

14th Austrian Stable Isotope Network Meeting

Tulln/Donau, November 26th-27th 2015

**Austrian Institute of Technology GmbH
Health and Environment Department**

**University of Natural Resources and Life Sciences
Department of Chemistry (VIRIS Lab)**

Austrian Institute of Technology and University of
Natural Resources and Life Sciences

14th Stable Isotope Network Austria Meeting

Tulln/Donau 26th-27th November 2015

PROGRAM AND ABSTRACT VOLUME

Editorial: STEFAN WYHLIDAL, ANDREA WATZINGER, REBECCA HOOD-NOWOTNY,
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Hosted by:

- Austrian Institute of Technology GmbH, Health and Environment Department
- University of Natural Resources and Life Sciences Department of Chemistry (VIRIS Lab)

PROGRAM

THURSDAY 26th NOVEMBER 2015

12:00 – 13:00 Registration

13:00 – 13:15 Welcome & Introduction

SESSION 1 (Chair: Martin Jung)

13:15 – 13:50 *Key Note Address*

Martin Kralik et al. (Department of Environmental Geosciences, University of Vienna): Austrian Atlas of Isotope Hydrology– Applications, Extreme and Trends

13:50 – 14:05 **Hermann Häusler et al.** (Department of Environmental Geosciences, University of Vienna): The use of stable isotopes $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ for characterizing recharge areas of groundwater bodies in the Northern Burgenland (Austria)

14:05 – 14:20 **Wyhlidal Stefan et al.** (AIT Austrian Institute of Technology, H&E Department): Mineralogy, hydro- and isotope chemistry of thermal water and scalings in hydrogeothermal plants and preliminary results of Batsch experiments

14:20 – 14:35 **Ronny Boch et al.** (Institut of Applied Geosciences, Graz University of Technology): Carobante scaling of Pannonian Basin geothermal wells: first results from stable C, O & clumped isotopes

14:35 – 15:00 *Coffee and Tea Break*

15:00 – 15:15 **Filip Volders et al.** (Elementar Analysensysteme GmbH): Automatic data calibration strategies with IONOS

15:15 – 15:30 **Lukasz Pytlak et al.** (Chair Petroleum Geology, Montanuniversitaet Leoben): Mixing of microbial gas and thermogenic hydrocarbons; the Austrian Molasse Basin case study

15:30 – 15:45 **Sylvain Richoz et al.** (Institute of Earth Sciences, University of Graz): Ocean Acidification at the Permo-Triassic Mass Extinction. Clues from Boron isotope

15:45 – 16:00 **Jan Wiederhold et al.** (Department of Environmental Geosciences, University of Vienna): Mass-dependent and mass-independent fractionation of stable Hg isotopes as two-dimensional tracer for mercury cycling in the environment

16:00 – 17:30 **Poster Session**

From 19:30 **Social Dinner**

Rebhuhn, Berggasse 24, 1090 Vienna

FRIDAY 27th NOVEMBER 2015

SESSION 2 (Chair: Andrea Watzinger)

- 10:20 – 10:55 *Key Note Address*
- Rebecca A. Kraft et al.** (Department of Nuclear Sciences and Applications, International Atomic Energy Agency): Scientific framework for combatting illegal logging: The development of wood standard reference materials for stable isotopes
- 10:55 – 11:10 **Micha Horacek et al.** (BLT Wieselburg, Lehr- und Forschungszentrum Francisco-Josephinum): Differentiation of wood origin in the Austrian Alps for the determination of possible growth regions of prehistoric wood
- 11:10 – 11:45 *Coffee and Tea Break*
- 11:45 – 12:00 **David Psomiadis et al.** (Imprint Analytics GmbH): Authenticity and traceability testing of vanillin by compound specific stable isotope analysis
- 12:00 – 12:15 **Simon Leitner et al.** (AIT Austrian Institute of Technology, H&E Department): Carbon isotope enrichment of chlorinated ethenes by local anaerobic microbial communities
- 12:15 – 12:30 **Eva Oburger et al.** (Department of Forest and Soil Sciences, University of Natural Resources and Life Sciences Vienna): Mineralization dynamics of ¹³C-labeled phytosiderophores in the rhizosphere of wheat
- 12:30 – 12:45 **Ondrej Hanousek et al.** (Dep. of Chemistry - VIRIS Laboratory, University of Natural Resources and Life Sciences Vienna): Measurement of $\delta(^{34}\text{S}/^{32}\text{S})\text{VCDT}$ in bioviable soil sulfate by DGT MC ICP-MS
- 12:45 – 14:00 *Lunch Buffet*

SESSION 3 (Chair: Rebecca Hood-Nowotny)

- 14:00 – 14:35 *Key Note Address*
- Leonard Wassenaar et al.** (Department of Nuclear Sciences and Applications, International Atomic Energy Agency): Isotope Forensics: Applications in Migratory Wildlife Studies
- 14:35 – 14:50 **Rebecca Hood-Nowotny** (AIT Austrian Institute of Technology, H&E Department): Insect isotope forensics
- 14:50 – 15:05 **Martina Burnik Sturm et al.** (Research Institute of Wildlife Ecology, Vetmeduni Vienna): The tale of the hoses' tails: stable isotopes reveal differences in the feeding ecology of three sympatric equid species in the Dzungarian Gobi, Mongolia
- 15:05 – 15:20 **Juliane Meyer et al.** (Institute of Earth Sciences, University of Graz): Environmental differences reflected by stable isotopes of *Cytheridella* in the Neotropics: a comparison of Florida and Mexico
- 15:20 – 15:30 *Closing*
- 15:30 General assembly

Poster

- Melanie Hager et al.** (Austrian Institute of Technology, Tulln): Determination of the H/D isotopic fractionation during biodegradation of n-decane in a laboratory study.
- Micha Horacek et al.** (HBLFA Francisco-Josephinum, Wieselburg): Origin of woodcocks (*Scolopax rusticola*) hunted in Austria.
- Horsky Monika et al.** (Department of Chemistry, VIRIS Laboratory, University of Natural Resources and Life Sciences Vienna): Towards a Sr isoscape of Austria for the determination of growth regions of prehistoric wood.
- Humer Franko et al.** (Environment Agency Austria): Literature Database for Karst-hydrologic studies in Austria.
- Kathrin Karer et al.** (Austrian Institute of Technology, Tulln): The Austrian network for isotopes in precipitation (ANIP).
- Katharina Schott et al.** (Austrian Institute of Technology, Tulln): Preliminary results of isotope patterns for selected precipitation stations in Austria from 2005-2014.
- Stefan Wyhlidal** (Austrian Institute of Technology, Tulln): Age determination of river and spring waters using the climate signal of the long-term $\delta^{18}\text{O}$ trend of precipitation stations.
- Martin Kern et al.** (Institute for Environmental Biotechnology, University of Natural Resources and Life Sciences Vienna): Monitoring of anaerobic PH-biodegradation by analyzes of shifts in terminal electron acceptor isotopic $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ ratios.
- Christine Opper et al.** (Department of Chemistry, VIRIS Laboratory, University of Natural Resources and Life Sciences Vienna): Provenancing of Strawberries using Sr Isotopes and Multielement Pattern: Investigation of Elemental Sources in the Bioavailable Fraction of Soils.
- Anika Retzmann et al.** (Department of Chemistry, VIRIS Laboratory, University of Natural Resources and Life Sciences Vienna): Human mobility along the Nile: Preliminary Strontium isotope analyses for migration studies in ancient Nubia.
- Marlene Sakoparnig et al.** (Institute of Applied Geosciences, Graz University of Technology): Stable Isotope studies (C, O, H) of active stalagmites & drip water in Katerloch cave (Austria).
- Dorothea Summer et al.** (Austrian Institute of Technology, Tulln): Synergistic degradation of chlorinated hydrocarbons with microorganisms and zero valent iron.
- Anastasiya Tchaikovsky et al.** (Department of Chemistry, VIRIS Laboratory, University of Natural Resources and Life Sciences): Elemental and $87\text{Sr}/86\text{Sr}$ isotope pattern as a tool for provenancing sturgeon caviar.
- Katrin Teufl et al.** (Josephinum Research): Discriminating between different origin of Ayous (*Triplochiton scleroxylon*) from West- and Central African countries.
- Anna Wawra et al.** (Austrian Institute of Technology, Tulln): Using stable isotope labelling as a tool to monitor the bioremediation of two contaminated soils.
- Bernhard Wimmer et al.** (Austrian Institute of Technology, Tulln): $\delta^{13}\text{C}$ -DIC of Municipal Waste Leachate is an Integrative Parameter for Characterising the Biological Stability of Landfill Bodies.
- Erik Wolfgring et al.** (Department of Palaeontology and, University of Vienna): Integrated stable isotope cyclostratigraphy of the Campanian stage (Upper Cretaceous).

1 Keynote

WATER – ISOTOPE – MAP ($\delta^{18}\text{O}$, $\delta^2\text{H}$, ^3H) OF AUSTRIA: APPLICATIONS, EXTREMES AND TRENDS

Kralik, M.¹, Benischke, R.², Wyhlidal, S.³

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²Joanneum Research, Graz

³Austrian Institute of Technology (AIT), Tulln

The isotopic ratios of oxygen and hydrogen in water ($^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$) are important tools to characterise waters and their cycles. This starts in the atmosphere as rain or snow and continues in the surface water (rivers and lakes) and ends in shallow groundwater as well as in deep groundwater. Tritium formed by natural cosmic radiation in the upper atmosphere and in the last century by tests of thermonuclear bombs in the atmosphere, is characterised by its radioactive decay with a half-life of 12.32 years and is an ideal age-marker during the last 60 years or whether a sample consists of considerable proportions > 60 years.

To determine the origin and mean age of waters in many projects concerning water supply, engineering (e.g. tunnels, hydroelectric power plants) and scientific projects in the last 45 years on more than 1,350 sites more than 40,000 isotope measurements were performed in Austria. To give an overview about the mean isotope distribution in different regions of Austria and as an important information for further practical and scientific applications the sampling sites were determined from many reports and publications and the median values classified and shown in different colours in the map.

In an electronic version of the “water isotope map of Austria” (www.umweltbundesamt.at) most of the data are available in the internet. The median value of all sites of oxygen-18 is $\delta^{18}\text{O}$ -10.7 ‰ and for hydrogen-2 $\delta^2\text{H}$ -75 ‰. These isotopes are measured as the negative per mille deviation from the heavier Vienna Mean Ocean Water standard (V-SMOW). As the fractionation is mainly temperature dependent the lowest negative values are observed in winter precipitation (oxygen-18 as low as $\delta^{18}\text{O}$ -23 ‰) and in springs in the Tyrolean Kauner valley ($\delta^{18}\text{O}$ -15.1 ‰) deriving their water from high mountains and glaciers. The majority of the Alpine springs due to the altitude of their recharge areas show relatively light $\delta^{18}\text{O}$ -values (< - 12.4 till - 11.4 ‰ (green colour in the map)).

In contrast the highest values were observed in summer precipitation (up to $\delta^{18}\text{O}$ - 0.5 ‰) and in shallow lakes further depleted in oxygen-18 by evaporation in the Seewinkel area close to the Hungarian border (up to $\delta^{18}\text{O}$ + 5 ‰).

