

# 9<sup>th</sup> Austrian Stable Isotope User Group Meeting

20<sup>th</sup> & 21<sup>st</sup> November 2009

Hotel Kranebitterhof, Innsbruck

## Organising committee

Christoph Spötl  
Michael Traugott  
Tatjana Weiler

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Geogene Stoffe**

# Welcome

Dear colleague,

Welcome to Innsbruck and to the **9<sup>th</sup> Austrian Stable Isotope User Group Meeting**. We are delighted that some 30 researchers and students from universities and governmental institutions have registered for this meeting. This positive response allowed us to organize an exciting and diverse program for this one and a half day meeting.

We invited three keynote speakers, each an international leader in his field. These keynotes as well as the regular talks and poster presentations will synthesise the latest progress made in this research field and help to identify promising avenues for future research.

The venue is in the "Kranebitter Hof" (Kranebitterallee 203, 6020 Innsbruck). The meeting will consist of three blocks of oral sessions, ranging from Biological Sciences to Earth Sciences.

**Keynote lectures** will be held by Tony Fallick (SUERC, Glasgow), Jurian Hoogewerff (UEA, Norwich), and Stuart Bearhop (University of Exeter).

Regular **oral presentation** will be 15-minute talks (plus 5 min discussion). Each **poster** will be presented by a 5 min "poster speed" presentation.

Please hand your presentation (PowerPoint) over to Tatjana Weiler at the registration and wear your name badge at all times during the meeting.

We hope that you find the Austrian Stable Isotope User Group Meeting a rewarding and productive conference.

Thank you for participating and helping to make this symposium a success.

Christoph Spötl, Michael Traugott, Tatjana Weiler  
(Conference organisers)

# Conference program

## Friday 20<sup>th</sup> November

- 12:00 - 13:30 Registration
- 13:30 - 13:35 Welcome & Introduction
- Session 1  
Chair: Michael Traugott
- 13:35 - 14:15 **Keynote 1**  
Stuart Bearhop: **Stable isotopes as dietary markers: where do we go from here?**
- 14:15 - 14:35 Julia Seeber: **Dwarf shrub litter as food source of macrodecomposers on abandoned alpine pastureland: a field experiment using stable isotopes**
- 14:35 - 14:55 Nikolaus Schallhart: **Isotopic tracking of dietary choices in soil-living insect larvae**
- 14:55 - 15:15 Elizabeth Yohannes: **Stable isotope ratios in winter-grown feathers of great reed warblers**
- 15:15 - 15:35 Nina Welti: **Mimicking floodplain reconnections and disconnections using 15N mesocosm incubations**
- 15:35 - 15:55 Andrea Watzinger: **Stable isotopic labeling of phenanthrene to identify degrading microorganisms and quantify biodegradation**
- 15:55 - 16:15 Coffee Break
- Session 2  
Chair: Martin Kralik
- 16:15 - 16:35 Michael Bahn: **Does photosynthesis affect grassland soil-respired CO<sub>2</sub> and its carbon isotope composition on a diurnal timescale?**
- 16:35 - 17:15 **Keynote 2**  
Julian Hoogewerff: **Forensic provenancing with natural isotopes**
- 17:15 - 18:00 **"Poster speed" presentations & poster discussion**
- 18:00 - 18:30 **SINA (Stable Isotope Network Austria) general assembly**
- 18.30 **Dinner**

## Saturday 21<sup>st</sup> November

Session 3

Chair: Christoph Spötl

- 9:00 - 9:40     **Keynote 3**  
Anthony E. Fallick: **Stable isotope geochemistry: following the leaders**
- 9:40 - 10:00     Yuri Dublyansky: **Stable isotopic analysis of nanomole amounts of water**
- 10:00 - 10:20     Konstantin Horkel:  **$\delta^{13}\text{C}/\delta^{18}\text{O}$  Isotope studies of cryptocrystalline magnesite in Anatolia (Turkey) and Kraubath (Austria)**
- 10:20 - 10:40     Micha Horacek: **Sulfur isotopes across the Permian/Triassic boundary - trace sulfate versus evaporite data**
- 10:40 - 11:00     Coffee Break & Posters
- 11:00 - 11:20     Christoph Spötl: **Isotopes and climate change: a tale from a small cave**
- 11:20 - 11:40     Marc Luetscher: **Kinetic fractionation processes in speleothems**
- 11:40 - 12:00     Martin Kralik: **Austrian Network of Isotopes in Precipitation and Surface Waters (ANIP): 40 years network of natural isotope-tracers in rain, snow, rivers and lakes**
- 12:00 - 12:20     Dieter Rank: **Mean Residence Time (MRT) of baseflow water in river catchments derived from decadal climatic signals in long-term isotope records of river water**
- 12:20 - 12:30     Closing & Outlook
- 12:30                Lunch

## Posters

Margarete Watzka: **The use of isotope measurements for the separation of discharge components during hydrological events in a riparian forest ecosystem, Lunz/See, Austria**

Franko Daniel Humer: **Identification and quantification of the diffuse nitrogen input in the catchment area of Ybbs and Wulka by the stable isotopes of nitrogen and oxygen in nitrate**

Maria Schaffhauser: **Stable isotope composition of carbonate cements in the Lower Permian Trogkofel massif, Carnic Alps**

Martin Kralik: **Heterogeneous mean transfer-times in an Alpine dolomite-karst massif, Austria:  $\delta^{18}\text{O}$ ,  $^3\text{H}$ ,  $^3\text{H}/^3\text{He}$ , CFC, SF<sub>6</sub>, chloride and dye tracer – investigations**

