

# Stable Isotope Mass Spectrometry User Group Meeting



5-7<sup>th</sup> July 2017

British Geological Survey, UK



**British  
Geological Survey**

NATURAL ENVIRONMENT RESEARCH COUNCIL



CENTRE FOR ENVIRONMENTAL  
GEOCHEMISTRY





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## Practical Information

### Internet Access

For Wi-Fi access, please use:

- 'eduroam' (if you have institutional login details)
- 'BGS Visitor' (password = bgsvisitoraccess)

### On-site parking

Free parking is available on the BGS site.

At the security gate, please let the guard know your name and that you are attending a conference. They will then let you through the barriers. Turn left immediately after the barriers to access the front car park. Proceed to reception.

### Meeting location and registration

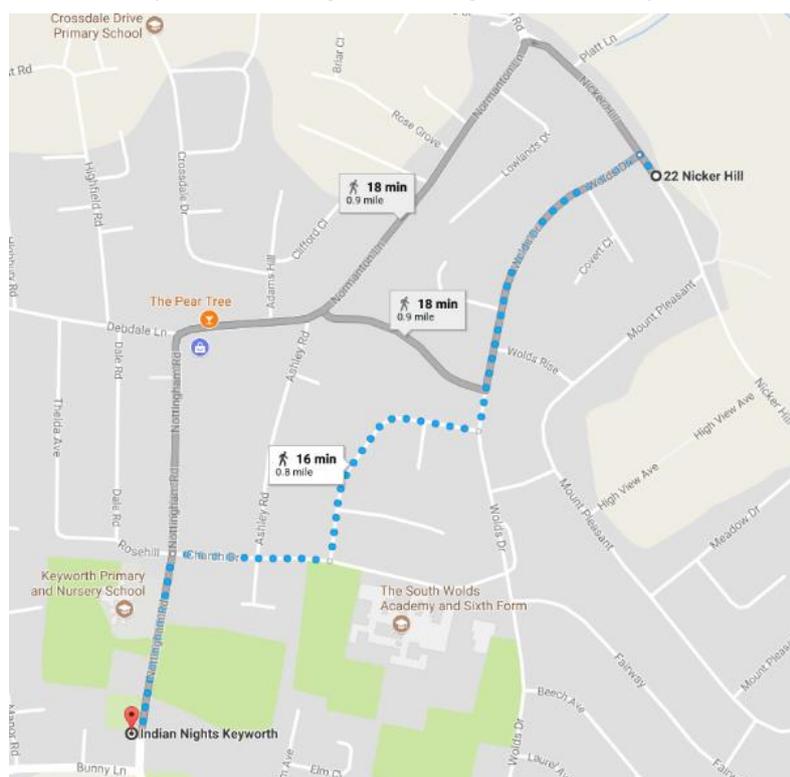
The meeting will be held at the British Geological Survey, Nicker Hill, Keyworth, Nottingham, NG12 5GG.

Upon arrival on either Wednesday 5<sup>th</sup> (for BGS tour) or Thursday 6<sup>th</sup> July, please go straight to reception and a member of the SIMSUG organising committee will be waiting to greet you.

All presentations will be in the De le Beche conference suite on Thursday 6<sup>th</sup> and Friday 7<sup>th</sup> July, which is situated directly above the main reception, and poster sessions/refreshments will be in the exhibition area directly behind main reception.

### Optional informal dinner at Indian Nights – Wednesday 5<sup>th</sup> July

Location map for Indian Nights, Nottingham Road, Keyworth, NG12 5FB:

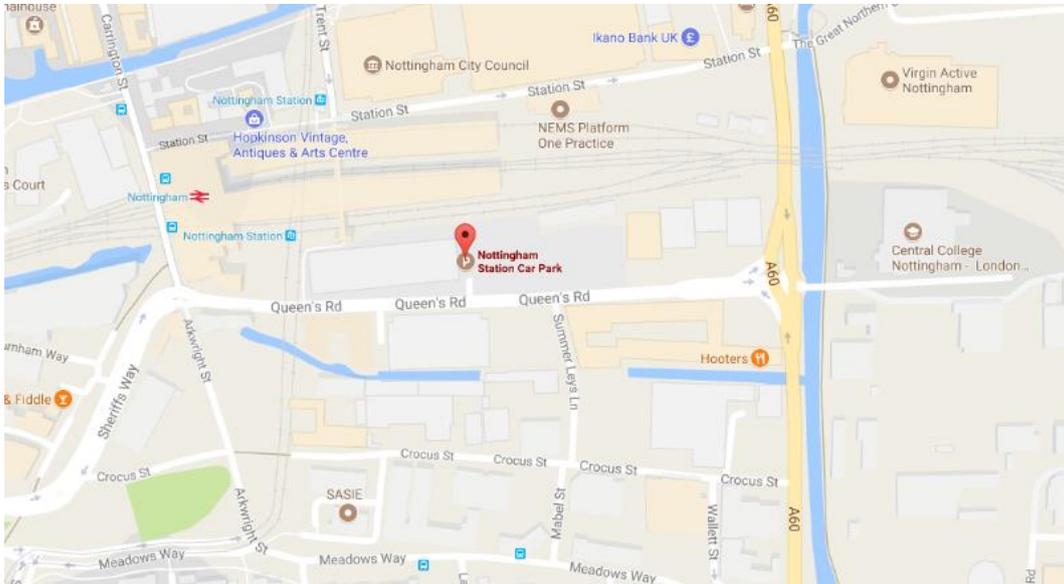


#### Walking Directions BGS-Indian Nights

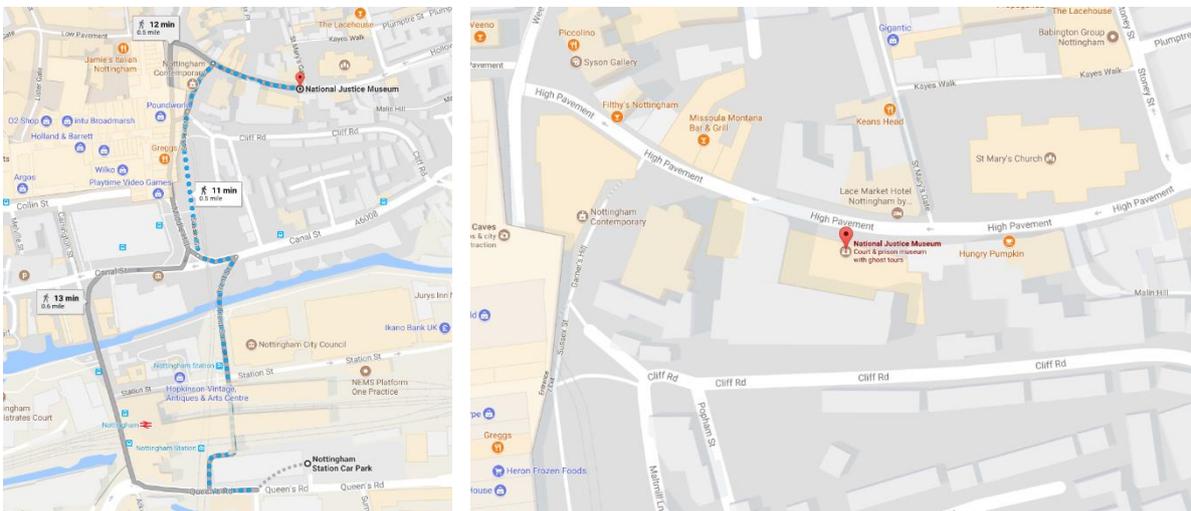
- Opposite the BGS main entrance, walk to Wolds Drive
- Continue on Wolds Drive until Co-Op store, turn right onto Church Drive
- Walk to the end of Church Drive and turn left onto Nottingham Road
- Indian Nights is roughly 200 meters along Nottingham Road on the right hand side
- Members of the SIMSUG committee will be on hand to accompany those going straight from the BGS tour to Indian Nights

## Conference Dinner

Transport will be provided from the BGS to the conference dinner following presentations on Thursday 6<sup>th</sup> July. For those driving to the city centre, we recommend parking at the Nottingham Station car park, located on Queen's Road, Nottingham, NG2 3AQ:



The conference dinner will be held at the National Justice Museum, High Pavement, Nottingham, NG1 1HN:



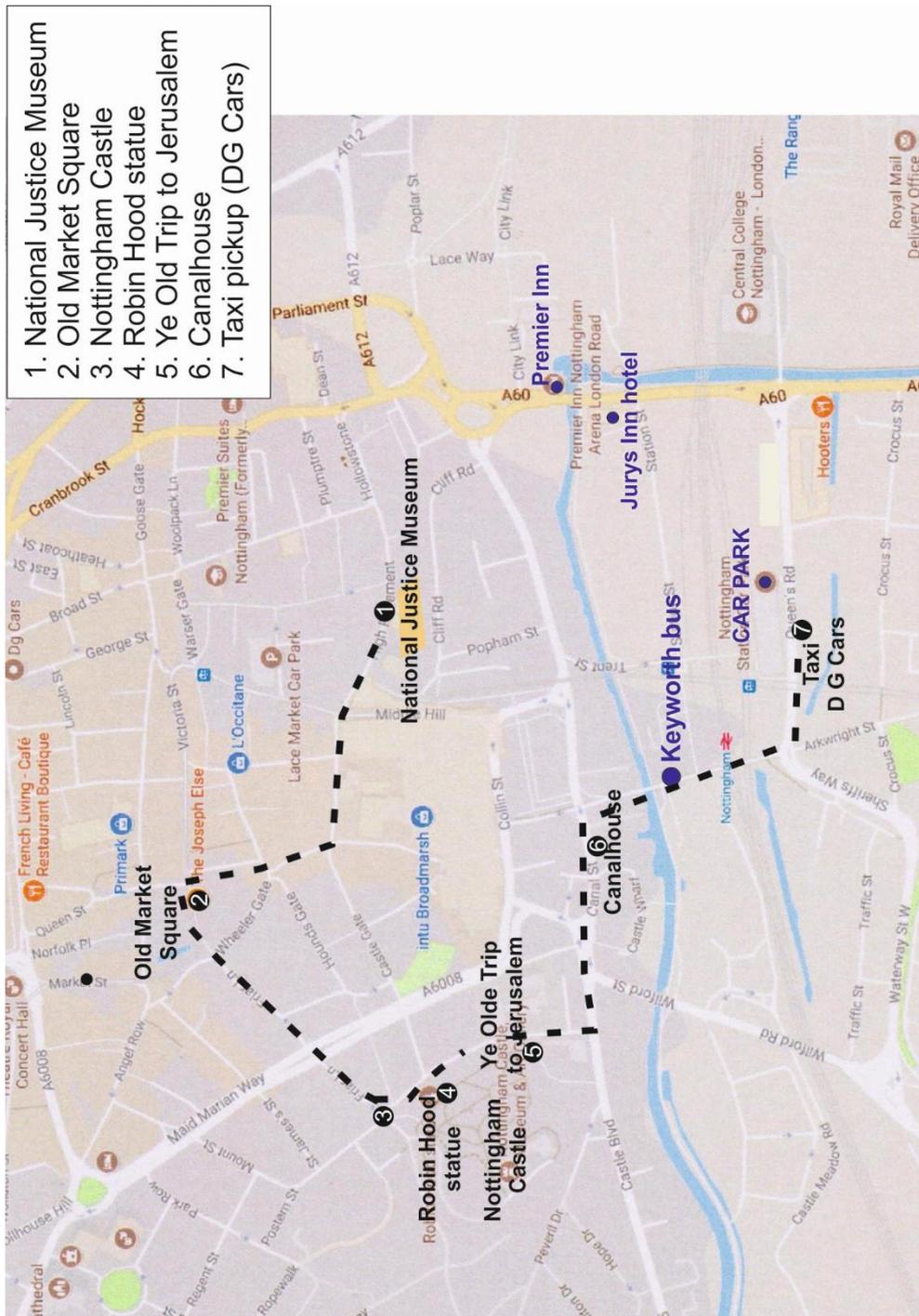
Conference dinner menu (after tour of the National Justice Museum)