As the isotopic ratios of the Austrian waters besides the dominant temperature effect at the site of precipitation are influenced by the origin of the evaporated water masses (clouds) as well, obvious regional differences are observed in Austria. Therefore the precipitation and the shallow groundwater in the region of South of the main Alpine crest (East-Tyrol, Carinthia and South-East Styria) is approximately 1 ‰ higher in $\delta^{18}\text{O}$ -values as sites at the same altitude and temperature as the rest of Austria. This is most probably caused by the stronger influence of precipitation from the Mediterranean area. This is supported by the highest oxygen-18 median values of a precipitation station in Graz ($\delta^{18}\text{O}$ - 8.3 ‰) and the relatively high values of shallow groundwater along the river Mur ($\delta^{18}\text{O}$: -9.7 to -8.9 ‰ (orange colour in the map)) in the South-East of Austria.

The median value of all 1,120 sampling sites of decay corrected (2015) tritium measurements is 6.2 tritium units (TU). This is somewhat smaller than the median value of all precipitation stations with 7.2 TU. This can be explained by the fact that in most cases in groundwater the median value has been reduced by decay according to the residence time underground. Similar to the $\delta^{18}\text{O}$ -values the tritium concentration increases in the summer up to 10 – 11 TU and decreases in winter down to 3 – 4 TU. This is due to the better circulation in the atmosphere in spring which brings the tritium formed by cosmic radiation down to the lower atmosphere and precipitation. Mean tritium concentration in water smaller than approximately 3.5 TU or smaller 0.3 TU contains large amounts of water or consists completely of water older than 60 years.

Waters containing approximately more than 12 TU or more than approximately 23 TU consists of older water containing still tritium from the 1960s and 1970s formed originally by thermonuclear bomb experiments or of tritium contamination coming e.g. from waste disposal sites or nuclear power plants along rivers. In Austria the rivers Danube and March at the Czech – Slovakian border show periodic or permanent tritium contamination up to 70 TU coming from nuclear power plants in the neighbouring countries.

In a regional context remarkable are the low tritium concentration of less than 2.8 TU in many springs and wells in the North – East of Austria (Weinviertel and parts of Marchfeld) which is related to low precipitation and older groundwater in this region.

The frequent occurrence of higher tritium values (^3H : > 9 TU) in the Seewinkel area at the Hungarian border is a sort of artefact as in investigations before about 1990 the tritium decay can be corrected, but not the dilution effect by young tritium-poor waters .

The Austrian water isotope map shows that in an alpine country with different climatic influences water isotopes are a useful tool to differentiate between water sources of variable, mostly short residence times.

2 Keynote

SCIENTIFIC FRAMEWORK FOR COMBATting ILLEGAL LOGGING: THE DEVELOPMENT OF WOOD STANDARD REFERENCE MATERIALS FOR STABLE ISOTOPES

Rebecca A. Kraft¹, Sergey S. Assonov¹, and Manfred Groening¹

¹International Atomic Energy Agency, Vienna, Austria

The international trade of illegally logged timber is an issue with far reaching environmental and economic consequences. In response to recent international regulation the International Atomic Energy Agency Terrestrial Environment Laboratory (IAEA TEL) is developing wood standard reference materials characterized for light stable isotopes to aid in the verification of the geographical origin of timber. As wood producer and consumer countries struggle to comply with international requirements for certification of the legality of wood products a scientific frameworks for assessing the geographical origin of wood is of vital importance.

Light stable isotopes have long been employed to authenticate the origin of a range of organic materials of economic importance by capitalizing in the characteristic global distribution of δD and $\delta^{18}O$ in meteoric water (Craig, 1961) and local-scale variation in $\delta^{13}C$ and $\delta^{15}N$. Together, these signals recorded in vegetation represent a powerful tool for the determination of geographic provenance (Kelly et al, 2005). The δD composition of wood is especially important in determining geographic provenance but presents the additional issue of exchangeable hydrogen. After a tree is cut hydrogen bound to oxygen and nitrogen continues to exchange with moisture in the ambient air obscuring the original δD isotopic signal as the wood moves from the location it was harvested through the export process (Schimmelmann et al, 1993). The production of wood standard reference materials and related analytical methods, particularly for exchangeable hydrogen, are critical to ensure data are reproducible across laboratories. As a subsequent step, a corollary project to sample the geospatial variations of stable isotopes in legislatively important species of timber across key wood producing countries is necessary. Together these tasks represent the first step towards distinguishing wood origin on a scientific basis rather than administrative documentation such as timber harvesting permits or shipping manifests, which can be easily falsified.

This talk will feature the role and challenges of using stable isotopes as part of a scientific framework to combat illegal logging, progress towards the isotopic characterization of candidate wood reference materials for $\delta^{13}C$, $\delta^{15}N$, and δD , and method development to address the issue of exchangeable hydrogen for δD in wood.

3 Keynote

ISOTOPE FORENSICS: APPLICATIONS IN MIGRATORY WILDLIFE STUDIES

Leonard Wassenaar¹

¹International Atomic Energy Agency, Vienna, Austria

Over the past decade, an increasing suite of environmental isotope forensic and fingerprinting techniques have been successfully developed as potent tracers for determining the geographical origins of animals and migratory species. Predictable or ecosystem scale H, O, C and N isotopic patterns in nature are intrinsically incorporated into organisms and plant tissues via geology, water or diet. Hydrogen isotopes in particular, have exceptional patterns in the hydrosphere and biosphere driven by spatially and temporally predictable hydrologic patterns (e.g. IAEA GNIP maps), which can be used to interpolate and predict origins of wildlife into regions not covered by field data collections or observational networks. These hydrology-driven isotope tools based on IAEA GNIP data have revolutionized isotopic spatial assignments of animals and wildlife materials globally, that were previously intractable. This presentation will provide a review of the development of H isotope applications specifically to questions of wildlife migration issues and spatial connectivity, and some of the analytical challenges that still remain. The approaches developed for wildlife over the past 15 years are nowadays sufficiently advanced to be transferred to other disciplines (e.g. food, narcotics origin).

4 Oral Presentation

THE USE OF STABLE ISOTOPES $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ FOR CHARACTERIZING RECHARGE AREAS OF GROUNDWATER BODIES IN THE NORTHERN BURGENLAND (AUSTRIA)

Häusler, H.¹, Tchaikovsky, A.², Kralik, M.^{1,3}, Müllegger, C.¹, Bichler, A.¹, Irrgeher, J.⁴, Mykhaylyuk, I.¹ & Prohaska, T.²

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21 water samples taken in the Wulka catchment were analysed both for their $^{87}\text{Sr}/^{86}\text{Sr}$ -values and $\delta^{18}\text{O}$ isotopic composition and revealed values ranging from 0.7090 to 0.7120 and -12.0‰ to -10.5‰, respectively. It can be concluded that artesian wells and thermal ground water bodies in Neogene indicate infiltration of fresh water from areas of crystalline composition in Late Quaternary times (Figure 1). Recharge areas can be identified as Leitha Mountains and Rosalia Mountains, both with maximum altitudes of 400 to 700 m above sea level. It can be further excluded that saline groundwater of a marine deep-seated aquifer charged the shallow groundwater horizons below the salt ponds of the Seewinkel, as was postulated since the 1960s, because relatively high strontium isotope ratios and very low oxygen isotope ratios cannot be interpreted as evaporation signals. Due to $^{87}\text{Sr}/^{86}\text{Sr}$ -values exceeding 0.7090, the Seewinkel deep seated aquifers are not composed of basic volcanic rocks, the strontium isotope ratios of which, according to Voerkelius et al. (2010), should range between 0.7035 and 0.7070.

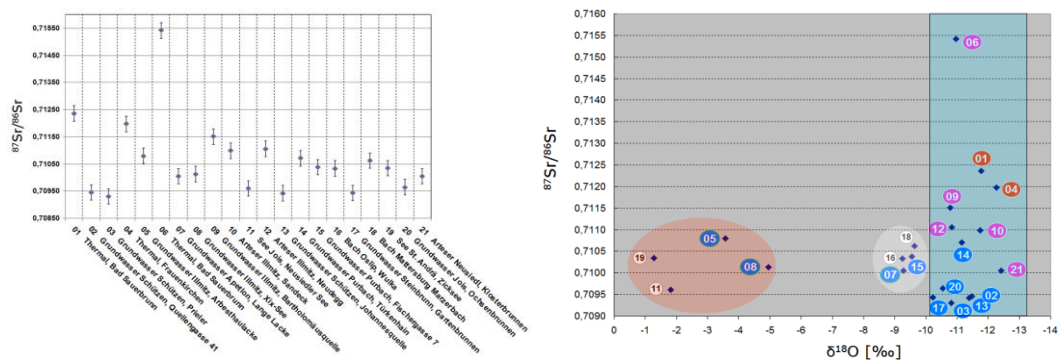


Figure 1. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of 21 water samples from the Wulka catchment; error bars represent combined standard uncertainties (U_c , $k=2$; left) and $^{87}\text{Sr}/^{86}\text{Sr}$ -values plotted against $\delta^{18}\text{O}$ -values (right).

Voerkelius, S., Lorenz, G.D., Rummel, S., Quélet, C. R., Heiss, G., Baxter, M., Brach-Papa, C., Deters-Iltzelsberger, P., Hoelzl, S., Hoogewerff, J., Ponzevera, E., Van Bockstaele, M. & Ueckermann, H. (2010): Strontium isotope signatures of natural mineral waters, the reference to a simple geological map and its potential for authentication of food.- Food Chemistry, 118, 933-940, 2 fig., 1 tab.

5 Oral Presentation

MINERALOGY, HYDRO- AND ISOTOPE CHEMISTRY OF THERMAL WATER AND SCALINGS IN HYDROGEOHERMAL PLANTS AND PRILIMINARY RESULTS OF BATSCH EXPERIMENTS

Wyhlidal, S.¹, Haslinger, E.¹, Boch, R.², Fröschl, H.³, Dietzel, M.², Leis, A.⁴, Knaus, R.⁴, Goldbrunner, J.⁵, Shirbaz, A.⁵ & Plank, O.¹

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The aim of the research project NoScale is to assess the risk of precipitation (scaling) and corrosion in the use of deep thermal groundwater. On the basis of comprehensive and complex chemical and mineralogical experiments and building upon detailed hydrochemical modeling the potential impact of the use of the thermal waters on the technical components of hydrogeothermal systems are to be shown. 15 hydrogeothermal plants were sampled in Austria as well as in Bavaria. At six plants, scalings could be sampled and analysed. The sampled plants are located in different (hydro)geological settings; the purpose of the geothermal plants (thermal, electricity, balneological) and therefore the exploitation depths varied to a great extent, therefore the isotope and hydrochemistry as well as the encountered scalings were different in each plant. The scalings were mostly carbonate scalings in pipes and on heat exchangers, but also precipitation of elemental sulphur occurred. In two plants, the scalings were so massive that they completely blocked the groundwater pump and the heat exchanger which subsequently led to a temporary shut-down of the plants after only one year of operation (Fig. 1). In ongoing laboratory experiments accompanied by thermodynamic-kinetic modelling, the nature and kinetics of the scaling processes shall be clarified. The investigated scaling processes in the different plants will result in recommendations for plant operators how to avoid scaling with the best suitable operating conditions.

