. ....	23
<i>Isotope geothermometry within the southern Tauern Window</i>	
Rabitsch, R. Fritz H. ....	26
<i>Automatic determination of content and <math>^{15}\text{N}</math> abundance of total dissolved nitrogen in water samples and soil extracts by Analyser-Mass spectrometer coupling</i>	
Russow, R., Kupka, H.-J., & Götz, A. ....	28
<i>Sulphur isotope distribution at Bleiberg lead-zinc deposit and its genetic implication</i>	
Schroll, E. & Rantisch, G. ....	29
<i>New applications of hydrogen isotopes in geo- and biochemistry</i>	
Sharp, Z.D. ....	31
<i>The stable isotopic composition of DIC in karst groundwater: Methodology and applications</i>	
Spötl, Ch. ....	32
<i>Continuous-flow IRMS analysis of carbonates using the Gas Bench II</i>	
Spötl, Ch., Wimmer, M., Offenbacher, K.-H. & Tooth, A.F. ....	33
<i>Raingauge with implemented isotope-sampling application</i>	
Stadler, H. ....	34
<i>The <math>^{13}\text{C}/^{12}\text{C}</math> fraction upon the setting of calcium carbonate mortars</i>	
Usdowski, E. ....	36
<i>Stable carbon and nitrogen isotopes as tracers of eutrophication process in mountain lakes</i>	
Vreca, P. ....	37

## Automatic, sensitive determination of the $^{15}\text{N}$ abundance of inorganic N compounds in aqueous samples using the SPINMAS measuring system

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The  $^{15}\text{N}$  determination of tiny amounts of N in the form of nitrite and nitrate can be carried out quickly and precisely in a single step by chemically converting the nitrogen in these compounds selectively into nitrogen monoxide (NO), which is then introduced into a suitable mass spectrometer using helium as carrier gas (Russow, 1999). In order to use this method for automated routine analysis, a set-up was developed in which the chemical conversion of the inorganic nitrogen compounds nitrite and nitrate as well as ammonium and hydroxylamine to form the gases NO as well as  $\text{N}_2$  and  $\text{N}_2\text{O}$  takes place automatically under PC control (SPIN – Sample Preparation of Inorganic N compounds, Russow et al., 1999). The SPIN unit is connected to a GAM 400 quadrupole mass spectrometer (InProcess Instruments GmbH, Bremen) and an automatic 222 XL Liquid Handler (GILSON). The entire measuring process is PC-controlled thanks to measuring sequences being programmed. The material problems caused by the very aggressive reaction solutions call for the use of especially corrosion-resistant materials.

Each measurement takes no longer than 8 min. The concentration of the respective N compound can also be determined by the measuring system described here, if medium accuracy is sufficient.

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- Russow, R., Schmidt, G., Fischer, H., Nitschke, W., 1999: Verfahren und Vorrichtung zur automatischen  $^{15}\text{N}$ -Bestimmung von Ammonium-, Nitrit- und Nitrat-Stickstoff in wäßrigen Lösungen. Deutsches Patent 197 35 927, Deutsches Patent- und Markenamt, Munich, approved on 16 September 1999.

## Factors controlling the performance of IRMS Systems

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Since 1950 the focus in isotope ratio mass spectrometry (IRMS) is to enhance the precision of isotope ratio determination while reducing the sample size. However, the “classical” dual inlet technique limits the minimum sample size in the range of 5 bar- microliter.

With the introduction of continuous flow applications in 1988 for compound specific isotope analysis (CSIA) using GC combustion a major breakthrough for smallest sample sizes was achieved. This was followed by bulk stable isotope analysis (BSIA) coupling an elemental analyzer via an open split interface to the IRMS. This boost in overall sensitivity had to be balanced by accepting a lower precision due to the transient GC peaks used in continuous flow analysis when compared to dual inlet applications.

Today all major isotopes in organic samples (CHNOS) are available in continuous flow IRMS heavily reducing the workload of sample preparation. Subsequently the focus of CF-IRMS research moves towards reading very small isotope signatures in nature within total ranges of a few ‰, like for CO<sub>2</sub> and other trace gases in air and in water currents, seasonality in tree rings and calcareous materials.

The research and monitoring of such minor isotope signals requires improved sensitivity, stability and linearity of the IRMS as well as of the continuous flow interfaces providing sample preparation, transfer and automation.

For all these applications the long term accuracy and precision is one of the most crucial parameters combining high performance with robustness.

The factors controlling the performance of continuous flow IRMS systems will be demonstrated on basic tests. Improved routine performance will be shown on specific applications.

### **Temperature effects on delta 13C of soil-respired CO<sub>2</sub>: an incubation study with arctic soils**

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The delta 13C value of soils is mainly determined by the delta 13C value of the incoming litter and fractionation processes during organic matter decomposition. Thus, the C isotopic composition of soils and respired CO<sub>2</sub> varies with composition of SOM, activity of heterotrophs and soil depth.

Arctic ecosystems store vast amounts of the earth's soil carbon. In a global warming scenario this represents a ticking time bomb of potential increase of atmospheric CO<sub>2</sub>, one of the most important greenhouse gases. Although a loss of CO<sub>2</sub> from arctic ecosystems to the atmosphere has been reported recently, it is as yet unclear whether microorganisms are able to utilize the large pool of more stable, recalcitrant C compounds.

In order to analyze the effect of temperature on the biological sources of heterotrophs in arctic soils we measured respiration rates and delta13C values of respired CO<sub>2</sub> and soils incubated at 2, 12 and 24°C. We found a consistent increase in respiration rates across the entire temperature range in organic horizons. In mineral horizons, respiration rates increased between 2°C and 12°C, but were similar between 12°C and 24°C. The relationship between soil temperature and the stable C isotope ratio of CO<sub>2</sub> produced by heterotrophs was linear, with depleted delta13C values of CO<sub>2</sub> at higher temperatures relative to lower temperatures. Additionally, the delta13C values of CO<sub>2</sub> were highly correlated to the delta13C value of bulk soil at 24°C but not at 2 and



12°C. The study clearly demonstrates that temperature has a major impact on the isotopic composition of soil-respired CO<sub>2</sub> and, thus, on the substrate utilized by microorganisms. The results further suggest that, at higher temperatures, the SOM decomposed by microorganisms reflects the SOM pool of the soil. It seems that certain groups of soil microbes with preference for specific C compounds display characteristic temperature optima.

In summary, warming caused a shift in the carbon pool being mineralized and, thus, may play an important role in the ability of microorganisms to use different substrates.

## **Climatic record in the Maastrichtian continental deposits of Southern Carpathians**

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The Hateg basin is an intra-mountainous depression situated in the central western part of the South Carpathians. From Maastrichtian to Early Paleogene two different formations are known: the Densus-Ciula and the Sinpetru Formation, both of them representing mollase type deposits (Grigorescu et al., 1990; Grigorescu & Csiki, 2002). Both Formations are critical for determining paleoenvironment conditions and tectonic processes of the area during Maastrichtian. Therefore, facies analyses, petrographic and geochemical data (stable isotope analysis on calcretes) have been carried out along representative profiles within these two formations.

Maastrichtian climate was not as warm and equable as the overall climate of the Cretaceous. Worldwide, the isotopic record from foraminifers and bulk sediments indicate temperature fluctuation during Maastrichtian time. These fluctuations are represented by: 1) progressive cooling during the Lower Maastrichtian; 2) accelerated cooling during Early to Late Maastrichtian transition (70 to 71 Ma); 3) abrupt warming at the end of Cretaceous (c. 65.4 to 65.1 Ma) and subsequently temperature decrease during the last 100 k.y. of Maastrichtian.

Continental climates in mid-latitude were still warm, despite cooling trends. Because ocean temperature does not always reflect land temperatures, additional data are in process in order to constrain continental paleoclimatic conditions from the Hateg basin at that time.

The Sanpetru formation consists of cyclic sedimentation of alluvial sequences deposited in a braided meandering river sequence. Within the overbank deposits numerous horizons of fossil soils with carbonate concretions develop. For the channel deposits, paleocurrent directions indicate an E-W flow, parallel to the strike of the detachment fault which borders northward the Retezat metamorphic dome. The Retezat dome which rose at the end of the Cretaceous time (Bojar et al., 1998, Willingshofer, 2000) constituted most probably a natural barrier for the adjacent river systems. Paleomagnetic studies within the Sanpetru Formation (Sibisel Valley), show one site with normal polarity, while all the other sites distributed upstream for more than 4 km, have reverse polarity (Panaiotu & Panaiotu, 2002). The data suggest a lower Maastrichtian age for the profile (Chron 31, 68.7-71.0). Oxygen stable isotope composition of calcretes from a

4 km sequence (Sibisel Valley) vary systematically from 25 to 23 permil. The data are interpreted to indicate progressive cooling of the continental climate within this interval.

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## **Middle Miocene seasonal temperature changes in the Styrian Basin as recorded by the isotopic composition of Pectinide and Brachiopod shells**

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An important interval in the global climatic and cryospheric development of the Cenozoic was the early to middle Miocene from 17 to 12 Ma. The climatic optimum near the early/middle Miocene was followed by global cooling at around 14 Ma. This event was concomitant with the expansion of the east Antarctica ice sheet. Thus the middle Miocene is characterised by climatic changes which resulted in a rapid shift from relative high-latitude warmth to high-latitude refrigeration.

The mechanisms that may have been responsible for global cooling include: 1) changes in ocean circulation and thus heat transport; 2) CO<sub>2</sub> draw down related to topographic uplift; 3) long-term orbital forcing.

In this study molluscs and brachiopod shells have been used to evaluate paleoclimatic parameters for a shelf environment during the Middle Miocene times. The studied outcrop which is stratigraphically well documented (Friebe, 1990, 1991; Fritz and Hiden, 2001) belongs to the Miocene of the Styria basin, which was part of the Paratethys realm, a land-locked remnant sea which formed subsequent to the collision of Europe and Africa-derived microplates.

When molluscs grow, their shells become biogeochemical recorders of climatic and environmental condition during their lifetime. Previous studies have shown that the calcitic

shell of pectinides and of brachiopods are suitable for paleoclimatic reconstruction as they secrete their skeleton in oxygen isotopic equilibrium with seawater. As pectinides are supporting little salinity variation they are particularly suitable in reconstructing water paleo-temperatures.

A geochronological age from a tuff intercalation from the studied outcrop made possible to correlate the evaluated Middle Miocene temperatures and seasonal variations with the interpreted oceanographic changes at that time, which occurred world-wide. The  $^{39}\text{Ar}/^{40}\text{Ar}$  age of the fresh volcanic biotites from the tuff intercalations shows a value of  $14.2 \pm 0.1$  Ma

Moreover the  $\delta^{18}\text{O}$  profiles measured on molluscs have been used to evaluate growth rates and to determine the relationship between growth interruption and seasonal variation.

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## Recharge Area of mineral springs in Jezersko area (N Slovenia)

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The geological conditions in the Karavanke mountains are strongly related to Periadriatic lineament. In the geological sense the lineament divides Karavanke into northern and southern part. This tectonic structure of first order has also big influence on hydrogeology of the area. In the central part of Southern Karavanke, along Slovenian and Austrian border, extensive Košuta unit of dachstein carbonate rocks is present. In the Southern Karavanke mountains springs from carbonate rocks prevail, however in the central part of the mountain ridge some other interesting springs can be found, among them mineral springs are very important. Mineral springs are positioned in the area between Jezersko to Solčava in Slovenia and between Vellach and Eisenkappel in Austria. Heterogeneous chemical composition is significant for them and in mainly all springs free  $\text{CO}_2$  is present.

In the area of Zgornje and Spodnje Jezersko in Slovenia three springs that are very likely to be from mineral origin were studied. The first spring Ankova slatina is situated in a valley northern from farm Anko (Zgornje Jezersko). The altitude of the spring is 985 m above sea level. In the past the spring was captured by small water capture that is nowadays abandoned. Above the capture site two boreholes were drilled. Usually water flows out from boreholes under the pressure but it sometimes happens that water completely dries up. Due to the presence of  $\text{CO}_2$  gas water outflow from the borehole mouth pulsate. Few meters below boreholes the spring occurs. During the research period it was established that the spring is intermittent. The outflow from spring and boreholes varies between 0 to 8 l/s.

In the area of Spodnje Jezersko famous tufa quarry is positioned. The deposits of tufa are very big and thick. In the western part of the quarry the relatively strong spring is present. The altitude of the spring is 860 m above sea level. Water flows out from fissures in limestones that are likely to be of Carboniferous age. Bellow the spring very strong and fast precipitation of recent tufa is present. The capacity of spring was estimated to be between 26 and 45 l/s.

