The 15\textsuperscript{th} meeting of the Stable Isotope Mass Spectrometry Users Group

26\textsuperscript{th}-28\textsuperscript{th} June 2019

Organic Geochemistry Unit, School of Chemistry, University of Bristol
SIMSUG2019 is supported by
PROGRAMME

Thursday 27th June

8:00-8:30 Registration – School of Chemistry, Staff and Postgraduate Lounge
8:30-8:40 Welcome and housekeeping – Ian Bull

Lecture Theatre 3
8:40-8:55 Oral slot 1 – Whale I never! Biosynthesis of ambrein by the Sperm whale and other animals
Rowland, S.J., Sutton, P.A. and Wolff, G.

Lecture Theatre 3
8:55-9:10 Oral slot 2 – Collision course: Accurate and precise measurements of stable and radiogenic Ca isotopes using collision cell MC-ICPMS
Lewis, J., Luo, T., Coath, C.D., Wehrs, H., Elliott, T. and Schwieters, J.B.

Lecture Theatre 3
9:10-9:25 Oral slot 3 – Multi-trophic role of the sponge Hyrtios erecta revealed by different bio-tracers

Lecture Theatre 3
9:25-9:50 Oral slot 4 – Using stable-isotope probing to investigate biotic uptake of organic nitrogen in a riverine system

Lecture Theatre 3
9:50-10:05 Oral slot 5 – Seals as indicators of spatial variability in Arctic food webs
de la Vega, C., Mahaffey, C., Yurkowski, D.J., Ferguson, S.H., Stenson, G., Haug, T., Bluw, M. and Jeffreys, R.M.

Lecture Theatre 3
10:05-10:20 Poster Introductions – Posters 1-8
10:20-10:50 Tea break & posters/exhibitors – School of Chemistry, Staff and Postgraduate Lounge

Lecture Theatre 3
10:50-11:05 Oral slot 6 – Oxygen triple-isotope ratio measurements of silicate rocks and minerals – applications and standardisation
Miller, M.F., Pack, A. and Greenwood, R.C.

Lecture Theatre 3
11:05-11:20 Oral slot 7 – Plant, animal and microbial nitrogen use efficiencies in a grassland ecosystem using 15N-stable isotope probing approaches
Reay, M.K., Marsden, K.A., Powell, S., Jones, D.L. and Evershed, R.P.

Lecture Theatre 3
11:20-11:35 Oral slot 8 – Stable carbon and nitrogen isotope ratios of bell pepper samples in correlation with greenhouse cultivation practices
Kruäš, S. and Vetter, W.

Lecture Theatre 3
11:35-11:50 Oral slot 9 – The Age of the Saharan Desert and C4 grassland expansion on Africa
Crocker, A.J., B. Naafs, B.D.A. Thomas Westerhold, T., James, R.H., Cooper, M.J., Ursula Röhl, Pancost, R.D., Osborne, C.P., Beerling, D.J. and Wilson, P.A.

Lecture Theatre 3
11:50-12:05 Oral slot 10 – Diet-provenance and mobility on the Maltese islands
Naflioti, A. and Rowan McLaughlin, T.

12:05-13:00 Buffet lunch & posters/exhibitors – School of Chemistry, Staff and Postgraduate Lounge

Lecture Theatre 3
13:00-13:15 Oral slot 11 – The Sercon CryoGas: for automated, high precision δ2H and δ13C analysis of gaseous and dissolved methane
Smith, A.C., Welsh, S., Atkinson, H. and Leng, M.

Lecture Theatre 3
Dunn, P.J.H., Malinovskiy, D., Cowen, S. and Goenaga-Infante, H.

Lecture Theatre 3
13:30-13:45 Oral slot 13 – EA-IRMS: Getting more by using less thanks to front-end sensitivity
Brodie, C., Kracht, O. and Hilker, A.

Lecture Theatre 3
13:45-14:00 Oral slot 14 – Introducing Analytical Results Database (ArDB): Intuitive Database Management, Data Visualisation and Quality Control
Taylor, K.W.R., Seed, M. and Sudnik, M.

Lecture Theatre 3
14:00-14:15 Oral slot 15 – Using Cavity Ring-Down Spectroscopy (CRDS) to measure stable isotopes: overview and recent developments
Peters, R.

14:15-14:30 Poster Introductions – Posters 9-16
14:30-15:00 Coffee break & posters/exhibitors – School of Chemistry, Staff and Postgraduate Lounge
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| 15:00-16:00  | **Plenary Lecture** – Advances in the analysis and interpretation of the oxygen isotope composition of diatom silica  
*Leng, M.J and Lacey, J.H.* |
| 16:00-16:15  | Group photograph – Outside Staff and Postgraduate Lounge                                  |
| 16:15-17:45  | Posters/exhibitors and mixer – School of Chemistry, Staff and Postgraduate Lounge         |
| 18:30-19:30  | Complimentary access to Bristol Zoological Gardens – Entrance via the Pavilion            |
| 19:30 onwards| Conference meal – The Pavilion, Bristol Zoological Gardens                               |

**Friday 28th June**

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<tr>
<td>9:00-9:10</td>
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<td>9:10-9:25</td>
<td><strong>Lecture Theatre 3</strong> CHAIR: Jens Holtvoeth</td>
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| 9:25-9:40    | Oral slot 16 – Investigation of microbial activity using clumped isotope thermometry along carbonate vein in granite host rock  
*Herlambang, A.* |
| 9:40-9:55    | Oral slot 17 – GC-IRMS measurements of $^{15}$N in amino acids to unravel ancient diets of humans and cave bears  
*Tung, P., Naito, Y., Drucker, D., Wijffling, C. and Bocherens, H.* |
| 9:55-10:10   | Oral slot 18 – Application of organic residue analysis and GC-C-IRMS techniques to decipher subsistence strategies employed at hillfort assemblages in the early Piast dynasty  
*Brown, S.F., Evershed, R.P., Tabaka, A., Krysztofiak, T., Miciak, M. and Klimowicz, P.* |
| 10:10-10:25  | Oral slot 20 – Metabolism of orally administered medium-chain triglyceride                   
*van Harskamp, D., Knotterus, S., Bleeker, J., van Goudoever, J., Wanders, R., Wijburg, F., Visser, G. and Schierbeek, H.* |
*Adlon, Q., Davies, A.J. and John, C.M.* |
| 10:40-11:10  | Tea break & posters/exhibitors – School of Chemistry, Staff and Postgraduate Lounge         |
| 11:10-11:25  | **Lecture Theatre 3** CHAIR: Julie Dunne                                                 |
| 11:25-11:40  | Oral slot 23 – Isotopic analysis of groundwater ecosystem response to climatic and anthropogenic change  
*Saccò, M.; Blyth, A.J.; Humphreys, W.F.; Kuhl, A.; Mazumder, D.; Meredith, K.; Hua, Q.; Smith, C. and Grice, K.* |
| 11:40-11:55  | Oral slot 24 – Functional response of an Austrian forest soil to experimental N deposition  
| 11:55-12:10  | Oral slot 25 – Open natural microcosm study Ecosystem function in the tropical rainforest canopy  
*Donald, J.D., Ellwood, M.D.F. and Maxfield, P.J.* |
*Casanova, E., Lefranc, P., Denaire, A., Arbogast, R-M., Jeunesse, C. and Evershed, R.P.* |
| 12:25-12:40  | Oral slot 27 – $^{13}$C values of bacterial hopanoids and leaf waxes as tracers for methanotrophy in peatlands  
*Inglis, G., Naafs, B.D.A.; Zheng, Y.; Schellekens, I. and Pancost, R.D.* |
| 12:40-13:00  | Closing remarks, prize-giving and decision on SIMSUG 2021 venue                          |
| 13:00-14:30  | Buffet lunch – School of Chemistry, Staff and Postgraduate Lounge                          |
School of Chemistry, University of Bristol, Cantock’s Close, BS8 1TS
Ice breaker 26/06/2019
Zerodegrees, Colston Street, BS1 5BA
Conference meal 27/06/2019
The Clifton Pavilion, Bristol Zoo Gardens, College Road, BS8 3HH (29 min walk)
ADDITIONAL INFORMATION

Schedule
The main academic conference will take place on Thursday 27th and Friday 28th. On the evening of Wednesday 26th there will be an informal ice breaker starting from 18:00 at Zerodegrees (see map). The venue is a microbrewery-restaurant (see https://www.zerodegrees.co.uk/restaurants/bristol/) so caters for both food and drink.

Prior to this there will, by arrangement, be an opportunity to tour our laboratories and facilities. If you would like to take part in the tour then please email Diane Foster (d.foster@bristol.ac.uk) who will provide you with further details.

After the posters/exhibitors and mixer session on Thursday 27th, delegates attending the conference meal will need to make their own way to Bristol Zoo Gardens (see map). We have allowed 45 minutes for people wishing to walk to the venue but buses (First Bus – no. 8) and taxis are all available close by. Please note that the entrance to the venue is through the Pavilion on College Road and NOT through the main entrance to the zoo. Limited parking is available opposite the College Road entrance. Prior to the meal, you will have complimentary access to the gardens until 19:30 when the zoo closes and the conference dinner begins.

Registration
Registration will take place from 08:00 onwards, Thursday 27th, and shall be in the level 3 staff and postgraduate lounge (just follow the signs from the School of Chemistry reception). There may be other conferences taking place in the School so please ensure that you don’t try to register with a completely different meeting!

Presentations
Poster boards are in the level 3 staff and postgraduate lounge along with the exhibitor stands; this is also where tea/coffee and lunches will be served. Ensure that posters are only displayed using the magnets provided, please do not use adhesive materials to mount them. Each delegate will be given the opportunity to introduce their poster between the main conference sessions on Thursday 27th. Introductions should be no longer than 1 minute in length and may be accompanied with a single slide.