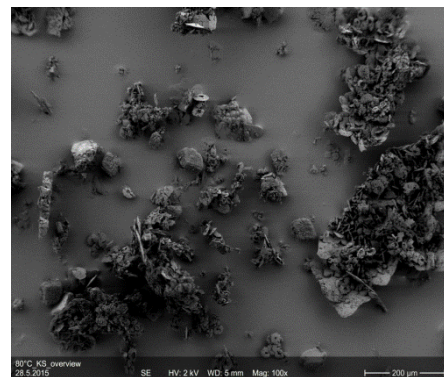


Figure 1: cm-thick carbonate scalings (left). scalings of Mg-calcite, Aragonite and Vaterite at the experiments (right)

6 Oral Presentation

CARBONATE SCALING OF PANNONIAN BASIN GEOTHERMAL WELLS: FIRST RESULTS FROM STABLE C, O & CLUMPED ISOTOPES

Boch, R.¹, Leis, A.², Mindszenty, A.³, Szanyi, J.⁴, Deák, J.⁵, Kluge, T.⁶, Sipos, P.⁷, Demeny, A.⁷,
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Solid precipitates in wells, pumps, pipes and heat exchangers cause severe problems in thermal water and energy production, i.e. clogging or reduction of inner diameters. Depending on natural and man-made environmental conditions spatiotemporally variable deposition (scaling progress) is common. Using high-resolution analytical techniques the mechanisms determining nucleation and growth dynamics of these chemical sediments are studied in detail focusing on forensic tasks and retarding/preventive measures. Scalings were collected from pipes at the wellhead of selected geothermal sites in Hungary. The geothermal installations comprise different aquifer and depth conditions, i.e. fluid-temperature, discharge, operating pressure and hydrochemistry. Mostly laminated and cm-thick carbonate scalings of individual macroscopic appearance represent mineral deposition (e.g. Mg-calcite), from two weeks up to 45 years. Subsamples for C and O isotope analysis via CF-IRMS were recovered using a dentist drill or computer-controlled micromill device. Oxygen isotopic compositions revealed a large range from -24.8 to -10.3 ‰ (VPDB), mostly reflecting differences in temperature, origin and age (aquifer depth) of the thermal water. In contrast, $\delta^{13}\text{C}$ values of (Mg)-calcite show a small range from -2.6 to 2.7 ‰ (VPDB). With regard to established oxygen- and novel clumped isotope geothermometers, geothermal scalings of well characterized precipitation conditions hold a great potential in evaluating isotope fractionation and calibration. O-isotopic fractionation calculations of thermal water and precipitating carbonate from different sites and temperature regimes reveal a clear T-dependence of the measured isotope values based on empirical (and extrapolated) calibration curves, i.e. in most cases approximating the measured scaling formation temperatures very well. Using such temperature relationships we analyzed a 7.5 cm thick (deposited from 1967-2012) scaling from a pipe leaving a thermal water storage tank towards Széchenyi Spa (Budapest) at high resolution. Isotope analyses reveal an increase in water-temperature from ≈ 65 °C to the currently measured 73 °C based on a distinct O-isotope shift in the upper portion (recent past) of the chemical sediment, i.e. a working hypothesis to be tested in-situ. Considering multiply-substituted (clumped) isotopologues, we currently apply scaling samples to study a pH and corresponding DIC (dissolved inorganic carbon) speciation effect on ^{13}C - ^{18}O clumping in carbonate resulting in a systematic deviation between actual and calculated temperature at high precipitation rates.

7 Oral Presentation

AUTOMATIC DATA CALIBRATION STRATEGIES WITH IONOS

Volders, F.¹, Sudnik, M.², Seed, M.², Wheeler, P.²

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²Isoprime Ltd, Isoprime House, Earl Road, SK8 6PT, Cheadle Hulme, UK

The data processing in the stable isotope ratio software has always been characterised by the off-line nature of this process. The commercially available software has so far not contained any option to go from the so-called raw data to the final useable data point. Isoprime Ltd, has in conjunction with their new IRMS system, the visION, also released a completely new software for data processing, IONOS.

The new software from Isoprime, allows the import from all types of data, directly into the software, so that all users can take advantage of the software to provide the final data for their research. The software is characterised by a multitude of automated calibration and correction set-ups for both bulk and compounds specific data analysis. With fully configurable reporting and lookup of the data one can always retrace the data correction scheme that has been used. The IONOS software will allow users to easily standardise their data analysis protocols.

8 Oral Presentation

MIXING OF MICROBIAL GAS AND THERMOGENIC HYDROCARBONS; THE AUSTRIAN MOLASSE BASIN CASE STUDY

Pytlak, L.¹, Gross, D.¹, Bechtel, A.¹, Gratzner, R.¹, Sachsenhofer, R.F.¹, Linzer, H.-G.²

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The Molasse Basin, extending from Geneva to Vienna, is the classical asymmetric foredeep and comprises Eocene to Miocene shallow to deep marine sediments. Within the Austrian sector two petroleum systems can be distinguished: a thermal petroleum system comprising Lower Oligocene source and Cenomanian/Eocene reservoirs rocks and a microbial gas system in Oligocene and Miocene strata.

The aim of the study is to understand the origin, mixing and alteration of natural gas associated with oil in the Austrian part of Alpine Foreland Basin. To do so forty eight wells producing oil from Cretaceous and Eocene reservoirs were sampled for oil and associated gas. Samples were investigated for molecular and stable C and H isotope composition of hydrocarbons and CO₂.

Based on stable carbon isotopes as gas was expelled from source rock at various maturity levels (0.6 – 1.2 %Rr) thus at the beginning of thermal maturation processes and in peak of oil window. Gas maturities established based on stable carbon isotopes are in general agreement with those of oils. Nevertheless, results revealed that most fields trap methane derived from source different to the thermogenic. Shallow northeastern reservoirs trap methane interpreted as methanogenic microbial oil biodegradation. The same process is suspected as source of methane in western deposits. Moreover those gases are enriched in ²H isotope suggesting different methanogenesis pathway. Fields along the southern margin of the Alpine Foreland Basin where reservoir temperature exceeds 80°C host methane generated during primary organic matter degradation. Thus, Eocene and Lower Oligocene layers should be considered as potential source rocks. Study gave new insight to filling history of traps and revealed more complicated geological background and hydrocarbons generation than have been thought until now.

9 Oral Presentation

OCEAN ACIDIFICATION AT THE PERMO-TRIASSIC MASS EXTINCTION. CLUES FROM BORON ISOTOPE

Clarkson M. O.¹, Kasemann S. A.², Wood R.³, Richoz S.⁴, Lenton T. M.⁵, Daines S. J.⁵,
Ohnemüller F.², Meixner A.², Poulton S. W.⁶, Tipper E. T.⁷

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Ocean acidification triggered by Siberian Trap volcanism is considered as possible kill mechanism for the Permian Triassic Boundary (PTB) mass extinction, but direct evidence for an acidification event is lacking. We present a high resolution seawater pH record across this interval, utilizing boron isotope data ($\delta^{11}\text{B}$) combined with petrographic analysis and quantitative modeling approach. We analyzed boron and carbon isotope data from two complementary transects in a shallow marine, open water carbonate succession from the Musandam Peninsula (United Arab Emirates, U.A.E.), where depositional facies and biostratigraphy are well constrained. During the PTB interval the U.A.E were part of the Arabian Platform, an expansive carbonate platform that remained connected to the central Neo-Tethyan Ocean.

Through the integration of geochemical and petrographical data and quantitative modeling, we are able to produce an envelope that encompasses the most realistic range in pH, which then allows us to resolve three distinct chronological phases of carbon cycle perturbation, each with very different environmental consequences for the Late Permian-Early Triassic Earth system. In the latest Permian, increased ocean alkalinity, primed the Earth system with a low level of atmospheric CO₂ and a high ocean buffering capacity. The first phase of extinction was coincident with a slow injection of carbon into the atmosphere and ocean pH remained stable. During the second extinction pulse, however, a rapid and large injection of carbon caused an abrupt acidification event that drove the preferential loss of heavily calcified marine biota.

The boron signal cuts across primary lithological boundaries, including micritic carbonates, grainstones, and intervals with calcispheres. $\delta^{11}\text{B}$ trends are therefore both facies and fabric independent but the short-lived acidification event is manifest in a loss of any biotic component, and unusual and anomalous carbonate precipitates that may indicate profound carbon cycle disruption.

10 Oral Presentation

MASS-DEPENDENT AND MASS-INDEPENDENT FRACTIONATION OF STABLE Hg ISOTOPES AS TWO-DIMENSIONAL TRACER FOR MERCURY CYCLING IN THE ENVIRONMENT

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Mercury (Hg) is a toxic heavy metal that represents a serious hazard for human and ecosystem health at local and global scales. Anthropogenic activities (e.g., coal combustion, industry, mining) have increased global Hg cycling by a factor of three compared with pre-industrial times. Although biogeochemical Hg cycling has been studied extensively over the past decades, many questions concerning sources, transformations, and the fate of Hg in natural ecosystems still remain unclear. New analytical techniques, namely cold-vapor multicollector inductively-coupled plasma mass spectrometry (CV-MC-ICP-MS), resulted in the detection of significant variations of stable Hg isotope ratios in natural samples. Thus, Hg isotope signatures represent a new tool to trace environmental Hg cycling by providing information on sources and transformation processes. Interestingly, depending on the fractionating process both mass-dependent and mass-independent fractionations occur and affect the even- and odd-mass Hg isotopes to a different extent (Figure 1) adding an additional dimension to the interpretation of Hg isotope signatures of natural samples. Here, we present Hg isotope data from different anthropogenically polluted field systems (e.g., mining environments [1], sediments contaminated by local industrial sources [2], ongoing work in contaminated aquifers) measured by CV-MC-ICP-MS (Nu Plasma II) to demonstrate the potential of Hg isotopes as tracer for environmental Hg cycling.

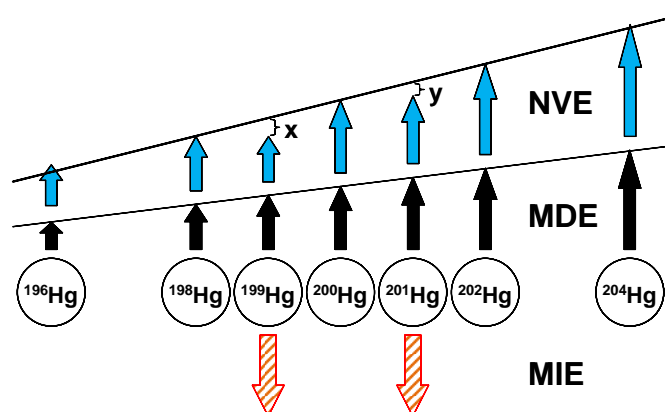


Figure 1. Schematic illustration of fractionation mechanisms in the Hg isotope system [3]. The arrows indicate qualitatively the influence of the mass difference effect (MDE), the nuclear volume effect (NVE), and the magnetic isotope effect (MIE) on the fractionation of the seven naturally occurring stable Hg isotopes.

