

# **Stable Isotope Network Austria**

## **Program & Abstracts**

**16<sup>th</sup> Stable Isotope Network Austria (SINA) Meeting**

**22<sup>th</sup> & 23<sup>rd</sup> November 2018**

**Lecture Hall 2, Alte Technik Campus,  
Rechbauerstr. 12, 8010 Graz**

## PROGRAM

**Thursday, 22<sup>nd</sup> November 2018**

12:30 – 13:30 Registration

13:30 – 13:45 Welcome & Introduction

### SESSION 1 (Chair: A. Leis & W. Piller)

13:45 – 14:30 **Keynote: M. Böttcher**

Stable isotopes as tracers in (Paleo-) hydrography and biogeochemistry of the Baltic Sea

14:30 – 14:45 **M. P. Stockinger**

Time-variability of the fraction of young water in a small headwater catchment

14:45 – 15:00 **Ch. Stumpp**

Which information can we get out of depth profiles of stable isotopes of water in snow and soils?

15:00 – 15:15 **M. Kralik**

Analysis of  $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ ,  $\delta^{88}\text{Sr}/^{86}\text{Sr}$  (SRM987),  $\delta^{18}\text{O}/^{16}\text{O}$  (VSMOW) and  $\delta^2\text{H}/^1\text{H}$  (VSMOW) isotopes to characterise groundwater and recharge in the Lake Neusiedl area

15:15 – 16:00 *Coffee & Tea Break*

16:00 – 16:15 **T. Harum**

Rhine river plume tracking with stable isotopes in Lake Constance

16:15 – 16:30 **G. Höfer-Öllinger**

Torrener Joch Fault Zone Hydrogeology – The Contributions from Stable Isotopes Investigations

16:30 – 18:30 *Open Discussion & Posters*

17:15 – 18:00 **Special talk in TU Graz Seminar Series „Geotechnics“ (located in HS L)**

**H. Madritsch** (NAGRA, Switzerland): Die Standortsuche für ein geologisches Tiefenlager für radioaktive Abfälle in der Schweiz: Überblick und Schlüsselaspekte

starting 19:30 **Social Dinner**

[Herzl Weinstube](#), Prokopigasse 12, 8010 Graz, (traditional restaurant)

**Friday, 23<sup>rd</sup> November 2018**

## **SESSION 2** (Chair: R. Boch & G. Winkler)

09:00 – 09:45 **Keynote: S. Bernasconi**

Measuring the temperature of geological processes with clumped isotopes: current state and future opportunities

09:45 – 10:00 **O. Schlegel**

$^{13}\text{C}$  and  $^{18}\text{O}$  Isotope Effects Resulting from High Pressure  $\text{CO}_2$  Cylinder Depletion

10:00 – 10:15 **D. Smajgl**

Laser based technique for  $\text{CO}_2$  flux measurements

10:15 – 10:30 **A. Füger**

Oxygen Isotope Fractionation During Smithsonite Formation From Aqueous Solutions

10:30 – 11:00 *Coffee & Tea Break*

11:00 – 12:30 **Poster Session** (including 3 min oral presentation in front of poster)

12:30 – 13:30 *Lunch Buffet in front of the Lecture Hall*

## **SESSION 3** (Chair: M. Dietzel & M. Kralik)

13:30 – 14:00 **Invited talk: A. Eisenhauer**

*Calcium Isotopes - Sensitive biomarkers for early diagnosis of osteoporosis and renal dysfunction*

14:00 – 14:15 **A. Demény**

Stable isotope analyses of the carbonate component of bones and teeth: The need for method standardization

14:15 – 14:30 **C. Martinez-Perez**

Stable isotope incubations and nanoSIMS analysis reveal that a small unicellular diazotroph is a key player in the marine N cycle

14:30 – 14:45 **K. Schmittner**

Impact of nitrogen deposition on forest biogeochemical processes investigated using a tool kit of stable isotope methods

14:45 – 15:00 **V. Mavromatis**

Zinc incorporation in calcite – Insights from Zn isotopes

15:00 – 15:15 **D. Hippler**

Genesis of Austroalpine magnesite deposits: Constraints from light stable C, O and Mg isotopes

15:15 – 15:45 *Coffee & Tea Break*

starting 15:45 **General Assembly** – Stable Isotope Network Austria (SINA)

## POSTERS

- |                          |   |
|--------------------------|---|
| <b>A. Baldermann</b>     | Carbon and oxygen isotope geochemistry of authigenic carbonates from the Miocene Islam Dağ section (eastern Azerbaijan)   |
| <b>R. Boch</b>           | Calcium- and iron carbonates from Erzberg – New insights from stable, unstable and clumped isotope data   |
| <b>D. Cseresznyés</b>    | Stable isotope compositions of dawsonite and other carbonates from the West-Hungarian natural CO <sub>2</sub> occurrence: implication for their origin                                    |
| <b>S. Eichinger</b>      | Calcium carbonate precipitation impairing the draining of tunnels – Stable C and O isotope fractionation and growth dynamics  |
| <b>N. C. Freistetter</b> | Deuterium as an intrinsic biogeochemical indicator of insects' invasiveness—A method development study  |
| <b>A. Föger</b>          | Lithium isotope fractionation during its incorporation in calcite affected by precipitation rate and pH   |
| <b>C. Grengg</b>         | How stable isotopes can be used to decipher reaction mechanisms within microbial induced concrete corrosion   |
| <b>G. Höfer-Öllinger</b> | Isotope Hydrogeology of S16 Perjen Tunnel Monitoring Programme, Tyrol, Austria  |
| <b>M. Horacek</b>        | Stable isotope analysis for control of declared geographic origin of Austrian apricots (from the Wachau area)   |
| <b>P. Koeniger</b>       | Long-term stable isotope ( $\delta^2\text{H}$ , $\delta^{18}\text{O}$ ) and hydro-chemical patterns of precipitation collected in weekly resolution in Hannover, Germany                  |
| <b>M. Kralik</b>         | Multi-tracer approach ( $\delta^{18}\text{O}$ , $^3\text{H}/^3\text{He}$ , CFC, SF <sub>6</sub> , $^{35}\text{S}$ ) to find the best emergency drinking water supply, Vorarlberg, Austria |
| <b>S. Leitner</b>        | Feasibility study to measure $\delta^{18}\text{O}_{\text{water}}$ via GC-IRMS   |
| <b>T. Meador</b>         | Stable isotope probing of microbial lipid biomarkers  |
| <b>T. Rinder</b>         | Origin of mine water and groundwater from the Ibbenbüren coalfield, North Rhine-Westphalia, Germany – interpretation of Sulfur, Oxygen and Hydrogen isotopic ratios                       |
| <b>B. Rossegger</b>      | Using stable isotopes for lube oil consumption measurement on combustion engines  |
| <b>K. Schott</b>         | Austrian Meteoric Water Line – a proxy based on isotope ratios in river water   |
| <b>D. Smajgl</b>         | Precision and accuracy of the Delta Ray Connect by yearlong measurements of $\delta^{18}\text{O}$ on water reference material   |

## POSTERS continued

- |                        |  |
|------------------------|--|
| <b>A. Spiridon</b>     | Consequences of climate change for agroecosystem carbon and nitrogen cycling – a stable isotope labelling study                          |
| <b>J. A. Stammeier</b> | Magnesium isotope evidence for enhanced crustal reworking as a cause for the Ediacarian mass extinction                                  |
| <b>J. A. Stammeier</b> | Potential Temperature Dependence of Zinc Isotope Fractionation during the precipitation of Smithsonite from Aqueous Solutions            |
| <b>A. Strick</b>       | Mechanisms and reaction kinetics of calcite precipitation from Novinjak-spring (Carinthia) traced by stable C, O, Ca, Mg and Sr Isotopes |
| <b>A. Wawra</b>        | Fate of <sup>15</sup> N fertilizer in plants and microbes following Biochar addition in an Austrian agricultural soil                    |
| <b>G. Winkler</b>      | Flow component characterization of alpine aquifers – an isotopic approach  |
| <b>E. Ziss</b>         | Biochar: Negative Emission Technologies are nice to the environment – Using stable isotopes in a citizen science approach                |

# SINA 2018

16th STABLE ISOTOPE NETWORK AUSTRIA MEETING

## Book of Abstracts

### Scientific Organizing Committee

Ronny Boch<sup>1</sup>

Martin Dietzel<sup>1</sup>

Albrecht Leis<sup>2</sup>

Werner E. Piller<sup>3</sup>

Gerfried Winkler<sup>3</sup>

<sup>1</sup>Institute of Applied Geosciences, Graz University of Technology

<sup>2</sup>JR-AquaConSol GmbH, Hydrological Concepts and Solutions

<sup>3</sup>Institute of Earth Sciences, University of Graz

## Oral Presentations

### Time-variability of the fraction of young water in a small headwater catchment

M.P. Stockinger<sup>1, 2</sup>, H.R. Bogen<sup>1</sup>, A. Lücke<sup>1</sup>, C. Stumpp<sup>2</sup> and H. Vereecken<sup>1</sup>

<sup>1</sup>Forschungszentrum Jülich GmbH, IBG-3: Agrosphere Institute, Jülich, Germany

<sup>2</sup>University of Natural Resources and Life Sciences Vienna, Institute of Hydraulics and Rural Water Management, Vienna, Austria.

Email: michael\_stockinger@boku.ac.at

The time precipitation needs to travel through a catchment to its outlet is an important descriptor of a catchment's susceptibility to pollutant contamination, nutrient loss and hydrological functioning. The fast component of water flow can be estimated by the fraction of young water (Fyw) which is the percentage of streamflow younger than 3 months. Fyw is calculated by comparing the amplitudes of sine waves fitted to seasonal precipitation and streamflow tracer signals. This is usually done for the complete tracer time series available neglecting annual differences in the amplitudes of longer time series. Considering inter-annual amplitude differences, we here employ a moving time window of one-year length in weekly time steps over a 4.5-years stable isotopes of water tracer time series to calculate 189 distinct Fyw results to test the following null hypotheses: (1) Fyw does not deviate more than  $\pm 2\%$  from the mean of all Fyw results indicating long-term invariance. Larger deviations would indicate either flow path changes or a change in the contribution of different flow paths; (2) within any four weeks Fyw does not change more than  $\pm 2\%$  indicating short-term invariance. Larger deviations would indicate a high sensitivity of Fyw to a 1-4 weeks shift in the start of a full one-year tracer sampling campaign; (3) for a given calendar month Fyw does not change more than  $\pm 2\%$  indicating seasonality of Fyw. In our study, all three null hypotheses were rejected. Thus, the Fyw results were time-variable, showed a high uncertainty in the chosen sampling time frame and had no pronounced seasonality. Based on high short-term variability of Fyw when the mean coefficient of determination  $R^2$  for precipitation and streamflow sine wave fits was below 0.2, we recommend an  $R^2$  of at least 0.2 when calculating Fyw. Furthermore, while investigated individual meteorological factors could not sufficiently explain variations of Fyw, the runoff coefficient showed a negative correlation with Fyw. This indicates that when annual runoff exceeds annual precipitation the catchment samples the deficit from storage which is old water, decreasing Fyw.

## Oral Presentations

### Which information can we get out of depth profiles of stable isotopes of water in snow and soils?

Christine Stumpp<sup>1</sup>, Kerstin Hürkamp<sup>2</sup>, Nadine Zentner<sup>3</sup>, Romain Chesnaux<sup>4</sup> and Benjamin Gralher<sup>3</sup>

<sup>1</sup>Institute of Hydraulics and Rural Water Management, University of Natural Resources and Life Sciences Vienna, Austria

<sup>2</sup>Institute of Radiation Protection, Helmholtz Zentrum München, Germany

<sup>3</sup>Institute of Groundwater Ecology, Helmholtz Zentrum München, Germany

<sup>4</sup>Centre d'Études sur les Ressources Minérales, Research Group "Risk Resource Water", Université du Québec à Chicoutimi, Chicoutimi, Canada

Email: [Christine.stumpp@boku.ac.at](mailto:Christine.stumpp@boku.ac.at)

Stable isotopes of water can give integrative information about water flow and transport processes. In cold regions during winter times, the isotopic composition of precipitation is preserved in the snow pack and partly altered due to fractionation processes. When melting, this melt water can be further traced in the pore water of the unsaturated zone for getting information about transit times and groundwater recharge rates. Both, information about fractionation processes in snow and about snow melt infiltration in the unsaturated zone can be gained from high resolution depth profiles of isotopes in the snow pack and in pore water.

We showed in snow cores in the Alps, that the isotopic composition from precipitation is generally well preserved in the snow. Differences mainly resulted from the difficulty in comparing precipitation amount and snow water equivalents and the temporal resolution of precipitation samples versus spatial information from high resolution profiles.

At two sites with and without vegetation in Canada, we used snow melt as a natural tracer and identified groundwater recharge rates. From high resolution depth profiles in the unsaturated zone, we found much deeper snow melt infiltration at the site without vegetation; however, the actual quantification of recharge rates was challenged by structural heterogeneities.

These high-resolution depth profile analyses in the unsaturated zone get more popular because recent developments in water-vapor equilibration laser spectroscopy allowing measurements of isotopes in the vapor phase not requiring any pore water extraction. However, we showed that some of the measured data were biased by carrier gas changes. Therefore, we developed a post-correction scheme resulting in the disappearance of apparent fractionation effects in upper soil layers.



## Oral Presentations

### Analysis of $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ , $\delta^{88}\text{Sr}/^{86}\text{Sr}_{\text{SRM987}}$ , $\delta^{18}\text{O}/^{16}\text{O}_{\text{VSMOW}}$ and $\delta^2\text{H}/^1\text{H}_{\text{VSMOW}}$ isotopes to characterise groundwater and recharge in the Lake Neusiedl area

A. Tchaikovsky<sup>1</sup>, H. Häusler<sup>2</sup>, M. Kralik<sup>2</sup>, A. Zitek<sup>1</sup>, J. Irrgeher<sup>3</sup> and T. Prohaska<sup>4,1</sup>

<sup>1</sup>Department of Chemistry, University of Natural Resources and Life Sciences Vienna, Division of Analytical Chemistry, Tulln, Austria

<sup>2</sup>Department of Environmental Geosciences, University of Vienna, Vienna, Austria

<sup>3</sup>Department for Marine Bioanalytical Chemistry, Helmholtz-Centre for Materials and Coastal Research, Institute for Coastal Research, Geesthacht, Germany

<sup>4</sup>Chair of General and Analytical Chemistry, Montanuniversität Leoben, Leoben, Austria

Email: martin.kralik@univie.ac.at

Isotopic pattern of  $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ ,  $\delta^{88}\text{Sr}/^{86}\text{Sr}_{\text{SRM987}}$ ,  $\delta^{18}\text{O}/^{16}\text{O}_{\text{VSMOW}}$  and  $\delta^2\text{H}/^1\text{H}_{\text{VSMOW}}$  were used to characterise groundwater and recharge of saline ponds in a clastic aquifer in East Austria. Therefore, shallow, artesian and thermal groundwater of the investigated aquifer along with rainfall and rivers were analysed using (MC) ICP-MS and IRMS. The  $n(^{87}\text{Sr})/n(^{86}\text{Sr})$  isotopic pattern changed with aquifer depth because of progressing bedrock leaching and dissolution with increasing groundwater residence time. The  $n(^{87}\text{Sr})/n(^{86}\text{Sr})$  isotope composition of shallow groundwater below saline ponds of  $0.71019 \pm 0.00042$  ( $U$ ,  $k=2$ ) was significantly different to thermal groundwater of  $0.71205 \pm 0.00033$  ( $U$ ,  $k=2$ ). In contrast to previous theories this result suggested no recharge of saline ponds by upwelling paleowater. Isotope pattern deconvolution revealed that rainfall accounted to about 60 % of the  $n(^{87}\text{Sr})/n(^{86}\text{Sr})$  isotope composition of shallow groundwater below saline ponds [1]. Analysed  $\delta^{18}\text{O}/^{16}\text{O}_{\text{VSMOW}}$  and  $\delta^2\text{H}/^1\text{H}_{\text{VSMOW}}$  isotopic composition of the same groundwater samples supported these findings.