Micha Horacek: **Control of authenticity of Tyrolean milk by stable isotope Measurements**

Barbara Post: **Food web analyses with stable isotopes of Tardigrades: a comparison between cryoconite-communities of Spitzbergen and a glacier in the Alps**

# Keynotes

## **Stable isotopes as dietary markers: where do we go from here?**

*Stuart Bearhop*

*School of Biosciences, University of Exeter, UK*

The use of stable isotopes in foraging studies has been something of a "slow burner" and remains a surprisingly underused technique among animal ecologists. I will review the principles behind the use of stable isotopes as dietary markers drawing on a series of case studies to illustrate the power and breadth of the approach. I will then go on to discuss some more recent ideas about potential applications of stable isotope analyses such as elucidating individual specialisations and as descriptors of community structure. I will close with some ideas as to why some researchers have been hesitant about using the approach, highlighting some common errors and misconceptions that can make data interpretation equivocal.

## **STABLE ISOTOPE GEOCHEMISTRY: FOLLOWING THE LEADERS**

*A. E. FALLICK*

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Tony Fallick T.Fallick@suerc.gla.ac.uk*

The objective of the presentation will be to illustrate the power and versatility of the stable isotope approach in biogeochemistry via a series of case studies involving different elements ( S, C, O and H ). Each example is also considered from the perspective of the sophistication of the techniques used and the underlying philosophy of the approach.

In the first case, sulfur isotope ratios are used to investigate the genesis of a world-class Zn-Pb ore deposit. Conventional analytical methods, available for fifty years, reveal a surprising conclusion concerning the important role of bacteria in the formation of the orebody. The second case exemplifies the use of advanced techniques ( CSIA : compound specific isotope analysis ) in an ecological context. The issue of provenance ( stable isotope ratios as fingerprints) is addressed by examining the carbon isotope ratios of essential fatty acids in the unusual ecosystem of deep-sea hydrothermal vents, often posited as independent of the Sun's energy. Finally, coupled oxygen and hydrogen isotope ratios of clay minerals are discussed to illustrate the advantages of new technologies ( eg laser fluorination ) yet highlight how much remains to be understood about fluid-rock interactions.

The overall leitmotif will be the wonderful insights of the pioneers of stable isotope geochemistry.

## **Forensic Provenancing with Natural Isotopes**

*Jurian Hoogewerff<sup>1</sup> and the TRACE consortium<sup>2</sup>*

*1 Centre for Forensic Provenancing, School of Chemistry, University of East Anglia UK,*

Geologists have long realized that the spatial compositional differences in the earth's crust can be used to trace the origin of many materials. So far, large scale studies assessing the potential and validating the methods against forensic criteria, (eg "the Daubert criteria") have not been performed except recently for one specific application; the development of effective analytical means for investigating food fraud and to independently validate paper and electronic traceability systems in the food industry. The existing traceability systems are reliant on the operators in the supply chain and therefore by definition not independent. As plants and animals are integral parts of their natural or managed local ecosystem they will contain bio-geo-chemical fingerprints that allow discrimination between those ecosystems by analytical means. The challenge for the scientific community is to investigate which markers deliver the most cost-effective and relevant geographical discrimination for each class of products. In the last two decades small scale proof of concept research projects have demonstrated that foods from different geographical regions have both varying natural isotope-ratio and trace element profiles (NITE). As these studies were very small scale, only involving maybe two or three source regions, there has been reasonable doubt that when using a larger number of source regions the apparent uniqueness of each region might break down.

To investigate the consequences of such up-scaling the European Commission funded a large scale (9M€) work-package on geographical profiling, within the (20M€) TRACE project on traceability in 2005-2009. The TRACE profiling investigation focussed on 650 mineral waters from the whole of Europe and a detailed comparison of wheat, honey, olive oil and lamb from 21 test regions with the regional soil and surface water composition and additional analysis of chicken and beef samples from different continents. From the first results of the TRACE project it is emerging that NITE profiling also works on large scales but that individualisation of production regions is probably not possible by NITE alone as indistinguishable climatological and geochemical conditions can occur at different, often far away, geographical locations. Thus NITE profiles can be very useful in answering specific compliance questions like "can this wheat come from a specific region" but not yet at finding the origin of an unknown batch, although it can indicate most likely (if known) areas and often even more valuably, exclude unlikely areas. The developments in and around the TRACE project have provided new insights that can now be applied in other forensic provenancing issues. One of the "insights" is that modelling or predicting soil composition from lithology alone is extremely challenging and that probably the best way forward is to produce empirical geochemical soil maps, especially Isoscapes (isotope maps) for relevant areas of food production, water production, protected plant and animal species habitats, and validate those maps with Isoscapes of required target foods and tissues. At the CFP one of our main lines of research is now to develop and validate robust spatial models for human provenancing, to assist forensic investigations into unidentified remains from murders, mass disasters and war crimes.