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11 Oral Presentation

DIFFERENTIATION OF WOOD ORIGIN IN THE AUSTRIAN ALPS FOR THE DETERMINATION OF POSSIBLE GROWTH REGIONS OF PREHISTORIC WOOD

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Wood artefacts from a prehistoric salt mine in Hallstatt, Austria, present a unique archive of information on Bronze and Iron Age mining. As trade is assumed for certain prehistoric tools the analysis of stable isotope signals of the elements C, O and H has been applied to investigate the geographic origin of these artefacts, in order to allow conclusions on trade routes.

In addition to Hallstatt, 26 locations in Austria were selected for sampling of modern trees based on known settlements in the time period of interest. The locations are located in Upper Austria, Salzburg, Styria and Carinthia. Drill cores from four tree species present in the archaeological finds (*Picea abies*, *Abies alba*, *Fagus sylvatica* and *Quercus* sp.) were sampled at the locations upon availability. The bulk wood samples were analysed for their C, O and H isotope ratios by isotope-ratio mass spectrometry.

The isotopic signature obtained from the modern trees enables a classification of the modern samples in two groups: One represents the locations of the northern and central Alps and the second one contains the locations of the southerly Alpine ones, the locations in the northern foothills of the Alps and the non-Alpine one. Prehistoric wood artefacts assumed to stem from the Hallstatt mine immediate vicinity show almost identical isotope patterns as modern wood from Hallstatt. Thus it is assumed that prehistoric wooden artefacts from other localities will have a very similar isotope pattern to modern wood from these localities and can be compared to and correlated with the modern wood isotope patterns.

12 Oral Presentation

AUTHENTICITY AND TRACEABILITY TESTING OF VANILLIN BY COMPOUND SPECIFIC STABLE ISOTOPE ANALYSIS

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The authenticity and traceability of food products is increasingly attracting the consumers' interest. The trend is not only toward more natural products and ingredients, but geographic origin and method of production can also affect the consumer's choice of products. It is illegal in the European Union (EU) to label a product with false information; however, falsification can be difficult to verify using traditional analytical methods.

Vanilla is the most important flavor in the food industry and is extensively applied in fragrance and pharmaceutical production. But where actually does our vanillin flavor come from? Natural extracts from vanilla beans represent only approximately 1% of the whole market volume and therefore fraud and adulterations as well as mislabelling are known to be a significant issue. To address this issue the analysis of stable isotopes of different compounds of the vanilla extract can help to identify origin and production processes.

Previous isotopic studies have investigated the authenticity of vanilla flavor using either elemental analyzer-IRMS (EA-IRMS) or gas chromatography-IRMS (GC-IRMS) (eg John and Jamin, 2004; Greule et al., 2010; Hansen et al., 2014). In these studies, it was shown that GC can be used to separate vanillin from the other components of a vanilla extract and after combustion or pyrolysis of the vanillin, the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ can be determined, respectively. The combined use of results of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ analyses for vanillin shows a relatively narrow clustering pending upon species, synthesis, raw materials and geographic location of growth.

Here we are presenting compound specific stable carbon and hydrogen isotope method (CSIA) for the analysis of the vanillin component of the vanilla extracts by GC-IRMS. This method allows the separation of artificially produced vanilla from those extracts made from pure vanilla with a natural origin. The multi-isotopic application allows the estimation of approximate region of growth of the vanilla bean. This reliable and robust application incorporates limited sample preparation and the use of small amounts of vanilla. The method can be securely applied to pure vanilla extracts or food flavor extracts and due to internationally scaling of the results inter-laboratory comparisons are easily possible.

13 Oral Presentation

CARBON ISOTOPE ENRICHMENT OF CHLORINATED ETHENES BY LOCAL ANAEROBIC MICROBIAL COMMUNITIES

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Chlorinated ethenes are xenobiotic volatile organic compounds (VOC) comprising Perchloroethene (PCE), Trichloroethene (TCE), Dichloroethene (cDCE, tDCE) and Vinyl Chloride (VC) representing a serious group of groundwater and soil contaminants (toxic and carcinogenic). Due to miserable handling or unappropriated storage chlorinated ethenes were likely to enter the subsurface at industrial sites (e.g. dry cleaning, metal degreasing). Leaching into an aquifer VOCs, as dense non aqueous phase liquids (DNAPL), tend to form a highly concentrated source zone and a contamination plume (as a consequence of groundwater movement). Within the plume and source zone VOCs can be degraded by dehalorespiration of bacteria.

Compound specific isotope analysis (CSIA) of carbon of VOC is a reliable tool to distinguish in-situ concentration level changes of VOC arising from microbial degradation or dilution by hydrogeological processes (dispersion, convection). Monitoring the VOC concentrations behaviour on-site or by laboratory experiments (microcosms) can indicate the possibility of site remediation by natural attenuation (MNA).

The aim of this study was to show the complexity of MNA by evaluating a geologically simple seeming contaminated site. The methodology was focused on data evaluation by CSIA (Purge & Trap – GC-C-MS/IRMS) of VOC degradation experiments (anaerobic microcosms) and groundwater sample analysis. To confirm data quality and improve data interpretation DNA sequencing was performed too. In addition degradation rates and kinetics of the microbial communities were evaluated. Furthermore the adsorption behaviour of the sediment samples was analysed to evaluate if adsorption can enhance the availability of solute chlorinated ethene concentrations for bacterial degradation.

Results of the site characterisation showed indications of bacterial degradation activity at some spots along the small contamination plume. This was proven by significant changes in the isotope composition of the initial contaminant PCE as well as its metabolites (TCE, cDCE). Geo-hydrological parameters and groundwater analysis evidenced that these spots permit anaerobic bacterial growth. The results of the microcosm study showed a variety of microbial communities (different degradation end products), which could be grown out of sediment samples. These results were fostered by the DNA-Analysis. Analysing the isotope enrichment of the residual VOC concentrations by the Rayleigh-Equation displayed isotope enrichment factors which could be grouped and correlated to differences in the microbial communities. In addition to the different carbon isotope enrichment factors degradation rates and first-order rate constants scattered too, underlying the complexity of a geo-hydrologically as homogeneous depicted contaminated site. Plotting the adsorption parameters of the sediment samples against the degradation rates within these samples showed that increasing adsorption might enhance degradation rates.

14 Oral Presentation

MINERALIZATION DYNAMICS OF ¹³C-LABELED PHYTOSIDEROPHORES IN THE RHIZOSPHERE OF WHEAT

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Being low molecular weight carbon (LMW-C) compounds, phytosiderophores (PS) released by strategy II plants are highly susceptible to microbial decomposition. However, to date very little is known about the fate of PS in soil. Using in-house synthesized ¹³C-2'-deoxymugineic acid (DMA), the main PS released by wheat, we traced DMA mineralization dynamics, including microbial incorporation into phospholipid fatty acids (PLFA), in the wheat rhizosphere and bulk soil of two alkaline and one acidic soil. Half-lives of the intact DMA molecule (3-8 hours) as well as of DMA-derived C-compounds (8-38 days) were in the same order of magnitude as those published for other LMW compounds like sugars, amino acids and organic acids. Combining mineralization with PLFA data showed that between 40 and 65% of the added DMA was either respired or incorporated into soil microbial biomass after 24 hours, with the largest part of total incorporated DMA-¹³C being recovered in gram negative bacteria. Considering root growth dynamics and that PS are mainly exuded from root tips, the significantly slower mineralization of DMA in bulk soil is of high ecological importance to enhance the Fe scavenging efficiency of PS released into the soil.

15 Oral Presentation

MEASUREMENT OF $\delta(^{34}\text{S}/^{32}\text{S})_{\text{VCDT}}$ IN BIOAVAILABLE SOIL SULFATE BY DGT MC ICP-MS

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Sulfur may undergo various biogeochemical processes in soil, many of which are affecting its bioavailability. Moreover, these processes are known to influence the isotopic composition of readily available soil $\text{SO}_4\text{-S}$. Therefore, analysis of stable sulfur isotopes is a tool to follow biological activity and geochemical processes, which affect the availability of sulfate to plants in soils.

A classical procedure to determine the isotopic composition of bioavailable $\text{SO}_4\text{-S}$ consists of porewater sampling using lysimeters or soil extraction (e.g. using NH_4NO_3), sulfate precipitation and a mass spectrometric analysis applying the isotope ratio mass spectrometer (IRMS). This approach is however sample consuming and/or demands high contents of sulfate in the sample. Recently, multi collector inductively coupled plasma mass spectrometry (MC ICP-MS) has become a method of choice for $^{34}\text{S}/^{32}\text{S}$ analysis when small amounts (sub-mg/g) of sulfate are targeted. The measurement is however limited due to effects of co-extracted matrix elements (K, Na, Ca etc.) on the measurement precision and accuracy. Therefore, a method is required combining the selective extraction of sulfate from soil and the high sensitivity and isotope ratio measurement accuracy of MC ICP-MS.

We present a DGT method for direct sampling of bioavailable sulfate from soil, even at low concentrations and small amounts of sample. The sampled sulfate can be leached from the resin gel easily in $1 \text{ mol L}^{-1} \text{ HNO}_3$. The eluate is then directly measured by MC ICP-MS without the need for further matrix element separation. Method parameters (diffusion coefficient in APA2 gel, elution efficiency from resin gel) were determined using ^{35}S as radiotracer. Isotope ratio analysis was optimized using the high resolution capabilities of MC ICP-MS and effects of the sampling procedure on the isotope ratio were investigated in order to ensure that an unbiased isotopic composition of bioavailable S can be assessed.

16 Oral Presentation

INSECT ISOTOPE FORENSICS

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With an increasing emphasis on area wide pest management a full understanding of the ecology and biology of insect-pest species is required to efficiently implement these area-wide strategies. Marking tools are invaluable in addressing the scientific knowledge gaps in the ecology and biology of insects such as distribution, movement, and larval host origin.

However there is currently a lack of widely available, simple and ethically acceptable methods for marking economically important species, including mosquitoes, moths and fruit flies. Stable isotope marking is one approach which could be used to naturally or synthetically label the vast numbers of insects required for genetic control or sterile insect technique programs, as it fulfils the universally defined marking criteria of: retention, not affecting the insect's fecundity or behaviour, durability, non-toxicity, easily applied, clearly identifiable and inexpensive.

Stable isotope tools offer a number of opportunities to trace the, source, distribution and movement insect populations across the landscape safely, posing no environmental threats or hazards; allowing estimates of population size, range and diet. Moreover using isotope signatures it is possible to determine which males, wild or sterile? are inseminating the native female population, yielding invaluable information on mating success.

It is often argued that stable isotope analysis using mass spectrometry is expensive. However we present and explore the economics of this issue and the feasibility of using a newly developed laser based systems in an operational context which could significantly reduce the cost of isotope analysis, therefore expanding the scope and applicability of this technology.