The  $\delta^{88}\text{Sr}/^{86}\text{Sr}_{\text{SRM987}}$  isotope composition of groundwater decreased from about 0.25 ‰ in most shallow, to predominantly negative values of about -0.24 ‰ in artesian groundwater indicating leaching and dissolution of minerals formed by weathering processes. In turn, the  $\delta^{88}\text{Sr}/^{86}\text{Sr}_{\text{SRM987}}$  isotopic composition of deep thermal groundwater showed positive values of about 0.12 ‰ suggesting removal of  $^{86}\text{Sr}$  from solution by carbonate precipitation.

These results highlight the potential of  $\delta^{88}\text{Sr}/^{86}\text{Sr}_{\text{SRM987}}$  isotope ratios as an additional geochemical tracer.

#### References:

[1] Tchaikovsky, A., Häusler, H., Kralik, M., Zitek, A., Irrgeher, J., and Prohaska, T. (2018): Analysis of  $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ ,  $\delta^{88}\text{Sr}/^{86}\text{Sr}_{\text{SRM987}}$  and elemental pattern to characterise ground-water and recharge of saline ponds in a clastic aquifer in East Austria. *Isotopes in Environmental & Health Studies* (submitted)

## Oral Presentations

### Rhine river plume tracking with stable isotopes in Lake Constance

Till Harum<sup>1</sup>, Albrecht Leis<sup>1</sup>, Vera Winde<sup>2</sup>, Anna Noffke<sup>2</sup> and Thomas Wolf<sup>2</sup>

<sup>1</sup>JR-AquaConSol, Graz, Austria

<sup>2</sup>LUBW, Institute for Lake Research, Langenargen, Germany

Email: [till.harum@jr-aquaconsol.at](mailto:till.harum@jr-aquaconsol.at)

Lake Constance is an intensively used lake (e.g. fishing) and serving as a drinking water reservoir for more than 4 million people. The main tributaries of the lake (Rhine, Bregenzerach) are the dominant influence on its physical and chemical properties and thus a potential source for pollutants. The water body circulation of the lake have been intensively examined and modelled, but the river plumes, e. g. intrusion depth and mixing behavior of the main rivers input, were not yet well known. The BMBF–ReWaM Project “SEEZEICHEN” was established with one focus on the investigation of propagation paths of these river plumes. River water and lake water each show characteristic stable isotope signatures. The aim of the project is to examine the expansion, thickness and mixing of the river plumes through Lake Constance by combining isotope and element measurements for the identification of river water. These measurements involve the isotope composition of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of water as natural conservative tracers, the principal chemical composition (Cl,  $\text{SO}_4$ , Mg, Ca, Na) and the in situ investigation of physical parameters (conductivity, temperature, oxygen) using multi parameter probes.

To identify river plumes in Lake Constance at 4-7 transects through the Lake each with 4-6 depth profiles has been sampled in October 2016, February 2017 and July 2017. The isotope signatures have been measured on board of a research ship with Wavelength-Scanned Cavity Ringdown Spectroscopy. To gain a better insight on the input signal of the incoming river monitoring stations (Rhine, Bregenzerach) and the outflow (Seerhein) from the Lake Constance region has also been sampled including long-term isotope data from the river Rhine from the official Austrian and Swiss stations.

Results from the 3 measuring campaigns are presented (Figure 1). The isotopic compositions of the water body indicate an isotopic stratification in the metalimnion between 15-30 m during summer and fall, cause of the intrusion of river water with specific isotopic signature. The river water layer is in about 20m and can be tracked over the whole lake. In winter the lake showed no stratification and a well mixing.

The results show that stable isotopes are representing an “ideal” conservative tracer to detect river water plumes in lakes with input originating from high mountainous areas.

# SINA 2018

16th STABLE ISOTOPE NETWORK AUSTRIA MEETING

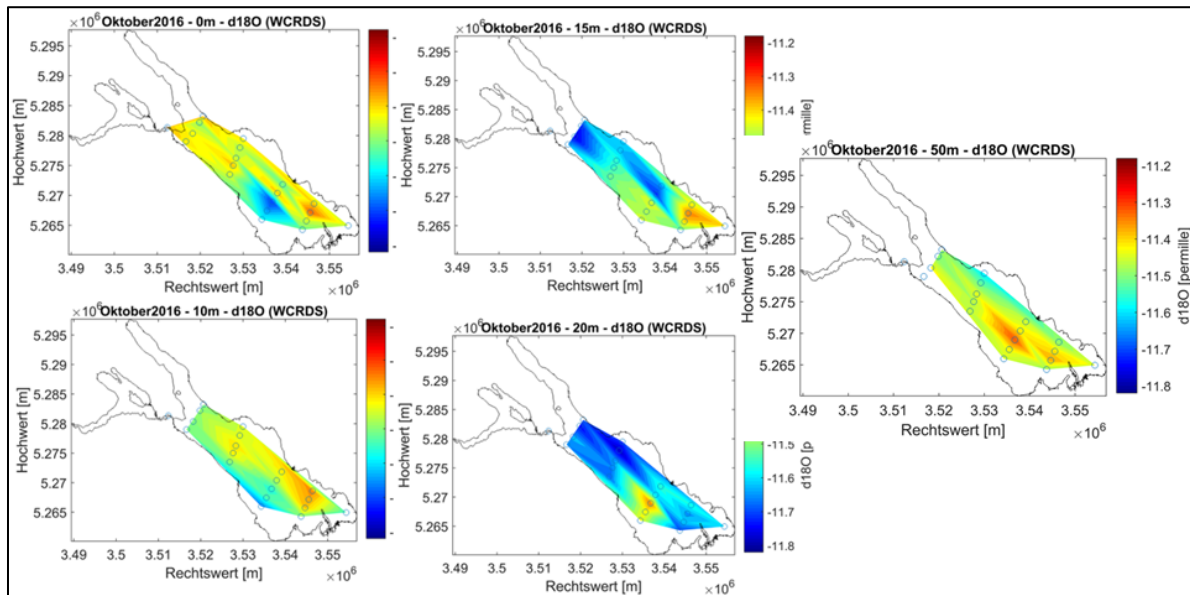


Figure 1: Dispersion of the stable isotope  $18O$  in different depths of the lake Constance

## Oral Presentations

### Torrener Joch Fault Zone Hydrogeology – The Contributions from Stable Isotopes Investigations

Giorgio Höfer-Öllinger<sup>1</sup> & Tim Schöne<sup>2</sup>

<sup>1</sup>Geoconsult ZT GmbH, Wals/Salzburg, Austria

<sup>2</sup>Freie Universität Berlin, Berlin, Germany

Email: giorgio.hoefer-oellinger@geoconsult.eu

The Torrener Joch Fault Zone is part of the sinistral Königsee-Lammertal-Traunsee strike-slip fault system (KLT, Decker et al., 1994) that cuts the Torrener Joch in East-West direction. It separates the Hoher Göll massive in the north from the Hagengebirge plateau in the south.

The hydrogeological processes of this fault zone are governed both, by karst and fault bound groundwater flow in the southern part of the fault zone. As the groundwater seems to percolate through Riedel structures in the Hagengebirge, a special emphasis was given to the tectonic setting of this zone (Höfer-Öllinger et al, 2018).

The southern branches of the Torrener Joch Fault Zone are commonly intercalated by upper Triassic and Jurassic rock mass on the one and by lower Triassic evaporate on the other hand. Due to high fluctuations of the karst groundwater level, water is in contact with the evaporates and dissolves them. This study provides a profound background for a new understanding of tectonic and landscape development in combination with hydrogeological processes. The interdisciplinary study combines findings of structural geology, modern monitoring techniques, conventional tracer tests, hydrochemical and numerical groundwater models with stable isotope measurements.

Since 2015, 175 water samples were taken in hydrogeological surface mappings and 362 in a weekly monitoring programme. The 537 samples were analysed for stable isotope (oxygen 18, oxygen 17 and deuterium) content.

In combination with regular measurement of in situ parameters (runoff, temperature, and electrical conductivity) the results of these analyses on the one hand confirm school book examples. On the other hand surprising new findings confirm conceptual models given in Buske (2018) and contribute to the understanding of groundwater runoff in the Bluntatal Valley, a distinctive geomorphological appearance of the Torrener Joch Fault Zone.

Fig. 1 shows the outcome of only one isotope (oxygen 18) in only 4 measurement points (1 karst spring, 1 surface creek, 1 groundwater seepage to a lake and 1 lake discharge). The very first findings of this study show that

- In spring snow melting governs the karst spring (“Schwarze Torren”) while the surface creek (“Fischbach”) shows most depleted values already in late winter and increases O<sup>18</sup> with the time.

- Increase of  $O^{18}$  during snow melting period may be governed by selective melting: This effect definitely seems to overprint a possible effect of increasing 0-degrees limit during early springtime.
- Filtration time between Schwarze Torren (and Fischbach surface creek, they merge immediately after the spring) and the Bluntau Lake is two months with surprising consistency.
- The process within the Bluntau Lake meanwhile is not so clear and can only be understood by additional groundwater accesses from other parts of the aquifer what coincidents with the existing hydrogeological model.

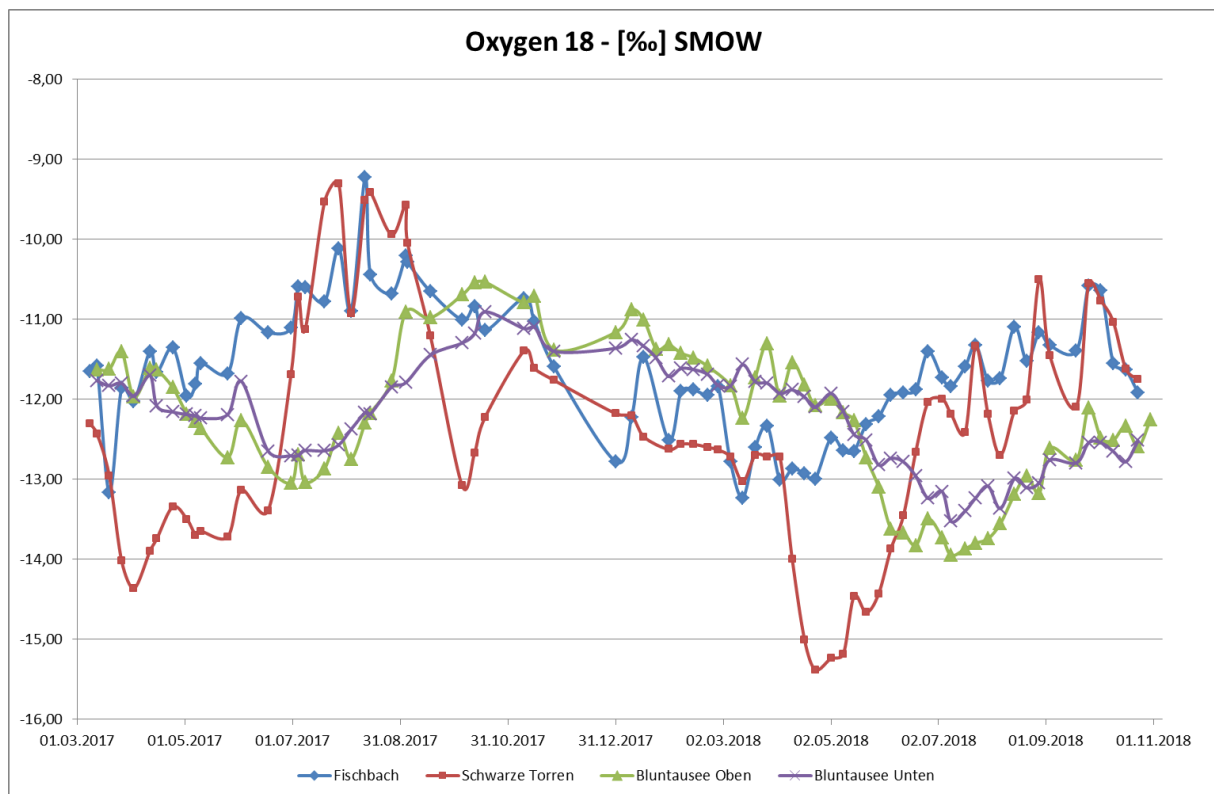


Fig. 1: Oxygen 18 values of selected hydrogeological monitoring points in the “Bluntau Valley”. “Fischbach” is the surface creek, “Schwarze Torren” the karst spring, “Bluntausee” is the lake where “oben” means groundwater seeping into the lake and “unten” the lakes discharge. The lake has no surface recharge.

## References:

- Buske, E. (2018) Hydrogeologische Untersuchung des Hagengebirges (nördliche Kalkalpen) mittels zeitlich hochauflösender Methoden – Grundwasserbeschaffenheit, -dynamik, -verfügbarkeit. – Unpub. MSc. thesis, 110 pp, Freie Universität Berlin.
- Decker, K.; Peresson, H.; Faupl, P. (1994) Die miozäne Tektonik der östlichen Kalkalpen: Kinematik, Paläospannungen und Deformationsaufteilung während der „lateralen Extrusion“ der Zentralalpen. Jahrbuch der Geologischen Bundesanstalt, 137 (1), pp. 5-18.
- Höfer-Öllinger, G.; Schneider, M.; Buske, E.; Volkmer, F.; Schöne, T.; Kessler, T.; Neubauer, F.; Müggenburg, K. & Heimlich, K. (2018) Hydrogeology of the Torrener Joch Fault Zone, Salzburg, Austria.

## Oral Presentations

### **Measuring the temperature of geological processes with clumped isotopes: current state and future opportunities**

Stefano Bernasconi<sup>1</sup>, Alvaro Fernandez-Bremer, Inigo A. Müller, Joep van Dijk and Nathan Looser

<sup>1</sup> Geological Institute, ETH Zürich, Zürich, Switzerland

Email: stefano.bernasconi@erdw.ethz.ch

Carbonate clumped isotope thermometry, which is based on the measurement of the abundance of <sup>13</sup>C-<sup>18</sup>O bonds in carbonate minerals, is a very promising tool for many applications in geosciences ranging from paleoceanography to the study of diagenesis and tectonics. The application of this tool in many fields of research, however, has been limited by the large sample sizes (15-30 mg) required by traditional measurement methods, the complex analytical methodology and contrasting published temperature calibrations which add considerable uncertainty in temperature reconstructions.

In this contribution I will shortly describe the latest improvements in small sample analysis developed at ETH and demonstrate that it is now possible to obtain measurements with errors of less than  $\pm 3^\circ\text{C}$  (at the 95% CI) with only 1-1.5 mg of carbonate. I will also show that with the introduction of a carbonate-based standardization scheme, differences in temperature calibrations across different laboratories are being resolved. New unpublished and published temperature calibrations suggest that clumped isotopes in calcite, siderite and dolomite all have the same temperature dependence, but that individual calibrations are necessary due to the different phosphoric acid fractionation factors. These improvements in analytical methods and interlaboratory consistency is improving the applicability of this tool to many fields. I will discuss applications in Mediterranean paleoceanography using foraminifera, reconstruction of terrestrial temperatures from paleosol siderites and, in combination with U/Pb Dating, how clumped isotope can provide new insights on the burial history and tectonics in mountain belts.