# Talks

## **Does photosynthesis affect grassland soil-respired CO<sub>2</sub> and its carbon isotope composition on a diurnal timescale?**

*Michael Bahn*

*Institute of Ecology, University of Innsbruck, Sternwartestr 25, A- 6020 Innsbruck, Austria.*

Soil respiration is the largest flux of carbon (C) from terrestrial ecosystems to the atmosphere. Here, we tested the hypothesis that photosynthesis affects the diurnal pattern of grassland soil-respired CO<sub>2</sub> and its C isotope composition ( $\delta^{13}\text{C}_{\text{SR}}$ ). A combined shading and pulse-labelling experiment was carried out in a mountain grassland.  $\delta^{13}\text{C}_{\text{SR}}$  was monitored at a high time resolution with a tunable diode laser absorption spectrometer. In unlabelled plots a diurnal pattern of  $\delta^{13}\text{C}_{\text{SR}}$  was observed, which was not explained by soil temperature, moisture or flux rates and contained a component that was also independent of assimilate supply. In labelled plots  $\delta^{13}\text{C}_{\text{SR}}$  reflected a rapid transfer and respiratory use of freshly plant-assimilated C and a diurnal shift in the predominant respiratory C source from recent (i.e. at least 1 d old) to fresh (i.e. photoassimilates produced on the same day). We conclude that in grasslands the plant-derived substrates used for soil respiratory processes vary during the day, and that photosynthesis provides an important and immediate C source. These findings indicate a tight coupling in the plant–soil system and the importance of plant metabolism for soil CO<sub>2</sub> fluxes.

## **Stable isotopic analysis of nanomole amounts of water released from fluid inclusions**

*Yuri Dublyansky and Christoph Spötl*

*Institut für Geologie und Paläontologie, Universität Innsbruck*

A dedicated analytical line built at Innsbruck University allows the analysis of small amounts of water released from fluid inclusions in minerals.

Mineral samples are crushed in a custom-built crushing cell with a small internal volume. The working zone of the crusher is kept at 130-150°C to minimize the adsorption of water on freshly crushed calcite and on the internal surface of the cell. The released water is transported by a He flow through a heated stainless-steel tube into the computer-controlled cryo-focusing cell (Humble, USA). The temperature and gas-flow parameters ensure quantitative collection of water, whereas CO<sub>2</sub> (and/or other poorly condensable gases) are not trapped. Upon completion of the cryo-focusing the cell is flash-heated (3600°C/min) to 280°C, which ensures that the released water arrives in the TC/EA conversion unit (Thermo, Germany) as a concise pulse. In the TC/EA the water is converted into H<sub>2</sub> and CO through reaction with glassy carbon at 1400°C. The evolved gases are separated in a chromatographic column and admitted, via the ConFlow III interface, into a Delta V Advantage mass-spectrometer (Thermo, Germany). Prior to crushing the line is conditioned by several injections of water with isotope compositions broadly similar (i.e., within ±20 ‰  $\delta$ ) to the expected composition of the inclusion water. For samples yielding more than ca. 0.1  $\mu$ l (60 nmol) H<sub>2</sub>O the precision is better than 1.5 ‰ for  $\delta$ D and ca. 0.5 ‰ for  $\delta^{18}$ O (1 $\sigma$ ).

To ascertain accuracy, multiple analyses of inclusion water were made of "pool spar" calcite collected from the two shallow pools in the Obir cave (Carinthia, Austria), which was deposited continuously over the last 11,000 yrs (determined by U-Th dating). The isotopic composition of the lake water ( $\delta$ D = -70.1±0.3 ‰;  $\delta^{18}$ O = -10.4±0.06 ‰), its temperature (5.2±0.2°C), as well as the relative humidity (97-100±3 %) at both sampling sites remained stable over the 1.5 to 4 year-long monitoring periods. The hydrogen isotope compositions measured for fluid-inclusion water in the pool spar ( $\delta$ D<sub>fi</sub> = -70.0±0.6 ‰, n = 4) match the lake water and the oxygen isotope values ( $\delta^{18}$ O<sub>fi</sub> = -9.92±0.40 ‰, n = 4) agree within ca. 0.5 ‰.

## **Sulfur isotopes across the Permian/Triassic boundary - trace sulfate versus evaporite data**

*Micha Horacek<sup>1</sup>, Rainer Brandner<sup>2</sup>*

*1 Business Unit Environmental Resources and Technologies, Austrian Institute of Technology GmbH – AIT, 2444 Seibersdorf, Austria*

*2 Department of Geology and Palaeontology, University of Innsbruck*

The Permian - Triassic boundary marks the severest mass extinction in Earth history. More than 90 % of all skeleton building species became extinct in this event. Despite numerous investigations the responsible mechanisms still are not unequivocally identified. Among the more popular hypotheses are bolide impact, global warming, global cooling, global ocean water poisoning, marine anoxia and volcanism. It was followed by a prolonged survival interval, probably due to the severity of the extinction and harsh environmental conditions still existing after the extinction event. To identify the really relevant processes during this crucial period geochemical proxies are investigated.

Here we present some sulphur isotope data of evaporites from the Permian-Triassic Boundary and the Lower Triassic in the Dolomites (Northern Italy). The curve shows low values in the uppermost Permian and the basal Lower Triassic and increases steeply to significantly enriched values in the vicinity of the Dienerian-Smithian Boundary. The sulphur isotope values remain elevated for the Smithian and Spathian substages of the Lower Triassic. Changes in ocean circulation are the most plausible causes for the presented isotope curve. The sulphur isotope curve of evaporites does not fit with the curve of CAS (carbonate associated sulphate) investigated in the Dolomites and elsewhere. The available data makes it appear plausible that CAS isotope data not always represents primary marine signals.

## **$\delta^{13}\text{C}/\delta^{18}\text{O}$ Isotope studies of cryptocrystalline magnesite in Anatolia (Turkey) and Kraubath (Austria)**

*Konstantin Horkel<sup>1)</sup>, Fritz Ebner<sup>1)</sup>, Heinrich Mali<sup>1)</sup>, Thomas Unterweissacher<sup>1)</sup> & Christoph Spötl<sup>2)</sup>*

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Cryptocrystalline magnesite occurs predominantly in ultramafites of ophiolites and associated sediments. Thereby it is discriminated between the Kraubath type (KT), which occurs strictly controlled by tectonics in ultramafites as veins and networks, and the Bela Stena type (BST), which occurs in sediments as nodulars and layers.