17 Oral Presentation

THE TALE OF THE HORSES' TAILS: STABLE ISOTOPES REVEAL DIFFERENCES IN THE FEEDING ECOLOGY OF THREE SYMPATRIC EQUID SPECIES IN THE DZUNGARIAN GOBI, MONGOLIA

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Stable isotope analysis of continuously growing and isotopically inert tissue such as hair has become a powerful tool to address individual seasonal variation in diet, water use and movement pattern in a suite of large herbivores, providing insight into long-term ecological dynamics and a species niche [1–3]. We studied the feeding ecology of three sympatric equid species in the Dzungarian Gobi in southwestern Mongolia: the re-introduced endangered Przewalski's horse (*Equus ferus przewalskii*), the endangered Asiatic wild ass (*Equus hemionus*), and a potential competitor the domestic horse (*Equus caballus*). Using segmentally cut tail hair, a biological archive that contains chemical information about what the animals have been eating in the form of C and N stable isotopes obtained from food, we were able to reveal species specific differences in the feeding patterns. A stable isotope mixing model revealed that both horse species are grazers (C3 grasses) that only include higher amount of C4 shrubs (>20%) in their food under extremely severe environmental conditions. The feeding pattern of the Asiatic wild asses, on the other hand, is highly seasonal switching from being grazers in the summer to mixed-feeders (including up to 65% C4 shrub) in the winter when food availability is lowest and competition with other wild and domestic grazers highest. The drastic isotopic dietary niche shift observed in Asiatic wild asses in winter suggests resource partitioning in order to avoid competition which facilitates the coexistence of horses and asses in the same habitat. The competition between Przewalski's horses and domestic horses on the other hand is likely high, particularly during times of food shortage. Our findings will help optimize resource allocation (grazing permits and winter camp position) between semi-nomadic people and their domestic animals on the one hand and Asiatic wild asses and Przewalski's horses on the other hand and will thus help to improve ongoing conservation strategies.

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18 Oral Presentation

Environmental differences reflected by stable isotopes of *Cytheridella* in the Neotropics: a comparison of Florida and Mexico

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Geochemical signatures of ostracod valves have become important proxies for paleohydrological conditions. The environmental factors and mechanisms which govern the isotopic composition ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) are, however, not yet fully understood, and hydrochemistry of recent sampling localities are rare.

Within the project FWF P26554 we investigate the Neotropical ostracod *Cytheridella* from recent freshwater habitats. *Cytheridella* covers a wide biogeographical range along the Neotropics, which gives us the opportunity to examine the isotopic composition of ostracod valves of *Cytheridella* and their host water on different spatial scales.

We used 18 water samples from different freshwater habitats (rivers, lakes, cenotes, marsh lands, lagoons) from Florida and Mexico sampled in August 2014 to analyse their isotopic composition (δD , $\delta^{18}\text{O}$, $\delta^{13}\text{C}$). In addition, valves of *Cytheridella* from surface sediment samples from the same sites were analysed for stable oxygen and carbon isotopes.

Water isotopic values range from -22.97 to 16.85‰, from -3.28 to 3.22‰ and from -12.36 to -3.06‰ for δD , $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, respectively. δD and $\delta^{18}\text{O}$ values separate Floridian from Mexican water bodies and characterise three different groups of waters. The first group is indicated by high values due to evaporation processes, the second is influenced by groundwater mixing reflected by the lowest values and the third median group represented mostly by rivers.

Data from stable isotope measurements of *Cytheridella* valves show a total range from -5.39 to 2.34‰ for $\delta^{18}\text{O}$ and -9.76 to -1.75‰ for $\delta^{13}\text{C}$. The values differ between the sample sites but reside in the dimension of their host waters. In addition, all valves of *Cytheridella* have a constant positive vital offset in comparison to calcite formed in equilibrium. This offset differs between sites ranging from +1.41 ‰ to +4.32 ‰. The range of the isotopic values and the vital offset of *Cytheridella* at a single site depend on the stability of the host water. Seasonally changing environmental conditions lead to higher differences in the range of the isotopic composition of the valves up to 1.89 ‰ for $\delta^{18}\text{O}$. For a temperature reconstruction with stable oxygen isotopes this would lead to a deviation of up to 9.45 °C for a seasonally changing environment.

19 Poster Presentation

DETERMINATION OF THE H/D ISOTOPIC FRACTIONATION DURING BIODEGRADATION OF N-DECANE IN A LABORATORY STUDY

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The usage of constructed wetlands with different filter materials for the clean-up of diesel hydrocarbon polluted water was tested in a pilot-study. This bioremediation method is cost-effective but still at its infancy concerning industrial pollutants. It is still challenging to quantitatively assign the reduction of organic contaminants in CWs to the responsible removal mechanisms. The assessment of the extent of biodegradation in CWs with compound specific isotope analysis (CSIA) is an innovative approach to get direct proof of microbial contaminant breakdown on-site since biodegradation is the only removal process that may lead to an accumulation of heavy isotopes in the unreacted substrate pool. This is only possible if the fractionation factor α for the transformation of the pollutant of concern is known. The magnitude of α depends on the actual bond that is broken in the initial transformation step and accordingly on the metabolic pathway. Secondly, the actual fractionation might be considerably smaller than expected if the bond cleavage of the pollutant is not the rate-determining step in the overall transformation process. The biodegradation process in the CWs is simulated in the laboratory with incubated filter material from the CWs and the n-alkane C10, which is one of the major constituents of diesel oil. The $\delta^2\text{H}$ of n-decane was determined with GC-IRMS during biodegradation in gastight sealed laboratory flasks. N-decane was reduced at high rates when applied to microcosms containing 'expanded clay' and sand amended with biochar, but the biodegradation was not accompanied by any isotopic fractionation. On the contrary, a slower reduction of the added compound was observed in laboratory microcosms containing sand from the CWs leading to an enrichment in $\delta^2\text{H}$ -values of 10 to 30 ‰. The fractionation factor α for the aerobic degradation of n-decane therefore ranges from 0.94 to 0.98. The observed isotope fractionation is by far lower than the one expected for a C-H bond cleavage suggesting that other non-fractionating steps were rate-determining during the degradation process in our laboratory microcosms. Therefore, it is too early to assess the extent of biodegradation of diesel hydrocarbons in the field with isotope measurements.

20 Poster Presentation

ORIGIN OF WOODCOCKS (SCOLOPAX RUSTICOLA) HUNTED IN AUSTRIA

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The woodcock in the EU is a protected species. Still, in several countries, among them Austria, its hunt is allowed. EU regulations, however, request the respective countries to protect their native woodcock population and to prove that the hunted woodcocks are alien migrants and not native ones.

For this purpose primary feathers of hunted woodcocks in Lower Austria have been collected and measured for their stable isotope signature. From the condition of the feathers juvenile and adult individuals are distinguished.

Expected are differences in isotope pattern between juvenile and adult woodcocks, as adult woodcocks have their moult in winter and thus report patterns representing the conditions in the wintering areas. Juvenile woodcocks report the conditions of the breeding sites in summer.

Preliminary results show the expected differences between juvenile and adult individuals. At least three different origins of the juvenile individuals are identified and at least two different ones for the adult ones. Furthermore there is evidence that woodcocks might not have a very high site-fidelity.

21 Poster Presentation

TOWARDS A SR ISOSCAPE OF AUSTRIA FOR THE DETERMINATION OF GROWTH REGIONS OF PREHISTORIC WOOD

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Wood artefacts from a prehistoric salt mine in Hallstatt, Austria, present a unique archive of information on Bronze and Iron Age mining. For instance, the geochemical signatures of growth locations are stored in the finds, though masked by contaminating minerals attributable to the storage conditions. Trade is assumed for certain archaeological finds. Consequently, analysis of the radiogenic strontium isotope amount ratio $n(^{87}\text{Sr})/n(^{86}\text{Sr})$ has been applied to investigate the geographic origin of these artefacts, in order to allow conclusions on trade routes.

In order to reveal the biogenic signatures of the prehistoric finds, a decontamination method based on acid leaching was developed. It enabled the separation of biogenic from diagenetic Sr. A mixing model was adopted to account for possibly incomplete removal of the latter. In addition to Hallstatt, seven regions in Austria were selected for sampling of modern trees based on known settlements in the time period of interest. The geological bedrock variability was considered within all regions for the definition of sampling spots, which resulted in a total of 26 locations. Drill cores from four tree species represented in the archaeological finds (i.e. *Picea abies*, *Abies alba*, *Fagus sylvatica* and *Quercus* sp.) were sampled upon availability. Sr isotope ratios were measured in wood digests after Sr/matrix separation using multicollector inductively coupled plasma-mass spectrometry (MC ICP-MS).

The isotopic signature of bioavailable Sr that was obtained from modern trees reflects the geological heterogeneity in Austria, which challenges the creation of an isoscape and its applicability to distinct provenance determination. Different bedrock types can be distinguished by their $n(^{87}\text{Sr})/n(^{86}\text{Sr})$. Furthermore, the data indicate that the isotope ratios of bio-available Sr within one geological substrate also vary strongly. The results highlight the importance to consider even small scale geological and environmental variability in a comprehensive sampling strategy for a reliable application of Sr isotope ratio analysis to the determination of origin of biogenic material.

This contribution was also presented at the DocDay 2015, Tulln, Austria.

22 Poster Presentation

LITERATURE DATABASE FOR KARST-HYDROLOGIC STUDIES IN AUSTRIA

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Referring to the Austrian Environmental Control Act (Federal Legal Gazette No. 152/1998) the Umweltbundesamt (Environment Agency) documents the karst-hydrologic studies in Austria.

According to this obligation two reports were published. The first report covers the period from the fifties up to the year 1991 (Umweltbundesamt, 1992). The second one covers the period from 1992 to 1997 (Umweltbundesamt, 2001). These two reports include master files of each study containing the most important and common terms like investigation area, author(s), working title, period of investigation, supplements, province(s) and a small outline map with the project area.

Tracing these papers was extraordinary time consuming. As electronic data processing and internet were not available in the past these first evaluations contain only short data sheets, sometimes listings of the methods or results of the investigations but no abstracts.

The documentation of the karst-hydrologic studies should be a support for persons working in the field of applied karst-hydrology and research scientists not only to get an overview of the amount of investigations in Austria but also to find specific karst-hydrologic studies sorted by the terms mentioned above.

Therefore the Umweltbundesamt provides a web based database that enables the user to search for those studies by author, year of publication, mountain group, groundwater body, province and the number of the Austrian Map.

There is also the possibility for authors to add their own work, to make them accessible to a wider audience or to update existing entries.

For many of these studies more detailed information (e.g. abstract, location of work) is available, if this was provided by the author.

Thus, the database is a state of the art method to document the karst-hydrologic studies. Not least, this database should to be a vibrant, ever-growing and comprehensive overview of the Austrian karst-hydrologic studies providing valuable support for all experts who deal with this topic.

In order to keep the database as up to date as possible, you are very welcome to enter your work on the homepage of the Umweltbundesamt:

<http://www.umweltbundesamt.at/karstdoku>

UMWELTBUNDESAMT (1992): Herlicska. H. & Graf, K.: Dokumentation karsthydrologischer Untersuchungen in Österreich. Reports, UBA-92-057. Umweltbundesamt, Wien.

UMWELTBUNDESAMT (2001): Herlicska. H. & Graf, K.: Dokumentarische Erfassung der karsthydrologischen Untersuchungen im gesamten Bundesgebiet Österreichs (1992-1997). Monographien, Bd. M-145. Umweltbundesamt, Wien.

23 Poster Presentation

THE AUSTRIAN NETWORK FOR ISOTOPES IN PRECIPITATION (ANIP)

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The Austrian Network for Isotopes in Precipitation (ANIP) started in 1972. All over Austria 50 stations, ranging from 120 to 2250 m in altitude, are presently in operation. The aim of ANIP is to provide input data for hydrological and hydrogeological investigations and database for climatological research.