The third spring is situated bellow Virnikova planina on the left bank of the creek. The altitude of the spring is 1200 m above sea level. On the both side of the creek channel tufa deposit are present. On the basis of high specific conductivity values in the creek water the spring was found during the hydrogeological mapping. The capacity of the spring is between 2 to 4 l/s.

On the monthly basis during the investigation period 14 samples were taken for each spring, except for Ankova slatina that dries up two times. The rudimentary chemistry ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ) and  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  were measured. On the basis of field parameters and analytical results basic chemical equilibrium parameters were calculated by PHREEQE computer code. The mean altitude of spring recharge areas were calculated with altitude effect 0,2‰/100m obtained in the Košuta region that is in the vicinity of investigated area.

For Ankova slatina the average of  $\delta^{18}\text{O}$  value is  $-10,00$  ‰ with the amplitude of 0,64 ‰. From the chemical point water can be determined as  $\text{Ca}^{2+}$  -  $\text{Mg}^{2+}$  -  $\text{Na}^+$  -  $\text{HCO}_3^-$  -  $\text{SO}_4^{2-}$  type. The average of  $\delta^{13}\text{C}$  value is  $-6,12$  ‰ with the amplitude of 3,39 ‰. The calculated values of  $\text{pCO}_2$  in spring water are between  $-1,66$  and  $-0,77$  and saturation indexes of calcite are between  $-1,03$  and 0,38.

For spring near tufa quarry the average of  $\delta^{18}\text{O}$  value is  $-9,35$ ‰ with the amplitude of 0,66 ‰. From the chemical point water can be determined as  $\text{Ca}^{2+}$  -  $\text{Mg}^{2+}$  -  $\text{Na}^+$  -  $\text{HCO}_3^-$  -  $\text{SO}_4^{2-}$  type. The average of  $\delta^{13}\text{C}$  value is  $-3,88$  ‰ with the amplitude of 5,15 ‰. The calculated values of  $\text{pCO}_2$  in spring water are between  $-2,45$  and  $-1,96$  and saturation indexes of calcite are between 0,16 and 0,74.

For spring bellow Virnikova planina the average of  $\delta^{18}\text{O}$  value is  $-9,75$ ‰ with the amplitude of 1,34 ‰. From the chemical point water can be determined as  $\text{Ca}^{2+}$  -  $\text{Mg}^{2+}$  -  $\text{Na}^+$  -  $\text{SO}_4^{2-}$  -  $\text{HCO}_3^-$  type. The average of  $\delta^{13}\text{C}$  value is  $-6,56$  ‰ with the amplitude of 5,01 ‰. The calculated values of  $\text{pCO}_2$  in spring water are between  $-0,29$  and  $-1,08$  and saturation indexes of calcite are between 0,08 and 0,52.

On the basis of hydrogeological mapping as well as hydrogeochemical and isotopic investigations it was determined that the recharge area of Ankova slatina spring is in the Devonian limestone lenses intercalated inside of Hochwipfel beds of Carboniferous age. The recharge area of tufa spring is surprisingly low in the altitude. It was determined that recharge area is in the slope materials and in the near vicinity of the spring and not in the Virnikov grintavec that is composed of Devonian limestones as we expect from the structural interpretation. The recharge area of spring below Virnikova planina is in the gypsum beds in the near vicinity.

It remains open what are the geochemical processes inside of tufa spring aquifer. From  $\delta^{13}\text{C}$  data it is clear that prevailing mechanism is dissolution of limestones but it is not clear why so large deposit of tufa appear only in this place and not on the others. We suppose that additional

source of CO<sub>2</sub> mixing with shallow water is the reason for this and that this source is similar as for other springs in the border region of Jezersko.

## Stable isotope ratios and the evolution of acidulous solutions

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In the present study 35 well and spring waters were sampled in the North of Hesse (Germany) and analysed with respect to the chemical compositions and stable isotope ratios ( $\delta^{13}\text{C}$ ,  $\delta^{34}\text{S}$ ,  $\delta\text{D}$ ,  $\delta^{18}\text{O}$ ). The solutions are used as drinking water, bottled mineral water or for medical applications. Several solutions are characterized by high concentrations of dissolved components. But most conspicuous are acidulous solutions with a high content of dissolved inorganic carbon (DIC). Although, the evolution of natural solutions is extensively studied significant gaps exist with respect to such acidulous solutions. The aim of the present study is to decipher the evolution of the solutions with respect to the sources and requirements of the catchment area.

In the acidulous solutions the source of the high amounts of dissolved inorganic carbon (DIC) and great proportions of carbonic acid is mostly vague. No recent magmatic activities are observed in the study area, but Tertiary basaltic rocks appear. If Tertiary basaltic magmas might be a primary source, CO<sub>2</sub> has to be stored until recent times within the underlying rocks and sediments.

The results show that the evolution of the solutions is characterized by the precipitation of meteoric water, the uptake of CO<sub>2</sub> and a subsequent dissolution of solids of the catchment area. Three types of solutions may be distinguished according to the chemical composition:

- 1: water with low concentration of dissolved ions (LOW)
- 2: brines dominated by Na<sup>+</sup> and Cl<sup>-</sup> (BRI)
- 3: acidulous solutions with high concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and DIC (CO<sub>2</sub>)

The dissolution of carbonate minerals, essential calcite and dolomite, is closely related to the uptake of gaseous CO<sub>2</sub>. The high P<sub>CO<sub>2</sub></sub>-values of the CO<sub>2</sub> type of about 1 atm requires a huge reservoir of CO<sub>2</sub>-gas, which cannot be provided by soil atmospheres. From the measured  $\delta^{13}\text{C}_{\text{DIC}}$ -values the <sup>13</sup>C/<sup>12</sup>C-signatures of the primary CO<sub>2</sub> are obtained. The respective  $\delta^{13}\text{C}_{\text{CO}_2}$ -values of the CO<sub>2</sub> type are either in the range of about -10 ‰ or lay between 0.8 and 3.7 ‰. The values of these two groups barely depend on the boundary conditions for the dissolution of carbonate (open and closed system with respect to the CO<sub>2</sub>-gas).

The <sup>13</sup>C/<sup>12</sup>C-signatures of CO<sub>2</sub> from magmatic origin (-6 and -3 ‰) lay between the  $\delta^{13}\text{C}_{\text{CO}_2}$ -values of above two groups. Higher and lower values may be explained by a <sup>13</sup>C/<sup>12</sup>C-

fractionation due to CO<sub>2</sub>-diffusion through micropores, faults, and interfaces of solids from a CO<sub>2</sub>-reservoir. Considering Tertiary basalts, but no recent magmatic activities in the study area, CO<sub>2</sub> may be referred to a subsequent liberation of CO<sub>2</sub>-gas from respective reservoirs of the underlying rocks of the study area, which is primarily gained from Tertiary basaltic magma. An accumulation of primary magmatic CO<sub>2</sub> may occur in reservoir rocks such as sandstones, which are secluded e.g. by clay-rich horizons of the Röt formation (Triassic) or by storage in marine evaporites. The high CO<sub>2</sub> content stimulates the ascent of the solutions until the earth surface is reached by an extensive formation of a gas-solution mixture.

High concentrations of silicic acid and an excess of dissolved sodium versus that derived from the dissolution of halite exhibit an intensive weathering of silicates. This appears especially in the CO<sub>2</sub> type and is also documented by the occurrence of kaolinite layers at the respective sites. Dissolved sulfate is mostly obtained from the dissolution of gypsum or anhydrite of the Zechstein formation. The stable sulfur isotope ratios at low SO<sub>4</sub><sup>2-</sup> concentrations show that sulfur is also gained by the oxidation of sulfides e.g. pyrite in shales. The presence of Sr<sup>2+</sup> and Ba<sup>2+</sup> reflects the dissolution of carbonate minerals, whereas iron and manganese is mostly controlled by precipitation of respective oxide/hydroxides as the solutions reach the earth surface.

The evolution of LOW and BRI type solutions is quite similar to that of the CO<sub>2</sub> type. However, a potential source of CO<sub>2</sub> for the dissolution of carbonate is mainly soil-CO<sub>2</sub>, and the BRI type solutions contain additional amounts of dissolved marine evaporates, especially halite.

## High Temperature Pyrolyses - a new field for isotope analyses

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A new method for the automated sample conversion and on-line oxygen isotope ratio ( $\delta^{18}\text{O}$ ) determination for organic and inorganic substances was developed a few years before. The samples are pyrolytically decomposed at 1400-1450°C (HTP) in presence of a nickel/ carbon powder (mixed, 10/90).

With the presented system solid and liquid samples are measurable. Organic as well as inorganic samples such as cellulose, nitrates, sulphates and phosphates of 50 - 100  $\mu\text{g O}$  can be analyzed for their  $\delta^{18}\text{O}$  values with a standard deviation of usually better than 0.3 ‰. Additionally, hydrogen isotopic ratios (standard deviation better than 3 ‰), carbon isotopic ratios of organic substances and nitrogen isotopic ratios of inorganic nitrogenous compounds are available in the same system.

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## $\delta^{15}\text{N}$ in soil profiles of differently managed temperate forest stands

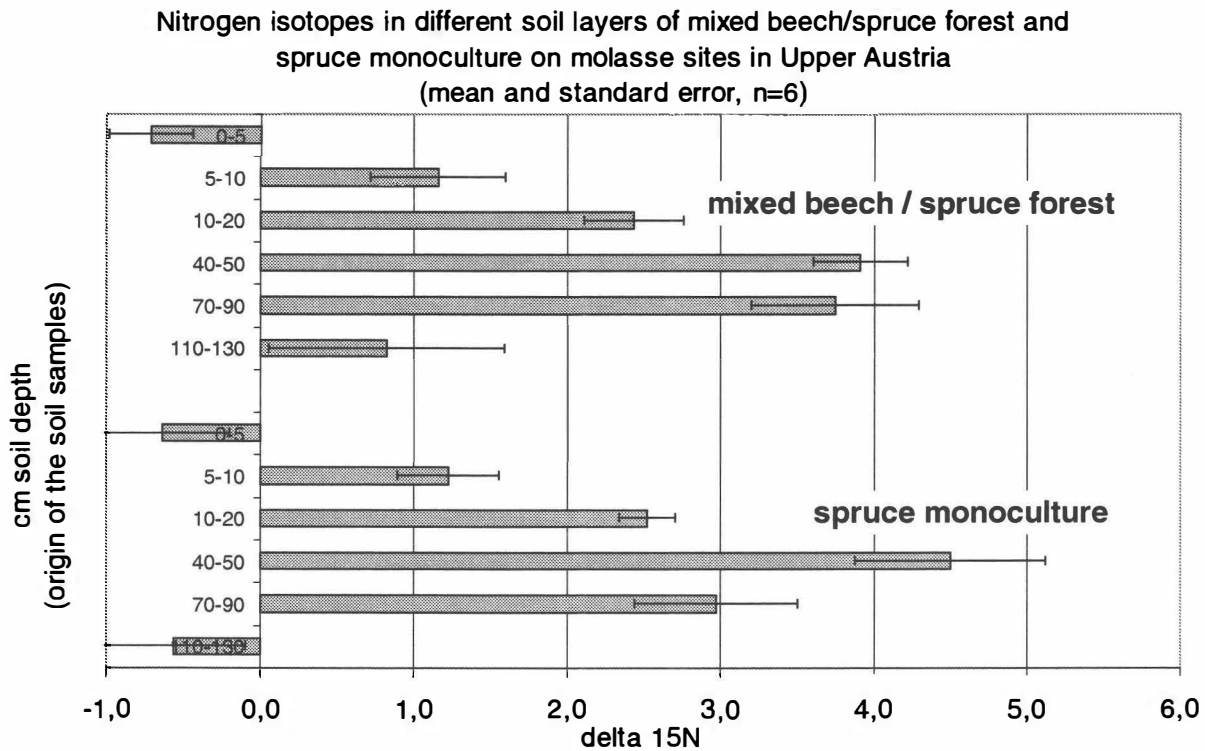
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Since the 19<sup>th</sup> century it became increasingly popular to plant Norway spruce (*Picea abies*) outside its climatic range. In areas, where the natural climax vegetation would comprise mixed broadleaf forests with high abundance of beech (*Fagus sylvestris*), large areas are covered by spruce monocultures now.