Both types differ from each other primarily by their stable C isotope values: -18 to -6‰ for KT versus -1 to +4‰  $\delta^{13}\text{C}_{\text{VPDB}}$  for BST.  $\delta^{18}\text{O}_{\text{VSMOW}}$  values overlap, whereby the KT shows tendency lower ones (+22 to +29‰) than the BST (+26 to +36‰).

Field studies and 260 samples from Austria (Kraubath) and Turkey (western and eastern Anatolia) allow following results.

Most investigated samples lay within the KT isotopic pattern.  $\delta^{18}\text{O}$  values indicate that almost all deposits have formed at temperatures of 60°C. The  $\text{CO}_2$  of the KT derives primarily by decarboxylation of organic rich shales, tributary by carbonates. The influence of volcanism as carbon source is unclear. The BST forms by precipitation in a sedimentary milieu.

The deposits Çırçır and Kuluncak (Eskişehir and Malatya/Turkey), where layered cryptocrystalline magnesite occurs within highly altered serpentinites at the border to sediments, contain positive  $\delta^{13}\text{C}$  (+2 to +6.6‰) and constant  $\delta^{18}\text{O}$  values (+26 ± 0.2‰). Positive  $\delta^{13}\text{C}$  values were caused by evaporation or biogenic fermentation.  $\delta^{18}\text{O}$  values again indicate formation temperatures of 60°C.

At the deposit Bathiyar (Eskişehir/Turkey) an interesting transition from network to layered magnesite was sampled. The former shows values typical for KT, the later shows values fitting with the BST. Whether this isotopic trend is primary or due to later processes will be investigated.

ZEDEF, V., RUSSEL, M. J., FALICK, A. E. & HALL, A. J. (2000): Genesis of vein stockwork and sedimentary magnesite hydromagnesite deposits in the ultramafic terranes of southwestern Turkey: a stable isotope study. – *Economic Geology*, 95, 429-446.

## **Austrian Network of Isotopes in Precipitation and Surface Waters (ANIP): 40 years network of natural isotope-tracers in rain, snow, rivers and lakes**

*M. Kralik (1), F. Humer (1), H. Lindinger (1), J. Grath (1)*

*Umweltbundesamt, Vienna, Austria*

The Austrian network of isotopes in precipitation and in surface waters (ANIP) is since 2007 a cooperation between Lebensministerium (BMLFUW) and the Ämter der 9 Landesregierungen. Before the network was conducted by a cooperation of the Austrian Environment Agency (Umweltbundesamt), the Austrian Institute of Technology (AIT) and the Helmholtz Institute Munich. ANIP is the effort to provide in an alpine country with quite different climatic regions nationwide with  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and Tritium isotope-data based on 50 stations all over the country. The monthly samples are collected at traditional meteorological stations of the Hydrographischer Dienst, the ZAMG and surface water stations virtually all run by the Hydrographischer Dienst.

Some ANIP-stations are since many years part of the [IAEA/WMO Global Network for Isotopes in Precipitation \(GNIP\)](#).

### **Why determining isotope composition of precipitation and surface water?**

Hydrology and hydrogeology: The determination of  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ -values allows in many cases and particularly in combination with hydrological and hydrochemical data to trace the water cycle more precisely. This concerns specially the mean altitude of recharge areas (e.g. springs, rivers), the exchange and mixture of river and groundwater and evaporation processes in lakes and back waters.

The radioactive decay of tritium in water permits by knowing the input and using hydrological models to calculate mean residence times ("groundwater ages") of water in the ground.

Climatology: The  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ -values are mainly dependent on the temperature during the precipitation process. Therefore research in the actual climate and even more in paleoclimatology uses water from ice cores or calcium carbonate in sediments or in flowstones as well as cellulose in tree-rings to reconstruct temperature records.

Food authentication and origin: Most foodstuffs contain water. Therefore isotope measurements in combination with other techniques are very useful to determine or narrow down the origin of food production.

Environmental forensic: deals with scientific investigations that address contamination within the environmental media as air, water, soil and biota. The origin of items of trade and related pending claims can be solved by isotope data. In addition, tritium emissions of nuclear plants by regular operation and accidents are monitored by this network.

## **Collection of precipitation and surface water samples**

The daily precipitation samples are unified to a monthly sample and send in 1L polyethylene bottles to the laboratory or stored in an underground cellar. From the surface waters (river or lakes) once a month a grab sample is collected and manipulated as the precipitation samples. Just at a single station (Hainburg, Danube) daily 1 liter samples are unified to a monthly sample.

## **Analyses**

The  $^{18}\text{O}$ - and deuterium ( $^2\text{H}$ ) – analyses are performed after equilibration in a gas-mass spectrometer or in a spectrometer based on infrared laser. The ratios are corrected by two laboratory standards calibrated with international standards as VSMOW and SLAP (IAEA).

Water samples for tritium analyses are prepared by electrolytic enrichment. The radioactivity measurements are done in low level liquid scintillation counters with high efficiency. The calculation of the tritium activity or concentration is based on the results of an international standard (NIST SRM 4361C).