Delegates giving oral presentations should ensure that their talk is loaded onto the lecture theatre computer BEFORE the session in which you are speaking, ideally as early as possible. Please make time to introduce yourself to your session chair, let them know of any special requirements that you may have and understand how they are running the session. Oral presentations, inclusive of any questions, are limited to 15 minutes in length. Please help your session chair by ensuring that your talk does not run longer.

There will be prizes (first and runner-up) for the best oral and poster student presentations. In addition, there will be a ‘People’s Vote’ prize, open to ALL oral and poster presenters.

Photograph
Weather permitting, there will be a SIMSUG 2019 photograph which will be taken on the patio outside of the level 3 staff and postgraduate lounge.

Abstracts
* denotes that the presentation is being given by a student.
ORAL PRESENTATIONS
Until very recently, the tricyclic triterpenoid alcohol, ambrein, which has long been important in perfumery, was known only in coproliths occurring in, or originating from, the Sperm whale, *Physeter microcephalus*. In *vitro*, ambrein can be produced by the action of bacterial enzymes on squalene, which is also the universal progenitor of the sterols. However, nothing is known of the *in vivo* biosynthesis of ambrein, either in the whale, or as has recently become apparent, in other mammals. In the present study we investigated the hypothesis that ambrein might be statistically isotopically ($^{13}$C/$^{12}$C) different in composition from the co-occurring sterols in whale coproliths. We determined using isotopic ratio monitoring gas chromatography-mass spectrometry (irm-GC-MS) the isotopic values of ambrein and epicoprostanol in about 30 coproliths, some taken directly from Sperm whales, others from beached jetsam. We report the results. We also investigated whether there was any evidence of possible biosynthetic intermediates in the pathway between squalene and ambrein. Some were identified in coprolith extracts by GC-MS, using synthesised compounds for identification. The results of this study thus shed new light onto the biosynthesis of an important and valuable industrial chemical, ambrein.
Collision course: Accurate and precise measurements of stable and radiogenic Ca isotopes using collision cell MC-ICPMS


*Bristol Isotope Group, University of Bristol, Bristol, UK
ThermoFisher Scientific (Bremen) GmbH, Bremen, Germany

Ca isotopes have a wide range of applications across the field of geochemistry. Measurements of radiogenic $^{40}$Ca excesses form the basis of K-Ca geochronology, whilst mass independent nucleosynthetic anomalies in the neutron-rich $^{48}$Ca nuclide provides evidence for unusual stellar contributions to our solar system. Measurements of mass dependent Ca isotope fractionation inform on a range of terrestrial processes from continental weathering cycles to igneous and metamorphic processes. In biological systems, Ca isotopes have been shown to be useful in assessing trophic level based on isotopic fractionation during mineralisation of calcified tissues. More recently there have been novel uses of Ca isotopes in the biomedical community to study body Ca homeostasis and the onset of disease. We report measurements of radiogenic and stable Ca isotopes using the prototype collision cell MC-ICPMS, Proteus. We add helium and hydrogen gases to the collision cell and utilise the resonant charge exchange between Ar$^+$ ions and H$_2$ molecules to almost completely remove the $^{40}$Ar$^+$ ion allowing the measurement of $^{40}$Ca isotope by MC-ICPMS without resorting to ‘cold’ plasma. We have characterised a range of reference materials for both their radiogenic and stable Ca isotope composition using Proteus. We find that radiogenic Ca ($^{40}$Ca/$^{44}$Ca) can be accurately measured with typical precisions better than 50 ppm (2SD). For mass dependent Ca isotope fractionations ($\delta^{44/40}$Ca), measurements using a double spike isotope tracer are accurate with respect to known values of reference materials with typical precisions of <0.05 ‰ (2SD).
Sponges are one of the most diverse marine animal phyla (Porifera), however, their trophic roles in coral-reef food-webs are scarcely looked at. In this study, we collected a non-cryptic high microbial abundance sponge *Hyrtios erecta* and both benthic and pelagic production sources in North Malé Atoll (the Maldives). As a mixotrophic species, the autotrophic role of *H. erecta* was analysed by comparing its bulk stable isotope data (δ\(^{13}\)C and δ\(^{15}\)N) with those of other primary producers; the results suggest that *H. erecta* might be utilising the same ultimate nutrient sources as the benthic macroalgae for photosynthesis or largely feeding on the DOM produced by these macroalgae. We also analysed its heterotrophic role by tracing its essential amino acid (EAA) intake using the carbon stable isotope values of five EAAs and found that *H. erecta* tended to feed on pelagic plankton as a source of EAAs. Our results confirm the multi-trophic role of *H. erecta* and the nutrient preferences of this sponge suggest that it might prefer DOM for metabolism and plankton for body building. Yet whether such a source utilisation pattern exists among other reef sponges (e.g. cryptic species more prominent on Indo-Pacific reefs) remains unclear. The findings point to the need of future research on the function of sponges in linking pelagic production sources to coral-reef food-webs.
Using stable-isotope probing to investigate biotic uptake of organic nitrogen in a riverine system

Lloyd, C.E.M.a, Johnes, P.J.b, Yates, C.b, Jones, D.L.c, Maberly, S.C.d, Mackay, E.4, Glanville, H.e, Brailsford, F.4 and Evershed, R.P.a

aSchool of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK
bSchool of Geographical Sciences, University of Bristol, University Road, Bristol BS8 1SS, UK
cSchool of Environment, Natural Resources and Geography, Deiniol Road, Bangor, Gwynedd, LL57 2UW, UK
dLake Ecosystems Group, CEH, Lancaster Environment Centre, Library Avenue, Bailrigg, Lancaster LA1 4AP UK
eSchool of Geography, Geology and the Environment, William Smith Building, Keele University, Keele, Staffordshire, ST5 5BG, UK

The flux of nitrogen (N) into rivers is rising due largely to inputs from the expansion and intensification of agriculture along with inputs from treatment of human waste. This trend is set to continue due to changing climate and increasing population, meaning extra pressure is being exerted on ecosystems while we attempt to balance food security and environmental impact. Research has shown that while water quality legislation focuses on inorganic nutrients due to their bioavailability, the proportion of the total river N flux, which is organic in its molecular composition is significant. Despite this, the impact of organic N on ecosystem function is currently poorly understood. We address part of this knowledge gap by investigating the extent to which organic N substrates are bioavailable to biota and if they can be directly assimilated. The use of $^{15}$N stable-isotope probing can provide insights into the routes of biotic uptake of organic N. Specifically, this work identifies and quantifies the uptake of $^{15}$N-labelled glutamate into epilithon and moss communities. An 8-day stream dosing experiment was carried out in a small headwater stream in the Conwy catchment, North Wales. Labelled substrate was added to the stream at 0.5 mL/min to produce an expected $^{15}$N enrichment of ~500‰. Samples of water, epilithon and moss were taken from the stream at over a 192 h period after the dosing commenced and the enrichment of the samples quantified, using bulk and compound-specific analysis of extracted amino acids. This method allowed us to directly demonstrate the assimilation of $^{15}$N-labelled organic substrates into newly biosynthesised proteinaceous amino acids. This experiment provides significant new insights into the biotic assimilation of organic-N substrates.
Seals as indicators of spatial variability in Arctic food webs

de la Vega, C.\textsuperscript{a}, Mahaffey, C.\textsuperscript{a}, Yurkowski, D.J.\textsuperscript{b}, Ferguson, S.H.\textsuperscript{b}, Stenson, G.\textsuperscript{c}, Haug, T.\textsuperscript{d}, Biuw, M.\textsuperscript{d} and Jeffreys, R.M.\textsuperscript{a}

\textsuperscript{a}School of Environmental Sciences, University of Liverpool, UK
\textsuperscript{b}Department of Biological Sciences, University of Manitoba, Canada
\textsuperscript{c}Fisheries and Oceans Canada, Newfoundland, Canada
\textsuperscript{d}Institute of Marine Research, Tromsø, Norway