This work is part of a project, that aims to characterize and compare spruce monocultures with mixed beech/spruce forests in close-by locations, where similar geology and climate can be expected. The goals of the project are i) the evaluation of the impact of forest management (mixed forest vs. monoculture) on nutrient cycling (improvement of the theoretical basis), ii) modelling and predicting effects of forest management on soil processes and nutrient fluxes, and iii) distinguishing pathways of nutrient turnover in these two types of forest management by means of natural abundance measurements of stable isotopes (C, N, O, Sr). On one hand, the sampling locations were chosen in the geological Flysh zone (sandstone formation) of Upper and Lower Austria. The natural forest vegetation of this area is classified as *Asperulo odoratae-Fagetum*. Secondly, locations were selected in the Molasse region, north of the Alps in the so-called Kobernausser Forest, Upper Austria. Natural forest vegetation is *Luzulo nemorosae-Fagetum*. The Molasse sites are characterized by lower pHs (2,6 – 3,4;  $\text{CaCl}_2$ ) compared to the Flysh sites (3,1 – 5,5); these sites are more sandy and exhibit a lower nutrient availability. All sites include forests of different stand age (sapling, pole, mature).

On Flysh, spruce monocultures caused distinct top soil acidification due to sequestration of basic cations in the canopy and O-horizon. At low pH (Molasse sites) this effect was not visible which is most likely not only the consequence of the logarithmic pH-scale but also the consequence of low base content, which does not allow for distribution of large amounts of base cations. Soil profiles were taken to measure the vertical distribution of stable nitrogen isotopes. In the upper soil layers (0-5 cm), negative  $\delta^{15}\text{N}$  values indicate that depleted plant material was deposited and incorporated after decomposition into the topsoil.  $^{15}\text{N}$  is discriminated in several steps during mineralization of organic material and uptake and assimilation of mineral N by plants, corresponding to commonly  $^{15}\text{N}$ -depleted plant litter.



On Flysh, no major differences in soil  $\delta^{15}\text{N}$  values could be found between mixed forests and monocultures. On Molasse, however, there were marked differences between both types of forest management (see Figure): monoculture caused more positive  $\delta^{15}\text{N}$  values in middle soil strata (40-70 cm depth), but much lower or even negative  $\delta^{15}\text{N}$  values in deeper soil layers (below 100 cm). The high  $\delta^{15}\text{N}$  values of middle soil layers could be due to the strong  $^{15}\text{N}$  discrimination during ammonium oxidation to nitrate (nitrification), resulting in  $^{15}\text{N}$ -depleted nitrate and the remaining ammonium pool becoming  $^{15}\text{N}$ -enriched. Nitrate can be further metabolized under wet conditions into gaseous nitrogen (oxides) by denitrifying microorganisms, leaving the soil thereafter. Denitrification also exhibits a significant isotope effect. On the other hand, nitrate may have been leached into deeper soil layers, where consequently  $\delta^{15}\text{N}$  values became more negative if nitrate was biologically or physico-chemically retained from percolating soil solution. However, it remains to be elucidated if the  $^{15}\text{N}$ -depleted deep soil layers, which were only detected in spruce monocultures but not in mixed forests of the Molasse zone, were related to nitrate loss.

In conclusion, the nitrogen isotope measurements clearly indicated that on the Molasse sites, spruce monoculture resulted in distinct changes in the soil N dynamics. On Flysh sites strong shifts were observed only in soil pH, but not in N isotope composition.



## Untersuchung der Sauerstoffisotopie von Conodonten aus dem Oberkarbon

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### Einleitung

Die Analyse von Sauerstoffisotopen stellt für alle geologischen Zeiträume ein zentrales Werkzeug zur Bestimmung von Temperatur und Salinität des Meerwassers dar und ermöglicht darüber hinaus Rückschlüsse auf das Ausmaß von Vereisungen in den hohen Breiten. Zur Erfassung von  $\delta^{18}\text{O}$ -Variationen im Paläozoikum wurde bisher vor allem auf Brachiopodenschalen zurückgegriffen (z.B. Veizer et al. 1999), da diese aufgrund ihrer primären Zusammensetzung (LMC) vergleichsweise wenig empfindlich gegenüber diagenetischen Überprägungen sind. Ein noch höheres Erhaltungspotential der primären Isotopensignatur ist aus chemisch-strukturellen Gründen sowie auf der Basis bereits vorliegender Untersuchungen für Conodontenapatit anzunehmen. Im Gegensatz zu Brachiopoden treten Conodonten in paläozoischen Sedimenten relativ häufig und weitgehend unabhängig von der Fazies und der geographischen Breite auf. Für die Analyse der Sauerstoffisotopie von Conodontenapatit wird nur der in der Phosphatgruppe gebundene Sauerstoff verwendet. Durch den Einsatz eines Hochtemperatur-Reduktionsofens (TC-EA) können relativ kleine Conodontenproben ( $\leq 1$  mg) untersucht werden.

### Ergebnisse und Schlußfolgerung

Oberkarbonische Conodonten wurden aus den Zyklolithemen des Mittleren Westens der USA untersucht, welche als Resultat glaziogener Meeresspiegelschwankungen interpretiert werden. Ein typischer Zyklus beginnt mit einem transgressiven Karbonathorizont, gefolgt von Grau- und/oder Schwarzschiefern, welche jeweils den Meeresspiegelhöchststand während des Interglazials widerspiegeln. Darüber folgt ein regressiver Karbonathorizont, der von kontinentalen Sedimenten überlagert werden kann, die den Meeresspiegelniedrigstand während des Glazials repräsentieren. Die analysierten Conodonten stammen aus den Karbonathorizonten und den Grau- sowie Schwarzschieferlagen. Die Analysen ergeben  $\delta^{18}\text{O}_{\text{Apatit}}$ -Werte zwischen 19,7 und 22,4‰ V-SMOW. Conodonten aus den Grauschiefern erbrachten  $\delta^{18}\text{O}_{\text{Apatit}}$ -Werte von 20,3 bis 21,4‰. Nimmt man für Meerwasser einen  $\delta^{18}\text{O}$ -Wert von 0‰ V-SMOW an, so errechnen sich Paläotemperaturen von 19,4 bis 24,1° C. Auf  $\delta^{18}\text{O}$ -Analysen an Brachiopodenschalen aus den Grauschiefern (Mii et al. 1999) basierende Berechnungen führen zu ähnlichen Temperaturen, allerdings mit wesentlich größerer Variationsbreite.

Innerhalb eines Glazialzyklus werden Unterschiede im  $\delta^{18}\text{O}_{\text{Apatit}}$  von bis zu 2‰ gemessen. Diese Variation wird überwiegend durch den „Eiseffekt“ und untergeordnet durch Temperaturschwankungen erklärt. Die Größe der Schwankungsbreite der Sauerstoffisotopenwerte innerhalb eines Zyklus ist vergleichbar mit der Änderung im  $\delta^{18}\text{O}$  während der pleistozänen Vereisungen (Schrag et al. 1996). Da jedoch im Falle der oberkarbonischen Zyklitheme die glazialen Maxima durch kontinentale Sedimente repräsentiert sind und somit keine Isotopenwerte vorliegen, ist anzunehmen, dass die Vereisungen und damit auch die Meeresspiegelschwankungen im Oberkarbon deutlich stärker ausgeprägt waren als während des Pleistozäns.

Die  $\delta^{18}\text{O}_{\text{Apatit}}$ -Kurve für Conodonten aus den Schwarzschiefern zeigt im Verlauf des Oberkarbons nach zunächst höheren Werten im Desmoinesian und Missourian ein Minimum im

frühen und anschließend wiederum höhere  $\delta^{18}\text{O}_{\text{Apatit}}$ -Werte im späten Virgilian. Ein Vergleich der Daten aus den Kansas-Zyklen mit den  $\delta^{18}\text{O}_{\text{Apatit}}$ -Werten von Conodonten aus dem Moskauer Becken zeigt einen deutlichen Unterschied im  $\delta^{18}\text{O}_{\text{Apatit}}$  zwischen beiden Lokalisationen mit teilweise signifikant schwereren Werten im Moskauer Becken. Dies kann eventuell mit dem Einfluss kalter Meeresströmungen erklärt werden.

## **Hydrochemical and Isotope Study of the Upper Part of the Kupa River Drainage Area - Croatia**

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Upper part of the Kupa river drainage area is typical karst terrain developed on part of the Dinaric carbonate platform. The terrain is made of rocks from under layered Palaeozoic deposits; Mesozoic and Tertiary carbonate rocks, limestones and dolomites. The complex structural relations were formed as a consequence of subduction of the African under the European plate in the combination with disintegration of the lower deposits of the carbonate platform during the younger geological period. Results are elements of overthrust tectonics that have special roles in shallow zones important for underground water flow paths.

Main characteristics of the region is a presence of the large water dividing zones between the Adriatic sea and the Black sea catchments, which is situated in the mountain area of the Risnjak massive. That area is very rich in precipitation what together with lithologic and structural characteristics cause the presence of the large groundwater reserves and few large karst springs in the Kupa river drainage area: Čabranka spring, Kupa spring, Zamost, Velika and Mala Belica, Kupica spring and Zeleni Vir spring. Also, on the other side of the mountain massive, in the Adriatic Sea catchment, is a large perennial spring of the Rječina river outflow. That spring is located at the same altitude as the spring of Kupa river. But, annual precipitation regime with long summer dry period has influence on high groundwater recharges amplitude of those springs.

Performed hydrogeological and isotopic studies have regional character to recognise the origin of spring waters regarding to recharge area of particular springs. During the 1997, 1998 and 1999, in different annual vegetation and hydrologic conditions were performed spring water sampling for hydrochemical and isotopic analysis and measurements of temperature, conductivity, pH and TDS on mentioned large springs and on the Rječina spring (Adriatic sea catchments). Hydrogeochemical facies of the study area mainly vary from Ca-HCO<sub>3</sub>, CaMg-HCO<sub>3</sub> to MgCa-HCO<sub>3</sub> main ionic composition as a result of dissolution of the carbonate rocks, limestones and dolomites. The presence of Palaeozoic clastic deposits in the drainage area of some springs causes increasing of magnesium, some heavy metals, non-metals, transition elements, actinide and lanthanide elements (Kupica spring, Zeleni Vir).

Usually, the stable isotope  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  ratios are influenced by temperature and pressure (altitude effect) prevailing during recharge as well as a consequence of the distance from the sea (continental effect). Therefore in our case, study spring waters become enriched towards to the sea (Figure 1). Also, established variations of the stable isotope content, which

have been observed, appear to result from local seasonal influx of precipitation into the particular drainage system.

Distribution of stable isotopes and tritium in the spring waters suggest that in that region, were distinguished a four different sub-catchments. The first one is the group of Rječina, Kupa and Kupari springs, which have, practically unique catchments area, situated in the Risnjak Mountain. The second group of the springs, Zamost, V. Belica, M. Belica and Kupica have the similar catchments situated in the middle part of the study area and they form tributaries of the north bank of the Kupa river upper part. Čabranka spring and Zeleni Vir spring drainage areas cover the larger part of terrains which borders are situated far from the springs. The Čabranka catchments is in the Slovenian mountains at higher altitudes while Zeleni Vir catchments lay deeply in the inland part of the Gorski Kotar region.