## **Data access**

All data can be downloaded from the internet:  
<http://www5.umweltbundesamt.at/h2ogispub/>

## **Kinetic fractionation processes in speleothems**

*Marc Luetscher, Christoph Spötl*

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Stable isotope variations in speleothems (cave carbonates) are increasingly used as a proxy for paleoclimatic changes. Most authors therefore focus on speleothems deposited close to isotopic equilibrium with the cave drip water, which implies a slow CO<sub>2</sub> degassing rate and no evaporation. In this case, temporal variations in  $\delta^{18}\text{O}$  mainly reflect changes in the cave air temperature and the isotopic composition of the seepage water, while  $\delta^{13}\text{C}$  values are chiefly controlled by the soil organic matter. Here, we explore the possibility to extract paleoenvironmental information also from speleothems subject to kinetic fractionation associated with rapid CO<sub>2</sub> degassing.

To assess whether calcite is precipitated in isotopic equilibrium or not, Hendy (1971) suggested two simple tests: 1) by checking if the  $\delta^{18}\text{O}$  values remain constant along individual growth layers, and 2) if there is a simultaneous enrichment of <sup>13</sup>C and <sup>18</sup>O laterally along these layers. Both tests are, however, strongly dependent on the sampling resolution and may fail even in absence of kinetic effects. To investigate possible changes in the CO<sub>2</sub> degassing rate we therefore sampled a stalagmite along a 0.5 mm spaced grid allowing for a 2D mapping of the stable isotope distribution. The data reveal phases with variable fractionation rates likely to be associated with major changes in the cave hydrological and ventilation regimes. Although analytically demanding, our sampling strategy offers new insights into stable isotope partitioning and aid in the identification of site-specific processes affecting the speleothem record (and hence paleoclimate interpretations drawn from these data).

## **Mean Residence Time (MRT) of baseflow water in river catchments derived from decadal climatic signals in long-term isotope records of river water.**

*Dieter Rank<sup>1</sup> & Wolfgang Papesch<sup>2</sup>*

<sup>1</sup>*Center of Earth Sciences, University of Vienna*

<sup>2</sup>*Austrian Institute of Technology - AIT, Seibersdorf*

Long-term stable isotope records of precipitation water exhibit significant decadal changes in the isotopic composition of H and O. Isotope ratios in river water are mainly determined by the isotopic composition in precipitation water in the drainage area. Several hydrological parameters and processes are modifying this isotopic signature and its temporal variations: delayed runoff of winter precipitation (snow cover), residence time of groundwater discharged to the river, confluence with tributaries, evaporation from lakes in the river system, climatic changes (changes in environmental temperature, spatial and temporal changes of precipitation distribution in the drainage area etc.) as well as anthropogenic influences on the hydrological regime (e.g. reservoirs, irrigation).

Since evaporation influences on the isotopic composition of river water play a minor role and can be neglected in most parts of the Danube Basin, the isotopic signals of precipitation water are transmitted through the whole catchment. A comparison of long-term stable isotope records of precipitation and river water, therefore, should tell us about the residence time of precipitation water in the catchment area. First evaluations show a shift of about 3 years for the climatic signal in Danube water at Vienna, most probably the mean residence time of baseflow water in the Upper Danube Basin. Typical alpine rivers – Inn, alpine section of the Rhine – exhibit a more pronounced climatic signal, the time-shift of the signal is similar to that of the Danube (except River Drau). The age distribution – residence time of river water in the catchment area – is responsible for the shape of the signals in river water.

Decadal stable isotope signals can possibly be used to determine MRTs of river and ground waters by model calculations in a similar way like the nuclear weapons' tritium signal. Such applications require long-term isotope records for the water bodies investigated. In this respect, ongoing activities of the Section of Hydrology of the IAEA to establish a global network for isotopes in rivers (GNIR) are an interesting initiative to make more long-term isotope records of river water available in the future.



## **Isotopic tracking of dietary choices in soil-living insect larvae**

*Nikolaus Schallhart, Manuel Tusch, Corinna Wallinger, Karin Staudacher & Michael Traugott*

*Mountain Agriculture Research Unit, Institute of Ecology, University of Innsbruck, Austria*

Stable isotope analysis is a useful tool to investigate trophic interactions in soil food webs, where direct observations are difficult due to the opaque habitat and the minuteness of many of the contributing species. In the present study we investigate the feeding behaviour of *Agriotes* larvae (Coleoptera: Elateridae), commonly known as wireworms, which are generalist plant feeders, abundant in soils and a serious pest worldwide. Using the analysis of stable isotopes under natural abundances, we aim at tracking the seasonal patterns in the dietary choices of wireworms in the field. Besides, mesocosm experiments are currently employed to experimentally examine the effect of plant diversity upon wireworm food choices, supplementing the field-derived data and conclusions.

The delta 13C signatures of *Agriotes* larvae collected in a weedy maize field in Tyrol (Austria) between May and October 2008 indicated a constant utilization of maize as a food source. A certain fraction of the population, however, was exclusively feeding on weeds during all time points investigated. Interestingly, the delta 15N values increased in both weed and maize feeding wireworms throughout the season. Delta 13C signatures of *Agriotes* larvae collected in September and October in a conventionally cultivated, weed poor maize field suggested that all of these insects had been feeding exclusively on maize. An increase in wireworms' delta 15N signatures, however, could not be observed in larvae collected in this conventional field.

Currently we are establishing mesocosm experiments where we aim at tracking the larvae's dietary choices at different plant diversity levels using a 15N labelling approach. First results indicate that individual plants can be efficiently labelled and that the isotopic label is not transferred to the soil or other unlabeled plants when the plants are grown together. These results provide an encouraging basis for the further experiments.