Understanding the ecological role of key indicator species in the structuring and functioning of Arctic food webs is crucial for improving management plans for conservation. Ringed (\textit{Phoca hispida}) and Harp (\textit{Phoca groenlandica}) seals, both reliant on sea ice, are excellent indicator species for assessing spatial variation in Arctic food web structure. $\delta^{15}$N of bulk tissue is commonly used to estimate food web structure but is strongly influenced by $\delta^{15}$N at the base of food web or baseline. Compound-specific stable isotope analyses of amino acids ($\delta^{15}$N\textsubscript{AA}) allow for robust determination of $\delta^{15}$N at the base of food web via phenylalanine ($\delta^{15}$N\textsubscript{Phe}), whilst simultaneously fingerprinting trophic structure in a food web via metabolic amino acids e.g. glutamic acid ($\delta^{15}$N\textsubscript{trophic}). We analysed $\delta^{15}$N\textsubscript{AA} in muscle of harp and ringed from European and Canadian Arctic to assess spatial variation at the base of food web and food web structure across the Arctic Ocean. We also measured $\delta^{15}$N of dissolved nitrate ($\delta^{15}$N\textsubscript{NO$_3$}). $\delta^{15}$N and $\delta^{15}$N\textsubscript{Phe} in Arctic seals varied between Arctic regions. There was a high correlation between $\delta^{15}$N and $\delta^{15}$N\textsubscript{Phe} and $\delta^{15}$N\textsubscript{Phe} and $\delta^{15}$N\textsubscript{NO$_3$}. Spatial variability in seal $\delta^{15}$N was triggered by spatial variability in the $\delta^{15}$N baseline. Differences were observed in $\delta^{15}$N\textsubscript{trophic} between ringed seals and harp seals reflecting differences in feeding strategy. Our results demonstrate the importance of accounting for spatial variability in the baseline when reconstructing food webs.
Accurate and precise measurements of the relative abundances of the three stable isotopes of oxygen can contribute to improved understanding of processes in Earth and atmospheric sciences, as well as in cosmochemistry. Recent diverse applications will be mentioned. Isotopic variations usually follow so-called ‘mass-dependent’ fractionation, with the relative variations in isotopic ratios being proportional to the difference in mass of the isotopes involved. In detail, however, there are subtleties which result in different natural processes defining distinct slopes in three-isotope diagrams. Improvements in analytical capabilities now allow precise measurement of these effects and make it possible to draw inferences about the processes that caused them (e.g. reaction kinetics versus equilibrium isotope exchange). With high precision measurements, a major challenge is to accurately calibrate the experimental data relative to reference materials such as VSMOW and to ensure that an assigned reference line is not (unintentionally) offset on the three-isotope diagram. For measurements on silicate rocks and minerals, the use of a water reference (VSMOW) presents technical challenges. We discuss a novel alternative to the usual calibration procedure and report the results of an inter-laboratory measurements comparison to assess this approach.
Grazed grasslands cover 40% of UK land and are an essential source of food however are also an important source of freshwater pollution due to loss of applied nitrogen (N) fertilisers. The N use efficiency (NUE) of grazed grasslands must be improved to reduce negative environmental impacts and improve food security. To fully evaluate NUE, the grazing system must be evaluated as a whole, which can be achieved using $^{15}$N-stable isotope probing (SIP). The fate of $^{15}$N-fertiliser in a grassland ecosystem was determined using a combination of field-feeding and lysimeter time course experiments and bulk and compound-specific $^{15}$N-SIP approaches. The plant NUE of applied $^{15}$N-fertiliser was 58.6±6.1% in a field setting, with a microbial NUE of 16.4±1.0%, determined using compound-specific $^{15}$N-isotope analyses of newly synthesised microbial amino acids. $^{15}$N-labelled grass was subsequently fed to sheep, and animal NUE determined to be 18.1±4.5%, with 19.5±0.8% and 21.0±5.2% excreted as urine and faces, respectively. Animal excreta is a major source of pollution from agriculture, particularly urine due to high N loading equivalent to 950 kg N ha$^{-1}$. A lysimeter study traced the fate of $^{15}$N-fertiliser excreted in urine, with 7.1±1.6% of fertiliser-derived $^{15}$N lost via leaching, alongside 1.7±0.7% as gaseous losses. Plant uptake and microbial assimilation increased in importance with time, accounting for up to 7.3±1.6% and 5.5±1.6% of $^{15}$N-fertiliser applied after 94 days, respectively. Combining the series of $^{15}$N-tracer studies with bulk and compound-specific $^{15}$N determinations provided a detailed mass balance for the fate of $^{15}$N-fertiliser, accounting for plant and animal incorporation and the central role of the microbial community in mediating the fate of fertiliser and excreta N.
Stable carbon and nitrogen isotope ratios of bell pepper samples in correlation with greenhouse cultivation practices

Krauß, S. and Vetter, W.

University of Hohenheim, Institute of Food Chemistry (170 b), 70599 Stuttgart, Germany

Bell pepper is a highly valued vegetable for human consumption and is therefore one of the most cultivated crops in the world. It can be grown as annual or perennial plant either in the open field or covered in greenhouses. Cultivation in greenhouses allows the exact adjustment of climatic growing conditions. Hence, not only light intensity and duration but also temperature can be controlled by adequate heating and ventilation cycles. Additionally, it is common practice to elevate CO$_2$ levels in the atmosphere of a greenhouse to enhance the photosynthetic rate to its optimum. Stable isotope ratios of carbon ($\delta^{13}$C) and nitrogen ($\delta^{15}$N) of bell pepper fruits from three different European countries (GER, NL, ESP) were determined by stable isotope ratio mass spectrometry (IRMS). Samples from Germany could be clearly distinguished from samples from the Netherlands or Spain by both their $\delta^{13}$C and $\delta^{15}$N values (‰). Bell peppers from Germany were extremely depleted in $^{13}$C with $\delta^{13}$C values of up to -46‰. Thus, they lay far outside of the typical range of $\delta^{13}$C values (‰) of C$_3$-plants. The depletion in $^{13}$C was ascribed to the supplementation of the greenhouses with CO$_2$ as growth regulator. The extremely negative $\delta^{13}$C values (‰) indicated that the added CO$_2$ had been derived from the combustion of fossil fuels which often are used for heating in greenhouses. This CO$_2$ shows a significantly more negative $\delta^{13}$C value (‰) compared to atmospheric CO$_2$. Additional discrimination against $^{13}$C by the plant during CO$_2$ assimilation could lead to the observed extremely negative $\delta^{13}$C values (‰).
The Sahara is the largest hot desert on Earth and the source of about half of the world’s atmospheric dust. Northern Africa is widely suggested to have dried progressively with global cooling through the late Cenozoic, favouring both desert and C₄-savanna expansion. However, the timing and cause of Saharan desert inception are vigorously debated, as are the drivers of the spread of C₄ grasslands. We present a high-resolution reconstruction of the accumulation and geochemistry of dust exported from northern Africa over the past 11 Million years from ODP Site 659 (situated underneath the major summer Saharan dust plume today) coupled with a leaf wax carbon isotopic record. We document persistent expansion and contraction of Saharan dust flux in North Atlantic deep-sea sediments throughout the past 11 Myr, contradicting suggestions of a landmark birthdate for the Saharan Desert associated with either the intensification of northern hemisphere glaciation (~2.7 Myr ago) or deposition of aeolian dunes in the Djurab (~7 Myr ago). Our results challenge suggestions of a long-term monotonic escalation in northern African aridity, with long-term expansion of northern African C₄ savanna ecosystems paused for several million years ~6–3 Myr ago, closely related to an interval of increased precipitation during insolation maxima. Our findings have important implications for floral and faunal evolutionary outcomes on Africa, including those of our hominid ancestors.
Diet- provenance and mobility on the Maltese islands

Nafplioti, A. and McLaughlin, T.R.

aMcdonald Institute for Archaeological Research, University of Cambridge, UK
bSchool of Natural and Built Environment, Queen’s University Belfast, UK

This paper investigates diet, provenance, migration and residential mobility in relation to early settlers on the Maltese islands. Multi-isotope (carbon, nitrogen, oxygen and strontium) ratio analysis of the remains of the people themselves from the mortuary contexts at Xaghra and Xemxija, carried out for the first time in the Maltese islands by the FRAGSUS project, explore the above issues. Current evidence points to a purposive Neolithic colonization of the islands. Covering a total surface area of 316 km², it appears that the earliest period when the islands would have offered a viable landmass for human permanent occupation would have been the Neolithic with the onset of agriculture. These newcomers are generally considered to be the first settlers. In this context, carbon and nitrogen isotope ratio data presentation and discussion focuses on understanding what nourished the ancient residents of the Maltese islands, on interpreting evidence for dietary variation and on elucidating the relationship between the remarkable prehistoric cultures of these islands and the landscape upon which human life depended. Oxygen and strontium isotope ratio signatures of human teeth from the above two sites are assessed with a view to reconstructing geographical origins and tracking residential change for the people analysed, while specific hypotheses for contact and mobility within the Maltese islands and also between the latter and the rest of the Mediterranean are being addressed.
Atmospheric methane (CH\textsubscript{4}) is one of the most abundant and potent greenhouse gases. As concentrations in the atmosphere have more than doubled since pre-industrial times, understanding methane formation pathways and sources of emission is critical to informing effective mitigation and limiting the role of methane in future climate change. Alongside impacts within the atmosphere, high concentrations of dissolved methane in groundwater pose a significant risk to human health, therefore fingerprinting methane sources within groundwater is becoming a critical concern for operators and regulators alike. The dual isotope analysis, hydrogen ($\delta^{2}$H) and carbon ($\delta^{13}$C), of methane is a key tracer tool for understanding sources, mixing and evolution of both dissolved and atmospheric methane. However, traditional methods of analysing methane for $\delta^{2}$H and $\delta^{13}$C are time consuming; involving offline, manual extractions. This processing time can drastically reduce the number of analyses that can be undertaken, limiting the scope of long-term isotope monitoring. Here we describe a new gas chromatography, pyrolysis/combustion, IRMS system for the automated analysis of CH\textsubscript{4} down to atmospheric concentrations (1800ppb). The system achieves precision of <0.2‰ for $\delta^{13}$C and <2.5‰ for $\delta^{2}$H. Depending upon CH\textsubscript{4} concentration and therefore bottle size, the system runs between 16 and 200 unknowns in an unattended run overnight. This system currently represents the only commercially available IRMS system for dual isotope analysis of methane and a step forward for the routine analysis of CH\textsubscript{4} in environmental studies.
For many years, it has been recommended that stable isotope analysts prepare their own in-house reference materials (RMs) for daily use either for instrument calibration or for quality control. In this way, commercially available RMs that provide traceability for all isotopic analyses are preserved, ensuring that the international isotope delta scales are maintained for a longer period of time. Also, in-house RMs that matrix-match samples or extend the available calibration range beyond commercial RMs play a role in assuring quality control of existing methods. While some guidance is available over the nature of an in-house RM, such as stability, homogeneity, hydroscopicity and other chemical properties etc., as well as how to prepare in-house RMs; there is far less guidance available regarding the process of assigning a value and uncertainty to an isotopic in-house RM. There are some general guidelines available for commercial RM producers, including the requirements of accreditation to ISO/IEC 17034:2016, but these tend to have much stricter requirements than might be necessary for an in-house QC material. Building upon the NML’s experience as an accredited RM producer, we present some detailed guidance with regards to value assignment based upon an in-house RM for δ\textsuperscript{18}O\textsubscript{VSMOW} in coffee. This includes the need for comprehensive planning, measurement uncertainty estimation, and on-going monitoring of the in-house RM. The need to “break” the principle of identical treatment, for example when extending the available isotope delta calibration range, will also be discussed.
The Thermo Scientific™ EA IsoLink™ IRMS System has provided a fresh perspective in EA-IRMS by introducing temperature variable gas chromatography and variable gas flow rates during sample analysis. These innovative features open doors to lower detection limits through more efficient sample gas transfer to the ion source, especially for the analysis of nitrogen, carbon and sulphur concentrations less than 5 µg and on very high C/N and C/S ratio samples. For example, sequential NCS analysis is now feasible on 1.0 – 1.5 mg of bone collagen, on wood samples and for sulphur measurements directly from water. This presentation will elaborate on these data, showing precisions that are generally better than those widely accepted in the literature for sequential NCS analysis and for sulphur analysis.