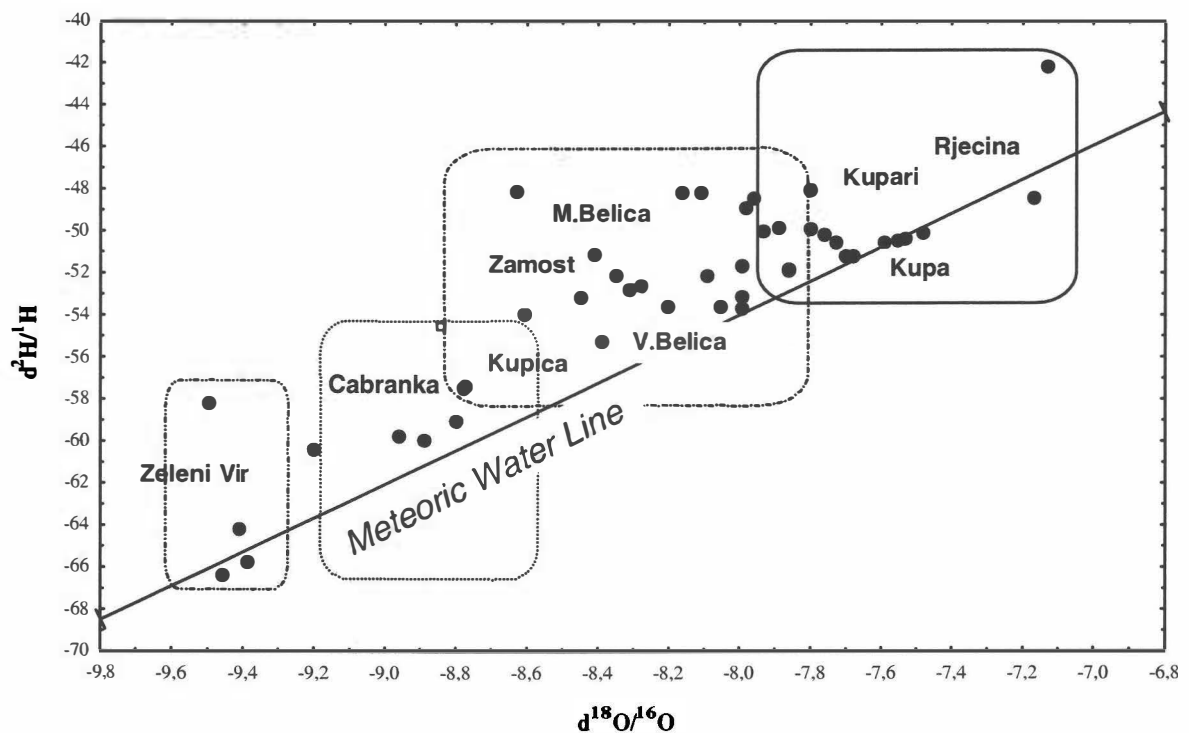


Figure 1. Stable isotope ratio  $\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$  in spring waters of the Kupa river drainage area

Tritium activity of the spring waters corresponds with tritium activity of the recent precipitation of the study area. Highest activities were detected during the spring hydrological maximum, while during the extremely dry summers at some springs outflow groundwaters with tritium activity below detected limits. It has shown that deep underground of the upper part of the Kupa river drainage area contains groundwater with relatively long mean residence time. Such circumstances reflect the high water potential suitable for the water supply, storage in the deep karstified underground of the study area.

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### **Water and anion transport conversion in highly heterogeneous, recultivated open mining fields with very different carbon levels and pH values: multitracer lysimeter studies**

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The movement of water and the related transport of bromide and nitrate were studied in soil used for agriculture from an open mining field near Espenhain/Saxony by means of tracer techniques (D<sub>2</sub>O, [<sup>15</sup>N]nitrate, Br tracer) in monolithic and reconstructed lysimeters. Despite the similarly high level of seepage, the breakthrough volumes were very different, namely 82 l (L 12/1), 147 l (L 12/3) and 30 l (L124) for D<sub>2</sub>O. After the experiments had continued for 36 months, the recovery standardised for 600 l seepage of bromide and deuterium respectively were calculated to be 22% and 39% for L 12/1, 15% and 19% for L 12/3, and 4% and 46% for L 124. The differences in the seepage recovery of the reactive tracer [<sup>15</sup>N] nitrate were even greater for the three lysimeters, namely 3,7% (L 12/1), 0,7 % (L 12/3) and 1,5 % (L 124).

The findings regarding the transport of D<sub>2</sub>O indicate that water transport in the soil monolith of L 12/1 is mainly determined by preferential flow, whereas in L 12/3 and L 124 conditions are largely shaped by piston flow and delays corresponding to the cascade model. Taking into account plant uptake, the sometimes much lower recovery of bromide compared to D<sub>2</sub>O in lysimeter L 12/1 and especially in L 124 could be attributed to reactions resulting from the strong acidic conditions (pH 1.5–2.0) in the soil water of these lysimeters, the extremely high sulphate levels (over 4%) and/or the reactive carbon from lignite residues. Under these conditions, the bromide appears to undergo temporary chemisorption and possibly even chemical conversion. The seepage recovery of [<sup>15</sup>N] nitrate in the open mining field soil is significantly lower than in natural soils. [<sup>15</sup>N] nitrate recovery in 600 l seepage of 3,7% (L 12/1), 0,7% (L 12/3) and 1,5% (L 124) are probably caused by nitrate decomposition via denitrification under the partly extreme soil conditions.

## Stable Isotope Analyses on Miocene Molluscs from the East Alpine Region: A Proxy for Paleoenvironmental Reconstructions

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In the framework of the FWF-project cluster “Changes in Eastern Alpine Miocene Ecosystems and their Geodynamic Control” a cooperative study within the projects “Stable isotopes and changing Miocene palaeoenvironments in the East Alpine region” and “Evolution versus migration: Changes in Austrian Miocene molluscan paleocommunities” was performed.

The Miocene of the East Alpine region is characterised by distinct changes in fossil communities. These bio-events can be detected in nearly all groups of organisms. Changes of environmental parameters, like temperature, water chemistry, salinity as well as alkalinity, water circulation, water depth, food supply etc., are considered as the main driving forces for such bio-events, and may reflect local or regional conditions, or even be related to global changes. The East Alpine region is an area well suited for studying these changes because of its richness in fossils and its differences in fossil biotopes. As most of the parameters cannot be reconstructed directly, the method of analysing stable isotopes in carbonate shells is a powerful tool in paleoecology. Oxygen isotope data are used as proxies for water temperature and salinity, and carbon isotope data as proxies for paleosalinities, reconstruction of water masses and productivity.

Molluscs are well suited for stable isotope analyses as it is supposed that molluscs precipitate their shells in isotopic equilibrium. Especially gastropods and bivalves were chosen for this study. Gastropod shells are built of metastable aragonite, therefore the ability of shell preservation is strongly reduced but diagenetic overprinting can be easily detected. If aragonitic shell material and primary aragonite crystals can be recognized, stable isotope signals can be considered as primary. Therefore the shells used for stable isotope analyses are examined for diagenetic overprinting by x-ray diffraction and electron microscopy. Bivalves are also often used for stable isotope analyses, although they are aragonitic or calcitic and some have mixed layered shells. Within super-families their mineralogy and shell structure remains constant. In this study we used shells of pectinids, which are mainly calcitic. Thin sections of the shells were cut for analysing the internal structure. From each gastropod as well as pectinid shell, several samples were drilled.

Various gastropod species (*Granulolabium* sp., *Ocenebra* sp. and *Turritella* sp.) with different life habitats of different localities were used for this study. Variations between different time slices can only be detected within one species in a constant environment. Many localities are also influenced by freshwater which affect the isotope signals of shells. Data from different time slices (Eggenburgium, Ottnangian, Karpatium, Badenium, Sarmatium) and localities will be presented. Special focus is given to shells from localities with constant marine conditions and from species which prefer fully marine environments.

Within the Central Paratethys the Early Badenian is a time of marine transgression. The location of Grund (Lower Badenian) represents a normal marine environment without any significant freshwater influx. It is located in the Molassezone north of the Danube. Mammal faunas indicate a biostratigraphic correlation with middle-late MN5, marine faunas indicate the Lower Lagenid Zone, and magnetostratigraphy shows normal polarity. Therefore the estimated

correlation from magnetostratigraphy is with chron C5Cn1 (Daxner-Höck, 2001). From Grund different gastropod species were measured, especially shells of *Ocenebra credneri* and *Turritella* sp. Additionally, stable isotope data of pectinid shells of *Pecten subarcuatus* and *Crassodoma multistriata* were established. Oxygen data from the bivalve shells vary within 3‰, but do not show the same maximum and minimum values. Especially the carbon isotope data exhibit some differences between the shells of *Pecten subarcuatus* and *Crassodoma multistriata*. Generally, *Turritella* sp. shows the highest oxygen and carbon values, and the values of *Ocenebra credneri* are similar to *Crassodoma multistriata*. These data can be compared with other Badenian localities and may help to understand local environmental differences.

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## Use of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotope ratios to identify sources of nitrate in the unsaturated zone.

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Anthropogenic nitrogen inputs have led during the last three decades to increased loads of nitrate in ground water in many regions of Europe.

Also, in the Leibnitzer Field in the south part of Styria a strong increase of the nitrate concentrations in the ground water could be observed during the past decades. The Leibnitzer Feld aquifer is extremely susceptible to surface derived contamination because of its largely unconfined nature and highly permeable sands and gravels. The source of nitrate contamination in the aquifer is attributed to local, long term agricultural land use practices such as spreading big amounts of liquid manure (mainly pig manure) above the soils. To determine what action should be taken to reduce nitrate contamination of the groundwater, it is important to identifying the source(s) and the origin of nitrate in unsaturated zone.

Several microbiological and isotope investigations were carried out in the unsaturated zone to assess these processes. In the result of the microbiological investigations, it was possible to show that nitrifying bacteria are located in the whole profile of the unsaturated zone. But the intensity of the nitrification process decreased under the top soil layer strongly. However, also soil samples from a depth of 1.8m have shown still a considerable potential nitrification rate. This conflicts with the widespread idea that nitrification in soils is limited to the root zone only.

To verify these results with a independent second method we have used  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  isotope ratios of nitrate in percolation water samples. The percolation water was sampled repeatedly at the outflows of the suction plates and cups between May 1998 and April 1999 for determining concentrations,  $\delta^{15}\text{N}$  values, and  $\delta^{18}\text{O}$  values of nitrate. The application of the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$

isotope ratios is a useful technique to help identify sources and fate of nitrate. Due to the large oxygen isotopic difference between nitrates produced in the atmosphere and those produced by microbial processes in the soil (nitrification), the oxygen isotopes in nitrate are particularly practical for the identification of nitrate from fertilizer (Amberger and Schmidt, 1987) and atmospheric nitrates (Kendall et al., 1998). In addition, the oxygen isotopes can be used to identify processes, such as denitrification, that may change the concentration and isotopic composition of nitrate (Böttcher et al., 1990). Beside this the isotope ratios in the unsaturated zone will be also influenced by mixing. In our case, we had two different main sources of nitrate, atmospheric nitrate (Nitrate Source A) and nitrate from nitrification in soil (Nitrate Source B). During nitrification in soil the value of  $\delta^{18}\text{O}$  in resulting nitrate normally decrease because the amount of isotopically heavy atmospheric nitrates decrease. Assuming also that in all depths of the unsaturated zone nitrification take place, the value of  $^{18}\text{O}$  in nitrate must decrease with increasing depth, because the amount of atmospheric nitrates is decreasing. The samples collected during our study are plotted in Figure 1. The mean isotopic composition of atmospheric nitrate (Source A) was determined with 9.1‰ for  $\delta^{15}\text{N}$  and 37‰ for  $\delta^{18}\text{O}$ . The outflow of the suction plates and cups in the unsaturated zone ranged from approximately 2‰ to 12.6‰ for  $\delta^{15}\text{N}$  and 2.2‰ to 19.1‰ for  $\delta^{18}\text{O}$ .

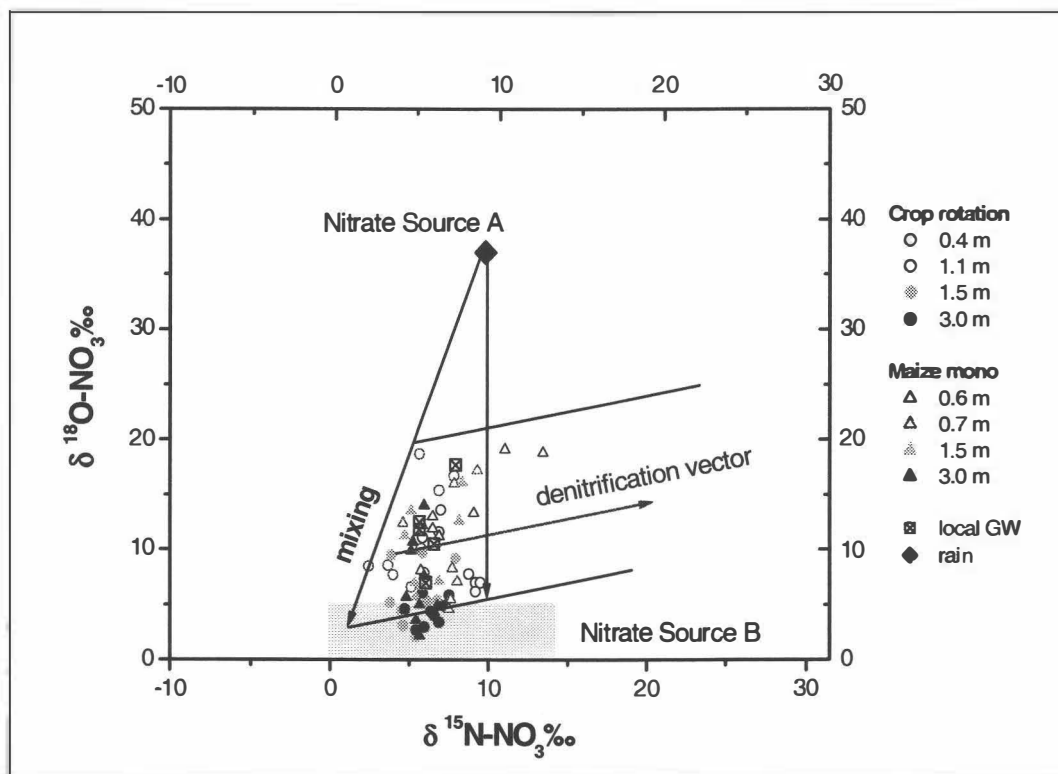


Figure 1: Mixing process actually found

The small transparent symbols indicate nitrate isotope ratios of percolation water from the upper part of the unsaturated zone. The small solid symbols show the isotope ratios of nitrate in the underlying gravel zone. The lightest  $\delta^{18}\text{O}$  values were found on the deepest sampling points in the unsaturated zone. This indicates clearly that nitrification processes take place in this soil zone. It shows also very well, that nitrate produced by nitrification can be identified by  $\delta^{18}\text{O}$  of nitrate. The isotopic composition of nitrate is not only a powerful tool to determine its

sources, but can also provide hints about nitrogen transformation processes such as nitrification and denitrification in the unsaturated zone.