## **Dwarf shrub litter as food source of macrodecomposers on abandoned alpine pastureland: a field experiment using stable isotopes.**

*Julia Seeber, Alexander Rief, Erwin Meyer, Michael Traugott*

*Functional Biodiversity and Trophic Interactions Research Group, Institute of Ecology, University of Innsbruck, Technikerstr. 25, A- 6020 Innsbruck, Austria.*

Abandonment of alpine meadows and pastures leads to a change in litter composition, quality and quantity due to the emergence of dwarf shrubs. Dwarf shrub litter is thought to be of poor quality and palatability to macrodecomposers such as earthworms and millipedes, thus leading to a slower decomposition process.

In laboratory mesocosm experiments we previously have shown that earthworms and millipedes feed on dwarf shrub litter. It is not known, however, if and to what extent this is true under field conditions. Here, we report on the outcomes of a field experiment designed to determine to what extent earthworms and millipedes feed on dwarf shrub litter under natural conditions. Besides unlabelled grass litter, <sup>15</sup>N-labelled litter of the dwarf shrub *Vaccinium gaultheroides* was offered to the decomposers in an abandoned alpine meadow. Decomposers, plant- and soil material were sampled at several dates after applying the labelled substrate. This allowed us to determine by stable isotope analysis if and to what extent dwarf shrub litter was actually consumed and built-in into the topsoil by the decomposer species under field conditions. The outcomes of this field experiment provide new insights into the feeding habits of key decomposer species, the turn-over rate of litter material and its incorporation into the A-horizon on abandoned alpine pastureland.

## **Isotopes and climate change: a tale from a small cave**

*Christoph Spötl(1), Ronny Boch(1), Hai Cheng(2)*

*(1)Institut für Geologie und Paläontologie, LFU Innsbruck, Austria*

*(2)Department of Geology and Geophysics, University of Minnesota,  
Minneapolis, USA*

Speleothems are important terrestrial archives of the past climate and the principal proxy for paleo-precipitation is the O isotope composition of the calcite which is related to the drip water isotopic composition and the temperature. On orbital timescales speleothems from the greater alpine realm show high  $d^{18}O$  values during warm, interglacial periods and depleted values during cold climates. During the latter intervals, however, most caves, in particular those located high up on the mountains, are expected to freeze.

We will present a case study from a cave in the Allgäu Mountains, which contains speleothems as old as some 600,000 years. Contrary to conventional wisdom, speleothem deposition at this high-elevation site (close to 2000 m) was not limited to warm climates which supported soil formation above the cave. U-series ages demonstrate that specific conditions kept the karst fissure network warm enough to allow water-rock interactions and the subsequent precipitation of calcite even during full glacials, such as Marine Isotope Stage 12, one of the most prominent glacials of the Pleistocene. Stable isotope data record very large shifts in  $d^{18}O$  of up to 7 per mil at the transitions from interglacials into glacials, which cannot be accounted for by cooling alone.

## **Stable isotopic labeling of phenanthrene to identify degrading microorganisms and quantify biodegradation**

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A project to study in-situ stabilization of polycyclic aromatic hydrocarbons (ISPAK) was conducted to investigate the extraction efficiency of vegetable oil addition on polycyclic aromatic hydrocarbons (PAH) contaminated soil. One part of the project was to characterize the soil microbial community and its ability to degrade remaining PAHs and vegetable oil after successful remediation. The soil microorganisms were characterized by phosphate ether linked fatty acid (PLFA) analysis. The usage of <sup>13</sup>C natural labeled oil (maize oil) proved uptake of <sup>13</sup>C into the microbial biomass hence confirming biodegradation, however it did not allow quantification of the involved microorganisms owing to high fractionation during maize oil incorporation into PLFAs. For the investigation of PAH degradation a <sup>13</sup>C artificially labeled phenanthrene was used and incorporation of labeled PAH into single PLFAs was quantified. Generally the biodegradation of PAH in the soil without vegetable oil application was low (3 %), which corresponded well with the calculated uptake of labeled PAH into PLFAs. Under vegetable a higher proportion of PAH (14%) was degraded as indicated by measurements of the PAHs in the soil, while the incorporated percent incorporation of PAH into PLFAs was only 4.5%. One possible mechanism might be incomplete phenanthrene degradation i.e. generation of metabolites which were not further metabolized.

## **Mimicking floodplain reconnections and disconnections using <sup>15</sup>N mesocosm incubations**

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The Danube River and its floodplains along with all other large rivers in the industrialized world have been changed to fit the needs of society for agriculture and hydro-power. Human impacts, canalization and flood protection measures reduce the retention capacity of the riverine landscape in braided sections and limit the exchange of matter to short periods of high flow between the river main channel and adjacent floodplains. Particularly, there is a significant decrease of hydrologic exchange of surface waters. The secondary channels and various water bodies within the floodplain are disconnected from the main river flow for long periods. In order to counteract these negative impacts on the floodplains, large scale restoration projects are focusing on the need to increase hydrologic exchange with the floodplain below bankfull levels. The impact of these changes on biogeochemical cycling, particularly denitrification, within the floodplains has not been previously considered. The presented study quantified the rates of denitrification using short term mesocosm incubations with <sup>15</sup>N-NO<sub>3</sub> tracing to follow the pathway of nitrate uptake within different floodplain sections. Two sections were compared, one close to the Danube main channel in a restored section of the Orth floodplain, the other in a backwater pool in the non-restored floodplain Lobau. Triplicate sediment samples were incubated in the laboratory for five days in 25L mesocosms. The overlying water was exchanged either with Danube River water or water originating from a backwater pool, thus changing the composition and quality of DOM and the microbial communities. In order to trace the route of nitrate uptake, <sup>15</sup>N-NO<sub>3</sub> was added to the average background concentration of the Danube River and followed through the denitrification pathway. Denitrification rates were calculated based on isotopic analysis of a sampled N<sub>2</sub> mixture and the determination of the <sup>15</sup>N abundance of ammonium, nitrite, and nitrate. The introduction of Danube River water increased denitrification rates in both observed sites, whereas the introduction of water originating from the backwaters decreased denitrification rates.