This presentation will focus on the analysis of small concentrations of carbon, nitrogen and sulphur and illustrate with data, how the EA-IRMS utilises chromatographic principles to routinely increase the sensitivity on various NCS measurements. This will be further supplemented with new data that takes us into the so-called “nano-EA” territory.
Introducing Analytical Results Database (ArDB): Intuitive Database Management, Data Visualisation and Quality Control

Taylor, K.W.R., Seed, M. and Sudnik, M.

Elementar UK Ltd, Cheadle Hulme, United Kingdom

Analytical Results Database (ArDB) is an intuitive software tool developed by Elementar UK which has been created to extend the envelope of analytical data analysis beyond simple data processing. Ultimately, ArDB simplifies and centralises the management of data, a particularly critical issue when generating large quantities of data associated with high-resolution and/or high-throughput analysis.

ArDB allows users to simply construct or import, maintain and manage their databases of any analytical results, including (but not limited to) results from stable isotope, elemental, and total organic carbon analysis instruments. ArDB allows users to visualize their data with 2D & 3D charts and maps, reducing the need to export data to complex additional statistical or GIS software programs. Statistical transformations such as linear discriminant analysis (LDA) and principle component analysis (PCA) are available to generate predictive models against which unknown samples can be tested, whilst compatibility with R ensures further extended statistical analysis is also possible. Launched in 2018, the software has since been utilised by analysts with applications in ecology, food authenticity and biogeochemistry.

Recently, ArDB has been expanded to offer comprehensive quality control (QC) statistics which allows the software to also be used to monitor instrument performance over short and long-time scales. Performance of both internal QC (e.g. instrument tuning, stability, linearity) as well as external QC (analysis of certified reference materials, laboratory standards) are recorded, centralised and monitored so the base performance can be continuously evaluated for multiple instruments across multiple laboratories.

ArDB performs QC statistics calculations using the Shewhart Tests, which can be enabled or disabled, allowing consistent testing of all data sets. However, it is not always desirable to apply the same control limits to all results, so it is also possible to independently assign different criteria for individual quality controls. Individual QC criteria can be set at an administrator level so that basic operators cannot make unauthorised alterations, ensuring a secure controlled data management environment. It is also possible for ArDB to group records together and to then apply QC statistics to each group independently, allowing for comparison of results e.g. across discrete time periods, or between individual instruments. This makes it easier for the analyst to detect any changes in instrument performance, or issues with the quality of the materials/standards being measured, and thus to ensure that any corrective action is performed before data is compromised.

One significant advantage of utilising ArDB for creating a database of analytical results as well as performing instrument QC evaluation is to be able to validate the results of new/unknown samples in ArDB, and to demonstrate quantifiable confidence in the database data. By being able to scrutinise internal and external QC results alongside sample data allows the analyst to ensure that only robust qualified data is accepted for population of their databases, and ultimately that the data used for the ongoing research themes they are pursuing is demonstrably robust and reliable.
Using Cavity Ring-Down Spectroscopy (CRDS) to measure stable isotopes: overview and recent developments

Peters, R.

Picarro, The Netherlands

TBA
PLENARY LECTURE

Advances in the analysis and interpretation of the oxygen isotope composition of diatom silica

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Diatom silica (frustules) are a form of biogenic opal and contain oxygen isotopes that are being increasingly used in palaeoclimate studies. Frustules are comprised of an inner tetrahedrally bonded silica skeleton (Si-O-Si) with an outer, hydrous layer. The hydrous layer is freely exchangeable and must be removed prior to oxygen isotope measurement using oxidising reagents and/or high temperatures. Analysis of the oxygen isotope composition of diatom silica requires samples that are almost pure diatomite since extraction techniques will liberate oxygen from all the components in the sediment. There is a generally acceptable protocol involving chemistry, sieving and settling techniques and more recently laminar flow separation. Recent studies of lacustrine diatoms have shown that even a small proportion of contaminant can have a significant influence on the oxygen isotope value. All lake sediments require their own specific procedure and every sample must be scrutinised by microscopy to check for the level of contamination prior to analysis. Where sediment cannot be purified sufficiently, a semi-quantitative assessment of the diatom content can facilitate mass balance techniques. When robust preparation methods are used, diatom silica offers an important palaeoclimate proxy, providing an additional complementary, rather than an alternative, host of oxygen isotopes in carbonates.

In palaeoclimate studies it is often assumed, but rarely proven, that diatom silica forms in isotope equilibrium and hence empirically derived palaeotemperature equations, usually made in-vitro, can be used. Most studies lack the detailed investigation of contemporaneous materials from natural waters of the region under study to test these equations. Further investigations need to be conducted in order to understand the systematic relationship between temperature, water isotope composition and diatom isotope composition to enable quantitative interpretation of the sediment record. Experiments to test for vital effects and interspecific differences have so far revealed little variation. It is useful to know when and where the diatom silica is formed in the modern environment, so details of diatom ecology are important in the interpretation of isotope data.

Here it is shown that valuable palaeoclimate data can be gained from the oxygen isotope composition of diatom silica, especially since diatoms are abundant in many lakes and parts of the oceans sensitive to climate variation where other hosts (e.g., carbonates) are absent. To date the most successful studies have been conducted in areas where the oxygen isotope data registers changes in the oxygen isotope composition of the water (rather than temperature) which is then related to other aspects of climate. In these studies the range of values obtained is often greater than the error introduced by contaminating materials.
Investigation of microbial activity using clumped isotope thermometry along carbonate vein in granite host rock

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Several investigations confirm that microorganisms thrive in oligotrophic fracture systems, surviving by consuming and producing methane. Methanogenesis and anaerobic oxidation induces a fractionation or kinetic isotopic effect of carbon (expressed in $\delta^{13}C_{VPDB}$). In our study area (Laxemar, Götemar and Forsmark, Sweden), microbial activity has caused carbon depletion, with $\delta^{13}C_{VPDB}$ in the range from -7.5‰ to -24.8‰ due to anaerobic oxidation processes. Here we apply a relatively new technique, carbonate clumped isotope thermometry to measure the $\delta^{13}C$, $\delta^{18}O$, and clumped isotope-derived temperature of the precipitating carbonate vein in granitic host rock. More important, this study is the first application of carbonate clumped isotope thermometry in granitic host rock. The method is based on measuring the clumping of $^{13}C-^{18}O$ within bonds of the carbonate lattice (indicated as $\Delta47$). The abundance of $\Delta47$ of CO$_2$ relative to a stochastic distribution depends only on the temperature of the fluid. The CO$_2$ purification processes for our measurements were done using two methods, a manual line and an automated line (called Imperial Batch Extraction System or IBEX). We compared the clumped isotope results to fluid inclusion results to investigate the precise temperature of fluid within the fracture. We show that mineralization of the fracture systems occurred at temperatures ranging from 45°C to 94°C, the lower end of this being a perfect environment to support microbial or thermophile activity. Our work demonstrates that the clumped isotope approach significantly reduces uncertainties and increases our ability to constrain temperature and fluid source related to microbial activity within fracture systems. This is especially true at temperatures <80°C where fluid inclusions are difficult to apply.
We apply compound-specific isotopic analysis of amino acids (CSIA-AA) to gain dietary information on trophic position (TP) of Late Pleistocene animals and hominins. Derivatized amino acids from preserved ancient bone collagen were measured for $\delta^{15}N$ using GC-IRMS. This method is based on the differential fractionation per trophic step of two amino acid groups: source amino acids (SAAs, i.e., phenylalanine) that fractionate $^{15}N$ very little (~0.4‰) compared to trophic AAs (TAAs, i.e., glutamic acid) that fractionate $^{15}N$ greatly (~8.0‰). Here $\delta^{15}N_{\text{Phe}}$ reflects the nitrogen source of the ecosystem, i.e. the primary producers. A mix of 10 AA standards are interspersed between samples to determine accuracy and normalize results. Reference standards of a known carnivore and herbivore are concurrently measured to provide TP reference points.