## Oral Presentations

### <sup>13</sup>C and <sup>18</sup>O Isotope Effects Resulting from High Pressure CO<sub>2</sub> Cylinder Depletion

Richard Socki<sup>1</sup> & Oliver Schlegel<sup>2</sup>

<sup>1</sup> Air Liquide, Research & Development, Newark, USA

<sup>2</sup> Air Liquide Austria GmbH, Wien Schwechat, Austria

Email: [oliver.schlegel@airliquide.com](mailto:oliver.schlegel@airliquide.com)

An equilibrium isotope fractionation in the liquid-vapor system of CO<sub>2</sub> for C and O isotopes is well established (i.e. Grootes, et al., 1969, Z. Physik 221). C isotopes tend to be enriched in <sup>13</sup>C in the vapor phase and O isotopes tend to be depleted in <sup>18</sup>O. This observation has particular relevance in contemporary stable isotope laboratory practices due mainly to the advent of Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS). For <sup>13</sup>C and <sup>18</sup>O measurements, CF-IRMS relies almost exclusively on incorporating a high pressure cylinder of CO<sub>2</sub> as a calibrated internal reference gas. If this reference gas contains a liquid phase, the laboratory's ability to produce reliable isotope data will be dependent on whether the isotopic composition of the CO<sub>2</sub> changes during cylinder depletion. Intuitively, one may presume that as the liquid CO<sub>2</sub> within that cylinder decreases, the vapor produced from that liquid will change isotopically to reflect known isotopic fractionation between those phases. This work quantifies the isotopic effect for <sup>13</sup>C and <sup>18</sup>O as a function of CO<sub>2</sub> cylinder depletion. CO<sub>2</sub> vapor samples from a cylinder that contains both liquid and vapor phases will be taken regularly and measured for both <sup>13</sup>C and <sup>18</sup>O. CO<sub>2</sub> will be depleted during sequential sampling and resulting cylinder contents monitored gravimetrically. Observed isotopic effects (fractionation) of the vapor from the depleted CO<sub>2</sub> cylinder will be reflected in the <sup>13</sup>C and <sup>18</sup>O composition of that vapor. Thus the last remaining liquid within the cylinder will likely show the largest isotope effects in both <sup>13</sup>C and <sup>18</sup>O in the CO<sub>2</sub> liquid-vapor system. These data will be useful for CF-IRMS researchers that rely on high pressure cylinders for CO<sub>2</sub> reference gas.

#### References:

Grootes, P.M., Mook, W.G. and Vogel, J.C. (1969) Isotopic fractionation between gaseous and condensed carbon dioxide. Zeitschrift für Physik, 221, 257-273.

## Oral Presentations

### Laser based technique for CO<sub>2</sub> flux measurements

Danijela Smajl<sup>1</sup> & Magda Mandic<sup>1</sup>

<sup>1</sup>Thermo Fisher Scientific GmbH, Bremen, Germany

Email: danijela.smajl@thermofisher.com

The isotopic composition of CO<sub>2</sub> has been widely used for studying ecosystem gas exchange. The carbon isotope ratio and oxygen isotope ratio of atmospheric CO<sub>2</sub> ( $\delta^{13}\text{C}$ ;  $\delta^{18}\text{O}$ ) can be used to partition the gross fluxes of CO<sub>2</sub> in terrestrial ecosystems, such as plant respiration, soil respiration and plant assimilation, as well as a tool for studying ocean-atmosphere interactions.

The characteristic  $\delta^{13}\text{C}$  value is modified by plant metabolism and photosynthesis, while the  $\delta^{18}\text{O}$  is affected by the oxygen exchange between the molecules of CO<sub>2</sub> and H<sub>2</sub>O which originate from different water pools.

Here we present new possibility for monitoring of CO<sub>2</sub> fluxes, Thermo Scientific™ Delta Ray™ spectrometers. Instrumentation is based on direct absorption spectroscopy and it uses mid-infrared laser that operates at 4.3  $\mu\text{m}$ . The laser scans over spectral region containing four CO<sub>2</sub> absorption lines and isotope ratios are calculated from the spectrum fit (Figure 1). Calculation of different CO<sub>2</sub> isotopologues and determination of stable isotope ratios from spectrum is possible due to absorption lines which are shifted relative to each other. In direct absorption laser spectroscopy, the calculated isotope ratios are highly dependent on the CO<sub>2</sub> concentration. Therefore, for maximal accuracy of the measurements, instrument has a possibility to adjust the concentration of reference gas to match the concentration of the sample gas. This technology enables simultaneous determination of  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and CO<sub>2</sub> concentration with precision better than 0.05‰. With measurement resolution of seconds, it is a great tool for monitoring quick changes in open systems and provides new insights in CO<sub>2</sub> fluxes.



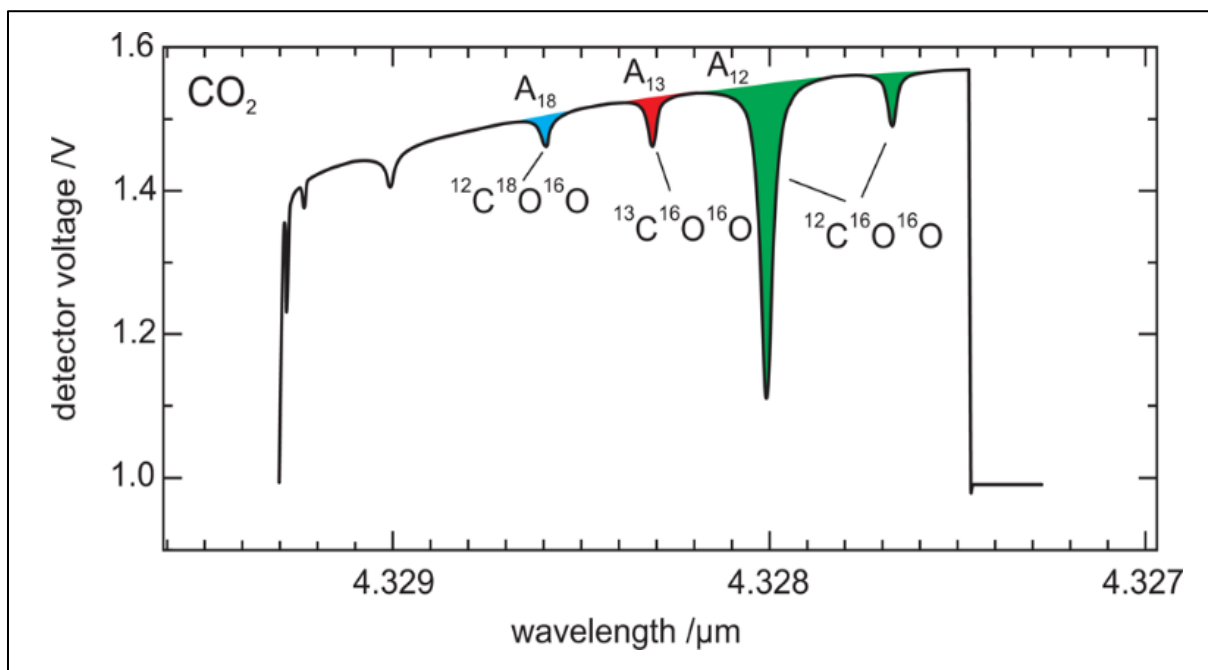


Figure 1: Mid-infrared spectral region at a wavelength of 4.3 μm and characteristic absorption lines for CO<sub>2</sub> isotopologues.

## Oral Presentations

### Oxygen Isotope Fractionation During Smithsonite Formation From Aqueous Solutions

A. Füger<sup>1</sup>, M. Méheut<sup>2</sup>, V. Mavromatis<sup>1,2</sup>, A. Leis<sup>3</sup> and M. Dietzel<sup>1</sup>

<sup>1</sup> Institute of Applied Geosciences, Graz University of Technology, Graz, Austria

<sup>2</sup> Géosciences Environnement Toulouse (GET), CNRS, UMR 5563, Observatoire Midi-Pyrénées, Toulouse, France

<sup>3</sup> JR-AquaConSol GmbH, Graz, Austria

Email: anja.fueger@student.tugraz.at

Owing to the large fractionation (i.e.  $\Delta^{18}\text{O}_{\text{solid-diss.}} \sim 30\text{‰}$ ) between carbonate minerals and aqueous fluids with respect to their  $^{18}\text{O}/^{16}\text{O}$  composition, the oxygen isotope composition of carbonates has been a fundamental tool for the estimation of mineral formation temperature by the geoscience community. Indeed the last 6 decades, a wide number of experimental studies investigated the temperature relation of  $\Delta^{18}\text{O}_{\text{solid-diss.}}$  between divalent metal carbonates and aqueous fluids. To date no experimental data exist for the oxygen isotope fractionation between smithsonite ( $\text{ZnCO}_3$ ) and water ( $\alpha_{\text{smithsonite-water}} = (^{18}\text{O}/^{16}\text{O})_{\text{smithsonite}} / (^{18}\text{O}/^{16}\text{O})_{\text{water}}$ ) and its temperature dependence. This lack of data is likely caused by the seldom occurrence of the physicochemical conditions required for smithsonite formation in Earth's surface environments and the competitive precipitation of hydrozincite ( $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ ). Smithsonite is a secondary zinc mineral that is one of the components of zinc ore bodies. It is formed through oxidation of primary zinc ores by the reaction with a carbonate source or by precipitation of zinc salt solutions with a  $\text{CO}_2$ -saturated and bicarbonate-rich solution. In the present study experimental work on smithsonite synthesis in the temperature range between 25 and 80 °C is coupled with ab-initio based theoretical calculations. The formation of smithsonite was induced by the transformation of hydrozincite at 25, 40, 60 and 80 °C. Our experiments were conducted in titanium batch reactors using Teflon-inlets where the  $\text{CO}_2$  pressure was adjusted to 10 bars. The low pH conditions provoked by the elevated  $p\text{CO}_2$  applied, lead to the dissolution of hydrozincite, which is initially formed by mixing of  $\text{Na}_2\text{HCO}_3$  (0.1 M) and  $\text{Zn}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$  (0.02 M) solutions, to yield - under the prevailing conditions - the thermodynamically stable mineral smithsonite. The experimental  $\alpha(^{18}\text{O})_{\text{smithsonite-water}}$  values fit within error in comparison to the theoretical values generated in this study and from the literature. Furthermore, the obtained  $\alpha(^{18}\text{O})_{\text{smithsonite-water}}$  values match with the general sequence of  $\text{Zn}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+} < \text{Ca}^{2+}$  for mono-cation trigonal Me-carbonate minerals suggesting incorporation of lighter oxygen isotopes in the carbonate mineral at increasing cation radius as indicated from thermodynamic considerations.

## Oral Presentations

### **Stable isotope analyses of the carbonate component of bones and teeth: The need for method standardization**

Attila Demény<sup>1</sup>, Ariana Gugora<sup>1</sup>, Dóra Kesjár<sup>1</sup>, Christophe Lecuyer<sup>2</sup> and Francois Fourel<sup>2</sup>

<sup>1</sup>Institute for Geological and Geochemical Research, RCAES, Hungarian Academy of Sciences, Budapest, Hungary

<sup>2</sup>Laboratoire de Géologie de Lyon, CNRS UMR 5276, University of Lyon, Lyon, France

Email: demeny.attila@csfk.mta.hu

Bones and teeth collected from archaeological excavations provide valuable bioarchaeological information, because their stable isotope compositions can be used in diet, migration and environmental studies. In addition to the collagen and phosphate components of bones and teeth, the stable carbon and oxygen isotope compositions of skeletal carbonate are frequently measured to determine paleodiet, environmental conditions and populational or individual migration. Despite the significance of these data, a standardized method for the stable isotopic analysis of skeletal carbonate has not been established. In this study, significant differences in the stable oxygen isotope values of bones and dental enamel were observed, which arose due to equipment- and methodology-based differences. The research samples were analysed at three laboratories, and stable isotope analyses were supplemented by Fourier Transformation Infrared Spectroscopy (FTIR) measurements that helped to detect a strong OH concentration-dependence in the stable oxygen isotopic shifts. Laboratory experiments were conducted to quantify the effects of reaction temperature and phosphoric acid concentration, both of which resulted in significant, though smaller  $\delta^{18}\text{O}$  changes than the OH-related  $\delta^{18}\text{O}$  change. As such, we suggest that the  $\delta^{18}\text{O}$  values of bones should not be included in anthropological interpretation and that the analysis of tooth enamel should be conducted at 70°C using 102%  $\text{H}_3\text{PO}_4$ , in order to make the results comparable. Furthermore, carbonated hydroxylapatite (CHAP) reference materials with varied isotopic compositions should be developed in the near future.

## Oral Presentations

### Calcium Isotopes – Sensitive biomarkers for early diagnosis of osteoporosis and renal dysfunction

Anton Eisenhauer<sup>1</sup>

<sup>1</sup>GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany

Email: aeisenhauer@geomar.de

We assessed the potential of Calcium (Ca) isotope fractionation measurements in blood ( $\delta^{44/42}\text{Ca}_{\text{Blood}}$ ) and urine ( $\delta^{44/42}\text{Ca}_{\text{Urine}}$ ) as a new biomarker for the diagnosis of osteoporosis and renal dysfunction. In a registered clinical study one hundred post-menopausal women aged 50 to 75 years underwent dual-energy X-ray absorptiometry (DXA), the gold standard for determination of bone mineral density (BMD). By multiple regression analyses it can be shown that the  $\delta^{44/42}\text{Ca}_{\text{Blood}}$  values are the best biomarker for osteoporosis and that no other clinical parameters need to be taken into account in order to improve diagnosis. Cut-off and equilibrium values for discrimination of patients suffering from osteoporosis were calculated from ROC (Receiver Operated Characteristics) analyses and mathematical modelling for  $\delta^{44/42}\text{Ca}_{\text{Blood}}$  and  $\delta^{44/42}\text{Ca}_{\text{Urine}}$ , respectively. It can be shown that DXA reflects BMD of selected bones only (femur and spine) whereas the Ca isotope biomarker reflects bone Ca loss of the whole skeleton. In addition, the close correlation between Ca isotopes and biomarkers of bone demineralization suggest that early changes in the range of days in bone demineralization are detected by Ca isotope values, long before radiological changes in BMD can manifest on DXA. Based on a simple quantitative model, it is made clear that the  $\delta^{44/40}\text{Ca}_{\text{Blood}}$  value in humans will provide a quantitative indication of the relative rates of bone mineral formation to mineral dissolution. Organisms experiencing an excess in bone Ca loss should have  $\delta^{44/40}\text{Ca}_{\text{Blood}}$  values that are below the equilibrium value. Whereas organisms experiencing a gain in bone Ca are characterized by  $\delta^{44/40}\text{Ca}_{\text{Blood}}$  values above the equilibrium value. In future individuals who fall below the ROC determined Ca isotope biomarker threshold values in blood and urine still undergo DXA examination to determine their individual risk of a broken bone. However, based on its high sensitivity to exclude osteoporosis in individuals with  $\delta^{44/42}\text{Ca}_{\text{Blood}}$  and  $\delta^{44/42}\text{Ca}_{\text{Blood}}$  values above the threshold limit, DXA measurements and exposure to radiation may be avoided.