The Alpine mountain range highly influences the amount of precipitation in Austria (400-3000 mm/a). The amount of annual precipitation increases towards the mountain ranges, in particular at the high altitude regions. However, between the north and south of the Austrian Alps strong regional differences exist.

The isotope time series of the stations of the Austrian precipitation network show significant but not uniform long-term trends. The 10-years running mean of some mountain stations indicates a pronounced increase in $\delta^{18}\text{O}$ of about 2‰ since 1975, the increase of $\delta^{18}\text{O}$ at valley stations compared to stations in higher altitudes however is much lower.

The differences in $\delta^{18}\text{O}$ values of sampling stations at similar altitudes can be explained by the origin of the air moisture. Lower $\delta^{18}\text{O}$ values (e.g. Patscherkofel) are caused by an Atlantic influence, whereas higher $\delta^{18}\text{O}$ values are the result of a Mediterranean one (e.g. Villacher Alpe). We will present long time series and some key results of the last four project years.

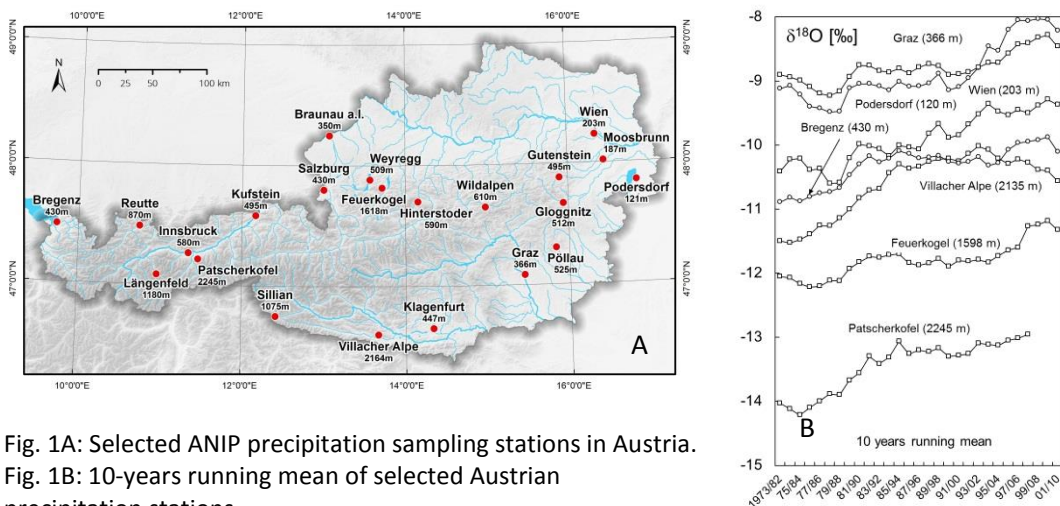


Fig. 1A: Selected ANIP precipitation sampling stations in Austria.
Fig. 1B: 10-years running mean of selected Austrian precipitation stations.

ANIP 2015. (Austrian Network of Isotopes in Precipitation and Surface water) database. Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft. H2O Fachdatenbank, Vienna. Online:

<https://secure.umweltbundesamt.at/h2odb/>

S. Wyhlidal, D. Rank: "Zur Geschichte des österreichischen Messnetzes für isotopenhydrologische Basisdaten (ANIP)"; ÖWAV Tagung, Praktische Isotopenanwendung, Vienna; 15.03.2011; S. 1-11

24 Poster Presentation

PRELIMINARY RESULTS OF ISOTOPE PATTERNS FOR SELECTED PRECIPITATION STATIONS IN AUSTRIA FROM 2005-2014

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Austria possesses one of the worldwide most long-standing and dense isotope networks (ANIP, 43 years of operation) and therefore unique isotope time series. Stable isotope variations in precipitation are a consequence of isotope effects accompanying each step of the water cycle. Therefore, stable isotope ratios of oxygen ($^{18}\text{O}/^{16}\text{O}$) and hydrogen ($^2\text{H}/^1\text{H}$) in past and present precipitation provide important (integrated) information about the origin and atmospheric transport of water vapour. The separation of a remote moisture source signal from local influences is thereby challenging.

Deuterium excess (d-excess) is a second-order isotopic parameter which is often interpreted as a tracer of the evaporation conditions of water vapour at the moisture source in terms of relative humidity, wind speed, and sea surface temperature, but can also be modified by local influences, such as below-cloud evaporation and equilibrium fractionation under very cold conditions.

The long-term variation of d-excess in precipitation at selected stations shows a significant difference in the behaviour of the d-excess at mountain (Villacher Alpe, Feuerkogel; Figure 1) and valley stations. It is well established that there is a slight increase of the yearly mean of the d-excess with increasing altitude of the sampling station (e.g. Rank and Papesch, 2005). But, moreover, the seasonal pattern of the d-excess differs considerably between mountain and valley stations. We present preliminary results of precipitation patterns for selected mountain and valley stations including the altitude effect based on isotopic data of the time period 2005-2014.

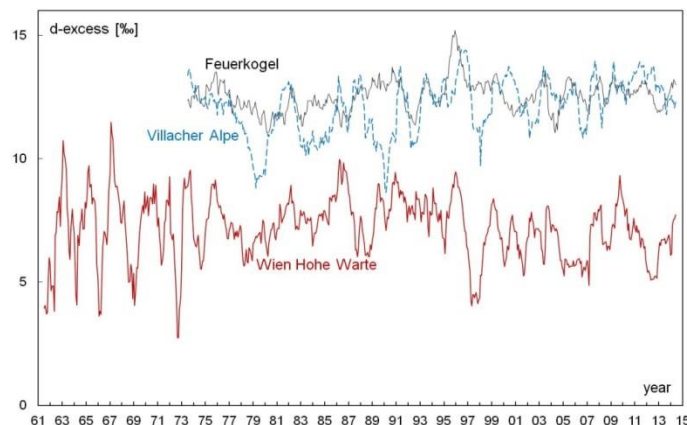


Figure 1. Long-term variations of deuterium excess in precipitation of Feuerkogel, Villacher Alpe and Vienna (12-month running mean).

Rank, D., Papesch, W., 2005. Isotopic composition of precipitation in Austria in relation to air circulation patterns and climate. In: Isotopic composition of precipitation in the Mediterranean Basin in relation to air circulation patterns and climate. IAEA-TECDOC-1453, IAEA, Vienna, 19-36.

25 Poster Presentation

AGE DETERMINATION OF RIVER AND SPRING WATERS USING THE CLIMATE SIGNAL OF THE LONG-TERM $\delta^{18}\text{O}$ TREND OF PRECIPITATION STATIONS

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Long-term stable isotope records of precipitation water exhibit significant decadal changes in the isotopic composition (e.g. Rank, Wyhlidal 2015; accepted). As a consequence, the stable isotope time series of river and spring waters show also significant changes on a decadal scale such as a remarkable increase of $\delta^{18}\text{O}$ in the 1980s mainly due to rising environmental temperature. The long-term $\delta^{18}\text{O}$ trend of several Austrian precipitation stations is similar to that of the Danube (RANK et al. 2010). This trend represents a general climatic long-term isotopic signal – input from precipitation – in all hydrological systems and suggests using it for the determination of water ages (MRTs) in a similar way like ^3H input by nuclear weapons in the past.

As a first attempt we compared $\delta^{18}\text{O}$ trends of precipitation and Danube water at Vienna on the basis of 10-year averages as well as exfiltrating groundwater from the Fischa Dagnitz spring area. The $\delta^{18}\text{O}$ time series of four precipitation stations of the Austrian Network for Isotopes in Precipitation (ANIP) were used for an average input signal for the Danube (Vienna, Bregenz, Feuerkogel and Patscherkofel) and for the Fischa Dagnitz spring area (Gloggnitz, Vienna, Gutenstein and Moosbrunn), respectively.

The best agreement between the two $\delta^{18}\text{O}$ trend curves could be achieved with a shift of the precipitation curve (input) by about 3 years for the Danube (Figure 1) and 15 years for the Fischa Dagnitz spring water (Figure 2), respectively.

The MRT of about 3 and 15 years found out from $\delta^{18}\text{O}$ time series correspond well with the values calculated from tritium time series of river and spring water. Those agreements confirm that reasonable MRT values can be achieved by using long-term $\delta^{18}\text{O}$ signals.

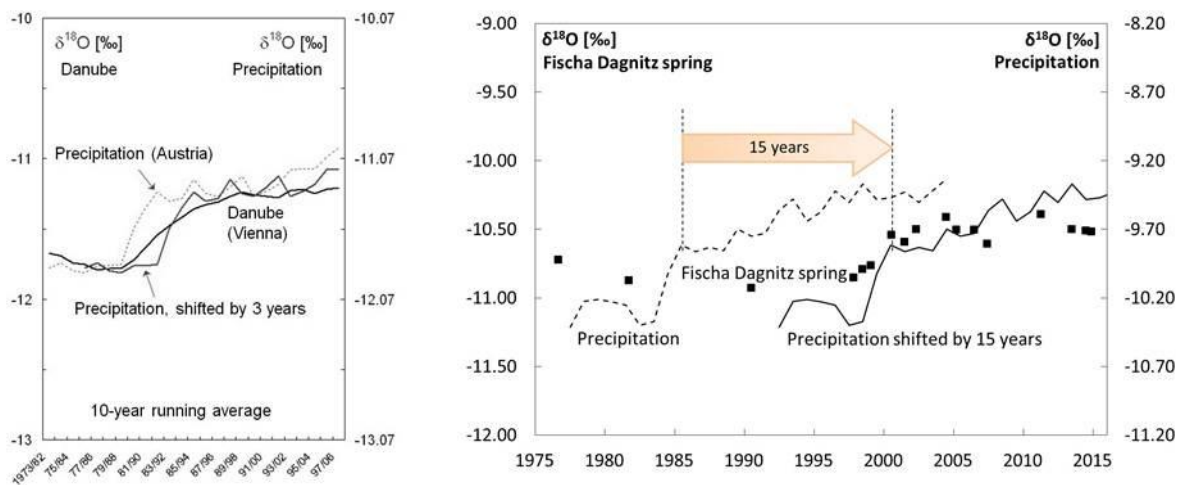


Fig. 1a. Comparison of $\delta^{18}\text{O}$ long-term trends of selected Austrian precipitation stations and of Danube water at Vienna. Fig. 1b. Comparison of $\delta^{18}\text{O}$ long-term trends of selected Lower Austrian precipitation stations and of the Fischa Dagnitz spring water at the Southern Vienna Basin.

26 Poster Presentation

MONITORING OF ANAEROBIC PH-BIODEGRADATION BY ANALYZES OF SHIFTS IN TERMINAL ELECTRON ACCEPTOR ISOTOPIC $\delta^{15}\text{N}$ AND $\delta^{34}\text{S}$ RATIOS

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Anaerobic clean-up methods for petroleum hydrocarbon (PH)-contaminated aquifers that rely on the capability of microorganisms to degrade toxic organic chemicals using terminal electron acceptors (TEA), termed in situ bioremediation, are promising approaches. However, in situ process control is difficult in the presence of discrete PH-phases (NAPL) due to compensation of PH-degradation by resolubilisation from the NAPL.