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## **Geology, stable isotope and fluid inclusion studies of the serpentinised Kenticha ophiolites, south eastern Ethiopia**

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The Adola granite-greenstone terrane covers an area of approximately 5000 km<sup>2</sup> in southern Ethiopia. It is characterised by two linear, closely spaced, N-S trending belts of metamorphosed supracrustal rocks, namely the Megado volcanosedimentary belt in the west and Kenticha ultramafic belt in the east. The former consists of ultramafic and tholeiitic basic volcanics and intrusives which are intercalated with sediments made up predominantly of arkoses, feldspathic quartzites, quartzites and pelites together with subordinate polymictic conglomerates and graywackes. In contrast, the Kenticha belt is dominated by ultramafic rocks, with subordinate amphibolites, biotite schists, minor graphitic schists and marbles (Gilboy 1970; Chater 1971, Billay et al., 1997). The two volcanosedimentary belts are surrounded and separated by a gneissic terrane which comprises para- and orthogneisses with subordinate muscovite-quartz schists, staurolite-garnet-biotite schists, impure marbles and amphibolites. The Kenticha belt has been affected by amphibolite-facies metamorphism of the staurolite-almandine and kyanite-almandine-muscovite subfacies. The ultramafic rocks generally trend north-south (7-8 km long and up to 1 km wide) and occur as hill- and ridge-forming bodies extending for about 30 km. They occupy higher structural levels in the granite – greenstone succession. The Kenticha serpentinite is composed of more than 70 vol.% serpentine, olivine, pyroxene, and opaque (chromite and magnetite). Mesh texture of chrysotile is common with minor antigorite. Olivine and pyroxene relicts imply a peridotitic protolith. Based on field relations, geochemical data and PGE over chondrite normalised plots, the Kenticha ultramafic rocks are considered to be ophiolites. Associated with these ophiolites are also complex pegmatites containing amazonites, columbo-tantalite among others. Within the granite-pegmatite system late-magmatic alterations (albitization, sericitization, kaolinization) and development of amazonite and microcline are widely developed.



The Kenticha ultramafic rocks are completely serpentinised and the nature of the fluid involved in the serpentinisation process is not known. When fluids interact with ultramafic rocks serpentine-group minerals and subordinate chlorite, talc, tremolite, brucite, magnesite and magnetite form. The temperatures, isotopic composition of the fluids and water/rock ratios during serpentinisation are recorded in the oxygen and hydrogen isotopic composition of the alteration products (e.g. Barnes and O'Neil, 1969; Wener and Taylor, 1973; 1974; Gregory and Taylor, 1981; Kyser et al., 1999).

Fluid inclusions in calcite within the serpentinised ultramafics are relatively small (7-15  $\mu\text{m}$ ), rounded to irregular and occur in intergranular cluster and intragranular trails. Many of them are monophasic at room temperature which is attributed to the metastable absence of the vapour bubble. The fraction of the liquid phase, when the inclusions contain a vapour and a liquid, is constant around 0.9. On reheating after cooling below  $-80^\circ\text{C}$ , first melting is observed from  $-52^\circ$  to  $44^\circ\text{C}$ , which may indicate either eutectic melting in the binary  $\text{H}_2\text{O}-\text{CaCl}_2$  or the ternary  $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$  system. Since melting of hydrohalite could not be observed we calculated inclusion properties assuming the binary  $\text{H}_2\text{O}-\text{CaCl}_2$  system. Ice melting was observed between  $-30$  and  $-20^\circ\text{C}$  from which salinities between 24 and 20 wt% salt can be derived. The inclusions presumably trapped a homogeneous fluid, indicated by the uniform fraction of the liquid phase. Homogenization temperatures ranging from  $100$  to  $140^\circ\text{C}$  are regarded as minimum temperatures for the calcite host formation.

Stable isotopic composition from the Kenticha ophiolite have been measured in order to define the nature of serpentinisation processes occurring in this region.

Stable isotope compositions have been determined from serpentines of a 50 meter deep borehole of the Kenticha ophiolite (drill-core 5/5).

$\delta\text{D}$ ,  $\delta^{18}\text{O}$  values ( $-99$  to  $-85$  and  $5.3$  to  $10.1$ , respectively) and mineralogy indicate that serpentinisation took place on continent at relatively low temperature in the presence of hydrothermal-meteoric fluids (Fig. 1). Two samples of chrysotile-lizardite have  $\delta^{18}\text{O}$  of  $14.1$  and  $12.3$  suggesting high water/rock ratios and low formation temperature. These two samples most probably come from depth levels situated near faults. The measured  $\delta\text{D}$  values of whole rock indicate that there is a correlation between the  $\delta\text{D}$  of the serpentine and that of local meteoric water, regardless of the age of the serpentinisation.

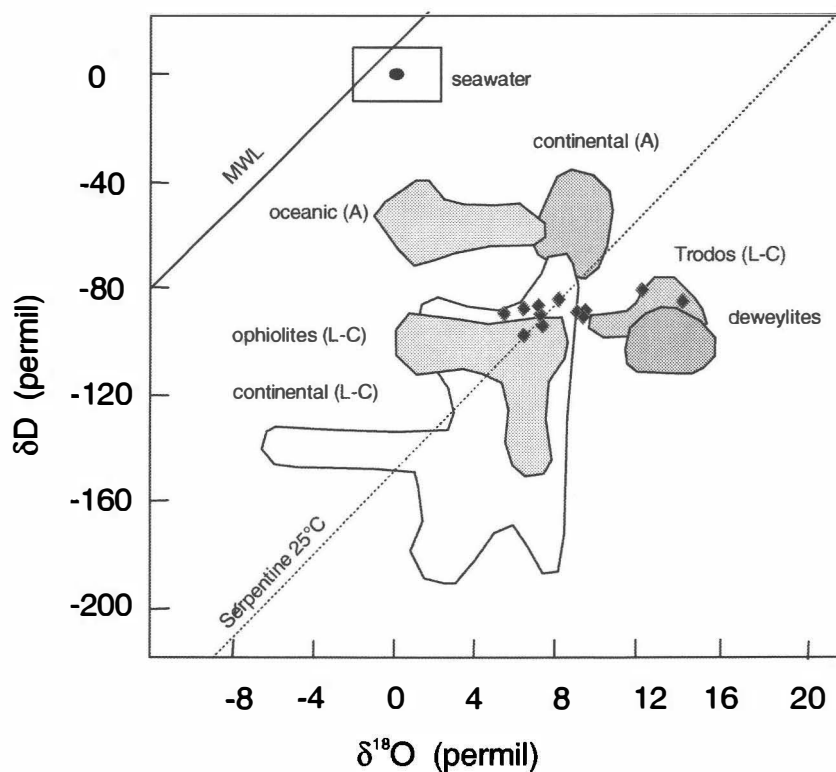


Fig 1:  $\delta D$  vs.  $\delta^{18}O$  plot showing the isotopic composition of Kenticha serpentinites, and the fields for oceanic and continental lizardite and chrysotile, continental antigorite, deweylites and Trodos serpentinites (after Wenner and Taylor, 1973, 1974, Kyser, 1999).

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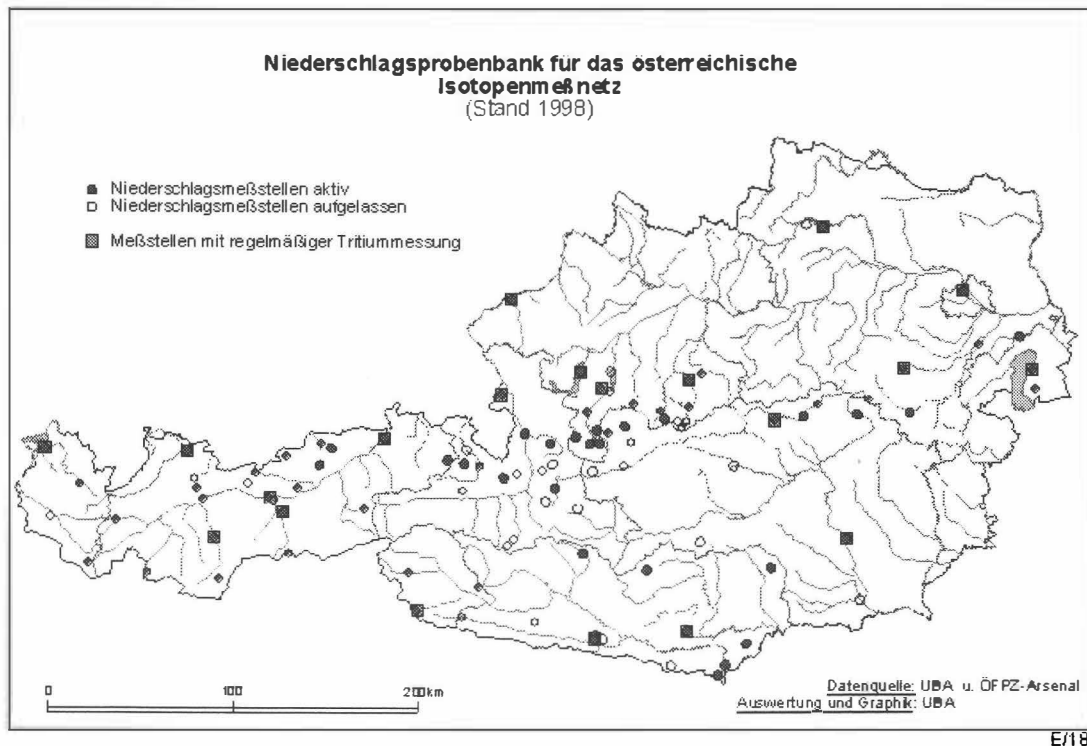
## The Austrian Network for Isotopes in Precipitation (ANIP)

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The Austrian Network for Isotopes in Precipitation (ANIP) started in 1972. At some stations samples have already been taken since the 1960s. 71 stations ranging from 120 to 2250 m in altitude are presently in operation all over Austria with some preference given to the Karst areas north and south of the Alpine mountain range (Fig. 1). The precipitation water is collected on a daily basis in ombrometers (500 cm<sup>2</sup>) and mixed to monthly samples. All samples not measured immediately have been stored in 1L bottles in a specially dedicated cellar (16000 samples) in Vienna and are available for analysis in the future. The aim of ANIP is to provide input data for hydrological and hydrogeological investigations and a data-base for climatological research.



*FIG. 1. Sampling stations of the Austrian precipitation network.*

The amount of precipitation in Austria is highly influenced by the Alpine mountain range (400-3000 mm/a). The amount of annual precipitation increases towards the mountain ranges, in particular at the high altitude regions. However, strong regional differences exist between the windward and the lee side of the Alpine ranges. Furthermore, the Alps as a weather divide sharply distinguish precipitation events caused by different air flow directions.

The isotope time series of the stations of the Austrian precipitation network show significant but not uniform long-term trends [1, 2]. While the 10-year running mean of some mountain stations exhibits a pronounced increase in  $\delta^{18}\text{O}$  of about 1 ‰ since 1975, the change of  $\delta^{18}\text{O}$  at the valley stations is much lower (Fig. 2). There are also differences in the time behaviour. The differences in the  $\delta^{18}\text{O}$ -values of sampling stations at similar altitudes can be explained by the origin of the air moisture. An Atlantic influence (moisture from NW) causes lower  $\delta^{18}\text{O}$ -values (e.g. Patscherkofel and Bregenz) than a Mediterranean one (e.g. Villacher Alpe and Graz). The main reason for this different  $^{18}\text{O}$ -content is the longer way of the Atlantic air masses over the continent along which the moisture becomes stepwise depleted in heavy isotopes by successive rainout (continental effect).