## Oral Presentations

### Stable isotope incubations and nanoSIMS analysis reveal that a small unicellular diazotroph is a key player in the marine N cycle

Clara Martínez-Pérez<sup>1\*</sup>, Wiebke Mohr<sup>1</sup>, Carolin R. Löscher<sup>2</sup>, Julien Dekaezemacker<sup>1</sup>, Sten Littmann<sup>1</sup>, Pelin Yilmaz<sup>1</sup>, Nadine Lehnen<sup>1</sup>, Bernhard M. Fuchs<sup>1</sup>, Gaute Lavik<sup>1</sup>, Ruth A. Schmitz<sup>2</sup>, Julie Laroche<sup>3</sup> and Marcel M.M. Kuypers<sup>1</sup>

<sup>1</sup> Max-Planck-Institute for Marine Microbiology, Bremen, Germany

\* *current affiliation*: Department of Limnology and Bio-Oceanography, University of Vienna, Vienna, Austria

<sup>2</sup> Department of General Microbiology, Christian-Albrechts University, Kiel, Germany

<sup>3</sup> Department of Biology, Dalhousie University, Canada

Email: ctinez.p@gmail.com

Biological dinitrogen (N<sub>2</sub>) fixation is yet the largest source of new N to the ocean and thus exerts control on the export of organic matter and the sequestration of atmospheric carbon dioxide (CO<sub>2</sub>). Although much of the N<sub>2</sub> fixation research has focused on larger N<sub>2</sub>-fixing microorganisms (diazotrophs) in the past (namely *Trichodesmium* sp.), more recent molecular and size-fraction studies suggested that smaller, unicellular organisms could be major contributors to oceanic N<sub>2</sub> fixation [1]. The abundance and expression of *nifH* phylotypes is usually used to determine their relative activity within the community. How this genomic potential translates into the relative contribution of any given phylotype to total N<sub>2</sub> fixation is, however, not clear.

To assess this question we conducted a study on a longitudinal transect through the tropical North Atlantic. We measured bulk N<sub>2</sub> fixation rates in the euphotic zone using the improved <sup>15</sup>N<sub>2</sub> dissolution method and determined the single-cell N<sub>2</sub> fixation rates of the two most abundant diazotrophs using nanometer scale secondary ion mass spectrometry (nanoSIMS). Beside the filamentous cyanobacterium *Trichodesmium* sp., we found the small, unicellular UCYN-A to be most abundant. UCYN-A is a cyanobacterium that lives in symbiosis with a small picoeukaryotic alga with which it exchanges carbon and nitrogen compounds [2]. Single-cell analyses showed that, surprisingly, both *Trichodesmium* and UCYN-A contributed equally to N<sub>2</sub> fixation in the tropical North Atlantic despite their large size difference. This was mainly attributable to the higher activity and faster growth of UCYN-A. In addition to the originally described, small UCYN-A type, we also found a larger UCYN-A type at lower abundances. Together, these two types of UCYN-A contributed ~ 20% to total N<sub>2</sub> fixation in the tropical North Atlantic indicating their importance in this region. Based on the analysis of publically available databases, we determined that UCYN-A is widely distributed in the ocean, much farther than the tropical and subtropical ocean in which N<sub>2</sub> fixation is typically found. We thus hypothesize that UCYN-A is not only important in the tropical ocean but is also a key player in the global oceanic N cycle [3]

**References:**

- [1] Zehr et al. (2001) Nature 412, 635-638
- [2] Thompson et al. (2012) Science 337, 1546-1550,
- [3] Martínez-Pérez et al. (2016) Nature Microbiology 1, 16163.

## Oral Presentations

### **Impact of nitrogen deposition on forest biogeochemical processes investigated using a tool kit of stable isotope methods**

Kathrin Schmittner<sup>3</sup>, Andrea Watzinger<sup>1</sup>, Markus Gorfer<sup>5</sup>, Ulf Grandin<sup>2</sup>, Nathalie Korboulewsky<sup>2</sup>, Rob Rose<sup>2</sup>, Jutta Stadler<sup>2</sup>, Ika Djukic<sup>4</sup>, Thomas Dirnböck<sup>4</sup>, Rebecca Hood-Nowotny<sup>1</sup>

<sup>1</sup>University of Natural Resources and Life Sciences, Vienna (BOKU), Vienna, Austria

<sup>2</sup>ALTER-net-MSII Network, Vienna, Austria

<sup>3</sup>University of Vienna, Vienna, Austria

<sup>4</sup>Umweltbundesamt GmbH, Vienna, Austria

<sup>5</sup>AIT Austrian Institute of Technology GmbH, Vienna, Austria

Email: K.Schmittner@gmx.at

Meta-data analyses and model-based hypotheses state that global soil C storage is controlled by microbial scale processes of fungal competition for available nitrogen (N). Global trends of increasing atmospheric N deposition and the continuing use of inorganic N fertilizer in both agriculture and forestry mean that the soils vital function as a carbon sink is potentially under threat. We set out to experimentally investigate these hypotheses across a trans-European gradient of forest soils and provide reliable information on soil microbial responses to nitrogen inputs for predictive climate change models.

Changes in soil nutrient status could result in a chain reaction of interacting microbial mechanisms which in turn could lead to the shifts in underlying ecosystem biogeochemical process rates. Recent meta-analysis has shown that plant fungal symbiont community structure exerts a greater fundamental control over soil C storage than temperature, precipitation or net primary production. Based on the hypothesis that plant associated fungi effectively scavenge all available organic and inorganic N leaving little N for the growth of the free-living decomposer microbial community and preventing further breakdown of soil organic matter (SOM).

We have set up an experiment in which a series of dual isotope labelled C and N ingrowth beech litter bags have been incubating in-situ in the forest. Moreover, the treatment plots have received additional inputs of inorganic nitrogen fertilizer over an eight year period. We have studied both nitrogen and carbon dynamics in these systems using a tool box of stable isotope techniques.

## Oral Presentations

### **Control of geographic origin of wine from border regions: Evaluation of different analytical methods and combinations of methods to identify the right side of the border**

M. Horacek<sup>1,7</sup>, K. Kolar<sup>2</sup>, M. Hla<sup>3,8</sup>, B. Tobolkova<sup>4</sup>, T. Vaculovic<sup>3</sup>, C. Philipp<sup>5</sup>, B. Marosanovic<sup>6</sup>, O. Mikes<sup>2</sup>, M. Polovka<sup>4</sup>, M. Lojovic<sup>6</sup>, E. Belajova<sup>4</sup>, L. Daško<sup>4</sup>, E. Jankura<sup>4</sup> and P. Eder<sup>5</sup>

<sup>1</sup>Lehr- und Forschungszentrum Francisco Josephinum, Wieselburg, Austria

<sup>2</sup>Czech Agriculture and Food Inspection Authority, Brno, Czech Republic

<sup>3</sup>CEITEC, Masaryk University, Brno, Czech Republic

<sup>4</sup>National Agricultural and Food Centre, Food Research Institute / Department of Chemistry and Food Analysis, Bratislava, Slovak Republic

<sup>5</sup>Höhere Bundeslehranstalt und Bundesamt für Wein- und Obstbau, Klosterneuburg, Austria

<sup>6</sup>SP LABORATORIJA a.d., Member of VICTORIA GROUP, Becej, Serbia

<sup>7</sup>Department of Lithospheric Research, University Vienna, Vienna, Austria

<sup>8</sup>Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic

Email: [micha.horacek@josephinum.at](mailto:micha.horacek@josephinum.at)

In the presented project the investigation on discrimination of geographic origin in border areas is carried out. Authentic wine samples from the border areas of Austria, Czech Republic, Slovakia (and from Serbia) are investigated and compared by applying different physico-chemical methods (e.g. IRMS, NMR, ICP-MS, ICP-OES, EPR, HPLC, polyphenols, etc). The comparison of the data sets from the participating countries and the different applied methods will show, to which extent a differentiation can still be achieved in the border areas of the respective countries, which methods prove most efficient and sensitive and if a combination of methods will lead to an increased sensitivity. Furthermore, we also investigate the causes for the potential differentiation, which might be environmentally determined, or due to different agricultural and/or enological practices. First results are surprisingly promising. Inter-laboratory comparisons are carried out to avoid lab-effects.



## Oral Presentations

### Zinc incorporation in calcite – Insights from Zn isotopes

Vasileios Mavromatis<sup>1</sup>

<sup>1</sup>Institute of Applied Geosciences, Graz University of Technology, Graz, Austria

Email: [mavromatis@tugraz.at](mailto:mavromatis@tugraz.at)

Recent experimental studies suggest that the incorporation of Zn in calcite is accompanied by an enrichment of the heavier isotope (i.e.  $^{66}\text{Zn}$ ) in the growing solid phase. This finding however contrasts the well accepted principle that heavy isotopes tend to exhibit higher concentrations in the phase that is characterized by shorter/stronger bond lengths. Indeed both molecular dynamic simulations and EXAFS spectroscopic analyses suggest that the Zn-O bond length in the octahedral  $\text{Zn}^{2+}$  aquo ion is significantly longer compared to the hexa-coordinated  $\text{Zn}^{2+}$  in the calcite lattice that is uniquely substitutes in the Ca site. This observation together with speciation calculations coupled with ab-initio derived species-specific isotopic fractionation suggest that incorporation of Zn aquo ion into calcite structure does not proceed via the direct attachment of the octahedral  $\text{Zn}^{2+}$  on mineral surface. In contrast incorporation and subsequently isotopic fractionation is controlled by the adsorption of tetrahedral  $\text{Zn}^{2+}$  on mineral surface during mineral growth. Herein we discuss how the mechanism of incorporation affects isotopic composition of the solid in this mineral surface controlled reaction.

## Oral Presentations

### Genesis of east alpine magnesite deposits: Constraints from light stable C, O and Mg isotopes

Dorothee Hippler<sup>1</sup>, Fritz Ebner<sup>2</sup>, Heinz Mali<sup>2</sup> and Martin Dietzel<sup>1</sup>

<sup>1</sup> Graz University of Technology, Institute of Applied Geosciences, Graz, Austria

<sup>2</sup> Montanuniversität Leoben, Department of Applied Geological Sciences and Geophysics, Leoben, Austria

Email: dorothee.hippler@tugraz.at

Major east alpine magnesite ( $\text{MgCO}_3$ ) deposits from carbonatic and metamorphic hostrocks consist of Veitsch-type, sparry (e.g. Breitenau, Hochfilzen, Hohentauern, Radenthein, Kaswassergraben) and cryptocrystalline magnesite (e.g. Kraubath), the first-mentioned often associated with secondary dolomite and/or talc. Although the genesis and geological provenance of most of these ore deposits has been well studied, some ore formation mechanisms, including the (re-) mobilization of Mg, are still a matter of debate. Two scenarios depict the deposition of magnesite ores: (1) through precipitation of evolved Mg-rich fluids (e.g. seawater) in an evaporative shallow setting or (2) by hydrothermal replacement of precursor carbonates, with the Mg being derived from either leaching of Ca-Mg-carbonates and/or Mg-rich silicates. The investigation of the isotopic ratios of carbon and oxygen ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ) and magnesium ( $\delta^{26}\text{Mg}$ ) in the different magnesites should hence contribute to an improved understanding of the geological-geochemical processes and potential Mg sources. We found that the  $\delta^{26}\text{Mg}$  values of the studied east alpine magnesite deposits, ranging from -2.88 ‰ to -0.49 ‰ (DSM-3), as well as fractionation factors between magnesites and respective hostrocks, first constrain interpretations from existing  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  data. And secondly, provide evidence for Mg-cycling during distinct water-rock interactions. Since the novel obtained  $\delta^{26}\text{Mg}$  signatures, furthermore, exhibit site-specific characteristics, they have been added to the „Austrian Isotope Catalogue of Ore Deposits“.

## Poster

### Carbon and oxygen isotope geochemistry of authigenic carbonates from the Miocene Islam Dağ section (eastern Azerbaijan)

Andre Baldermann<sup>1</sup> & Elshan Abdullayev<sup>2</sup>

<sup>1</sup>Institute of Applied Geosciences & NAWI Graz GeoCenter, Graz University of Technology, Graz, Austria

<sup>2</sup>Academician H. Aliyev Institute of Geography, Azerbaijan National Academy of Science, Baku, Azerbaijan

Email: baldermann@tugraz.at

The paleo-oceanographic and paleo-climatic evolution of the Euxinic-Caspian Basin in the Eocene to Miocene is recorded in the widespread deposition of mixed argillaceous-calcareous sediments of the “Maykop facies”, which represent source rocks for hydrocarbons of huge economic significance in eastern Azerbaijan. Sedimentary facies and chemical proxies (CIA values, element ratios etc.) indicate deposition of “carbonate-free” argillites under dominantly (semi)arid and anoxic conditions in the early Miocene, followed by a shift to oxygenated and more humid conditions in the middle Miocene, which is reflected by massive occurrences of “carbonate” argillites. Accompanying these changes in the depositional environment, distinct differences in the spatial distribution, mineralogy and isotopic composition of the authigenic carbonate fraction are recognizable: low-Mg calcite ( $-34.5$  to  $-16.0$  ‰ of  $\delta^{13}\text{C}$  and  $-48.7$  to  $-12.5$  ‰ of  $\delta^{18}\text{O}$ ) occurs in trace amounts (0-4 wt%) in the lower part of the Islam Dağ section, whereas high amounts (up to 30 wt%) of low-Mg calcite and high-Mg calcite ( $-10.6$  to  $+1.7$  ‰ of  $\delta^{13}\text{C}$  and  $-27.6$  to  $-4.8$  ‰ of  $\delta^{18}\text{O}$ ) occur at the top of the section. Noteworthy, the low-Mg calcite is strongly depleted in  $^{13}\text{C}$  and  $^{18}\text{O}$  with respect to common marine carbonates. The extreme enrichment in  $^{12}\text{C}$  is likely attributable to the microbial mediated anaerobic oxidation of methane, released from decaying organic matter, following alteration of methane to DIC and subsequent precipitation of isotopically light calcite. With respect to the oxygen isotopes, recent sub-surface alteration of pyrite into gypsum is thought to produce interstitial solutions that are heavily enriched in  $^{16}\text{O}$ , from which isotopically light carbonates can precipitate. In contrast, the isotopic composition of pure high-Mg calcite ( $-4.5$  to  $+1.7$  ‰ of  $\delta^{13}\text{C}$  and  $-5.1$  to  $-4.8$  ‰ of  $\delta^{18}\text{O}$ ) is similar to marine Miocene carbonates ( $\sim -5$  ‰, PDB, for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ), which suggests precipitation of this mineral phase during early marine diagenesis at elevated Mg/Ca ratios of the interstitial solutions. In this particular case, the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  isotopic signature of the authigenic carbonate fraction can be successfully used to distinguish between pristine marine signals and alteration processes linked to meteoric diagenesis.