Thus, the objective of the present study is to determine the practicability of interpreting acceptor sided stable isotopic shifts ($\delta^{15}\text{N}$ in nitrate and $\delta^{34}\text{S}$ in sulfate) as process parameter for the monitoring of PH-degradation in contaminated aquifers. Long-term anaerobic degradation experiments were carried out in laboratory scale anaerobic microcosms supplemented with PH-contaminated sandy aquifer and different concentrations of TEA. TEA-concentrations were monitored via ion chromatography (IC), total petroleum hydrocarbons (TPH) were analysed via gas chromatography with flame ionisation detector (GC-FID) and isotopic ratios were analysed via elemental analyzer and mass spectrometer (EA-IRMS). Statistical correlation between TPH-degradation and the shift of acceptor sided stable isotope ratios was analysed via linear regression analysis.

TEA-depletion and TPH-degradation was observed under all electron accepting conditions. All microcosms showed shifts in $^{14}\text{N}/^{15}\text{N}$ isotope ratios, while no significant $^{32}\text{S}/^{34}\text{S}$ isotope fractionation was observed. Good linear correlations between $\delta^{15}\text{N}$ -shifts in the residual TEA-fraction and the corresponding decline in TPH-concentrations with R^2 -values of at least 0.85 were found. Isotope enrichment factors (ϵ) derived from changes in isotopic ratios were dissimilar under different electron accepting conditions.

These results indicate that the monitoring of acceptor sided stable isotope ratios enables for quantitative and qualitative insight on the degradation progress. Further experiments and field observations are necessary for the calibration of this technique as an efficient monitoring approach.

Acknowledgements: Financial support for the project IsoMon by the European Regional Development Fund (EFRE) together with the Government of Lower Austria, contract No. WST3-T381/029/2011, is greatly appreciated.

Keywords: petroleum hydrocarbons, in situ bioremediation, terminal electron acceptors, stable isotope ratios, monitoring technique

27 Poster Presentation

PROVENANCING OF STRAWBERRIES USING SR ISOTOPES AND MULTIELEMENT PATTERN: INVESTIGATION OF ELEMENTAL SOURCES IN THE BIOAVAILABLE FRACTION OF SOILS

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The investigation of local - specific elemental and $^{87}\text{Sr}/^{86}\text{Sr}$ - isotopic fingerprints is a powerful tool for the determination of provenance of food. It is known that the fingerprint of the bioavailable fraction in soils is well reflected in the plant and consequently in the fruit. Nonetheless, a major concern is the influence of potential additional sources of strontium and other elements, such as fertilizers, rain water or irrigation. In case of Sr, liming was suspected to add a major contribution. Lime is used in conventional agriculture as a buffer substance to ensure optimal pH conditions for the growth of plants and is usually rich in Sr ($25 \mu\text{g g}^{-1}$). Therefore, it is of importance to know the impact on the elemental and Sr isotopic composition. As a consequence, the fingerprints of strawberry plants and strawberry fruits grown in limed and non-limed soil were determined, using ICP - QMS and multicollector ICP - MS. Additional influence parameters, such as the irrigation water and rain water, were taken into account, as well.

Small strawberry plants were purchased and planted on two patches with soil from Waldhausen (Waldviertel, Lower Austria) which exhibits a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71663 ± 0.00018 (U (k=2)). After a growth period of about four months, plants and strawberries were harvested. Sample preparation and analysis followed established protocols.

Although the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of the lime (0.70808 ± 0.00032 , U (k=2)), the irrigation water (0.71002 ± 0.00014 U (k=2)) and the rain water (0.71001 ± 0.00014 , U (k=2)) were significantly lower than the isotope ratio of the soil, the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of the plants (0.71331 ± 0.00014 , U (k=2)) and the strawberries (0.71363 ± 0.00014 , U (k=2)) showed a clear pattern: Plant and fruit Sr isotope ratios were shifted from the original signature at purchase towards that of the soil. Further, differences of the elemental pattern between limed and non-limed soil were insignificant.

According to these results, no significant influence of lime, irrigation water and rain water to the elemental and Sr isotopic fingerprint was observed. These results confirm that the elemental and isotopic information in the bioavailable fraction in soils is not altered by the investigated agricultural practices under the present conditions.

28 Poster Presentation

HUMAN MOBILITY ALONG THE NILE: PRELIMINARY STRONTIUM ISOTOPE ANALYSES FOR MIGRATION STUDIES IN ANCIENT NUBIA

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The “Across ancient borders and cultures”-project (FWF START Y615-G19) focuses on the establishment of a settlement on Sai Island (Nile) in Upper Nubia (modern Sudan) as a part of the southwards directed Egyptian expansion in the New Kingdom (c. 1539-1077 BC). In the course of the investigations, new insights on the life style, the living conditions and especially the coexistence and merging of cultures in the 2nd Millennium BC of Egypt and Nubia are expected [1].

During the last decades, strontium (Sr) isotopic analyses in human and animal skeletal remains as indicator of the locally specific fingerprint taken up from the environment via diet has evolved into a key tool in anthropology and archaeology for tracing residential changes and living conditions of ancient humans. Beside the Egyptian ‘colonialist’ (allochthonous), Nubian indigenes (autochthonous) were probably part of the ancient population of the Egyptian settlement on Sai Island. Therefore, Sr isotopic analysis in tooth enamel of individuals buried on Sai island will be performed and compared to Sr isotopic signatures assessed in the local proximity (via the establishment of so-called ‘isoscapes’).

The preliminary analytical work covered the multi-element and $^{87}\text{S}/^{86}\text{Sr}$ isotopic analyses of soil extracts (bioavailable Sr fraction), water, as well as recent and ancient animal tooth samples (hot-plate assisted acid digests) from the northern part of Sai Island. Multi-element analyses were performed with an ICP-QMS and the Sr isotope ratio were measured on a multi collector ICP-MS using standard procedures [2].

The Sr isotope ratio of the environmental samples from Sai Island showed a narrow range from 0.70660 to 0.70808. Herein, the paleo-sediments showed a higher Sr isotope ratio than the younger Nile silts and alluvial deposits. The Sr isotope ratio in enamel and dentin of the recent animal samples lay in the range of the younger sediments and that of the ancient animal samples overlapped with the excavation site. The isotopic map (isoscapes) of Sai Island will be used as basis for the further interpretation of autochtony or allochtony of the skeletal remains of excavated individuals.

An abstract with a similar content was submitted for DocDay Conference 2015, Tulln, Austria.

<http://acrossborders.oeaw.ac.at/about/about-acrossborders>.

J. Irrgeher, T. Prohaska, R. E. Sturgeon, Z. Mester and L. Yang, *Anal. Methods*, 2013, **5**, 1687.

29 Poster Presentation

STABLE ISOTOPE STUDIES (C, O, H) OF ACTIVE STALAGMITES & DRIP WATER IN KATERLOCH CAVE (AUSTRIA)

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Speleothems (secondary cave carbonates) are increasingly used in paleoenvironmental research based on their capability to archive climate information, their wide (global) distribution in karst areas, high preservation potential underground and precise age control based on uranium-series dating. Katerloch Cave located north of Graz (SE-rim of the Alps) is well known for its overwhelming speleothem decoration, e.g. up to several metres tall candle-stick-type stalagmites. In a current project we study modern (active) sites of stalagmite formation in Katerloch focusing on the site-specific growth dynamics and the connection of modern environmental conditions with petrographic, chemical and stable isotopic information captured in the speleothems. We recovered two actively growing stalagmites both of them comprising modern and past calcite deposition. In addition, fresh calcite precipitates on glass substrates underneath active drip sites were collected continuously from 2006 to 2014 (eight years!) in combination with cave monitoring (and meteorological data). The samples represent different cave sections of significantly different temperature and drip sites of partially different characteristics (e.g. drip rate).

Stable isotope profiles micromilled at 0.25 mm resolution from the upper (youngest) 20 cm of stalagmite K10 show $\delta^{13}\text{C}$ values ranging from -9.3 to -4.6 ‰ (VPDB) and $\delta^{18}\text{O}$ from -8.0 to -5.1 ‰. ^{238}U - ^{234}U - ^{230}Th measurements using MC-ICP-MS constrain the age of this youngest growth segment to the last ca. 6500 years next to supporting most recent precipitation. The entire stalagmite K10 (71 cm), however, comprises several distinct growth intervals starting from 129.1 \pm 1.2 kyr before present (Last Interglacial) up to now, mostly reflecting relatively warm and humid climate intervals and being separated by distinct growth interruptions. Consequently, the highly-resolved isotopic compositions in the youngest portion of K10 can be compared to older time intervals in the stalagmite and in relation to isotope data from other Katerloch stalagmites of different age and cave section. High-resolution (100 μm) isotope profiles micromilled from the multi-annual modern calcite precipitates on artificial substrates revealed low $\delta^{13}\text{C}$ values of -12.8 to -8.3 ‰ (VPDB) and relatively high $\delta^{18}\text{O}$ of -6.9 to -4.9 ‰. Interestingly, the $\delta^{18}\text{O}$ curves from all collection sites (of different modern calcite thickness) record a pronounced decrease during their most recent growth period most likely corresponding to a significant decrease towards lower O-isotope values observed in drip waters collected in the year 2014 compared with samples from 2005 to 2007. In general, the drip water $\delta^2\text{H}/\delta^{18}\text{O}$ values plot between the Western Mediterranean Meteoric Water Line and Global MWL indicating a significant influence of Mediterranean moisture sources to regional precipitation. The prominent shifts could be explained by significant changes in seasonality of precipitation and water infiltration.

30 Poster Presentation

SYNERGISTIC DEGRADATION OF CHLORINATED HYDROCARBONS WITH MICROORGANISMS AND ZERO VALENT IRON

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About one third of the expected 2000 severely contaminated sites in Austria are estimated to be polluted by chlorinated hydrocarbons (CHC). These sites are located mainly within build-up regions. Therefore in most cases only in-situ remediation methods can be used. This project examines a new in-situ remediation method, in which the biotic degradation via bacteria is combined with abiotic degradation via zero-valent iron particles. During chemical treatment by Fe⁰ the CHC-molecule is reductively dechlorinated. However Fe⁰ is also consumed by reaction with water leading to generation of H₂ without any CHC degradation. To achieve biotic degradation often strictly anaerobic strains of the bacteria *Dehalococcoides* are used. These bacteria can dechlorinate CHC by utilizing H₂. By combining these processes the H₂, produced during the anaerobic corrosion of Fe⁰, could be used by bacteria for further CHC degradation. Therefore the amount of used Fe⁰ and as a consequence also remediation costs could be reduced. Additionally the continuous supply of H₂ could make the bacterial degradation more controllable.

Different Fe⁰ particles (nano- and micro-scale) were tested for their perchloroethene (PCE) degradation rate and H₂ production rate in microcosms. PCE-degradation rate by bacterial cultures was investigated in the same microcosm system. In course of these experiments the ¹³C enrichment factors of the degradation of the different particles and cultures were determined to be able to differentiate between these degradation mechanisms.