This method has been applied to three cases studies in Europe. First, it was used to disentangle dietary patterns of late Neandertals (dated between 35,370 and 42,160 yrs BP) in Spy Cave, Belgium. The isotopic signature from bulk collagen place Neandertals close to predators (e.g., wolves and hyenas), indicating a diet heavily dependent on meat from large herbivores. However, using CSIA-AA, TPs of 2.7 – 2.8 (N = 3) were assigned and lower $\delta^{15}N_{\text{Phe}}$ meaning possibly a lower contribution of mammoth (high $\delta^{15}N_{\text{Phe}}$) than previously hypothesized based on bulk collagen isotopic analysis and up to ~20% dietary protein from plants based on SIAR mixing models.1,2

Second, early Upper Pleistocene modern humans (UPMHS) at Buran-Kaya III, south Crimea (35,488-36,912 yrs BP) exhibited relatively high $\delta^{15}N$ values for bulk collagen, leading to proposed consumption of freshwater resources and/or mammoth meat. Measured TPs of 2.5 – 2.6 (N = 3) indicated a solely terrestrial-based diet with a high contribution of mammoth meat and a significant plant protein intake of ~45%.3,4

A third case study involved Late Pleistocene cave bears (Ursus spelaeus) from Goyet Cave, Belgium, where although bulk collagen $\delta^{15}N$ and $\delta^{13}C$ results indicated herbivory these values were quite variable and may be affected by $\delta^{15}N$ baseline shifts unrelated to trophic position (e.g. environmental, behavioural or physiological traits). Here using CSIA-AA, TPs of 1.9-2.1 (N = 10) were determined for U. spelaeus confirming a pure herbivorous diet. In comparison brown bears (Ursus arctos) in the same cave had TPs of 2.0-2.4 indicating an omnivorous diet.5

Therefore, CSIA-AA is a powerful additional method in palaeodietary isotopic tracking for Late Pleistocene omnivores, including hominins.
Application of organic residue analysis and GC-C-IRMS techniques to decipher subsistence strategies employed at hillfort assemblages in the early Piast dynasty


Animal fats are primarily composed of triacylglycerols, which commonly degrade to n-alkanoic acids, predominantly palmitic (C_{16:0}) and stearic (C_{18:0}) acid. While mere detection of these saturated fatty acids is relatively undiagnostic, compound-specific isotope analysis allows a great deal to be inferred about the fat source. Due to varying metabolic and biosynthetic pathways by which fatty acids are produced in different organisms, it has been possible to separate lipid residues into various categories based on δ^{13}C values. Indeed, with the construction of scatterplots based on modern reference fats, it is now possible to distinguish between dairy, ruminant/non-ruminant adipose fats via determination of C_{16:0} and C_{18:0} δ^{13}C values. Due to the inherent ability of lipids to be preserved in ceramic matrices of antiquarian pottery, we are able to apply this proxy to extracted lipids recovered from archaeological cooking pots. From this we can infer subsistence strategies employed by inhabitants at a given site, thus initiating evaluation of settlement dietary habits and animal exploitation. This method has been applied to two Medieval hillfort sites (Ostrów Lednicki and Giecz) in the Wielkopolska region of Poland, attributed to the early dynasty of the Piasts. By performing GC-FID, GC-MS, and GC-C-IRMS analyses on sherd sub-samples, organic biomarkers of animal origin have been identified and can thus help to decipher dietary patterns. By cross-referencing with historical texts, faunal records, and other key artefacts recovered from excavation, we hope to use this compound-specific stable isotope proxy to further elucidate questions regarding animal husbandry during this key socioeconomic turning point in Polish history.
Comparing stepwise fluorination and MC-ICP-MS techniques for silicon isotope analysis using fossil diatoms

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Diatoms as primary producers play an important role in the biological carbon pump. Silicon isotopes from diatoms are a useful proxy to understand past variation in silicic acid (nutrient) utilisation in the ocean and therefore are an important link between the silicon and carbon cycle. The NERC Isotope Geosciences Facility (NIGF) in Nottingham offers two methods for analysing silicon isotopes, stepwise fluorination with Isotope Ratio Mass Spectrometry (IRMS) and Multi collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS). Here we compare the two methods using fossil diatoms extracted from two sediment cores from the North Pacific Ocean; ODP site 882 in the subarctic North Pacific Ocean and IODP site U1341 in the Bering Sea that span the last 2.5 Ma. Twenty diatom samples from each site were prepared using standard preparation techniques and checked for purity using a light microscope, XRF and SEM to ensure that only diatom material would be analysed. Results for both techniques were measured relative to the standard NBS 28. Here we present the results from the two techniques and show that in all but one sample there is excellent reproducibility (average difference between the two techniques is 0.07‰). We additionally compare the merits of the two analytical procedures for analysing diatom material for environmental research.
The utilization of orally administered MCT in humans is still unknown. Specifically, to which extent MCT is used as a direct energy source (oxidation) or for synthesis of longer fatty acids (elongation). The utilization is hypothesized to be different under various feeding circumstances. To investigate this, a $^{13}$C labelled MCT (tracer) was administered to healthy volunteers. They received either an oral infusion (1) exclusively MCT or (2) a combination of nutrients. The tracer was also continuously administered by oral infusion. Breath and plasma samples were withdrawn at regular intervals after the start of the tracer administration. In blood samples, the concentration and enrichments of the fatty acids ($C_8$ to $C_{18:2}$) were determined. These results were used to determine the uptake of MCT and potential elongation of several fatty acids. The rate of oxidation was determined by the analysis of $^{13}$C enrichment in breath. The samples were analysed by Gas Chromatography/Combustion/Isotope Ratio Mass Spectrometry (GC/C/IRMS). This technique is capable of very precise analysis of enrichments, especially at low levels. A new method, involving transesterification with isobutanol, was developed for analysis of $C_8$, as the standard method was not sensitive enough. Due to the outcome of this study, the current advise for patients with a disorder of long-chain fatty acid oxidation may need adjustment. Nowadays, they are advised to consume MCT before exercise. If the prescribed MCT is elongated in the body, this has no benefit compared to their standard diet advise, which is to avoid long-chain fatty acids.

The effect of Oxygen Plasma Ashing treatment on the carbonate clumped isotope parameter

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Carbonate clumped isotope paleo-thermometry is a technique based on measuring multiply-substituted isotopologues of $^{13}$C and $^{18}$O ($\Delta_{47}$). The application of this technique has led to a variety in the types of samples being measured, including organic-rich carbonate samples. High concentration of volatile organic compounds in the CO$_2$ during the purification process may produce isobaric effects on mass 47, and a static Porapaktm Q trap may not be sufficient to remove heavy organic material. Oxygen plasma ashing (OPA) is a method known to remove organic matter from samples. The effect of OPA treatment on bulk isotopic composition has been demonstrated as neglectable. Until recently, the mean offset in $\delta^{18}$O resulting from OPA alteration was around -0.12‰ for a 2-4 hours treatment. Clumped isotopes however rely on a high-resolution measurement, and even small offset could significantly impact the results. Here, we tested the OPA method for carbonate clumped isotopes. We used three samples, Imperial Oamaru Limestone, Imperial Carrara Marble and Oman calcite vein. The samples were treated using a Hennikertm Plasma HPT-100 for 10, 20 and 30 minutes. The initial $\Delta_{47}$ value of samples are 0.722‰, 0.402‰ and 0.622‰. Our results show a positive change of $\Delta_{47}$ and $\delta^{18}$O value with 0.045 - 0.027‰ and 0.111 - 0.187‰ offset for all three samples with a 30 minutes exposure time to OPA. An ANOVA test confirmed the population difference only between the 30 minutes exposure and the remaining dataset. Our result has thus provided an effective OPA pre-treatment time for safe clumped isotope analysis. This will help application of clumped isotope paleo-thermometry to complex samples, for instance samples contaminated with hydrocarbons.
Carbon isotope fractionation in algal lipids as a pCO$_2$ proxy – testing at a modern CO$_2$ seep (Shikine Island- Japan)

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As carbon dioxide concentrations in the atmosphere (pCO$_2$) continue to rise, understanding its role in earth system dynamics becomes increasingly more relevant. Geologic trends may offer critical context for such understanding but reconstructing these past pCO$_2$ remains a challenge. Stable carbon isotopic fractionation associated with CO$_2$-fixation during photosynthesis ($\varepsilon_p$) into organic matter has been shown to relate to carbon dioxide concentrations when tested in laboratory cultures and mesocosm experiments. Here, we analyze $\varepsilon_p$ at a new potential type of testing ground- a CO$_2$ vent which offers a natural environment with CO$_2$ concentrations ranging from ambient (ca. 310 µatm) to elevated (ca. 770 µatm). At a CO$_2$ vent near Shikine Island, Japan, we test $\varepsilon_p$ in a variety of general algal biomarkers, exploring molecular fossils other than the typically explored species-specific alkenone proxy. We observed strong, consistent $\delta^{13}$C shifts in several algal biomarkers from a variety of sample matrices over the steep CO$_2$ gradient, resulting in an $\varepsilon_p$ that positively correlates with pCO$_2$, in agreement with $\varepsilon_p$ theory and previous culture studies. pCO$_2$ reconstructed from this $\varepsilon_p$ trend with the measured pCO$_2$ values at the sites, as well as the correct control values, but with lower absolute reconstructed values. Our results show that naturally occurring CO$_2$ seeps may provide useful testing grounds for pCO$_2$ proxies and that general algal biomarkers show promise for reconstructing past pCO$_2$. 
(ORAL 23)

Isotopic analysis of groundwater ecosystem response to climatic and anthropogenic change


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Groundwaters host a diverse, endemic, but poorly understood ecosystem. Up to 80% of species are undescribed, and trophic functioning and response to perturbation is understudied due to the barriers to observation in this cryptic environment. The base of the groundwater food web is a microbial community feeding on carbon and nutrients within the aquifer. This in turn is grazed by microinvertebrate fauna, preventing microbial overgrowth and maintaining groundwater quality. Research questions include the origin of the carbon in different systems; changes in biogeochemistry with environmental perturbation; and the detailed functioning of the trophic web. We analysed stygofauna from a shallow calcrite aquifer in the Yilgarn region of Australia, comparing C and N isotope composition during periods of high and low rainfall. Results show that while the trophic chain is truncated and relatively stable, due to a high level of omnivory, carbon dynamics change with freshwater recharge. This is interpreted as reflecting preference changes between fresh and recycled carbon depending on availability, a hypothesis supported by hydrogeochemical analyses. Synthesising the geochemical results with ecological data indicates that, at least in shallow aquifers, freshwater recharge is a major control on groundwater ecosystem function, a finding which raises questions about the impact of climate aridification on these fragile systems.
Elevated atmospheric reactive nitrogen (N) deposition is considered one of the key components of global climate change, threatening biodiversity and possibly altering one of the forest’s key ecosystem services carbon sequestration. Ignoring the impact of N on plant growth, any major physical, biological or anthropogenic process that alters the rate of conversion of soil organic matter to atmospheric CO\textsubscript{2} (decomposition), will have profound implications for the global C budget and consequently climate change. Soil inorganic-N concentrations are predicted to increase as the result of increased deposition and mineralization due to temperature increases. However, experimental results on the effects of increased N input on SOM decomposition in the field are inconsistent, reporting positive, negative and neutral responses of SOM to N input.