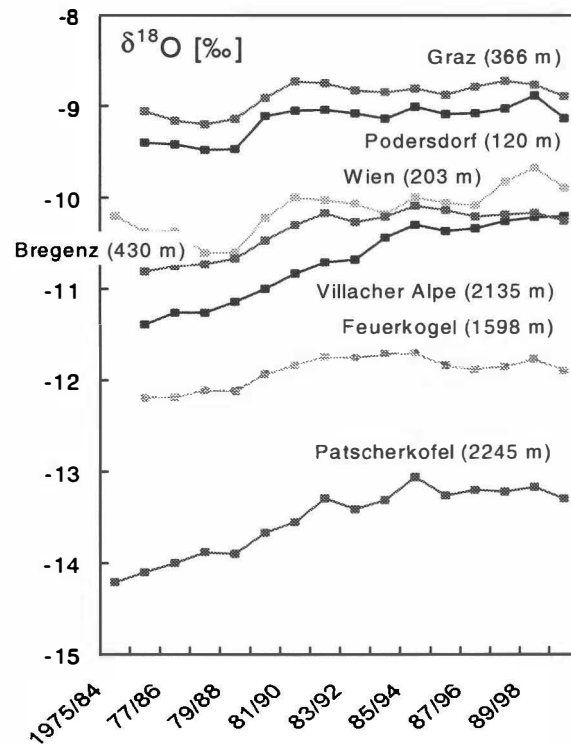


FIG. 2. Long-term  $\delta^{18}\text{O}$  variations (10-year running means) at several stations of the Austrian precipitation network [1, 2].

The stable isotope variations in precipitation are a consequence of the isotope effects accompanying each step of the water cycle. Temperature is the most influencing parameter, but there are also other influences like changes in the origin of air masses or in rain formation mechanisms [2, 3, 4].

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## Isotope geothermometry within the southern Tauern Window

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### Aim of the study

Remnants of South-Penninic oceanic sediments are now exposed in the Tauern Window, beneath the Austroalpine Complexes. During Cretaceous times this oceanic basin was flanked by the northern Middle Penninic continental block and the southern Austroalpine continental block. The Cretaceous sedimentary facies distribution includes (Kurz et al. 1998): 1) Oceanic basin sediments with carbonatic – clastic deep water sediments that grade upwards into flysch-type deposits (“Glockner Facies”). The sediments were deposited on oceanic crust. 2) Relatively pure carbonates have been deposited on northern (“Venediger Facies”) and southern (Austroalpine Complex, “Mattrei Facies”) continental margins. 3) An intermediate position with carbonatic and clastic sequences developed along the northern continental slope and along rift-related escarpments (Rote Wand – Modereck Facies). During closure of the oceanic domain, sediments and basement rocks have been incorporated into a nappe pile with the Venediger Nappe in footwall position, the Rote Wand – Modereck Nappe in an intermediate position and the Glockner Nappe in a hangingwall position. Closure of oceanic domains and subsequent underthrusting of Penninic continental units (Venediger Complex) beneath the Austroalpine caused crustal thickening, burial and heating of Penninic units. Final exhumation and cooling of Penninic Tauern Window units in Paleogene times left a distinct zonation of paleothermal isogrades with high tempered units in central Tauern Window portions and low tempered units along the Tauern window margin. Simultaneously with Tauern Window exhumation lateral extrusion tectonics (pronounced West – East stretch) modified the primary configuration of units and may have eventually disturbed the paleo-isograd pattern.

We performed an isotope study along a profile from the southern Tauern Window margin (Glockner Nappe) to central portions (Venediger Nappe). Aim of the study was to (1) obtain information on primary sedimentary environment, (2) to reconstruct the paleo-temperatures along the profile, and, (3) to check possible disturbances created by tectonics. This work expands on previous isotope studies by e.g. Hoernes and Friedrichsen (1978).

### Data and interpretation

We sampled very similar lithologies along a profile (“Kalkglimmerschiefer”) across Glockner Decke (GD), Rote Wand – Modereck Decke (RWMD) and Venediger Decke (VD) that consist essentially of three mineral types, calcite, quartz and muscovite. Calcite is major phase with 60%-90% (volume) in all samples, other phases are below 2% (volume). Calcite was analysed for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  using the automated system Kiel II,  $\text{O}_2$  ( $\delta^{18}\text{O}$ ) in silicate phases was analyzed using a Laser Fluorination line with  $\text{BrF}_5$  as reagent gas.

The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of all minerals are distinctly different within the three nappes as exemplarily shown for  $\delta^{18}\text{O}$  in Fig 1. This correlated with the reported facies distribution. Rocks from the GD are interpreted to represent clastic carbonatic sediments of anoxic environment. Degassing of  $\text{CO}_2$  may have caused the negative  $\delta^{13}\text{C}$  values. By contrast, the heavy  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values from the VD characterize sediment from a shallow marine swell position.

The three coexisting mineral phases do give concordant temperatures for samples from the VD but highly discordant temperatures for samples from the GD. Here two species of calcite occur with an early phase within the matrix and younger calcite grown in microveins an tension

gashes. Cathodoluminescence studies clearly indicate disequilibria between calcite and other mineral phases. Most plausible temperatures are obtained from calcite / muscovite pairs (Figs. 1, 2) and show increase of temperatures from ca. 380° in the south (GD) to c. 530° in the north (VD). This fits observed temperature estimations based on microstructures. Microstructures and stable isotope data suggest that the Glockner Nappe suffered a late, shallow level tectonic event during final exhumation of the Tauern Window and lateral extrusion tectonics. This event is not recorded in central Tauern Window portions.

With the “fast grain boundary” program package of Eiler et al. (1994) we started to model cooling rates from central and marginal Tauern Window portions. First results suggest rapid cooling and exhumation in the VD (Tauern Window interior) and slow cooling in the GD.

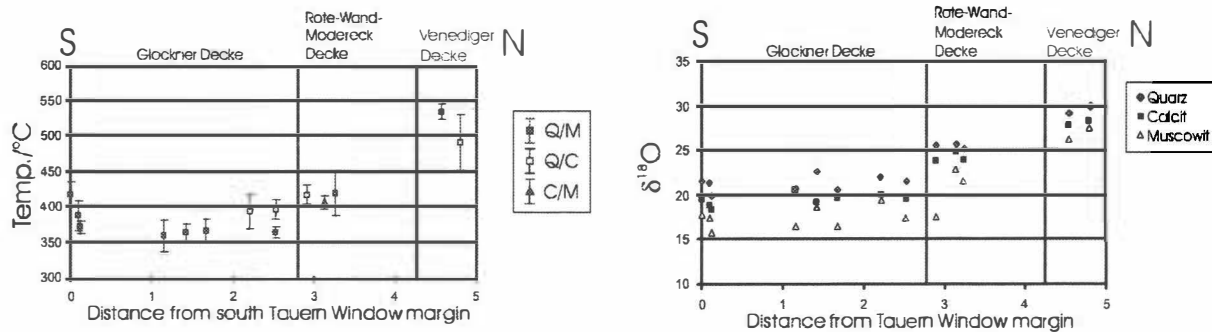


Figure 1: Temperature variation (left) and raw data (right) from the southern Tauern Window

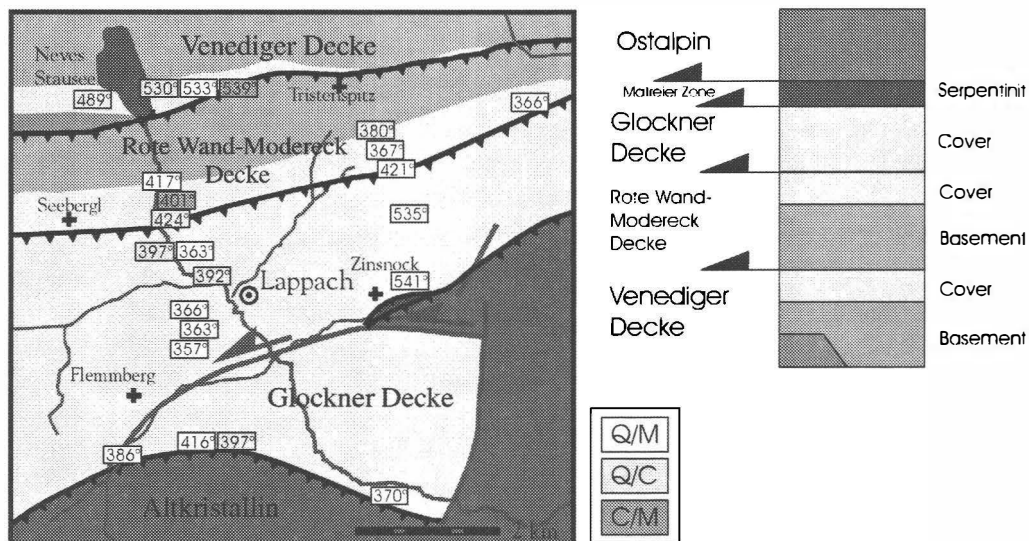


Figure 2: Temperature variation within three nappes from the southern Tauern Window

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## **Automatic Determination of Content and $^{15}\text{N}$ abundance of Total Dissolved Nitrogen in Watery Samples and Soil Extracts by TOC Analyser-Mass Spectrometer Coupling**

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The standard method for determining the  $^{15}\text{N}$  abundance of total dissolved nitrogen (TDN: org. N +  $\text{NH}_4^+\text{-N}$  +  $\text{NO}_3^-\text{-N}$ ) in aqueous samples (e.g. soil leachate, sewage, urine) is currently Kjeldahl digestion followed by steam distillation or diffusion to isolate the ammonium, and then  $^{15}\text{N}$  measurement using IRMS (Bremner & Mulvaney, 1982, Brooks et al., 1989). However, this technique is both time-consuming and laborious. Using elemental analyser-IRMS coupling is impossible owing to the required sample volumes of  $\geq 0.5$  ml. A solution to this problem emerged with the availability of TOC analysers to determine the total dissolved carbon and nitrogen in aqueous samples. The HighTOC analyser (Elementar Hanau, Germany), which catalytically oxidizes the sample's total nitrogen with a high, constant yield to form nitrogen monoxide (NO), appeared particularly suitable. As  $^{15}\text{N}$  determination of NO using mass spectrometry had already proved successful (Russow & Stevens, 1996, Sich & Russow, 1999) online coupling with a suitable MS via the combustion product NO ought to enable the rapid, automatic  $^{15}\text{N}$  determination of the total dissolved nitrogen in a sample with sufficient sensitivity and accuracy. The Quadrupol-MS ESD 100 (InProcess Instruments Bremen, Germany) proved to be a suitable mass spectrometer. It is known that oxygen, necessary for a sufficient combustion, has a big impact on the detection of the relevant masses 30 and 31 by the mass spectrometer. This causes changes in the background of the MS record which lead to unacceptable incorrect  $^{15}\text{N}$  determinations. This problem could be solved by an indirect coupling of the TOC analyser to the QMS via a cryotrap immersing into liquid nitrogen working after the "trap and flash" principle (Sich & Russow, 1998). The coupling of the instruments described was found in numerous measurements of standard and real samples to provide a workable method. The detection limit is about 2  $\mu\text{g}$  of nitrogen, corresponding to an N concentration of 0.07 mg/l in a maximum dosage volume of 3 ml. Depending on the N concentration,  $^{15}\text{N}$  abundances starting from 0.5 at.% can be measured with the required precision of better than 3% (simple standard deviation). For example, measuring the abundance of 0.5 at.% requires about 50  $\mu\text{g}$  N, whereas as of 1 at.% only about 5  $\mu\text{g}$  N is needed per analysis.

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### **Sulfur isotope distribution at Bleiberg lead-zinc deposit (Austria) and its genetic implication.**

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Bleiberg (Carinthia, Austria) is the Alpine type deposit (ATP) of the low-temperature carbonate-hosted lead-zinc mineralisations. The ores are hosted by 350m Ladinian to Carnian platform carbonates. Genetically related lead-zinc deposits are found in Mežica (Slovenia) and Raibl (Italy). These deposits are located along the Periadriatic lineament, which separates the Austroalpine from the Southalpine tectonic unit. Mining ceased at the end of the 20<sup>th</sup> century. With a total production of 2.4 Mio t Pb+Zn, the deposit of Bleiberg is the largest deposit of the ATP.

The genesis of this deposit is discussed controversially. A Carnian sedimentary-sydiagenetic origin (Brigo et al. 1977, Schroll 1996) is opposed against a (MVT) model of migrating brines during post-Norian (Jurassic) age (Zeeh et al. 199?, Kuhleemann et al. 2002).