Preliminary results showed, that the nano-scale particles reacted faster with PCE and water than their micro-scaled counterparts. The PCE degradation via micro-scaled particles lead to ¹³C enrichment factors in the range of -3,6 ‰ ± 0,6 to -9,5 ‰ ± 0,2. With one of the examined bacterial cultures a fast reduction of PCE to ethene was observed. Although PCE and TCE were completely degraded the metabolites DCE and VC could still be detected. Due to a fast PCE removal the ¹³C enrichment factors could not be examined yet.

In the future further microcosm experiments with the bacterial culture and the different ZVI particles are planned. Also the influence of existing substrate, possible toxicity of the particles, bacterial competition for the produced H₂ and the variation of different parameters (e.g.: C-source, temperature, nutrients) will be examined. The fate of H₂ in water and of carbon in CHCs will be traced by spiking with stable isotopes (D₂O, ¹³C-labeled CHC) and phospholipid fatty acid (PLFA) analysis. In addition a column and a lysimeter experiment will be conducted under conditions closer to the field situation.

31 Poster Presentation

ELEMENTAL AND $^{87}\text{Sr}/^{86}\text{Sr}$ ISOTOPE PATTERN AS A TOOL FOR PROVENANCING STURGEON CAVIAR

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Sturgeon caviar is one of the most expensive food commodities in the world. While farming of sturgeons for caviar production is emerging, there is a decrease in the natural populations due to illegal fishing. As a consequence, sturgeon caviar trade has been put under international regulations. However, unambiguous origin determination is still a basic necessity: Sound analytical methods are required to discriminate farmed from wild caviar, in order to control illegal trade and to foster sustainable farming. Therefore in this pilot study, untreated caviar, processed caviar (i.e. salted), water, fish feed and salt from five sturgeon farms in Central Europe (one in Austria and four in Italy) were investigated for their elemental and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition using (multi collector) inductively coupled plasma mass spectrometry ((MC) ICP-MS). Sample preparation was performed according to optimized standard protocols.

The elemental pattern and the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio of water of a fish farm is reflecting the local water chemistry that is expected to be transferred into the caviar, as well. Therefore, the chemical information can be used as a finger mark for provenancing. Nonetheless, the potential effect of fish food on the chemical signature of caviar needed to be considered, as well as the effect of caviar processing (e.g. salting).

Firstly, fish farms from geologically different areas could be differentiated by the elemental and isotopic signature of the water. Moreover, the chemical fingerprint of these fish farms was different from the water signature of the natural living habitat of the sturgeon in the river Danube. Secondly, the information of the water could also be found in the caviar allowing for the distinction between caviar produced in the investigated fish farms from caviar of wild fish from the Danube. However, a shift in the elemental and isotopic composition by the fish feed and salt used in the fish farms was observed.

Further investigations will use mixing models to evaluate the contribution of different sources to the final isotopic and elemental pattern in sturgeon caviar. The fully validated analytical protocol for identifying the original $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio and elemental composition of raw and processed caviar has great potential to act as a new tool in caviar provenancing.

An abstract with a similar content was submitted for RAFA 2015, Prague, Czech Republic

32 Poster Presentation

DISCRIMINATING BETWEEN DIFFERENT ORIGIN OF AYOUS (TRIPLOCHITON SCLEROXYLON) FROM WEST- AND CENTRAL AFRICAN COUNTRIES

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Controlling the declared provenance of timber is an important topic in view of illegal logging. Globally 20-40% of logging is estimated to be illegal. A large international project regarding the investigation of origin of tropical timber from Western and Central Africa has just been completed. The aim of this project was to establish DNA- and isotope methods to differentiate between the origins and to feed the produced data into a database to serve as a base for the identification of true origin. This shall serve as a reference for questions of provenance control in the future and combat illegal logging of tropical timber. Here we report the investigations of stable isotope patterns of Ayous (*Triplochiton scleroxylon*). The measured samples came from five countries: Ivory Coast, Ghana, Cameroon, Congo and Democratic Republic of Congo (DRC). The first two countries mentioned are in Western Africa while the others are in Central Africa. *Triplochiton scleroxylon* is one of the major timber logged in this region and intense harvesting resulted in over-exploitation. The samples were measured for their isotopic ratio of the elements hydrogen, oxygen, carbon, nitrogen and sulphur by IRMS (Isotope Ratio Mass Spectrometry). Sr isotopes were measured by TIMS (Thermal Ionisation Mass Spectrometry). The results show a strong influence of geology and climate on the isotope signatures. Samples from DRC can be identified due to the climatic situation of the Congo Basin and the western African countries possess a pattern influenced by the Precambrian bedrock. The results furthermore document a significant influence of the type of investigated sample material (drill core taken with a drill, wood chips, tree bark, the latter two types harvested with a bush knife).

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USING STABLE ISOTOPE LABELLING AS A TOOL TO MONITOR THE BIOREMEDIATION OF TWO CONTAMINATED SOILS

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Mixed contaminations are a frequently occurring contamination type, and their remediation can be challenging due to their persistency in soil. For this reason it is essential to work with a method that gives an indication about the success of the chosen remediation technology.

Stable isotope labelling is used as a tool to monitor the remediation of contaminated soils. Phospholipid fatty acid analysis (PLFA) is coupled with stable isotope probing in order to gain information about the metabolically active microbial communities living in soil.

As part of the ISOMON project ("Isotope application for remediation, aftercare and monitoring of contaminated sites"), the aim of this study was to investigate the microbial communities involved in the degradation process of an organic contaminant (phenanthrene, PHE) in a mixed contaminated soil. In a batch incubation experiment, two soils - contaminated with heavy metals and polycyclic aromatic hydrocarbons (PAHs) - were applied with a ¹³C-phenanthrene label and incubated for several weeks. Both experimental soils had a loamy texture. Soil A was slightly alkaline, soil B slightly acidic.

The results of the incubation batch experiment showed the uptake of ¹³C into the microbial biomass; each soil showed a distinct incorporation rate, and different phenanthrene degraders were identified for each soil. The PHE-degrading soil microorganisms in experimental soil A (especially 16:1w7+6, 16:0, cy17:0) incorporated more ¹³C than the communities in soil B (14:0, 16:1w7+6, 16:0, 18:1w9c, 10Me18:0+12Me18:0). Soil amendment (mixture of biochar, gravel sludge and iron oxide) application did not foster microbial degradation of PHE in neither soil. Soil A showed a higher microbial biomass than soil B; during the time of incubation microbial biomass dropped in both soils. Additionally, the reduction of the total PAHs was assessed. In soil A, the total concentration of the 16 EPA PAHs decreased by 80% after 100 days of incubation.

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$\delta^{13}\text{C}$ -DIC OF MUNICIPAL WASTE LEACHATE IS AN INTEGRATIVE PARAMETER FOR CHARACTERISING THE BIOLOGICAL STABILITY OF LANDFILL BODIES

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Characterising the stability of organic substances in landfills is important for assessing the duration of landfill aftercare or to determine the completion of an in-situ aeration of the waste body. At present many expensive and time consuming methods (solid sampling, gas measurements, chemical analysis of leachate) have to be combined to assess the current and future risk of emissions from a landfill. From previous investigations it is known that the prevailing condition (e.g. methanogenic phase, aerobic conditions) in the landfill influences the carbon isotope signature of the dissolved inorganic carbon ($\delta^{13}\text{C}$ -DIC) in the leachate. The aim of our investigations is therefore to develop a meaningful method to characterise the biological stability of the organic material in the waste body based only on the determination of $\delta^{13}\text{C}$ -DIC in the leachate.

In the laboratory landfill simulation reactors (LSR) filled with municipal solid waste (MSW) of different waste composition and reactivity were percolated under aerobic and anaerobic conditions. Leachates were monitored continuously for $\delta^{13}\text{C}$ -DIC and their chemical composition. Before and after the percolation the reactivity of the MSW was determined using conventional methods (TOC, Nt) as well as biological methods like gas generation potential and respiration activity. In addition we periodically collected the seepage water of several old landfills and analysed them for $\delta^{13}\text{C}$ -DIC and their chemical composition. One of the landfills was monitored during the whole process of an in-situ aeration.

The differences between $\delta^{13}\text{C}$ -DIC of the LSR leachates between aerobic and anaerobic treatments were highly correlated with the reactivity of the MSW. More reactive materials were showing higher positive $\delta^{13}\text{C}$ -DIC values ($> +5\%$) for the anaerobic and more negative values ($< -20\%$) for the aerobic treatment compared to less reactive materials. After switching the LSR from the initially anaerobic to aerated conditions the drop of the $\delta^{13}\text{C}$ -DIC to more negative values was considerably faster than the observed shift of the chemical composition (e.g. the decrease in ammonium) of leachates. This high sensitivity of the $\delta^{13}\text{C}$ -DIC signal to the oxidation-reduction status of MSW might also explain some discrepancies in the isotopic signatures and chemical composition of the landfill leachates. An old landfill showing low ammonium loads in the seepage water but still producing methane was characterised by high $\delta^{13}\text{C}$ -DIC values (+5 to +10%) while the natural occurring transformation to aerobic conditions in other landfills and the technical in-situ aeration caused a significant drop of $\delta^{13}\text{C}$ -DIC to less than -10% although the ammonium concentrations in the leachates were still high.

Our results indicate that monitoring of $\delta^{13}\text{C}$ -DIC of landfill leachates over a longer time period (e.g. during in-situ aeration) is a powerful and cost-effective tool for characterizing the oxidation/reduction status of landfilled municipal solid waste and is therefore an excellent tool for monitoring the progress of an in-situ aeration.

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INTEGRATED STABLE ISOTOPE CYCLOSTRATIGRAPHY OF THE CAMPANIAN STAGE (UPPER CRETACEOUS)

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The Upper Cretaceous Postalm section near Abtenau in the Northern Calcareous Alps was examined for stable isotopes, biostratigraphy, and palaeoenvironmental analyses. We use variations in stable carbon isotopes to link this section to a global reference curve. Stable isotope stratigraphy is, in combination with biostratigraphic and magnetostratigraphic constraints, a valuable tool for the correlation of sections and to give estimates on the duration of events in Earth history. At Postalm an almost complete continuous late Santonian to Maastrichtian succession (~10Ma) is exposed. The deposits indicate a pelagic to hemipelagic palaeoenvironment and can be classified as a Cretaceous Oceanic Red Bed (CORB). Furthermore, cyclic marly limestone-marl alternations show strong evidence for Milankovitch cyclicity (presumably precession cycles), and are thus particularly relevant for a cyclostratigraphic examination of this section aiming at establishing a floating timescale for the Tethyan Campanian stage. Over 400 samples from the late Santonian (*D. asymetrica* Zone) to the late Campanian (*G. gansseri* Zone) were examined for stable isotopes. Several distinct events recorded in the composite carbon isotope record of Cretaceous deposits can be recognized at the Postalm section. An increase in carbon isotope values around the Santonian-Campanian boundary can be correlated to the Santonian/Campanian boundary event (SCBE). Furthermore we can identify the Base Upper Campanian Event (BUCE), the Base Calcarata Event (BCE) as well as the Late Campanian Event (LCE) at Postalm section. Stable carbon as well as oxygen isotope signature curves show a cyclic pattern. Spectral analysis techniques reveal a strong signal for the 100 and the 405 ka eccentricity cycles.

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