Recent meta-data analyses and the model-based hypotheses suggest that global soil C storage is controlled by microbial scale processes of fungal competition for available nitrogen (N). It has been posited that higher SOM in ectomycorrhizal and ericoid mycorrhiza (EEM) systems is the result of EEM fungi’s ability to uptake and assimilate low molecular weight organic N. It has been hypothesized that EEM’s effectively scavenge all available organic and inorganic N leaving little N for the growth of the free-living decomposer microbial community and preventing further breakdown of SOM. We set out to test this hypothesis empirically in forest soils across Europe which had had received a medium-term N deposition treatment on soil plots only. We traced carbon and nitrogen transformations of added isotopically labelled litter into inorganic, soil microbial and gaseous pools and monitored concomitant changes in gross mineralization and nitrification rates and enzymatic activity. We found no evidence to suggest that substantially increasing available nitrogen increased the decomposition rates of the labelled litters added. On the contrary in-line with emerging consensus, N deposition significantly reduced gross N mineralization rates and enzyme activity.

Having dug deep into the secrets of the soil, using a suite of direct stable isotope labelling methods in the forest, we found no evidence of accelerated organic matter decomposition as a result of experimentally elevated nitrogen deposition in forest soils across Europe.
Open natural microcosm study Ecosystem function in the tropical rainforest canopy

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The relationship between the biodiversity and functioning of an ecosystem is not well understood, in particular, when exploring patterns across multiple trophic levels. This study uses the natural microcosm of the bird’s nest fern to explore this relationship at Danum Valley in Sabah, Malaysian Borneo. A large-scale manipulative experiment was installed into the canopy of eight trees, where 64 (open) fern microcosms were prepared to manipulate levels of invertebrate diversity and access to $^{13}$C-isotopically enriched organic matter within the fern suspended soil. By tracing the levels of this enriched organic matter over time, the experiments demonstrated that increasing invertebrate diversity resulted in increased rates of decomposition within the soil body. In particular, by examining subsequent enrichment of the microbial community of the soil, it was possible to determine the interacting effect of invertebrate biodiversity on microbial functioning. Increases in invertebrate biomass increased rates of decomposition, likely as a result of stimulation of the microbial community to break down organic matter, absorb the resulting carbon, assimilate it into cell walls, and subsequently respire and replace this with more carbon. These findings support the view that the loss of biodiversity will have negative effects on the functioning of ecosystems, through the breakdown of relationships in the invertebrate and microbial constituents of soil decomposer community.
Disparity of food subsistence in Neolithic Alsace revealed by stable-isotopes analyses of lipid residues preserved in pottery vessels

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The Alsace region was extensively occupied during the Neolithic by cattle-based societies with the first settlers in the area corresponding to two sub-groups of the Linearbandkeramik (LBK). The use of milk products could have started during the LBK, however, aDNA studies have failed to reveal the 13,910*T allele responsible for the digestion of lactose from milk by adults in this culture. Stable isotope analyses of lipid residues preserved in pottery vessels can provide direct evidence for milk exploitation by early farmers. Lipid residue analyses performed on ca. 800 potsherds from the region revealed that the Upper Alsatian (UA) groups exploited both dairy and carcass products, whereas in the Lower Alsatian (LA) groups the dairy products were almost absent from the subsistence package. Interestingly, dairy products were absent at LA sites which showed high frequencies of pig remains, but were present at UA sites largely dominated by cattle, supporting the diversity in animal exploitation for their secondary products. Additionally, ca. 90 potsherds from two Middle Neolithic cultures following the LBK tradition in Lower Alsace, revealed during the Grossgartach culture dietary practices were based on meat products. The following Rössen culture had, on the other hand, an economy based on dairy. Milk exploitation was widespread during the Early Neolithic with the LBK in Upper Alsace but this became commonplace in the Lower Alsace only several generations later during the Middle Neolithic supporting a model of diverse timing for dairy exploitation in the region.
Peatlands are the largest natural source of atmospheric methane and play an essential role in the global carbon cycle. The stable carbon isotopic composition ($\delta^{13}C$) of bacterial and plant lipids has been used to study modern and past peatland biogeochemistry, especially methane cycling. However, the small number of recent peatlands that have been characterised and the lack of consistency between target compounds means that this approach lacks a rigorous framework. Here, we undertake a survey of bacterial and plant lipid $\delta^{13}C$ values in peatlands from different geographic regions, spanning a wide range of temperature (-8 to 27°C) and pH (~3 to 8), to generate a reference dataset and to probe drivers of isotopic variability. Within our dataset, the carbon fixation pathway predominantly determines leaf wax ($n$-alkane) $\delta^{13}C$ values. Bacterial-derived $C_{31}$ hopane $\delta^{13}C$ values track those of leaf waxes but are relatively enriched (0 to 10‰), indicating a heterotrophic ecology and preferential consumption of $^{13}$C-enriched substrates (e.g. carbohydrates). In contrast, $\leq C_{30}$ hopanoids can be strongly $^{13}$C-depleted and indicate the incorporation of isotopically light methane into the bacterial community, especially at near neutral pH (~5-6 pH). Previous analysis of Eocene sediments has suggested isotopic decoupling between $C_{31}$ and $\leq C_{30}$ hopanoid $\delta^{13}C$ values. Our work suggests a profound and globally widespread decoupling in recent peatlands; this persists despite the profound diversity of hopanoid producing bacteria and associated controls on their $\delta^{13}C$ values and it has significant implications for future work. Re-analysis of published data from: (1) the (mid-to-early) Holocene and (2) latest Paleocene/earliest Eocene in this revised context highlights that perturbations to the peatland methane cycle occurred during the past, and we envisage that this approach could provide unique (qualitative) insights into methane cycling dynamics throughout the geological record.
POSTER PRESENTATIONS
Organic residue analysis of hunter-gatherer pottery from Zengpiyan, China, to investigate vessel use and diet

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The analysis of organic remains left on archaeological artefacts can show how humans used artefacts, unravel the ancient diet, trade and economy. The field of organic residue analysis (ORA) applies a suite of chromatographic (for separation) and mass spectrometric (for identification) techniques to investigate the amorphous or invisible biomolecules within archaeological findings. By applying the archaeological biomarker concept, assign biomolecular components to specific sources based on well-established biomarker criteria. Zengpiyan is an early Neolithic site in southern China, occupied between 9000 and 7500 years ago. The oldest cultural layer dated back to 12000 years ago. The lifestyle at that time was hunter-gatherer. Faunal skeletal remains indicate the predominance consumption of wild deer. No trace of any agricultural activities existing. The most controversial topic is whether it is the earliest site of pig domestication in China (or even amongst the earliest in the world). About 65% of individual pig clues from the faunal assemblages were only 1-2 years old and was classified as the early phase of this site. Previous archaeological investigation of Zengpiyan only utilized traditional techniques (e.g. phytolith), revealing limited results. The aim of this project is to apply a novel method, ORA, to investigate the subsistence practices in Zengpiyan, in combination with archaeological evidence to explain the established hypothesizes and develop a preliminary comprehensive picture of the people living at this site.
Glaciers have been shown to export isotopically distinct Si from the subglacial environment when compared to non-glaciated catchments. We can use the silicon isotope ($\delta^{30}$Si) composition of proglacial rivers to infer subglacial weathering processes, potentially improving our understanding of the dominant weathering regimes and subglacial water residence time.

We have conducted laboratory dissolution experiments to mimic the subglacial environment, testing the impact of physical erosion on the $\delta^{30}$Si composition of dissolved and amorphous Si phases. We show that the dissolution of freshly ground mineral surface layers result in very light $\delta^{30}$SiDSi composition, indicating that the high physical erosion rates beneath ice sheets likely drive the distinct signature of Si exported from these environments.

Based on our experimental findings, we may also be able to use the $\delta^{30}$SiDSi composition of proglacial rivers to infer the water residence times in subglacial environments, assuming rock-water interaction times are driving the $\delta^{30}$SiDSi composition due to Si dissolution from finely ground surface layers. A greater understanding of subglacial weathering processes is key to predicting fluxes of nutrients from these environments. We demonstrate the potential silicon isotope geochemistry has in improving our understanding of subglacial processes, highlighting the importance of mechanochemical weathering in these environments.
(Poster 3)*

Methanotrophy through biomarkers: Do we know how to recognize its full extent?

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Diploptene, a hopanoid biomarker (i.e. fossilized) lipid, is found in the membrane wall of numerous bacteria. Given its decay-resistant and ubiquitous nature, it has been often employed to study bacteria communities in present and past terrestrial and aquatic settings. While some studies rely on its concentrations relative to other biomarkers in order to assess changes in environment, other studies employ compound specific isotopic analysis (CSIA) of diploptene to determine carbon sources utilized by bacteria at a point in time. \(\text{CSIA}_{\text{diploptene}}\) (i.e. \(\delta^{13}C_{\text{diploptene}}\)) has thus been employed in research that investigates periods of relative high methane (CH\(_4\)) production, and consequently, consumption by methanotrophs. However, since diploptene is not produced only by methanotrophs, but by a wide range and metabolically distinctive bacteria, it is difficult to relate with high confidence “relatively depleted” isotopic signature of diploptene to CH\(_4\) consumption and to accurately approximate the size of methanotrophic community and activity (Davies et al., 2016). Here, we track CH\(_4\) incorporation into diploptene, and find the sites (CH\(_3\)-radicals) that, during CH\(_4\) consumption, would present depleted signatures. We further propose a position-specific isotopic analysis (PSIA) approach for the sites of interest in order to obtain a more accurate signature of CH\(_4\) consumption. Three well-known methanotroph strains have been selected due to their distinct pathways used for CH\(_4\)-C assimilation which are further discussed in this poster with respect to hopanoid production. Through this approach we expect to obtain \(\delta^{13}C_{\text{diploptene}}\) values that can accurately determine periods of high/low CH\(_4\) production, allowing thus diploptene to be employed as a proxy for methanotrophy.
A bioarchaeological study of intensification of pig husbandry during the Yangshao period: Implications for rising social complexity in the middle Yellow River Region