The interpretation of the sulfur isotope distribution in the Alpine ore district is an efficient contribution to evaluate these contrary models.

The Bleiberg deposit is characterized by a complex mineralisation, distributed in six ore horizons. In spite of the uniformity of the ore mineralization, differences in mineralogy, trace element geochemistry of sphalerite, and sulfur isotopes of sulfides are observed in dependence of the stratigraphic position and the structural setting of the mineralisation (Table 1). Geochemical data, e.g. Ga/Ge-ratio of sphalerite, indicate a leaching temperature around 100°C. The burial temperature of Carnian sediments at Bleiberg is estimated with ca. 130°C (Rantitsch 2001).



Ore horizon	Metal Zn+Pb mio t	Zn/Pb	Gangue	Ge (ppm)	$\delta^{34}\text{S}\text{‰}$ sulfides	$\delta^{34}\text{S}\text{‰}$ barite
3 <sup>rd</sup> Cardita	0.1	6/1	Ba, F		-22.1 to -15.1 (19)	15,3 to 16,3 (2)
2 <sup>nd</sup> Cardita	Subeconomic		Ba, F		-19.3 to -5.0 (5)	12.1 to 14,8 (2)
1 <sup>st</sup> Cardita	0.2	8/1	F	340	-31.9 to -13.7 (44)	
Crest	0.5	6/1	F	160	-31.9 to -10.2 (29)	
Erzkalk	1.5	1/1 to 10/1	Ba, F	180	-27.0 to -3.0 (181)	12.0 to 17,1 (27)
Maxer Baenke	0.1	8/1	F	550	-31.6 to -13.7 (48)	

Table 1: General characteristic (F=fluorite, Ba=barite, n=number of samples) of the Bleiberg ore horizons (Cerny 1989, Schroll 1996).

348 sulfur isotope data from the Bleiberg deposit, obtained during thirty years of exploration, are available for this study. The sulfur isotope distribution of the Bleiberg deposit is shown in Tab. 1 and Fig. 1. The  $\delta^{34}\text{S}$ -values of sulfides (n=303) display a wide variation from -3.0 (ZnS) to -31.6 (PbS). Three populations of  $\delta^{34}\text{S}$ -mean values around  $\delta^{34}\text{S}$  -7, -17 and -25 ‰ are identified. The  $\delta^{34}\text{S}$ -values of barite (n=28) vary between 12.0 and 17.1‰ (mean 14.7‰). An isotopic equilibrium between the mineral phases is not recognisable.

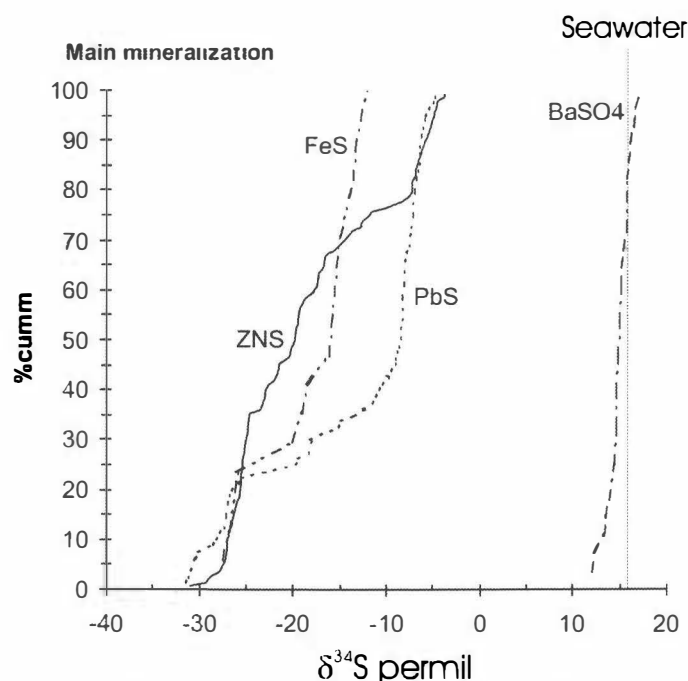


Figure 1. Sulfur isotope distribution in the Bleiberg deposit.

The  $\delta^{34}\text{S}$ -values of barite indicate precipitation of sulphate sulphur from the coeval seawater and evaporates of the Carnian stage (16‰). Main source of sulfidic sulfur is the coeval seawater produced by bacterial activity (Kucha et al 2002). Stratiform mineralizations show highly depleted sulphur (~-25‰) corresponding with the difference  $\Delta\delta^{34}\text{S}\text{‰}$  (sphalerite) –  $\Delta\delta^{34}\text{S}\text{‰}$  (seawater) of ~-41‰ and with bacterial sulphate reduction (BSR) in an open system.

The bacterial activity is confirmed by optical and instrumental methods (Kucha et al. 2001). The lightest sulphur (-31.6‰) is reported from late stage stalactitic botryoidally sphalerite. The origin of the sulfur isotope population which is characterized by a broad peak at -17‰ is multimodal: BSR, of pre-existing sedimentary iron sulphide or ore sulphide, mixing with hydrothermal sulphur (<-10‰) dominate in discordant ore structures. The hydrothermal sulfur probably originates from sedimentary iron sulphides of the basement or its cover. Sulphur isotope patterns of other carbonate-hosted Pb-Zn deposits in the Alps and anywhere support this assumption.

The detection of bacteriogenic activities during syndiagenetic sedimentary processes in sulphides from the most important ore horizons at Bleiberg deposit excludes the MVT-model, and confirms the model of Mid-Triassic age. The proposed model for the Bleiberg deposit corresponds with the interpretation of sulfur isotopes of the (Irish type) Lower Carboniferous giant lead-zinc deposit Navan in Ireland (Fallick et al. 2001).

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## **New applications of hydrogen isotopes in geo- and biochemistry**

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In spite of the enormous hydrogen isotope fractionations that occur in nature, the applications of hydrogen isotope geochemistry have been limited, in part due to the difficulty in making the isotopic analyses. However, new continuous flow analytical techniques, developed in the last several years, have made analyses vastly easier and less time consuming than those in the past. Much smaller amounts of material can be analyzed with a minimum of sample preparation. As a result, large number of analyses can be made in a relatively short time. In this communication, I present a number of varied applications of hydrogen isotope geochemistry, archaeology and ecology in order to illustrate the types of problems that can be addressed.

$\delta D$  values of bird feathers are related to their geographic location during molting (feather growing). An isotopic study of Wilson's warblers shows that birds migrating to the most northern latitudes in summer, also migrate to the most southerly latitudes in winter, 'leapfrogging' a second group of Wilson's warblers that migrate far less. This kind of migration information was unknown before our isotope study. In another study, the  $\delta D$  values of the Aconcagua Mummy sacrificed in the high Andes were measured. H, C, N and S isotope ratios all varied as a function of seasonality. We were able to show that the mummy child had not lived at high altitudes for a significant period of time prior to his death.

We have coupled the continuous flow hydrogen method with a laser extraction system to extract single fluid inclusions for  $\delta D$  determinations. We find that primary and secondary fluid inclusions have distinctly different  $\delta D$  values. Primaries have mantle values; secondaries have a strong meteoric component. We have also started a program of analyzing the  $\delta D$  of atmospheric water vapor. Unlike typical meteoric water measurements, which can only be made when it rains, we can analyze vapors at any time, and our data are consistent with the actual air, not the water modified by condensation-evaporation processes.

Because hydrogen is a major constituent of water and organic matter, and to a lesser extent, rocks, its applications are extremely varied. The advances of rapid turnover time, small amounts of material for analysis, and the high spatial resolution when coupled to a laser, means that a tremendous number of new applications will be seen in the coming years.

## **The stable isotopic composition of DIC in karst groundwater: Methodology and applications**

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The stable isotopic composition of dissolved inorganic carbon ( $\delta^{13}C_{DIC}$ ) is a useful parameter to trace the origin(s) of the bicarbonate ion, which is the dominant anion in shallow groundwater. In this setting, DIC has three main sources, soil carbon dioxide, dissolution of carbonate minerals, and atmospheric carbon dioxide exchanged through the air-water interface.

We use a gas evolution method that (a) avoids the use of toxic additives to prevent microbial activity, (b) requires only small sample volumes, and (c) works reliably and quickly even in difficult field conditions (e.g., caves). 10 ml sample vessels are preloaded with a few droplets of phosphoric acid, capped, and the head space is flushed with He. In the field, the sample is injected into the exetainer using a needle syringe. The amount of sample depends on the carbonate alkalinity and varies from fractions of a milliliter up to 2 ml. The  $CO_2$  in the headspace of the exetainer is analyzed within a few days using a Delta<sup>plus</sup>XL isotope ratio mass spectrometer operating in continuous-flow mode (GasBench II). We found no significant (i.e., > 0.1‰) C isotope shift during a few days of sample transport and storage (cf. Nelson, *Rapid Comm. Mass Spectrom.*, 14, 2000; Tu et al., *Rapid Comm. Mass Spectrom.*, 15, 2001).

Because there are no durable DIC standards available, we use the following procedure to calibrate the raw delta values against VPDB: DIC samples are run intermittently with calcite samples (DIC is measured during the working day, calcite runs over night). We use the calcite standard  $\delta^{13}C$  values of the runs before and after a DIC measurement to correct and calibrate the DIC values. A linearity correction is performed using the slope  $\delta^{13}C$  vs. intensity of mass 44

as measured during the calcite runs. Overall external precision quoted at the 1-sigma uncertainty level typically is 0.1‰ for  $\delta^{13}\text{C}$ .

In alpine karst aquifers  $\delta^{13}\text{C}_{\text{DIC}}$  depicts large variations that are seasonally controlled. In the Obir Caves underground study site (Carinthia) drip waters show a consistent pattern of low  $\delta^{13}\text{C}_{\text{DIC}}$  values during the warm season. The midpoint of the transition from high and low values (change from winter to summer regime) occurs between mid April and June, depending on the location in the cave system. Conversely, the midpoint of the rising trend of  $\delta^{13}\text{C}_{\text{DIC}}$  values at the end of the warm season occurs between early to mid November. The lowest values (during summer) are  $-12.7$  to  $-11.2$ ‰ (11 sites), whereas cold-season values typically reach up to  $-2.9$ ‰. The low  $\delta^{13}\text{C}_{\text{DIC}}$  values are consistent with a simple mass-balance calculation in which dissolved soil  $\text{CO}_2$  ( $-24$ ‰) and limestone host-rock ( $+3$ ‰) contribute approximately 85% and 15% of carbon to the solution, respectively. This mixing proportion deviates significantly from the stoichiometric calcite dissolution equation but is typically observed in karst systems based on  $^{14}\text{C}$  studies (e.g., Genty et al., *Radiocarbon*, 41, 1999). The tendency toward high  $\delta^{13}\text{C}_{\text{DIC}}$  values during the cold season could be attributed to low soil bioproductivity and hence a higher proportion of  $^{13}\text{C}$ -rich carbon in the aquifer. Comparison with other parameters, however, strongly implies that it is more likely to be a result of kinetic effects inside the cave environment and in particular due to seasonally changing underground air flow causing low  $\text{pCO}_2$  values in winter which give rise to degassing of cave seepage waters, secondary calcite precipitation and enrichment of the residual vadose waters in  $^{13}\text{C}$ .

## Continuous-flow IRMS analysis of carbonates using the GasBench II

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Stable isotope (C, O) analysis of carbonate minerals (predominantly calcite) is a standard procedure in a wide range of geoscientific research fields, including paleoceanography and terrestrial paleoclimate studies. The classical method used to obtain C and O isotope ratios in calcite (McCrea, *J. Chem. Phys.*, 18, 1950) is labor intensive and requires large sample sizes (tens of milligrams) and each sample must be prepared by hand. Automatization has led to the development of online carbonate preparation lines hooked up to dual-inlet isotope ratio mass spectrometers (IRMS). The advent of continuous-flow techniques has significantly simplified and streamlined this technique.