## Poster

### Calcium- and iron carbonates from Erzberg – New insights from stable, unstable and clumped isotope data

R. Boch<sup>1</sup>, T. Kluge<sup>2</sup>, X. Wang<sup>3</sup>, A. Leis<sup>4</sup>, K. Lin<sup>3</sup>, H. Pluch<sup>5</sup>, F. Melcher<sup>6</sup> and M. Dietzel<sup>1</sup>

<sup>1</sup>Institute of Applied Geosciences, Graz University of Technology, Austria

<sup>2</sup>Institute of Environmental Physics, University of Heidelberg, Germany

<sup>3</sup>Earth Observatory of Singapore, Nanyang Technological University, Singapore

<sup>4</sup>JR-AquaConSol GmbH, Graz, Austria

<sup>5</sup>VA Erzberg GmbH, Eisenerz, Austria

<sup>6</sup>Chair of Geology & Economic Geology, Montanuniversität Leoben, Austria

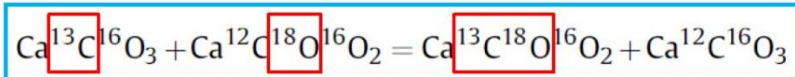
Email: ronny.boch@tugraz.at

The iron ore deposit Erzberg ranges amongst the most prominent places in Austria due to its historic and economic value. It mainly consists of various carbonate minerals including widespread siderite and ankerite, as well as rare aragonite-calcite veins (“erzbergite”) precipitated in vertical fractures. During several sampling visits, Fe- and Ca-(Mg)-carbonate host rocks and erzbergite fracture fillings, as well as modern water samples were recovered. Stable, radiogenic and multiply-substituted (clumped) isotope compositions were analyzed in order to evaluate genetic aspects of the aragonitic veins and Fe-rich carbonate minerals.

Stable  $\delta^{13}\text{C}$  vs.  $\delta^{18}\text{O}$  isotope values of siderite, ankerite, calcite and aragonite support lime-/dolostones as the principal source rock for erzbergite formation. The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  signatures of modern waters revealed systematic spatial differences regarding the water infiltration areas and hydrochemical evolution at Erzberg. The latter includes processes such as sulfide oxidation and prior  $\text{CaCO}_3$  precipitation in the aquifer. Radiometric  $^{234}\text{U}$ - $^{230}\text{Th}$  age determination yielded absolute ages from  $285.1 \pm 3.9$  to  $1.03 \pm 0.04$  kyr BP for different erzbergite samples ( $n=20$ ) including material from mineral collections. Most of these samples were dated with age uncertainties ( $2\sigma$ ) of 0.5 to 1 % (decades to few hundred years). Unexpectedly, all vein samples collected from fractures on-site are younger than the last glacial maximum ( $< \sim 20$  kyr BP). Considering the distinct erzbergite formation mechanisms (Boch et al., 2018, Sedimentology), the mostly vertical fractures are probably of young age too.

Clumped ( $^{13}\text{C}^{18}\text{O}$ ) isotope measurements of erzbergite aragonite ( $n=7$ ) revealed cool to near-freezing (water) temperatures of  $\sim 0$  to  $10$  ( $\pm 5$ ) °C, i.e. a rare case of aragonite crystallization at low temperature. The temperature range is in line with a higher elevation alpine meteoric setting restricted by recurrent freezing (and dryness) during cool climate intervals. This is further corroborated by meteoric paleo-fluid  $\delta^{18}\text{O}$  isotope compositions ( $-11.8$  to  $-8.7$  ‰ VSMOW) calculated

from the aragonite  $\Delta_{47}$  and  $\delta^{18}\text{O}$  analyses, as well as by measured  $\delta^{18}\text{O}$  isotope signatures of small water flows encountered in fractures of the open pit mine today. Clumped isotope data of the iron ore carbonates siderite and ankerite yielded temperatures from ca. 200 to 400 °C and the ankerites typically show higher temperatures. Parental fluid  $\delta^{18}\text{O}$  signatures calculated from the directly measured carbonate  $\Delta_{47}$  and  $\delta^{18}\text{O}$  compositions support prominently enriched fluid  $\delta^{18}\text{O}$  values (10.0 to 22.1 ‰ VSMOW) probably indicative of highly saline, reducing (redox) and episodically mobilized Fe-rich thermal fluids promoting the regional iron ore formation (cf. Prochaska, 2012).



”Clumped Isotopes”: Single-phase equilibrium describing the temperature dependent clumping of relatively rare and heavier  $^{13}\text{C}$  and  $^{18}\text{O}$  isotopes into a carbonate functional group during Ca-carbonate precipitation.

## Poster

### **Stable isotope compositions of dawsonite and other carbonates from the West-Hungarian natural CO<sub>2</sub> occurrence: implication for their origin**

Dóra Cseresznyés<sup>1</sup>, György Czuppon<sup>2</sup>, Csilla Király<sup>1</sup>, Zsuzsanna Szabó<sup>1</sup>, Csaba Szabó<sup>1</sup>, Attila Demény<sup>2</sup>, Martin Dietzel<sup>4</sup>, Bettina Purgstaller<sup>4</sup>, Mavromatis Vasileios<sup>4</sup> and György Falus<sup>1</sup>

<sup>1</sup>Eötvös University, Lithosphere Research Group, , Budapest, Hungary

<sup>2</sup>Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, HAS, Budapest, Hungary

<sup>3</sup>Geographical Institute, Research Centre for Astronomy and Earth Sciences, HAS, Budaörsi út 45, Budapest, Hungary

<sup>4</sup>Graz University of Technology, Institute of Applied Geosciences, Graz, Austria

Email: cherry.dori@gmail.com

Carbon capture and storage have become a vital problem in the last decades because the concentration of carbon-dioxide is constantly increasing in the atmosphere in relation with anthropogenic emissions. To reach long-term safety of geological storage of CO<sub>2</sub>, we need to know the geological environment, its behavior, and the influence of the complex physical and chemical reactions on the studied system. The investigation of natural CO<sub>2</sub> occurrences helps understand and predict what processes are likely to occur in CO<sub>2</sub> geological storage reservoirs over geological time scales. In the present work we provide a detailed insight into the stable isotope compositions of different carbonate minerals of a natural CO<sub>2</sub> reservoir from the Mihályi-Répcelak area, W-Hungary. The study of stable isotope systems gives important information on the origin of fluids (CO<sub>2</sub> and H<sub>2</sub>O). We measured the C and O isotopic compositions of different carbonate minerals (dawsonite: NaAlCO<sub>3</sub>(OH)<sub>2</sub> and siderite: FeCO<sub>3</sub>) and whole rock samples. In addition, we have determined the H isotopic composition of structural OH<sup>-</sup> in dawsonite. Using the obtained isotopic values and fractionation factor for calcite (as the determination of fractionation factor for dawsonite is in progress), the δ<sup>13</sup>C values of CO<sub>2</sub> in equilibrium with dawsonite and the δ<sup>18</sup>O values of water in equilibrium with carbonate minerals were calculated. The results indicate that the CO<sub>2</sub>, which was present during the formation of carbonate minerals, had magmatic origin, whereas the percolating water likely had a meteoric origin with an oxygen isotopic composition modified during prolonged water-rock interaction.

## Poster

### Calcium carbonate precipitation impairing the draining of tunnels – Stable C and O isotope fractionation and growth dynamics

Stefanie Eichinger<sup>1</sup>, Ronny Boch<sup>1</sup>, Albrecht Leis<sup>2</sup> and Martin Dietzel<sup>1</sup>

<sup>1</sup>Institute of Applied Geosciences, Graz University of Technology, Austria

<sup>2</sup>JR-AquaConSol GmbH, Graz, Austria

Email: stefanie.eichinger@tugraz.at

The unwanted formation of calcium carbonate deposits in tunnel drainage systems is a widespread phenomenon, which frequently causes disturbed flow regimes and water draining and finally severe clogging of the drainage system. Extensive and repeated maintenance procedures, e.g. mechanical and/or chemical removal of the scales, are cost and time intensive factors for tunnel operation companies. The formation of calcium carbonate and its prevention in such environments is still not completely understood with regard to the determining spatiotemporal processes. Therefore, in the present study, different scales and related aqueous solutions from different sections of the drainage system in a selected Austrian motorway tunnel were collected in order to decipher the distinct depositional mechanisms and environmental dependencies of calcium carbonate formation.

Mineralogical, petrographic and chemical analyses of the scales revealed complex precipitation features of the  $\text{CaCO}_3$  polymorphs calcite and aragonite, in which calcite is most dominant. The distribution of the stable C isotopes of dissolved inorganic carbon (DIC) and of C and O isotopes in the carbonate precipitates were used to decipher the origin of the mineral forming  $\text{CO}_3^{2-}$  ion, i.e. deriving from the local ground water DIC, as well as from the tunnel atmospheric  $\text{CO}_2$ . Stable C and O isotopic fractionation between solid and aqueous carbonate components can be used to trace the distinct although variable growth behavior of calcite and aragonite. Equilibrium versus kinetic fractionation patterns of stable C and O isotopes primarily reflects the dynamics of temperature variations,  $\text{CO}_2$  exchange and/or associated pH fluctuations, as well as intermittent evaporation and (turbulent) flow regimes. A remotely-controlled scale guard (alert) sensor system is currently implemented for *in-situ* monitoring of the ongoing scaling process in different sections of the drainage system. These robust sensors allow for an online and on-site tracking of temperature, pH, electric conductivity and redox potential over time focusing on a potential impact of natural and man-made environmental changes, which affect the isotopic composition of the aqueous solutions and the resulting precipitates. The principal goal of these studies is an advanced understanding of the variable scale formation conditions, scale characteristics and reaction mechanisms to reduce scaling in tunnel drainage systems.

## Poster

### Deuterium as an intrinsic biogeochemical indicator of insects' invasiveness – A method development study

N.C. Freistetter<sup>1,3</sup>; G. Simmons<sup>2</sup>; A. Watzinger<sup>3</sup> and R. Hood-Nowotny<sup>3</sup>

<sup>1</sup>University of Applied Sciences Technikum Wien, Vienna Austria

<sup>2</sup>USDA, APHIS, PPQ, CPHST, California Station, Salinas, USA

<sup>3</sup>University of Natural Resources and Life Sciences, Tulln, Austria

Email: freistetter.nadine@gmail.com

Gypsy moth (*Lymantria dispar*) caterpillars are a major pest to deciduous trees and cause extensive defoliation in US forests. Herein we present an evaluation strategy to distinguish established Gypsy moth populations from invasive, newly established ones. This could help improve insect pest management.

Natal provenance of Gypsy moths was determined based on the local isotopic water signatures imprinted in their biological tissues and global geographic variations in water isotope signals. It is well known that a proportion of the  $\delta^2\text{H}$  signature exchanges readily, however there are few values on the percentage exchangeable  $\delta^2\text{H}$  in insects. Gypsy moth samples from 22 locations in Europe, Asia and the USA were analysed for  $\delta^2\text{H}$  with a TC/EA-IRMS system by Thermo Fisher.

In parallel studies, we determined the percentage of exchangeable hydrogen in the moth's tissue. Ten samples were split into two groups, which then were put into two different micro-atmospheres. The samples were left to equilibrate and then dried before  $\delta^2\text{H}$  measurement. Based on two source mixing models, the percentage of exchangeable hydrogen was determined.

This percentage was used to calculate the true, intrinsic isotopic signature of the moth samples. Regressions between the intrinsic  $\delta^2\text{H}$  of moths and the  $\delta^2\text{H}$  of the precipitation at the moth capture sites were used to calculate back to the  $\delta^2\text{H}$  value of the moths' natal origins.

There was a strong correlation between the  $\delta^2\text{H}$  in precipitation and the  $\delta^2\text{H}$  in the moths for each continent (e.g. Europe:  $R^2=0,91$ ). The moths found in Europe, China and eastern USA appeared to be part of native populations, as expected. The data suggested that specimens from California and Louisiana were invasive non-native specimens, fortunately, since to date there are no confirmed established Gypsy moth colonies in those regions. However sadly, the eggs found in Juneau, west coast Alaska, suggest that they were the product of an established Gypsy moth population as their highly negative values were consistent with the snowy waters of Alaska. These data show the potential of isotope tools to address critical issues of invasive species encroachment and reveal possible entry pathways to target in achieving effective pest management.



## Poster

### Lithium isotope fractionation during its incorporation in calcite affected by precipitation rate and pH

A. Fuger<sup>1</sup>, M. Kussner<sup>2</sup>, C. Rollion-Bard<sup>2</sup>, A. Leis<sup>3</sup>, M. Dietzel<sup>1</sup> and V. Mavromatis<sup>1,4</sup>

<sup>1</sup>Institute of Applied Geosciences, Graz University of Technology, Graz, Austria

<sup>2</sup>Institut de Physique du Globe de Paris, CNRS UMR71541, Paris, France

<sup>3</sup>JR-AquaConSol GmbH, Graz, Austria

<sup>4</sup>Geosciences Environnement Toulouse (GET), CNRS, UMR 5563, Observatoire Midi-Pyrenees, Toulouse, France

Email: anja.fueger@student.tugraz.at

The isotopic signals of trace elements in carbonate minerals are routinely used as geochemical tools to unravel the environmental conditions during formation e.g. throughout the geological past. The Li isotope system has been received large attention mainly due to its isotope fractionation effects observed during continental silicate weathering and secondary mineral formation such as carbonates at the seafloor. However, the latter fractionation effects during calcite formation are still less explored. In the present study the influence of precipitation rate ( $10^{-8.2} < r_p \text{ (mol m}^{-2} \text{ s}^{-1}) < 10^{-7.1}$ ) and pH ( $6.3 < \text{pH} < 9.6$ ) on the behavior of lithium isotope fractionation during calcite formation was investigated. Therefore, calcite precipitation was induced by simultaneous pumping of two solutions ( $\text{CaCl}_2 + \text{LiCl}$ ;  $\text{Na}_2\text{CO}_3$ ) into a reaction vessel containing calcite seeds using a peristaltic pump at 25 °C. The pH was adjusted by distinct  $\text{pCO}_2$  of the introduced gas phase or by NaOH titration. The obtained  $\Delta^7\text{Li}_{\text{calcite-fluid}}$ , defined by the difference between  $\delta^7\text{Li}_{\text{calcite}}$  and  $\delta^7\text{Li}_{\text{fluid}}$ , shows a higher Li isotope fractionation ( $-2.6 \text{ ‰} < \Delta^7\text{Li}_{\text{calcite-fluid}} < -5.3 \text{ ‰}$ ) at elevated precipitation rate keeping pH = 8.5. The lithium isotope fractionation is positively correlated with the incorporation of Li during the growth of calcite and can thus be explained by a kinetically driven entrapment approach: Higher precipitation rates force the incorporation of Li ions at the growing surface, where lighter Li isotopes are preferential entrapped in calcite. In case of a constant precipitation rate (i.e.  $10^{-7.7} \pm 0.2 \text{ mol m}^{-2} \text{ s}^{-1}$ ) the  $\Delta^7\text{Li}_{\text{calcite-fluid}}$  values indicate a smaller Li isotope fractionation (from -5.3 ‰ to -2.3 ‰) with increasing pH up to 8.5 is reached, whereas at pH > 8.5  $\Delta^7\text{Li}_{\text{calcite-fluid}}$  increases from -2.3 ‰ to -4 ‰. The incorporation of lithium during the growth of calcite is lower at elevated pH corresponding to lower  $\text{HCO}_3^-$  concentration, assuming a co-entrapment with  $\text{HCO}_3^-$  in order to balance the positive charge during  $\text{Li}^+$  incorporation. Accordingly, it is postulated that changes in  $\Delta^7\text{Li}_{\text{calcite-fluid}}$  at a given precipitate rate can be affected by variability in  $\text{CO}_3^{2-}/\text{HCO}_3^-$  ratio of the fluid.