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After the early pig domestication by c. 8500 BP in Central China, zooarchaeological evidence manifests that it is during the Yangshao period (7000-4500 BP) that domestic pigs became widespread across China. At around this time a large number of sites and densely populated large settlements appeared, among which Xipo site (5800-5000 BP) as a regionally central settlement in the core area of Yangshao Culture is my research focus. This site displays preliminary features of early social complexity, which has great potential to provide clues about the development of pig husbandry during the flourishing climax of the Neolithic period in northern China and to explore the localised social developmental pattern in the middle Yellow River basin. Pig husbandry was well established during that time as the predominant subsistence pattern supplying the main animal protein to human diets. My hypothesis is that intensification in pig husbandry provided one of the main subsistence bases for developments in human settlements in the middle Yellow River basin during the Yangshao period, and that process can be tracked through examining pig remains using stable isotopes. The carbon and nitrogen isotopes of bone collagen could indicate the dietary compositions and trophic levels of Xipo pigs, and the sequential analysis of oxygen and carbon isotopes on pig lower incisors is applied to assess their birth seasonality and dietary shifts within a fine timescale. Intensified pig husbandry, sophisticated management strategies and specialised labour division in livestock raising probably occurred during the Yangshao period, which in turn boosted the early social complexity in the middle Yellow River basin.
Measurement of δ¹⁵NH₄ in ice core samples

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Polar ice cores are a unique climate archive: Enclosed air and aerosols provide information about past climate conditions and changes in the climate system. At our division the Continuous Flow Analysis (CFA) system has a long history and the measurement of high-resolution aerosol records (e.g. c(NH₄⁺)) is nowadays a routine application. With the coupling of CFA and mass spectrometry we want to extend our analytical capabilities and make also the δ¹⁵NH₄ measurable, where we envisage two different fields of applications:

1. Quantification of the nutrient cycling efficiency and the biological activity in the Southern Ocean.
2. Differentiation between terrestrial and marine sources of NH₄⁺ found in Greenlandic ice cores.

The low ammonium concentration in ice (1-10 ppb) and only small expected changes in the nitrogen isotopic ratio make this analysis challenging. The basis of our δ¹⁵NH₄ system is the well-established CFA system, which provides a continuous and contamination-free flow of meltwater including dissolved ammonium. We are currently developing an interface that comprises four main steps: In a first step, the dissolved NH₄⁺ is retained by an inorganic absorber (zeolite). The zeolite material is dried before ammonia is desorbed thermally (400°C). Secondly, the released NH₃ is oxidized to N₂ using Cu/CuO as redox agents. In a third step, combustion side products (i.e. CO, CO₂, NOx and H₂O) are separated using a series of cryotaps and a GC system. In the last step, the δ¹⁵N of the purified N₂ is determined by isotopic ratio mass spectrometry. While the setup for step 2-4 is already constructed and tested, the pre-concentration with zeolites is ongoing work and under development. In our poster we will present the current status of the analytical system.
BFC2: a new working standard for determining oxygen isotope compositions from biogenic silica

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In-house and tertiary reference standards for stable isotope measurements are critical for regular matrix-matched analysis, calibration, and normalisation of natural materials against internationally accepted delta scales. The use of appropriate working standard materials that are physicochemically similar to analytes is the principal method for obtaining accurate results in isotopic analyses. Here, we present a new reference material (BFC2) for the determination of the oxygen isotope composition (δ¹⁸O) of biogenic silica that was obtained from a diatomite collected in the Burney Mine, Shasta County, California, USA. The diatomite is a Tertiary lacustrine deposit of the Cascade Range and succeeds an existing diatomite standard (BFC, also called BFCmod) originating from the same location that was acquired from the British Geological Survey archive roughly 20 years ago. Previous studies on the original BFC using stepwise fluorination (SWF) shows the long-term reproducibility of the material to be δ¹⁸O = +28.9 ± 0.3 ‰ VSMOW (n > 1000) and data from an inter-laboratory comparison using different techniques gave a pooled value of +29.0 ± 0.3 ‰ VSMOW (n = 94)¹. Scanning electron microscopy and X-ray fluorescence indicate that BFC2 is of a similar nature to BFC, having negligible extraneous material and high purity (normalised SiO₂ = 97%), and isotope analysis using SWF gives δ¹⁸O = +27.8 ± 0.3 ‰ VSMOW (n = 33). The compositional similarity of BFC2 to the original BFC in conjunction with preliminary isotope data highlight the efficacy of the material as a new calibration and reference standard for isotopic measurements of biogenic silica.

Mass-dependent isotope variations in meteorites can provide valuable insights into processes that occurred during planet formation in the early solar system. Mass-dependent isotope studies on terrestrial rocks and chondrites, believed to be the planetary building blocks, provide evidence for Pt and Mo isotope fractionation during terrestrial core formation. These data provide important constraints on the conditions that prevailed during terrestrial core formation. Moreover, large isotope variations recorded for Cu, Zn and Ru in different iron meteorites from the same group were attributed to liquid-solid fractionation during cooling and solidification of planetary cores. Here we present the first mass-dependent Pd isotope data for the IIAB iron meteorites to evaluate the effects of fractional crystallisation of Pd isotopes during planet formation. We have analysed samples covering the entire IIAB fractional crystallisation sequence and the results show that Pd remains largely unaffected by fractional crystallisation. One sample, Sao Juliano, is notably heavier than the other samples which may reflect partitioning of Pd into schreibersite, a nickel phosphate mineral, present in this sample.
Changes in the carbon cycle during the Paleocene-Eocene Thermal Maximum (PETM)

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The Paleocene-Eocene Thermal Maximum (PETM) was a dramatic and transient warming event, triggered by the release of \textsuperscript{13}C-depleted carbon to the ocean-atmosphere system. The magnitude of the stable carbon isotope (\(\delta^{13}C\)) excursion (CIE) varies between PETM records, with different archives influenced by diverse secondary factors. The mean magnitude of the CIE varies not only among different realms, i.e. \(\approx 4.7 \pm 1.5 \%\) in terrestrial records and \(\approx -2.8 \pm 1.3 \%\) in marine deposits, but also differs among carbon archives such as: bulk marine carbonate \(\approx -2.7 \pm 1.1 \%\), soil carbonate \(\approx -5.5 \pm 1.7 \%\), bulk marine organic carbon \(\approx -4.1 \pm 2.2 \%\), bulk organic soil matter \(\approx -3.5 \pm 0.6 \%\), benthic foraminifers \(\approx -2.5 \pm 1.0 \%\), and planktic foraminifers \(\approx -2.7 \pm 1.0 \%\) (reviewed in McInerney and Wing, 2011). These variations are driven by one or a combination of different factors, including changes in the isotopic composition of the carbon source, mixed components with different \(\delta^{13}C\) values, or changes in isotope fractionation through physiological responses to higher temperatures and/or higher \(CO_2\) (Sluijs and Dickens, 2012), as well as a variety of regional or local climate factors. Therefore, the exact magnitude of CIE across the PETM remains uncertain (Dickens, 2011). Compound-specific \(\delta^{13}C\) analysis (Hayes et al., 1989; Pancost et al., 1998) bypasses many of these issues by removing concerns associated with mixing of marine vs terrestrial sources or different biosynthetic pools due to changes in OM preservation. However, there are almost no marine biomarker \(\delta^{13}C\) records for the PETM. Developing new records can refine estimates for the magnitude of the PETM carbon cycle perturbation, and therefore the source and quantity of released carbon. Here, we determine compound specific \(\delta^{13}C\) values for a range of marine biomarkers in PETM sediments from the northern Peri-Tethys (Guru-Fatima and Dzhengutay sections). Collectively, our data (\(\delta^{13}C_{Pr,Ph}\)) demonstrate that isotopic fractionation was stimulated \(\approx 4\%\) by marine algae during the PETM. However, in Guru-Fatima \(\delta^{13}C_{Pr}\) and \(\delta^{13}C_{Ph}\) CIE is likely influenced by enhanced marine productivity and physiological factors, as in Dzhengutay where marine productivity is relatively less, \(\delta^{12}C_{Pr}\) and \(\delta^{12}C_{Ph}\) are more depleted. The increase in the fractionation of stable carbon isotope in marine biomarkers, is an indicative of an increase in p\(CO_2\) during the PETM.
Laser sublimation extraction - the key to carbon isotope composition of atmospheric CO$_2$ in old ice

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Ice cores are unique archives of ancient atmospheric air providing the only direct record of past greenhouse gases. The project BEOI plans to drill an ice core extending over 1.5 Ma, nearly doubling the time span of the existing record. Due to glacial flow, the oldest section of the core is highly thinned, constraining the vertical sample size to cm-scales for a century-scale resolution. recovering the air to determine $\delta^{13}$C(CO$_2$) is technically challenging as acid/carbonate reactions in water limit the use of melt extraction. Mechanical extraction like crushing the ice only partially releases air and might result in a fractionated air sample. Sublimation extraction is the only dry method with 100% extraction efficiency for all gases. However, current sublimation methods do not have the necessary vertical resolution. We will present the development of an IR laser-based method that achieves such resolution by vertically sublimating a 3.5cm x 3.5cm x 8cm ice bar with subsequent collecting the air via cryo-trapping in a dip tube. Key to the necessary resolution is the homogenisation of the laser light by optical means. A remaining challenge are CO$_2$ adsorption/desorption effects in the extraction line with a possible solution of applying an inert coating. The $\delta^{13}$C(CO$_2$) composition, CO$_2$, CH$_4$ and N$_2$O concentration will be measured by a custom-made Mid-IR dual-laser spectrometer developed in this context without consuming the sample. The sample remains available for subsequent uses such as the determination of $\delta^{15}$N$_2$ using IRMS in dual-inlet mode.
Deuterium as an intrinsic biogeochemical indicator of insects’ invasiveness—
A method development study

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

Natal provenance of Gypsy moths was determined based on the local isotopic water signatures imprinted in their biological tissues and global geographic variations in water isotope signals. It is well known that a proportion of the δ²H signature exchanges readily, however, there are few values on the percentage exchangeable δ²H in insects. Gypsy moth samples from 22 locations in Europe, Asia and the USA were analysed for δ²H with a TC/EA-IRMS system.