A GasBench II linked to a Delta<sup>plus</sup>XL mass spectrometer was installed at the Department of Geology and Paleontology of Innsbruck University in 2000 and since spring of 2001 this system has been extensively used to run a large amount of powdered carbonate samples (ca. 27.000 samples since January 2001), which are being prepared using a video-controlled micromilling device. Our system routinely handles sample sizes between approximately 100 and 450  $\mu\text{g}$  that are directly loaded into 10 ml borosilicate exetainers and sealed using butyl rubber septa (Labco). 72 exetainers are placed into an aluminum tray kept at  $72.0 \pm 0.1^\circ\text{C}$ , including 12 standards and one quality assurance standard. During a first step the exetainers are automatically flushed with 6.0 He by penetrating the septa using a double needle. Afterwards, 5-7 drops of phosphoric acid (density 1.91) are deposited in each exetainer using

the autosampler while the second needle transfers the evolved gas from a neighboring vial into the GasBench. This procedure ensures identical reaction times. Following water removal using Nafion traps, CO<sub>2</sub> is separated from other components of the gas sample using a gas chromatographic column (heated to 70.0°C) and the peak of this CO<sub>2</sub> is then sent through an open split into the MS.

Measurements are performed on a Delta<sup>plus</sup>XL MS. Each sample run starts out with a peak centering, followed by three rectangular-shaped mass peaks of CO<sub>2</sub> reference gas, after which nine successive sample peaks are produced by delivering nine sequential aliquots of pure CO<sub>2</sub> into the ion source. The internal precision (1 sigma) is typically 0.03-0.06‰ and 0.04-0.08‰ for raw  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , respectively. We use an in-house calcite standard (sieved Carrara marble, calibrated against NBS 18, 19, CO-1 and CO-8) to calibrate the raw results versus the VPDB scale. The external precision calculated over 12 standards per batch is typically 0.05-0.06‰ for  $\delta^{13}\text{C}$  and 0.06-0.08‰ for  $\delta^{18}\text{O}$ . The standard deviation for the QA sample (Laas marble) over a 14 month measurement period is 0.065‰ and 0.075‰ for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , respectively, which compares favorably to other labs (e.g., Revesz et al., *U.S. Geol. Survey Open-File Report 01-257, 2001*; Werner & Brand, *Rapid Comm. Mass Spectrom.*, 15, 2001).

## Rain-gauge with integrated isotope-sampling device

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This precipitation station is designed to measure the rainfall and to offer the possibility to take samples for isotopic analyses of the total discharge during one month.

*Precipitation measurement:* Digital tipping bucket rain-gauge with a time resolution from one minute up to some hours (free of scaling) and a quantity resolution (depending on the type of bucket) from 0.1 or 0.2 mm rainfall.

*Sampling application:* For isotopic analyses it is necessary, that no part of the precipitation can evaporate. Therefore in this application the containers where the precipitation are stored, can be opened and closed. This procedure is working automatically. When the rainfall starts (=the moment of the first tipping), the container is opened. After the rainfall it is closed again. The time of delay can be chosen individually (for instance 1 to 10 minutes).

To get correct samples of one month, a second valve is changing the flow path between the two containers exactly at the beginning of the month.

The schematic construction of the isotope sampling device is shown in Fig. 1.

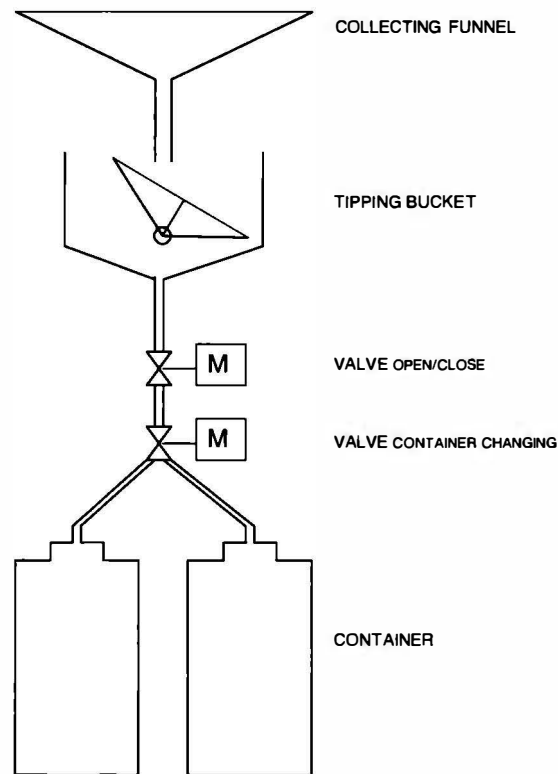


Fig. 1: Scheme of the automatic isotope-sampling device.

Both valves are controlled by the data-logger. Apart from precipitation also other parameter like temperature, wind speed, radiation, and so on can be stored.

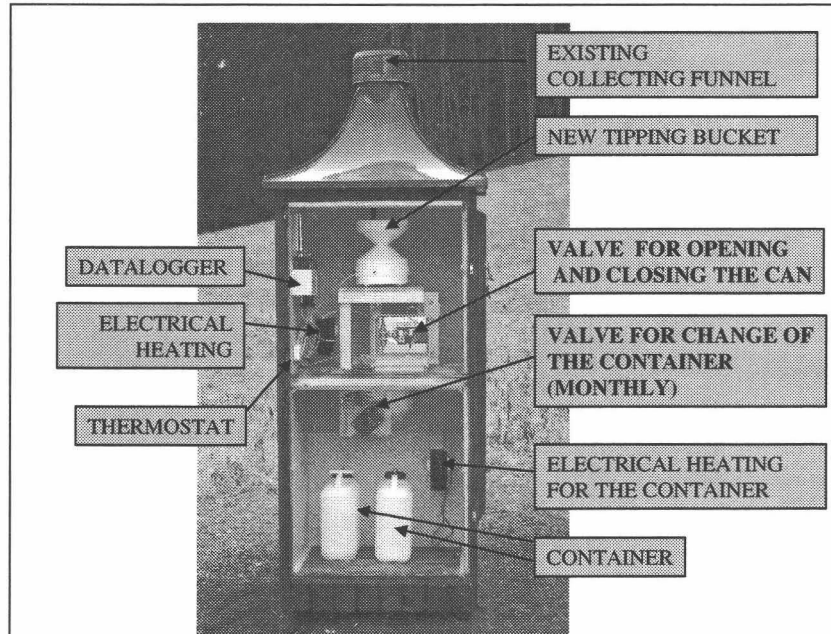


Fig. 2: Automatic precipitation station with integrated isotope-sampling device.

The picture shows a station of the Zentralwasserversorgung Hochschwab Süd, rebuilt with the digital equipment and the isotope sampling device.

The whole application can be mounted in existing measuring stations, without changing the existing collecting funnel (as shown in Fig.2). This is important for the continuity of the measurement at an existing station.

To avoid large changes of temperature of the sampled water, the containers can be isolated. The station must be heated in such a way, that the sample is not freezing. A simple funnel heating is not enough. The heating can be done with gas or electricity. Electrical heatings can be regulated by a thermostat. In stage of development are funnel-heatings with Peltier-elements. This devices are also able to cool the collecting funnel during hot periods.

The system (without the heating) can be supplied with solar panels and supplemented with remote data transfer systems like LEO-satellites, GSM or telephone.

## The $^{13}\text{C}/^{12}\text{C}$ fractionation Upon the Setting of Calcium Carbonate Mortars

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A number of sciences has become more and more concerned with the constituents of historical mortars. For example, in archaeology the objective is to deduce from the mineralogical and chemical compositions the provenance of material or even former recipes and methods for preparation, and environmental sciences are specially concerned with the carbon isotopes of the calcium carbonate of lime mortars in order to derive a former composition of atmospheric carbon dioxide. Under such auspices it has been shown that the sulfur isotopes of gypsum mortars may be used in order to trace the origin of the raw material. However, lime mortars represent a much more complicated case, because their calcium carbonate displays a rather wide range of compositions from  $\delta^{13}\text{C} \approx -25$  to  $-7$  ‰ (PDB) and from  $\delta^{18}\text{O} \approx 8$  to  $24$  ‰ (SMOW). Obviously, this range reflects various processes of isotopic fractionation which occurred during the history of an individual cement. But it is not clear which of the data may represent a primary composition.

In order to establish this composition experimental brickwork has been set up. Surprisingly, the measurements show that, unlike to the sulfur isotopes of gypsum mortar, the calcite of lime mortar does not have a unique carbon isotope composition. The  $\delta^{13}\text{C}$  values change systematically from  $-11$  ‰ at the outside of the brickwork to  $-2$  ‰ (PDB) within the interior at a very good correlation to the oxygen isotopes. This zoning along a mortar layer is caused by a kinetic fractionation factor  $\alpha_{\text{CaCO}_3-\text{CO}_2(\text{g})} = 0.9960$  which is given by the absorption of atmospheric carbon dioxide into a strong alkaline slurry of portlandite, sand and water and its subsequent reaction to calcite within a liquid boundary layer surrounding the  $\text{Ca}(\text{OH})_2$  particles. Thus, the diffusion and the reaction of carbon dioxide leads to an enrichment of  $^{13}\text{C}$  over  $^{12}\text{C}$  at the gas-side of a reaction front so that the calcite becomes continuously "heavier" from the exterior to the interior along a mortar layer. The overall process may be described by a fractionation according to zone melting. The variation of the oxygen isotopes follows the same principle. However, a reliable fractionation factor is difficult to assess.

## Stable carbon and nitrogen isotopes as tracers of eutrophication process in mountain lakes

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Stable carbon and nitrogen isotope investigations have proven to be a powerful tool in studies related to C and N cycles in aquatic environments. Organic matter produced and sedimented at the lakes bottom represents a time-averaged integration of processes affecting stable isotopic composition. The use of stable isotopes of bulk sedimentary organic matter (SOM) to study past environmental conditions is based on the assumptions that SOM originates from primary production in the water column and that the isotopic ratios reflect those of organic matter produced in the water column (Schelske and Hodell, 1991). If these assumptions are valid, then the stable isotopic composition of sediments should be a function of nutrient-driven productivity or trophic state in lake (Gu et al., 1996).

In the Julian Alps in NW Slovenia there are 14 small postglacial mountain lakes. All lakes are situated in the area of the Triglav National Park where human impact is limited by law. Lakes are situated at different altitudes, have different size, maximum depth and different trophic state. For the purpose of this study we investigated four lakes: Zgornje Krisko jezero, Jezero v Ledvicah, Krnsko jezero and Jezero na Planini pri Jezeru. The first two are oligotrophic and are situated above tree level while the other two are eutrophic and are situated just below tree level. In order to investigate the applicability of C and N stable isotope signatures in SOM to trace changes in lake trophic state sediment cores were taken from the deepest basin of the lake and sectioned into 1 cm segments. Dry sediment samples were used for determination of the stable isotopic composition of organic carbon ( $\delta^{13}\text{C}_{\text{org}}$ ) and nitrogen ( $\delta^{15}\text{N}$ ) that was performed on a Europa 20-20 continuous-flow mass spectrometer with an ANCA-SL preparation module. Ranges of  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  values are summarized in the Table below.

Lake	$\delta^{13}\text{C}$ [‰]	$\delta^{15}\text{N}$ [‰]
Zgornje Krisko jezero	-19.8 to -15.2	-1.0 to +0.9
Jezero v Ledvicah	-26.3 to -22.4	-3.0 to +1.6
Krnsko jezero	-31.5 to -24.9	-1.2 to +2.4
Jezero na Planini pri Jezeru	-36.0 to -29.6	+1.3 to +2.9

$\delta^{13}\text{C}_{\text{org}}$  values decrease with depth of the sediment in Zgornje Kriško jezero while in other three lakes the isotopic composition of organic carbon increases with depth. Isotopic composition of nitrogen increases with depth in all four lakes. Higher  $\delta^{13}\text{C}_{\text{org}}$  values are associated with lower  $\delta^{15}\text{N}$  values and are characteristic for oligotrophic lakes, while lower  $\delta^{13}\text{C}_{\text{org}}$  values are associated with higher  $\delta^{15}\text{N}$  values that are characteristic for eutrophic lakes. Very low  $\delta^{13}\text{C}_{\text{org}}$  values in eutrophic lakes are related to the presence of methanotrophic organisms that consume  $^{13}\text{C}$ -depleted methane during synthesis of microbial biomass in water column and consequent sedimentation of this  $^{13}\text{C}$ -depleted biomass at the bottom of the lake. Lower  $\delta^{15}\text{N}$  values in oligotrophic lakes can be attributed to the primary source of nitrogen. Above tree level nitrate deposition or atmospheric  $\text{N}_2$  comprise the primary source for dissolved lake nitrate, which is available to aquatic plants and phytoplankton and consequently  $\delta^{15}\text{N}$  values of the lacustrine biomass is close to 0‰ or negative (Mayer and Schwark, 1999). In contrast, terrestrial input of organic matter into the lake contributes material with more positive nitrogen isotopic



composition. This is evident in both eutrophic lakes that are situated below tree level and where SOM is a mixture of terrestrial and aquatic organic matter.

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