## Poster

### **How stable isotopes can be used to decipher reaction mechanisms within microbial induced concrete corrosion**

C. Grengg<sup>1</sup>, F. Mittermayr<sup>2</sup>, A. Leis<sup>3</sup>, M. Böttcher<sup>4</sup> & M. Dietzel<sup>1</sup>

<sup>1</sup>Institute of Applied Geosciences, Graz University of Technology, Austria

<sup>2</sup>Institute of Technology and Testing of Building Materials, Graz University of Technology, Austria

<sup>3</sup>JR-AuqaConSol GmbH, Graz, Austria

<sup>4</sup>Geochemistry & Isotope-Biogeochemistry, Leibniz-Institute for Baltic Sea Research (IOW), Germany

Email: [cyrill.grengg@tugraz.at](mailto:cyrill.grengg@tugraz.at)

Conventional studies, describing the phenomena of microbial induced concrete corrosion (MICC), are focused on material and environmental factors in order to understand the underlying reaction mechanisms and thus to increase construction material durabilities. This study aims to emphasize the application of distinct stable isotope distributions within an interdisciplinary approach. Therefore, data on stable isotopes of sulfur, oxygen and hydrogen were used to decipher reaction kinetics and pathways in MICC environments. Special focus was laid on fractionation trends of stable sulfur isotopes, caused by the microbiological controlled redox reactions, induced by primary sulfate reduction and subsequent re-oxidation by sulfate reducing bacteria and sulfide oxidizing bacteria, respectively. Hydrogen and oxygen isotope data of expressed concrete pore fluids trace fluctuations within the environmental parameters, e.g. relative humidity, temperature and evaporation, in the sewer system.

## Poster

### Isotope Hydrogeology of S16 Perjen Tunnel Monitoring Programme, Tyrol, Austria

Giorgio Höfer-Öllinger<sup>1</sup>; Richard Loidl<sup>2</sup> and Bernard Millen<sup>1</sup>

<sup>1</sup>Geoconsult ZT GmbH, Wals/Salzburg, Austria

<sup>2</sup>ASFINAG Bau Management GmbH, Wien, Austria

Email: [giorgio.hoefer-oellinger@geoconsult.eu](mailto:giorgio.hoefer-oellinger@geoconsult.eu)

The second tube of the 3 km long Perjen Motorway Tunnel was constructed between 2016 and 2018. The water rights monitoring programme started in 2011, comprising quantitative and qualitative measurements. The monitoring was carried out continuously at some sites with data loggers and at monthly intervals at all other sites for the quantitative parameters including electrical conductivity and temperature. At quarterly intervals samples were taken for hydrochemical and stable isotope (oxygen-18 and deuterium) analysis. Around 42 springs, two creeks, one production and five monitoring wells were monitored.

The geology surrounding the Perjen Motorway Tunnel consists to the North of Permian and Triassic aged carbonate nappes (mainly dolomite, limestone but including evaporites of Raibl and Reichenhall Formations) belonging to the Northern Calcareous Alps; to the South are crystalline bed rocks (phyllites, schist, gneiss) of the Silvretta Group. The boundary between these two major tectonic units is the East-West striking Stanzer Valley Fault. The bed rocks are partly covered by Pleistocene glacial deposits and more recent sedimentary deposits of various kinds.

At the start of the monitoring program, in 2011, there was a lack of understanding of the hydrogeology of some of the individual springs. In situ parameters showed electrical conductivities of up to more than 1.000 µS/cm and water temperature of up to more than 16 C. Apart from detailed hydrochemical and stable isotope analysis, strontium 87/86, sulphur-34 and oxygen-18 from sulphate, as well as tritium, were analysed from a selection of springs and a well.

The relation between strontium and sulphur isotopes helped define the origin of the spring water in a surprisingly distinct way: Only one spring ("Quelle Meinel") has a distinct strontium 87/86 signature from the crystalline or silicate rich bed rocks whereby the sulphur content of the spring water is probably a mixture of sulphide and sulphate dissolution. The spring "Leitenbauerquelle" and well "Brunnen Perfuchsberger Au" show mixtures of sulphide, sulphate, silicate and carbonate dissolution. At the spring "Holzspitzenquellen" the strontium 87/86 signature distinctly implies carbonate dissolution, however the sulphur content comes from the dissolution of sulphides. Very distinct strontium 87/86 and sulphur-34 signatures from the springs "Grinner Quellen 1+2" and "Quelle Perjentunnel" imply dissolution of evaporite rocks of the Raibl Formation, whereby the distinct signatures at the spring "Wildbadquellen" imply dissolution of evaporite rocks of the Reichenhall Formation. The other springs seem to depict mixtures of these origins (Fig. 1).

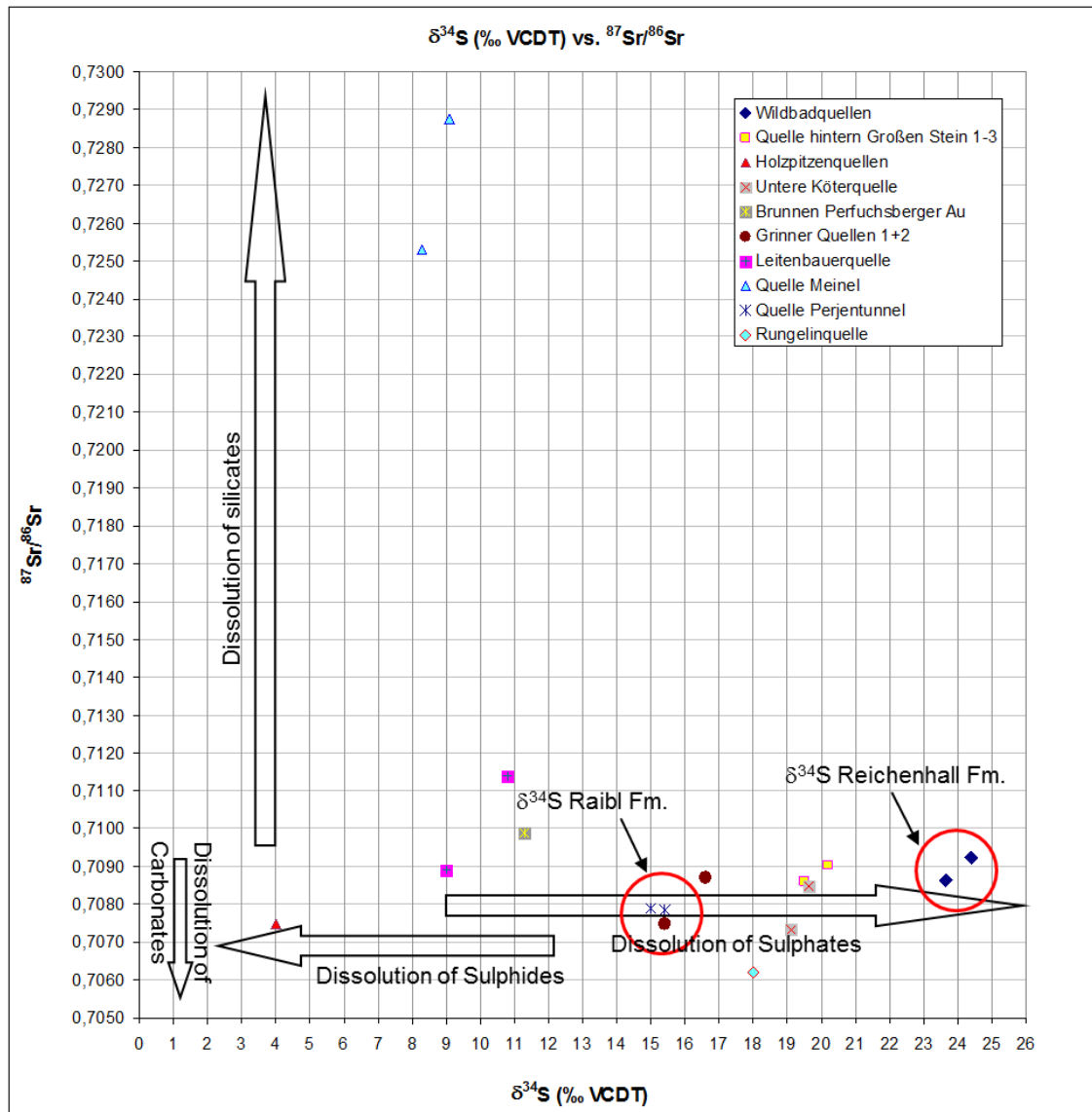


Fig. 1: Assumed origin of strontium and sulphate content of spring and groundwater

## References:

- Böttcher, M., Usdowski, E. (1993)  $^{34}\text{S}/^{32}\text{S}$  Ratios of the dissolved Sulphate of River, Well and Spring Waters in a Gypsum-Carbonate Karst Area at the Southwest Edge of the Harz Mountains - Z. dt. geol. Ges. 144, pp. 471-477
- W. H. Burke, R. E. Denison, \* E. A. Hetherington, R. B. Koepnick, H. F. Nelson and J. B. Otto (1982) Variation of seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  throughout Phanerozoic time. *Geology* 10, 516– 519.
- G. E. Claypool, W. T. Holser, I. R. Kaplan, H. Sakai and I. Zak (1980): The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation; *Chemical Geology*, Vol. 28, pp. 199-260
- Groottes, P.M., Mook,

## Poster

### **Stable isotope analysis for control of declared geographic origin of Austrian apricots (from the Wachau area)**

Micha Horacek<sup>1, 2</sup>

<sup>1</sup>Lehr- und Forschungszentrum Francisco Josephinum, Wieselburg, Austria

<sup>2</sup>Department of Lithospheric Research, University Vienna, Vienna, Austria

Email: [micha.horacek@josephinum.at](mailto:micha.horacek@josephinum.at)

Apricot samples of 3 vintages (2015-2017) were investigated to differentiate samples from the Austrian Wachau region from samples from other areas within and outside of Austria. The isotope composition of the elements hydrogen (H), carbon (C), nitrogen (N) and oxygen (O) of fruit pulp (H, C, N, O), fruit stone (H, C, O) and fruit juice (O) was analysed to find appropriate parameters for the differentiation of different geographic origin. This is, to my knowledge, the first study on geographic origin of apricots, evaluating the potential for discrimination of apricots from the Wachau from samples of other origin. The investigation of different sample tissues (pulp, stone, juice) supports a better differentiation of geographic origin. The results give a somewhat varying picture, as the values of the vintages significantly vary from year to year. However, overall there are promising prospects for the possibility of control of apricots with declared origin of the Lower Austrian Wachau region.

## Poster

### **Long-term stable isotope ( $d^2H$ , $d^{18}O$ ) and hydro-chemical patterns of precipitation collected in weekly resolution in Hannover, Germany**

Paul Koeniger<sup>1</sup>

<sup>1</sup>Federal Institute for Geosciences and Natural Resources (BGR), Geozentrum Hannover, Hannover, Germany

Email: Paul.Koeniger@bgr.de

Long-term observations of stable isotopes ( $d^{18}O$  and  $d^2H$ ) in precipitation were initiated in May 2008 at the Federal Institute of Geosciences and Natural Resources (BGR) in Hannover, Germany. Starting in October 2015 a routine analysis of hydro-chemical parameters was added whenever enough sample aliquot was available (major ions, trace elements).

A discussion of the ten-year precipitation series of stable isotope data in weekly resolution (about 500 samples) will be presented. Beneath general patterns (seasonality and trends) we also focus on importance of amount weighing procedures, corrections for minor rain amounts, aspects of sample storage and re-analyzes, as well as impacts through changes in analytical equipment over time (IRMS, CRD spectroscopy) which is visible from the data.

For stable isotopes a Thermo Fisher Scientific delta plus IRMS (Gasbench and H-Device) was used until 2011 and from 2012 on a Picarro L2120-i water vapor analyzer with long-term accuracies for quality check samples better than 0.2‰ and 0.8‰ for  $d^{18}O$  and  $d^2H$ , respectively.

## Poster

### **Multi-tracer approach ( $\delta^{18}\text{O}$ , $^3\text{H}/^3\text{He}$ , CFC, $\text{SF}_6$ , $^{35}\text{S}$ ) to find the best emergency drinking water supply, Vorarlberg, Austria**

Martin Kralik<sup>1</sup>

<sup>1</sup>Department of Environmental Geosciences, University of Vienna, Vienna, Austria

Email: martin.kralik@univie.ac.at

To provide an emergency drinking water supply in case of catastrophic events (regional chemical accidents, floods, earth quakes etc.), wells and springs should be known which are fed by a large reservoir. Such reservoirs provide a good filtering capacity and long Mean Residence Times (MRTs) of the raw water, which allow to set measures to protect the general water supply or to treat the drinking water before use.

After preselection of 16 wells and springs all over the territory of the province of Vorarlberg at the western end of Austria by the local administration, these wells and springs were measured (water temperature, electric conductivity, pH and dissolved oxygen content) and sampled monthly for  $\delta^{18}\text{O}/^2\text{H}$  over the winter half-year. At the same time the tritium concentrations of the first and last sample were measured as well.

Based on the variation of the monthly on-site measurements and the  $\delta^{18}\text{O}/^2\text{H}$  results 11 wells and springs were selected for further investigations. On these sites samples for  $^3\text{H}/^3\text{He}$ , CFC-11/12/113,  $\text{SF}_6$  and sulphur-35 measurements were collected in August 2014.

Based on these measurements five wells or springs are regarded as “suitable” (MRT 9-30 yrs) as emergency water supply and five as of “limited suitability” (MRT 5-13 yrs).

To ensure the fitness of all water extraction points for emergency drinking water supply even after extreme storms all springs and wells regarded as “suitable” and “of limited suitability” should be equipped with loggers measuring discharge, water temperature, and electric conductivity continuously for at least two years.

## Poster

### Feasibility study to measure $\delta^{18}\text{O}_{\text{water}}$ via GC-IRMS

Simon Leitner<sup>1</sup>, Andrea Watzinger<sup>1</sup> and Rebecca Hood-Nowotny<sup>1</sup>

<sup>1</sup> University of Natural Resources and Life Sciences, Institute of Soil Research, Tulln, Austria

Email: [simon.leitner@boku.ac.at](mailto:simon.leitner@boku.ac.at)

Measuring the isotopic signature of water above a crop canopy reveals crucial information about the way in which the crop is using the water resource, whether it is lost as evaporation or contributes to productive growth. Isotope flux partitioning of evapotranspiration is one empirical approach that has emerged as a robust method for measuring the ratio of transpiration to evapotranspiration, with uncertainties of less than 5% using Keeling plots. However, so far only a static real-time approach has been tested which requires expensive on-site equipment. We set out to explore an unmanned aerial vehicle (UAV) based approach to collect Keeling plot data which would allow trans-global assessment of water budgets.

It is well established that the oxygen isotope composition of water and dissolved  $\text{CO}_2$  equilibrates and enables the indirect determination of  $\delta^{18}\text{O}$  values of water by measuring  $\delta^{18}\text{O}$  ratios of gaseous  $\text{CO}_2$ . We hypothesized that water vapor contents in both forestry and agricultural contexts are sufficient to allow for water oxygen isotopes to equilibrate with atmospheric  $\text{CO}_2$  in gastight vials. Thus by measuring the  $\delta^{18}\text{O}$  of the  $\text{CO}_2$  we get an accurate measure of the water vapor collected at a specific point in time and space.

The presented method is embedded within a comprehensive approach of analyzing atmospheric gases ( $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ) collected by an UAV. Our overall goal is to provide a simple analytical setup. Sampling of 20 mL vials should enable the determination of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of  $\text{CO}_2$  by headspace injection and purge and trap auto sampling and subsequent IRMS analysis.