**Stable isotope ratios in winter-grown feathers of great reed warblers (*Acrocephalus arundinaceus*), clamorous reed warblers (*A. stentoreus*) and their hybrids in a sympatric breeding population in Kazakhstan**

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Understanding the spatial structure of migratory bird populations is essential to describe the ecological and evolutionary processes of distribution. Endogenous markers such as stable isotopes show significant promise as a means of tracking animal movement and distribution. We sampled feathers from adult great reed warblers (*Acrocephalus arundinaceus*) and clamorous reed warblers (*A. stentoreus*) in a sympatric breeding population in Kazakhstan to study natural variation in stable isotope signature and its power to delineate wintering origin of populations on a continental scale (Africa vs. Asia) than has typically been used in earlier studies. The great reed warbler is a long-distance migrant that over-winters in sub-Saharan Africa, whereas the clamorous reed warbler performs a short-distance migration to the Indian sub-continent. Feather carbon ( $\delta^{13}\text{C}$ ), nitrogen ( $\delta^{15}\text{N}$ ) and deuterium ( $\delta\text{D}$ ) isotopes were obtained from winter-grown feathers of adult birds of both species and a small sample (N=3) hybrid great  $\times$  clamorous reed warblers. We found pronounced, highly significant differences in  $\delta\text{D}$ , and a sufficient, yet significant difference in  $\delta^{13}\text{C}$  between the two species. Our results show a significant variation in feather isotope signature between the two species to allow the general application of the stable isotope technique to resolve continental variation in winter distribution between closely related *Acrocephalus* species with sympatric natal origin. The isotope signatures of the hybrids clustered with those of the great reed warbler. Hence, a parsimonious suggestion is that the hybrids undergo moult in Afro-tropical wintering grounds, as do the great reed warbler. We conclude that stable isotopes are potentially powerful predictors for studies of origins migratory populations wintering in different continents.

# Posters

## **The use of isotope measurements for the separation of discharge components during hydrological events in a riparian forest ecosystem, Lunz/See, Austria.**

*Florian Hofhansl, Margarete Watzka, Wolfgang Wanek*

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In a riparian forest ecosystem nutrients are generally transported along the hydrological pathway from the atmosphere to the pedosphere. It is along this runoff gradient that most of the major exchange processes take place.

The overall nutrient input to the ecosystem can derive from external and internal sources. External inputs come from wet deposition (rainwater, fog) and dry deposition (aerosols, atmospheric particles), while the internal inputs originate from soil and rock erosion processes. Therefore the chemical composition of the rainwater is changed during the runoff over the canopy (throughfall) to the soil (soil water) into the ground (groundwater) and lately to the surface runoff (fluvial water). These ecosystem processes comprise important ecosystem services like the retention, filtering and purification of rainwater and the recirculation of the runoff via evaporation and thus exhibit the maintenance of the hydrological cycle.

In order to understand and quantify these processes along the hydrological pathway, water samples of different categories (rainwater, throughfall, soil water, groundwater and fluvial water) were taken and analysed for their chemical composition (An- Cat Ions, TOC/TN,  $^{18}\text{O}$  and  $^2\text{H}$ ). The importance and origin of nutrients available in these categories is then analysed via statistical methods (PCA, ANOVA) and computed by a hydrograph separation model. The deriving End-member-mixing-analysis (EMMA) gives insight into the contribution of different sources of nutrients to the hydrological discharge by using conservative tracers (e.g. Chloride,  $^{18}\text{O}$ ). These analyses illuminate the flow paths between terrestrial and aquatic systems and the biogeochemical functions of mobilization and retention of nutrients within different discharge categories of a riparian ecosystem.

## **Control of authenticity of Tyrolean milk by stable isotope measurements**

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Consumers are willing to pay elevated prices for specific product qualities, e.g. for food from a certain region, therefore the declaration of origin of these products needs to be controlled. Conventionally this is done by estimating the flow of goods and by controlling the documentation accompanying the products. However, this means are often not sufficient to detect intentional deception. The measurement of the stable isotope composition of products offers the possibility to investigate the product itself. The stable isotope ratios of the elements H, C, N, O and S are varying geographically due to diverse environmental conditions (e.g.: climate, geology, soil, altitude, geography...) thus creating individual patterns for each region. These patterns are transferred in different ways into plants and animals originating from a certain region. Therefore analysis of the stable isotope pattern is a potent tool for geographic differentiation.

Tyrolean milk is regarded as a high quality good produced under strict regulations in a special (alpine) environment. To protect Tyrolean milk from incorrectly declared milk originating from other regions/countries, stable isotope investigations have been carried out over a period of one year on samples from all regions of Tyrol. Samples have been measured for isotopic composition of H, C, N and O.

The observed variation in the isotopic pattern of the Tyrolean milk within the year can be explained by different feeding regimes during summer and winter. Comparison of the isotopic pattern of the Tyrolean milk and milk samples of the same age from other regions gives evidence for significant differences in the isotope ratios. As the investigated "non-Tyrolean" samples have been produced in neighbouring regions that should have similar isotopic signals due to comparable environmental conditions, presumably it should be even easier to distinguish between milk from farther regions and milk from Tyrol.