In parallel, studies we determined the percentage of exchangeable hydrogen in the moth’s tissue. Ten samples were split into two groups, which then were put into two different micro-atmospheres. The samples were left to equilibrate and then dried before δ²H measurement. Based on two source mixing models, the percentage of exchangeable hydrogen was determined.

This percentage was used to calculate the true, intrinsic isotopic signature of the moth samples. Regressions between the intrinsic δ²H of moths and the δ²H of the precipitation at the moth capture sites were used to calculate back to the δ²H value of the moths’ natal origins.

There was a strong correlation between the δ²H in precipitation and the δ²H in the moths for each continent (e.g. Europe: R²=0.91). The moths found in Europe, China and eastern USA appeared to be part of native populations, as expected. The data suggested that specimens from California and Louisiana were invasive non-native specimens, fortunately, since to date there are no confirmed established Gypsy moth colonies in those regions.

These data show the potential of isotope tools to address critical issues of invasive species encroachment and reveal possible entry pathways to target in achieving effective pest management.
Nitrogen (N) is one of the key nutrients vital for the survival of all living organisms. But for N to be available to primary producers, it must first undergo nitrogen fixation. Biological N\textsubscript{2} fixation is the main non-anthropogenic input of fixed N\textsubscript{2} to be used by living organisms and is driven by an exclusive group of bacteria and archaea known as diazotrophs. As part of the NERC SPECTRA CZO Newton Fund project, we are developing a new \textsuperscript{15}N\textsubscript{2} stable isotope probing method for determining N\textsubscript{2} fixation in soils, based upon on gas chromatography-combustion-isotope mass spectrometry (GC-C-IRMS) of \textsuperscript{15}N-amino acids. Here, the rate and magnitude of assimilation of \textsuperscript{15}N\textsubscript{2} by the N-fixing bacteria will be measurable through the \textsuperscript{15}N content of newly synthesised amino acids determined by GC-C-IRMS. The method will also be adapted to assay N\textsubscript{2} fixation with potentially greater sensitivity and specificity compared to existing methods and provide hitherto unobtainable quantitative information on N\textsubscript{2} capture and flow in agricultural and semi-natural soils. Overall, this novel approach will contribute to our further understanding of the biological N cycle and assist in meeting current challenges on environmental sustainability and food security.
Changes in climatic and environmental conditions can affect both plant chemical and isotope composition. Nowadays, many studies use bulk isotope values which represent a weighed mean average of the different plant compounds. An isotopic characterization of individual biogeochemical compounds is needed in order to differentiate the isotopic composition of the main plant components i.e. polysaccharides, lignin, polypeptides, lipids and waxes, etc. Here, we investigate the link between molecular and isotope composition of wood from three Eucalyptus spp. using an analytical pyrolysis technique combining Py-GC with IRMS (Py-CSIA). Bulk samples and lignin extracted were analysed by Py-CSIA. Isotopic measurements were normalized to the accepted scale using a n-alkanes mixture containing 15 dissolved alkanes (C_{16} to C_{30}) (Indiana University). Values well fitted along a straight line with a linear regression R2 no lower than 0.999. Although pyrolysis induced thermal cracking in long chain molecules at high pyrolysis temperature (>400 °C) significant deviations from the acclaimed isotope composition were not observed in the standard solution nor in the wood samples. Our results support the idea that Py-CSIA can reveal major differences between compounds from different biogenic origin: polysaccharides- lignin-derived units and fatty acids. Despite that wood from different origins provide very similar Py-GC-MS pattern- Py-CSIA can make the difference giving additional valuable information.
During the harshest conditions of the last ice age European human populations abandoned northern latitudes, with their range contracting to southern refugia. By the time ice sheets retreated and large areas of land became available for resettlement there had been a hiatus of several thousand years. The ERC funded UP-North project is examining the relationship between climate change and the recolonisation of Northern Europe after the last glacial maximum. As people move eastwards and northwards to colonise uninhabited landscapes, increasing diversification is seen in their stone and bone tool industries. UP-North is exploring the relationship between this human dispersal, cultural development-prey ecology and climate change. Here we present the results of stable isotope analyses (C, N, S) of hunted fauna (reindeer, horse, bovids and red deer) which are providing new palaeoenvironmental and palaeodietary reconstructions that are directly linked to the archaeological evidence, thus allowing the relationship between cultural and climate change to be explored.
(Poster 14)

Which environmental parameters control the hydrogen isotope composition ($\delta^2$H) of long-chain n-alkanes? - An example from Early Pleistocene climate cycles recorded in sediments of Lake Ohrid

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Lake Ohrid in the Western Balkans (Albania, North Macedonia) is Europe’s oldest extant lake, dating back 1.4 million years (Ma). Its continuous sequence of sediments provides a rare archive of environmental change preceding the mid-Pleistocene transition (MPT). Carbonate precipitation in Lake Ohrid appears strongly controlled by temperature and shows pronounced obliquity-controlled glacial-interglacial cycles in pre-MPT sediments between 1.36 and 1.16 Ma. Palynological data reveals matching vegetation changes. However, these are typically controlled by changes in hydrology rather than temperature. We therefore analysed the isotopic composition of leaf wax-derived n-alkanes ($C_{25}$, $C_{27}$, $C_{31}$) in order to test if a reduction in supply of $^2$H-depleted moisture from NE-Atlantic sources through the dominant northerly air mass inflow is responsible for this pattern. Notably, the leaf wax $\delta^2$H values, ranging from -190 to -160 ‰, do not show a clear glacial-interglacial pattern. Instead, we observe a shift towards generally heavier values half-way through the record around 1.26 Ma that coincides with equivalent shifts in n-alkane distribution ($C_{31}$ becoming more abundant), a decrease in grass pollen, and an increase in deep-water diatom species. We therefore suggest that lake expansion and the associated decline in low-lying habitats with groundwater contact is responsible for the observed pattern rather than a steady increase in the supply of relatively $^2$H-enriched moisture from Mediterranean sources.
Biochar: Negative Emission Technologies are nice to the environment part two
Using stable isotopes in a citizen science approach

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

Again, in this project we offered citizens the opportunity of participating in their own experiment, so at each event we encouraged the public to participate in our next generation pot-scale Citizen Science endeavor. There was preliminary evidence that biochar could promote nodulation of legumes in the soil. We set out to further test this improved nodulation phenomena across a range of soils in Austria.

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

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

The results and conclusions from this project will be presented.
Simultaneous $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ analysis of 1 mg of bone collagen: analytical improvements

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The measurement and understanding of sulphur isotopes in bone collagen is a rapidly growing field. Sulphur isotopes in proteins preserved in archaeological material can potentially distinguish between marine and terrestrial diets, being especially useful when the dietary interpretation of $\delta^{15}N$ is complicated by aridity or nutritional stress. There is also potential to use sulphur isotope values as a provenancing tool because of their relationship to underlying geology. However, $\delta^{34}S$ studies are still not applied routinely in the same way as $\delta^{13}C$ and $\delta^{15}N$ analysis. This has in some way been hampered by the large amount of organic material required per measurement; at least 10 mg for an individual analysis. This is due to the low concentration of sulphur in bone collagen (0.2% to 0.3%). In contrast, a dual carbon and nitrogen analyses can be achieved with less than 1 mg of material. Additionally, it is usually necessary to analyse $\delta^{34}S$ separately from $\delta^{13}C$ and $\delta^{15}N$, often with equipment adaptations. Thus, this has made the analysis of $\delta^{34}S$ expensive, both in terms of time, sample destruction and cost. This presentation describes how a simultaneous triple $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ analysis is achievable in a single sample drop on a collagen sample of 1 mg using the Thermo Scientific™ EA IsoLink™ IRMS System. This means that the overall cost per sample analysis is reduced, less maintenance is required and system throughput is significantly enhanced. This is without compromising on analytical precision, which we show to be $\leq 0.1\%$ for $\delta^{13}C$, $\leq 0.15\%$ for $\delta^{15}N$ and $\leq 0.3\%$ for $\delta^{34}S$. This method provides new opportunities for data collection and, in the case of sulphur, the routine analysis of $\delta^{34}S$ in bone collagen.
The National Environmental Isotope Facility (NEIF) provides an integrated platform of state-of-the-art isotope bio-geochemistry analytical capabilities and specialisms to support the UKRI-NERC science communities. NEIF is comprised of five laboratories based at the British Geological Survey, the Scottish Universities Environmental Research Centre, the University of Bristol, the University of Oxford, and the Centre for Ecology and Hydrology. The new national facility provides: (i) unparalleled analytical capacity and data quality to help delivery of internationally competitive research projects and programmes, (ii) a diverse range of specialist expertise and instrumentation, not available locally in most HEIs, (iii) a national platform for innovation that supports training, development and the international competitiveness of the UK research community, and (iv) awareness of environmental research and related NERC activities. NEIF offers integrated capabilities, encompassing all the common stable isotopes and matrices from gases to solids and extant to extinct organisms, to track and interrogate a wide range of solid Earth processes, including the hydrosphere and biosphere, and to provide chronologies spanning 4.6 Ga of Earth System evolution. The facility provides a single access point to an extensive range of world-leading isotope capabilities for the UK research community, and the community-centred nature of NEIF means that it is effective at providing training to a broad cohort of early stage researchers in a range of analytical and application skills. NEIF is funded by UK Research and Innovation through the Natural Environment Research Council.