The approach was tested by separately incubating two internal laboratory water standards (ST) and a standard compressed air. Results showed that  $\delta^{18}\text{O}$  values of  $\text{CO}_2$  approached the reported values of the respective internal laboratory water standard; reaching a plateau after 12 h which is in good agreement with reported equilibration times. The equilibration process was indicated by drop in standard deviation of the measured triplicate samples over time (ST<sub>1</sub>:  $t_1=1.4\text{‰}$ ,  $t_6=0.1\text{‰}$ ; ST<sub>2</sub>:  $t_1=0.9\text{‰}$ ,  $t_6=0.02\text{‰}$ ). Finally, results suggested that the method was highly applicable and robust, and will now be tested in a field campaign.



## Poster

### Stable isotope probing of microbial lipids

Travis B. Meador<sup>1,2</sup>, Weichao Wu<sup>2</sup>, Kai Uwe Hinrichs<sup>2</sup>

<sup>1</sup>SOWA-RI, Biology Centre CAS, České Budějovice, Czech Republic

<sup>2</sup>MARUM Center for Marine Environmental Sciences & Department of Geosciences, University of Bremen, Bremen, Germany

Email: travis.meador@bc.cas.cz

In the context of changing climate and human activity, understanding the processes and pathways of soil C allocation and decay continue to be the subject of intense study, with particular attention devoted to determining the controls on microbial growth rate and growth efficiency in subsurface ecosystems. Whereas investigations of C and N stable isotopes have been useful to delineate C sources, C-fixation pathways, substrate transfers, and more, the natural abundance composition of hydrogen isotopes [i.e., <sup>2</sup>H, deuterium (D) versus <sup>1</sup>H, protium (H)] in microbial lipids was shown to be responsive to the metabolic pathways used for energy generation (Zhang et al., 2009). Additionally, dual stable isotope probing approaches that determine the assimilation of both deuterated water (D<sub>2</sub>O) and inorganic <sup>13</sup>C into microbial lipids are now being employed to constrain microbial growth rates and turnover time (Wegener et al. 2016). Because autotrophs incorporate almost exclusively inorganic C into biomass, and organic substrates serve as the principal C source for heterotrophs, the ratio of inorganic C assimilation rate to total lipid production rate ( $R_{a/p} = \text{assim}_{IC} / \text{prod}_{lipid}$ ) can further reveal the predominance of autotrophic versus heterotrophic production in natural systems; i.e., autotrophy ( $\approx 1$ ) or heterotrophy ( $< 0.3$ ), with the latter acknowledging up to 30% of inorganic C incorporation into lipids during heterotrophic growth (Sorokin, 1966).

To further investigate the potential for dual stable isotope probing methods to reveal ecosystem processes, an archaeal methanogen, *Methanosarcina barkeri*, was grown on autotrophic (H<sub>2</sub>/CO<sub>2</sub>) or heterotrophic substrates (acetate or methanol) in the presence of both <sup>13</sup>C-bicarbonate and D<sub>2</sub>O. We observed high  $R_{a/p}$  variability with C substrate that likely resulted from the biochemical pathways that control not only D/H fractionation (e.g., Zhang et al., 2009), but also C assimilation via anaplerotic reactions, for example. Because the proportion of inorganic C assimilated into heterotrophic biomass should vary with the relative demand of anaplerotic reactions during catabolism of organic C-substrates, we propose that the  $R_{a/p}$  proxy will be informative for interpreting C fluxes, microbial energy sources, and metabolism in natural systems.

## Poster

### **Origin of mine water and groundwater from the Ibbenbüren coalfield, North Rhine-Westphalia, Germany – interpretation of Sulfur, Oxygen and Hydrogen isotopic ratios**

Thomas Rinder<sup>1</sup> & Sylke Hilberg<sup>1</sup>

<sup>1</sup>Department of Geography and Geology, University of Salzburg, Salzburg, Austria

Email: thomas.rinder@sbg.ac.at

Mine dewatering is necessary to allow excavation of hard coal below the groundwater table. After closure this is no longer needed and a mine can be flooded. However, during all operational cycles, coal mine drainage is potentially harmful to the environment. The waters are often acidic, comprise high loads of total dissolved solids and toxic metals, thereby potentially polluting receiving streams and surrounding groundwater reservoirs. Understanding of the chemical evolution of mine waters is a crucial factor for successful mine water management and the mitigation of environmental problems after the closure of the coal mines.

The colliery in the Ibbenbüren coalfield is one of the two last remaining active collieries in Germany. It is planned to close and flood the mine beginning with December 2018. In summer 2018 a sampling campaign of the mine water and groundwater surrounding the coalfield was conducted. A coupled hydrochemical and isotopic approach is applied to identify the processes which govern the chemical evolution of the mine drainage and to understand the hydrogeological framework of the region with the greater aim to facilitate the prediction of the future long-term development.

The carboniferous sedimentary rocks of the Ibbenbüren coalfield host anthracite coal bearing layers, which were brought up to the surface during a tectonic uplift in the Cretaceous. The coalfield is surrounded by Permian, Triassic and Jurassic sediments. Preliminary results show that the isotopic composition of sulfate in waters, that are relatively close to the surface, points to pyrite oxidation as the main source of sulfate, with  $\delta^{34}\text{S}$  values between -8,3 and +0,3 ‰. In contrast the  $\delta^{34}\text{S}$  values of the brines in the deepest part of the mine resemble the values of upper Jurassic or mid Triassic evaporites. In this case the infiltration of groundwater from outside of the coalfield is likely. Finally the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  isotopic composition of the brines points to a meteoric origin.

## Poster

### Using stable isotopes for lube oil consumption measurement on combustion engines

Bernhard Rossegger<sup>1</sup>, Michael Schneider<sup>2</sup>, Albrecht Leis<sup>3</sup>, Michael Engelmayer<sup>3</sup> and Andreas Wimmer<sup>2</sup>

<sup>1</sup> Large Engines Competence Center, Graz, Austria

<sup>2</sup> Institute of Internal Combustion Engines and Thermodynamics, Graz University of Technology, Graz, Austria

<sup>3</sup> JR-AquaConSol GmbH, Graz, Austria

Email: [rossegger@ivt.tugraz.at](mailto:rossegger@ivt.tugraz.at)

Three of stakeholders major requirements to modern combustion engines basically are low life cycle cost (LCC), long time before overhaul (TBO) and low exhaust gas emissions. All of them may be addressed by optimizing the lube oil consumption (LOC), as it exerts a major influence on chemical deterioration of the exhaust gas aftertreatment system, hydrocarbon emissions, particle emissions and lubricating oil auto ignition. Since the amount of lubricating oil emitted by modern engines via the exhaust gas stream is very low compared to the amount of air and fuel streaming through the engine, state-of-the-art methods for measuring LOC are reaching their limits. Especially gravimetric and volumetric measurement methods are considered to bring along a tough trade-off between accuracy and measurement time. Therefore, tracer methods are the mean of choice for LOC measurement in various R&D applications in the field of combustion engines. However, many different tracer substances have already been investigated, all having their advantages but downsides as well. Thus, the investigation of a newly developed tracer substance based on deuterium and first promising engine test bench results are being presented in this publication in the form of a poster contribution.

## Poster

### Austrian Meteoric Water Line – a proxy based on isotope ratios in river water

K. Schott<sup>1</sup>, S. Wyhlidal<sup>2</sup>, D. Rank<sup>3</sup>, A. Watzinger<sup>1</sup>

<sup>1</sup>University of Natural Resources and Life Sciences Vienna, Inst. of soil research, Tulln, Austria

<sup>2</sup>AIT Austrian Institute of Technology GmbH, Tulln, Austria

<sup>3</sup>Center of Earth Sciences, University of Vienna, Vienna, Austria

Email: Katharina.Schott@boku.ac.at

For the reconstruction of paleoclimate and paleohydrology it is of major interest to build on robust and detailed information about isotopic patterns in the modern hydrological cycle. The variability of these patterns can also contribute to current ecologic issues, for instance changes in food webs under changing climate conditions. Austria's Network for Isotopes in Precipitation and Surface waters (ANIP) is one of the densest and most long-standing worldwide and thus provides unique isotope time series of precipitation, groundwater and river water of a landscape with complex topography.

The Global Meteoric Water Line states the average relationship between isotope ratios in natural terrestrial waters ( $\delta D = 8 \cdot \delta^{18}O + 10\text{‰}$ ), at a regional scale it can be described with local meteoric water lines. In Austria the Alpine main ridge acts as a weather divide, which leads to prominent differences in the isotopic composition in precipitation water North and South. Therefore, general conclusions for the whole Austrian territory are difficult to draw. River water has the advantage that it can be understood as a spatial and temporal integrator of the isotopic composition of precipitation water received in the respective catchment (Figure 1, Rank et al., 2018), thus it might be a better choice for a general statement for Austria than data from single precipitation stations therein. We present an approach to define the Austrian Meteoric Water Line based on isotope ratios in river water. For the alpine part of Austria, the preliminary result is  $\delta D = 7.87 \cdot \delta^{18}O + 9.35\text{‰}$  ( $R^2 = 0.999$ ).

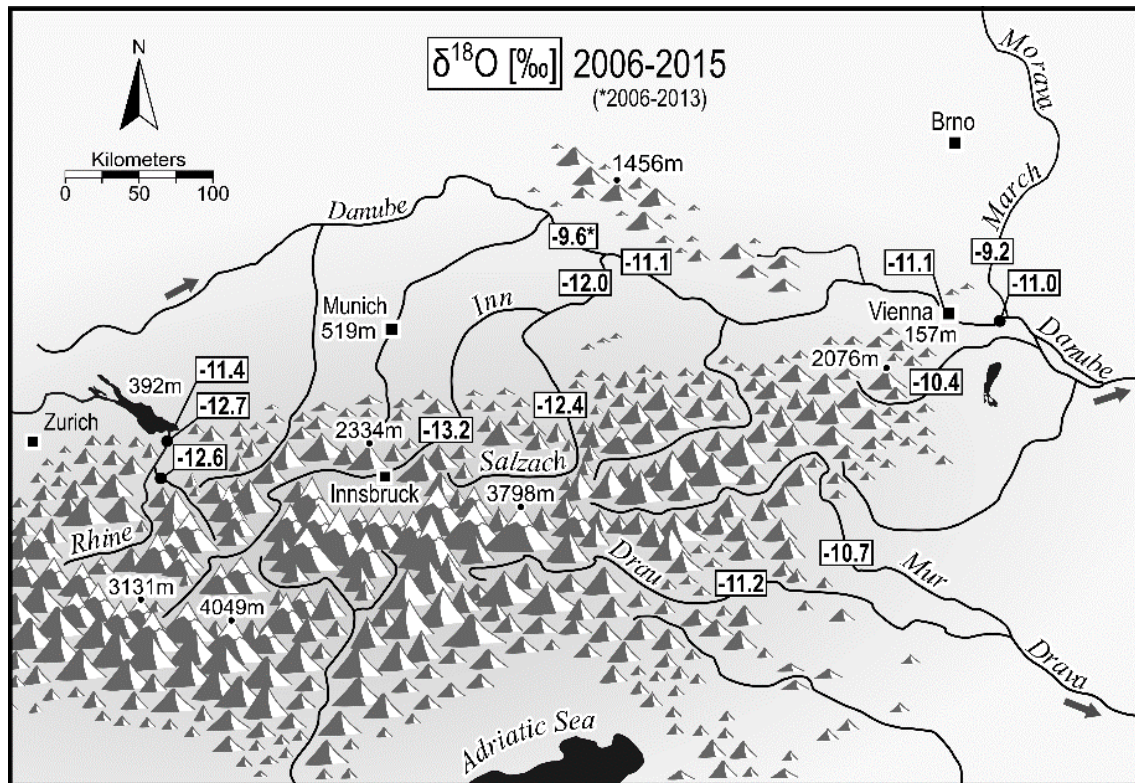


Figure 1: Sampling stations for isotope measurements on Austrian rivers (mean  $\delta^{18}\text{O}$  values 2006-2015)

## References:

Rank D., Wyhlidal S., Schott K., Weigand S., Oblin A. (2018) Temporal and spatial distribution of isotopes in river water in Central Europe: 50 years experience with the Austrian network of isotopes in rivers. *Isotopes Environ Health Stud.* 54 (2), 115-136.

## Poster

### **Precision and accuracy of the Delta Ray Connect by yearlong measurements of $\delta^{18}\text{O}$ on water reference material**

Danijela Smajgl<sup>1</sup>, Anja Kovac<sup>1</sup> and Magda Mandic<sup>1</sup>

<sup>1</sup>Thermo Fisher Scientific, Bremen, Germany

Email: danijela.smajgl@thermofisher.com

It is known that traditional methods, such as isotope ratio mass spectroscopy, show high accuracy and precision when measuring  $\delta^{18}\text{O}$  of water, but in addition to traditional methods, isotope ratio infrared spectroscopy is a new option for performing laboratory analysis.

Thermo Scientific™ Delta Ray™ Isotope Ratio Infrared Spectrometer (IRIS) with the Universal Reference Interface (URI) Connect is a laser-based instrument which is operating in mid-infrared range at 4.3  $\mu\text{m}$ . It allows continuous measurements of isotope ratios and concentration of  $\text{CO}_2$  as well as discrete sample measurements, such as head space analysis or direct sample transfer from gas bags or injection by syringe.

Here we present automated measurements of  $\delta^{18}\text{O}$  with equilibration method. In the sample preparation step, 0.8 mL of standards were added into vials, after which the headspace was flushed with 1%  $\text{CO}_2$  by autosampler-assisted flushing procedure. Samples were placed on a shaker and equilibrated at room temperature, overnight.

Measurements were done in a time period of one year. For referencing, several certified international standards were used, while USGS 48 was treated as quality control sample. The Principle of Identical Treatment was applied for sample and standard preparation, in measurement procedure, as well as in the evaluation of the results. Two-point calibration was used.

The results are confirming high precision and accuracy of the method over one year. This shows that Delta Ray Connect can be used for determination of  $\delta^{18}\text{O}$  of water samples. Furthermore, the preliminary results of tap water and wine measurements with the Delta Ray Connect allow us to further extend the Delta Ray Connect applications to food and beverage, with special attention to different liquid matrix samples e.g. fruit juices, soft drinks or vinegars.

## Poster

### Consequences of climate change for agroecosystem carbon and nitrogen cycling – a stable isotope labelling study

Andreea Spiridon<sup>1,2</sup>, Rebecca Hood-Nowotny<sup>2</sup>, Simon Leitner<sup>2</sup>, Helene Berthold<sup>3</sup>, Johannes Hösch<sup>3</sup>, Erwin Murer<sup>4</sup>, Johannes Wagenhofer<sup>4</sup>, Herbert Formayer<sup>5</sup>, Alexander Bruckner<sup>6</sup>, Wolfgang Wanek<sup>1</sup>, Andrea Watzinger<sup>2</sup>

<sup>1</sup>Institute of Terrestrial Ecosystem, Department of Microbiology and Ecosystem Science, University of Vienna, Vienna, Austria

<sup>2</sup>Institute of Soil Science, University of Natural Resources and Life Sciences Vienna, Vienna, Austria

<sup>3</sup>Department for Soil Health and Plant Nutrition, AGES Austrian Agency for Health and Food Safety, Vienna, Austria

<sup>4</sup>Institut für Kulturtechnik und Bodenwasserhaushalt, BAW Bundesamt für Wasserwirtschaft, Petzenkirchen, Austria

<sup>5</sup>Department of Water – Atmosphere – Environment, University of Natural Resources and Life Sciences Vienna, Austria

<sup>6</sup>Department of Integrative Biology and Biodiversity Research, University of Natural Resources and Life Sciences Vienna, Vienna, Austria

Email: andreea.s@students.boku.ac.at

The impact of climate change on the determining factors of plant production, such as precipitation amounts and patterns are rarely studied in the Pannonian area. Even less is known to what extent different soils might alter ecosystem responses. To investigate the effects of future rainfall patterns on different soils, a regionalized scenario RCP6.0 derived from the 5<sup>th</sup> IPCC Assessment Report is used on a long-term lysimeter facility.