## **Heterogeneous mean transfer-times in an Alpine dolomite-karst massif, Austria: $\delta^{18}\text{O}$ , $^3\text{H}$ , $^3\text{H}/^3\text{He}$ , CFC, $\text{SF}_6$ , chloride and dye tracer – investigations**

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According to the European Water frame Directive it is a requirement that surface and groundwater in the EU should show good quality conditions by 2015. For the implementation of this goal it is necessary that any measures to improve groundwater quality show an impact within the upcoming 5 years. A prerequisite for any change of groundwater chemistry within this time frame is that the mean residence times of the groundwater bodies are shorter than 5 years.

A dolomite massif at the north front of the Eastern Alps (Upper Austria) was examined to establish the water cycle in respect of mean residence time (MRT) and recharge area with various isotope systems and tracer chemicals. Besides a previous tracer test for quick water movements during storm events (days) along karstified fracture zones, oxygen-18, deuterium, chloride and tritium were analysed over a time period of 18 years to estimate the MRT of the groundwater in this fractured dolomite aquifer. In addition,  $^3\text{H}/^3\text{He}$ , CFCs and  $\text{SF}_6$  were analysed at two springs covering a young (month) and an old water discharge ( $\sim 20\text{y}$ ) characteristic for karstwater dynamics.

The oxygen-18 and deuterium measurements fit well in the altitude dependent oxygen shift ( $0.2\text{‰} / 100\text{m}$ ) and indicate a water recharge close to the plateau of the dolomite massif at an altitude of 800-900m. A small shift towards higher deuterium excess in the springs compared to the valley precipitation in a nearby station indicate that part of the precipitation evaporates and is included in the rain at the top of the mountain plateau.

## **Food web analyses with stable isotopes of Tardigrades: a comparison between cryoconite-communities of Spitzbergen and a glacier in the Alps**

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Cryoconite holes are unique freshwater environments, which can cover 0,1-10 % of the ablation zone of a glacier. They are formed when solar heated dark debris melts down into ice. They occur globally in glaciated environments of polar and alpine glaciers. These individual ecosystems which resemble mini lakes with a sediment layer and a water column have distinct boundaries, energy flow and nutrient cycling. The supernatant water in a hole is frozen throughout the winter or even during a day-night cycle implying harsh conditions for cryoconite communities. During melting periods nutrients are available for the cryoconite communities. These nutrients may be stored from the sediment in the hole or originate from melt water and allochthonous input of the wind-deposited material. Cryoconite holes are settled by mainly microbial communities (viruses, bacteria, microalgae and protozoa). Depending on the geographic region also metazoa such as tardigrades, rotifers, nematodes, copepods and insect larvae can be found. Tardigrades have a high tolerance to a variety of extreme environmental conditions. They can enter an ametabolic dry stage called anhydrobiosis. The stable isotopes of nitrogen ( $\delta^{15}\text{N}$ ) and carbon ( $\delta^{13}\text{C}$ ) provide powerful tools for estimating the trophic positions of and carbon flow to the consumer, the tardigrade, in food webs.

## **Stable isotope composition of carbonate cements and replacement dolomites of the Trogkofel massif, (Lower Permian, Carnic Alps)**

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The Trogkofel massif, situated at the Austrian-Italian border, consists mainly of a succession up to 400 m in thickness of limestones deposited along a platform margin (Trogkofel Limestone). Shallow-water bioclastic grainstones, packstones and rudstones alternate with cementstone mounds rich in foliose algae, *Tubiphytes*, bryozoans and *Archaeolithoporella*. In the cementstone mounds, bioclasts are coated by thick fringes and botryoids of fibrous calcite that probably represents calcitized aragonite. Primary and intrinsic pores are filled by microbialite, and/or by mudstone to bioclastic wackestone.

Localized dolomitization is common in the Trogkofel section. Replacement dolomites show a wide range of shapes and fabrics, including anhedral xenotopic fabric, subhedral to euhedral hypidiotopic to idiotopic fabric, and replacement saddle dolomite.

The Trogkofel succession is riddled by palaeokarstic dykes and caverns filled by (a) isopachous cement fringes up to a few decimetres in thickness, and/or (b) by red, geopetally-laminated lime mudstone to bio-lithoclastic wackestone; geopetal laminasets locally are convoluted.

The top of the Trogkofel Limestone is a truncation surface which, in turn, is overlain by the Tarvis Breccia. The breccia is poorly sorted, typically clast-supported, and consists of angular lithoclasts embedded in a matrix of former lime mudstone. Both, matrix as well as lithoclasts, are dolomitized.

Various types of cement (isopachous, botryoidal, microbialite, calcite spar), karstic cavity fills (isopachous cements, internal sediment), and replacement dolomites of the Trogkofel section, as well as the Tarvis Breccia were analysed for their stable isotopic composition.  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  data produced so far allow to differentiate between replacement dolomites versus saddle dolomite of the Trogkofel section, and the Tarvis Breccia. Saddle dolomite shows the most depleted O isotope values, suggesting formation during relatively high temperatures. C isotope values are invariably positive in all dolomite types indicating no influence of organic diagenesis on the alkalinity of the deep-burial pore water. Matrix dolomite from the Tarvis Breccia shows slightly positive  $\delta^{18}\text{O}$  values. Calcite cements show a wide range in  $\delta^{18}\text{O}$  values (ca. -1 to -7 permil VPDB), which overlaps the composition of unaltered brachiopod shells (ca. -3 permil VPDB).

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# Map