Stable isotope labelling is one of the more practical ways of tracing fate and behavior of nutrients in agricultural soils. In this study, white mustard (*Sinapis alba*) dual labelled with <sup>13</sup>C and <sup>15</sup>N stable isotopes is being used as green manure and applied to the 3 m<sup>2</sup> lysimeters where future rainfall patterns are compared with current precipitation patterns on two different soil types – sandy calcareous phaeozem and calcic chernozem, representing the Marchfeld region in Austria.

Green manure provides nutrients and serves as a major component for the build-up of soil organic matter. Mineralization and cycling of carbon and nitrogen from the green manure will be calculated after measuring <sup>13</sup>C and <sup>15</sup>N isotopes in major pools (<sup>13</sup>C - CO<sub>2</sub> gas, <sup>15</sup>N - N<sub>2</sub>O gas, <sup>13</sup>C in the soil and in the soil microorganisms – PLFAs, <sup>15</sup>N in total soil, inorganic and organic pools, soil microorganisms, plants and soil solution).

First results of <sup>13</sup>C CO<sub>2</sub> and <sup>15</sup>N - N<sub>2</sub>O gas measurements indicated prompt release of C and N added with the labelled mulch. The impact of precipitation on the mineralization was not significant, while plant biomass was significantly affected (decreased plant biomass for the future scenario). Plant and bulk soil analysis emphasized the importance of plant growth, which was diminished under future scenario on the N uptake, and hence the pathway of mineralized <sup>15</sup>N. The study will allow for a better understanding of soil-water-plant interaction processes under changing conditions and contribute to better adaptation and mitigation strategies for climate change.







## Poster

### Temperature Dependence of Zinc Isotopes Fractionation during the precipitation of Smithsonite from Aqueous Solutions

J. A. Stammeier<sup>1\*</sup>, A. Föger<sup>1\*</sup>, V. Mavromatis<sup>1,2</sup>, A. Leis<sup>3</sup> and M. Dietzel<sup>1</sup>

<sup>1</sup> Institute of Applied Geosciences, Graz University of Technology, Graz, Austria

<sup>2</sup> Géosciences Environnement Toulouse (GET), CNRS, UMR 5563, Observatoire Midi-Pyrénées, Toulouse, France

<sup>3</sup> JR-AquaConSol GmbH, Graz, Austria

\* equally contributing authors

Email: j.stammeier@tugraz.at

Smithsonite is a secondary zinc carbonate mineral that is one of the key components of zinc ore bodies. In nature, it is commonly formed via its precursor phase hydrozincite by (i) the reaction with a carbonate source or by (ii) precipitation of zinc salt solutions with a CO<sub>2</sub>-saturated and bicarbonate-rich solution. Smithsonite may be used in respect to isotope proxies to calculate transformation temperatures. However, this is not straight forward as (trans-) formation occurs via a precursor phase and is dependent on pCO<sub>2</sub>. Theoretical calculation demonstrated that Zn isotope fractionation between fluid and precipitating solid is temperature dependent. Thus, knowledge about the Zn isotope composition could constitute a potential temperature proxy. In order to investigate this hypothesis, a pilot study was conducted based on previous experimental work in which smithsonite was precipitated at varying temperatures yet constant pCO<sub>2</sub>. In these experiments, formation of smithsonite was induced by the transformation of hydrozincite at 25, 40, 60 and 80 °C. Preliminary results of the solids reveal a temperature dependent fractionation ( $\Delta^{66}\text{Zn}_{\text{smith-H}_2\text{O}} = \delta^{66}\text{Zn}_{\text{Smith}} - \delta^{66}\text{Zn}_{\text{H}_2\text{O}}$ ) between 25 and 80°C. This contribution invites discussions about potential mechanisms producing Zn isotope fractionation in smithsonite.

## Poster

### **Mechanisms and reaction kinetics of calcite precipitation from Novinjak-spring (Carinthia) traced by stable C, O, Ca, Mg and Sr Isotopes**

Andreas Strick<sup>1</sup>, Dorothee Hippler<sup>1</sup>, Ronny Boch<sup>1</sup>, Jessica Stammeier<sup>1</sup>, Albrecht Leis<sup>2</sup>, Florian Böhm<sup>3</sup>, Anne-Desiree Schmitt<sup>4</sup>, Martin Dietzel<sup>1</sup>

<sup>1</sup>Institute of Applied Geosciences, Graz University of Technology, Graz, Austria

<sup>2</sup>JR-AquaConSol, Graz, Austria

<sup>3</sup>GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany

<sup>4</sup>Laboratoire d'HYdrologie et de GEochimie de Strasbourg, Université de Strasbourg, Strasbourg, France

Email: andreas.strick@student.tugraz.at

The Novinjak-spring near Köttmannsdorf (Carinthia) is a typical example of an active calcite precipitating spring and acts as natural laboratory for studying apparent isotopic fractionation behavior (C, O, Ca, Mg, Sr) between the atmosphere, fluid and precipitate along its flow path. The water has its origin in local meteoric precipitation ( $^{18}/^{16}\text{O}$ , D/H) and is bearing calcium and bicarbonate through dissolution of limestone within the aquifer ( $^{13}/^{12}\text{C}$ ). Precipitation of calcite is due to the fluids starting to equilibrate with the Earth's atmosphere by degassing of  $\text{CO}_2$ . Loss of  $\text{CO}_2$  causes a rise of pH,  $\text{CO}_3^{2-}/\text{HCO}_3^-$  ratio and thus precipitation of  $\text{CaCO}_3$ . Precipitates consist of low Mg-calcite as porous tufa, showing a high structural variability due to molding of the calcified organic material. Distinctive isotopic trends along the flow path show the enrichment of  $^{13}\text{C}$  and  $^{44}\text{Ca}$  with respect to  $^{12}\text{C}$  and  $^{40}\text{Ca}$  within the fluid and the precipitated calcite caused by the preferred degassing of  $^{12}\text{CO}_2$  ( $\alpha = 0.986 \pm 0.009$ ) and the preferred incorporation of the isotopically lighter Ca within the calcite ( $\alpha = 0.99916 \pm 0.00021$ ), respectively. The latter isotopic and Sr elemental fractionation between fluid and solid and also within the fluid composition along the flow path documents the environmental conditions during calcite formation in particular the precipitation rate, yielding  $10^3$  to  $10^5 \mu\text{mol}/\text{m}^2/\text{h}$   $\text{CaCO}_3$  ( $15 \pm 2^\circ\text{C}$ ). The distribution of  $^{26}/^{24}\text{Mg}$  and  $^{88}/^{86}\text{Sr}$  isotopes indicate constant values of the solution along the flow path due to limited incorporation of both ions into the precipitating calcite. From ongoing isotope analyses of the precipitate a significant fractionation between fluid and calcite is expected to be preferential incorporating the light Mg and Sr isotopes in the calcite. Above elemental and isotope data are discussed to assess and validate the above multiproxy approach for reconstructing environmental conditions for calcite formation in aqueous media.

## Poster

### **Fate of $^{15}\text{N}$ fertilizer in plants and microbes following Biochar addition in an Austrian agricultural soil**

Rebecca Hood-Nowotny<sup>1</sup>, Anna Wawra<sup>1</sup> Andrea Watzinger<sup>1</sup> and Gerhard Soja<sup>2</sup>

<sup>1</sup>Institute of Soil Research, University of Natural Resources and Life Sciences (BOKU), Vienna, Austria;

<sup>2</sup>Environmental Resources & Technologies, Austrian Institute of Technology (AIT), Tulln, Austria;

Email: Rebecca.Hood@boku.ac.at

Field studies of biochar addition to soil and nutrient cycling using  $^{15}\text{N}$  fertilizers in temperate agriculture are scant. These data are required in order to make evidence based assessments, we have shown in a series of field experiments that Biochar applications of up to 72 tonnes  $\text{ha}^{-1}$  did not cause significant N yield or plant yield depression as a consequence of N immobilization when mineral N fertilizer was added. Charring carbon appeared to reduce the N immobilization impact of carbon, in contrast when one tonne  $\text{ha}^{-1}$  of un-charred maize carbon was added to a temperate Austrian soil with similar climatic conditions in a previous study, it resulted in a significant 20% decrease in maize N yield compared to controls over similar time scale. This lack of yield depression on the application of Biochar is important to farmers if we are to promote carbon farming and appeared to be a Biochar specific effect. We set out to explore the mechanisms behind this phenomenon. In a glasshouse experiment similar quantities of pyrolysed and un-pyrolysed carbon was added to the soil and  $^{15}\text{N}$  fertilized barley grown. Results showed that in the uncharred carbon treatments grain yields were halved as a consequence of immobilization, but the impact was not observed in the Biochar treatments. Immobilization of N was evident from the significantly higher  $^{15}\text{N}$  enrichment of the soil microbial biomass in the un-charred carbon treatment ( $615\text{‰} \pm 116$ ) which was twice that of both the NPK ( $343\text{‰} \pm 146$ ) and BCN ( $278\text{‰} \pm 23$ ) treatment confirming our hypothesis that microbial N immobilization was significantly altered as a consequence of charring. Indeed, these experiments suggest little or no immobilization of nitrogen on the addition of  $\sim 58,000$  kg of C  $\text{ha}^{-1}$  in the form of Biochar which resulted in similar if not improved rates of plant fertilizer nitrogen uptake, with a potential maximum carbon credit value of around  $\$7000 \text{ ha}^{-1}$  based on social cost of carbon values obtained from the literature.

## Poster

### Flow component characterization of alpine aquifers – an isotopic approach

Gerfried Winkler<sup>1</sup>, Simon Kainz<sup>1</sup>, Thomas Wagner<sup>1</sup>, Albrecht Leis<sup>2</sup> and Karl Krainer<sup>3</sup>

<sup>1</sup>Institute of Earth Sciences, NAWI Graz Geocenter, University of Graz, Graz, Austria

<sup>2</sup>JR-Aquaconsol, Graz, Austria

<sup>3</sup>Department of Geology, University of Innsbruck, Innsbruck, Austria

Email: [gerfried.winkler@uni-graz.at](mailto:gerfried.winkler@uni-graz.at)

Alpine aquifers are characterized by a heterogeneous and complex internal structure which causes aquifer components with different hydraulic properties. In addition alpine aquifers incorporate and mix water from multiple recharge components such as rain, snowmelt, melting of glacier- or permafrost-ice related to the alpine environment. Thus, the discharge of springs draining alpine aquifers such as e.g. rock glaciers is complex and contains multiple flow components incorporating the different recharge components and the groundwater as a mixture thereof. Based on the meteoric diurnal and seasonal variation, the recharge and the ratios of the individual recharge components of such aquifers vary over time. The discharge and the varying individual flow component ratios of the total discharge reflect these diurnal and seasonal variations of recharge and the heterogeneous internal structure.

For the use and protection of groundwater in such an environment e.g. for drinking water it is crucial to have information about the different flow components, their ratios and their variation over time. Hydrograph analysis enables the identification of different flow components but is very limited in the quantification of the individual flow component ratios. Analyses of stable isotopes in combination with electric conductivity of the water as a conservative tracer provide a proper and helpful tool to identify and characterize the individual flow components and their ratios. With the isotopic signature of the individual recharge components i.e. glacier- or permafrost-ice, snow, rain, and groundwater a mixing component model enables the identification of the diurnal and seasonal variations.

This isotopic approach in combination with electric conductivity of the water was applied to identify and characterize the individual flow components of two springs draining active rock glaciers in the Austrian Alps. The rock glacier catchments contain a small glacier or remnants of a glacier in their upper area. The results show that the seasonal discharge is dominated by snowmelt in June, in general by rain during July and August, and by groundwater from autumn to spring. During dry warm summer periods the springs also show a distinct diurnal variation of the discharge with a time shift of about 12 hours (depending on the size of the rock glacier) of the discharge peak relative to the maximum daily air temperature. The isotopic signature shows that the daily shift of the discharge peak is dominated by meltwater of the glacier ice in the upper catchment. The analysis clearly indicates that different flow components dominate the discharge during different times and

meteoric conditions. The knowledge of the dominant flow component is also very important for a better understanding of the melting processes of the glacier- and permafrost-ice. Thus, prognoses of the impacts of climate warming on alpine regions are possible.

## Poster

### **Biochar NET-2-U-2: Negative Emission Technologies are nice to the environment part two Using stable isotopes in a citizen science approach**

Elisabeth Ziss<sup>1</sup>, Anna Wawra<sup>1</sup> and Rebecca Hood-Nowotny<sup>1</sup>

<sup>1</sup> University of Natural Resources and Life Sciences Vienna, Department of Forest and Soil Sciences, Vienna, Austria

Email: [elisabeth.ziss@boku.ac.at](mailto:elisabeth.ziss@boku.ac.at)

The aim of this follow up project was to build on our successes and lessons learnt from our previous project “Biochar NET-2-U” and further communicate our FWF funded and further biochar research findings to a wider public through a participation model of communication. Making the public aware of nature-based negative emission technologies (NETs), specifically this year we made tangible links to the Paris-COP Four per Mille campaign, which is an International Soils for Food Security and Climate Change initiative. Biochar addition to soil fits well into this framework as a viable climate change combating strategy. By making links with this global initiative we wanted to further engage the public in a horizontal dialogue on the important role of soils and agriculture in combating climate change globally.

This year too we offered the opportunity of participating in their own experiment, so at each event we encouraged the public to participate in our next generation pot-scale Citizen Science endeavor.

There is preliminary evidence that biochar could promote nodulation of legumes in the soil. We set out to further test this improved nodulation phenomena across a range of soils in Austria.

We wanted to test this hypothesis in using a citizen science approach in combination with the  $\delta^{15}\text{N}$ -stable isotope method to assess biological nitrogen fixation. The beauty of this method is that it allowed us to assess biological nitrogen fixation over the growing season and that it is incredibly simple to apply, in a citizen science context. Moreover, it gave the citizen scientists the chance to run the experiment from seed to harvest and observe the effects of the biochar directly on their balcony. But it also gave us the chance to collect useful data on the impact of biochar on nitrogen fixation across a range of soils. In doing so it provided an entry point for the citizen scientist's into the more technical world of stable isotopes and allowed them to expand their knowledge in this area.

Finally, we collected, collated, discussed and interpreted the data bringing together all social actors and Citizen Scientists in a second Biochar Day where we fostered a global outlook by making tangible links to on-going projects in developing countries.

The results and conclusions from this project will be presented.

# THANK YOU

to all of our sponsors!



## Sponsored by:

**Thermo Fisher Scientific** - Wehlstrasse 27b/1, A-1200 Wien, Austria  
**Elementar Analysensysteme GmbH** - Elementar Strasse 1, D-63505 Langenselbold, Germany  
**IVA Analysentechnik** - Alte Seilerei Haus 5, Meerbuscher Str. 64-78, D-40670 Meerbusch, Germany  
**HEKAtech GmbH** - Friedrich-List-Allee 26, D-41844 Wegberg, Germany  
**Springer-Verlag GmbH**, D-69121 Heidelberg  
**Air Liquide Austria GmbH** – Sendnergasse 30, A-2320 Schwechat, Austria  
**Picarro Inc.** - 3105 Patrick Henry Dr. Santa Clara, California 95054, USA