- Italian lasagne with rocket salad, coleslaw & garlic bread
- (vegetarian option available)
- Chocolate fudge brownie & cream
- Wine, courtesy of our sponsors

## Walking Tour of Nottingham

The optional walking tour will take place following the conference dinner. The tour will end in the Canalhouse for drinks (Canal Street, Nottingham, NG1 7EH). Taxis back to Keyworth are booked for 23:00 from DG Cars opposite the station car park on Queen's Road (organisers will walk from Canalhouse pub following walking tour). A bus to Keyworth is also available from outside Nottingham train station at 21:35/22:35/23:35 (Trent Barton Keyworth Connection).

Map of walking tour:



## Further information

If there are any questions, or for additional information, please email Beatrice Bullock-von Moos at [bbullock@bgs.ac.uk](mailto:bbullock@bgs.ac.uk) or phone (+44) 0115 936 3425

## Scientific Programme

### Wednesday 5th July 2017 (optional itinerary)

15:00	17:00	Tour of the British Geological Survey
17:30	20:00	Informal dinner at Indian Nights, Keyworth

### Thursday 6<sup>th</sup> July 2017

09:00	09:30	Arrival at British Geological Survey and registration
09:30	09:45	Welcome and introduction to SIMSUG 2017

#### Session 1 – Methodological Advances and Calibration Studies

Chair: Melanie Leng

09:45	10:00	Paul Dennis (University of East Anglia) How pure is pure? A cautionary tale for clumped isotope ratio measurements
10:00	10:15	Angela Lamb (British Geological Survey) Fractionation of inorganic phosphate oxygen isotopes during mineral dissolution by microbially produced organic and inorganic acids
10:15	10:30	Lucy Roberts (University College London) Effects of cleaning methods upon preservation of isotopes and trace elements in ostracods
10:30	10:45	Sabine Lengger (University of Plymouth) The isotopic characterisation of tetraether lipids (GDGTs) by high temperature GC-IRMS
10:45	11:00	Andrew Smith (British Geological Survey) Extracting the $\delta^{18}\text{O}$ - $\text{PO}_4$ record from carbonate speleothems – methods development and potential applications
11:00	11:30	Posters and refreshments

#### Session 2 – Palaeoclimate of the Terrestrial Realm

Chair: Jack Lacey

11:30	11:45	Matthew Jones (University of Nottingham) Approaching proxy data – climate model comparison using lake isotope Proxy System Models
11:45	12:00	Heather Moorhouse (Lancaster University) Catchment-scale lake Nitrogen isotopes from sediments of headwaters to terminal basins and their relationship to algal community change
12:00	12:15	Jonathan Dean (University of Hull) Using stable isotope analysis of stromatolites from a lake in Ethiopia to investigate the African Humid Period termination
12:15	12:30	Jenni Sherriff (University of Winchester) Oxygen isotope values of freshwater gastropod carbonate in temperate fluvial systems; implications for palaeoenvironmental studies in fluvial sequences
12:30	12:45	Maarten van Hardenbroek (Newcastle University) Stable carbon and nitrogen isotopes of invertebrate remains: a glimpse of food web structure change?
12:45	14:00	Lunch

**Session 3 – Advances in Stable Isotope Geochemistry**

Chair: Andrew Smith

14:00	15:00	Peter Wynn (University of Lancaster) <b>KEYNOTE:</b> Subglacial methane sources and sinks – an isotopic approach
15:00	15:15	Jan Kaiser (University of East Anglia) The oxygen-17 excess of stratospheric and oceanic nitrous oxide
15:15	15:30	Michael Singer (Cardiff University) Source Water Isotope Identification Toolkit (SWIIT) for detecting historical water use by forest trees
15:30	16:00	Posters and refreshments

**Session 4 – Systems and Software Innovation**

Chair: Jack Lacey

16:00	16:15	Chris Brodie (Thermo Fisher Scientific) Pushing research boundaries: Benefits of temperature ramped gas chromatography in EA-IRMS
16:15	16:30	Helen Atkinson (Sercon Ltd.) Improvements in sensitivity in IRMS measurements
16:30	16:45	Mike Seed (Elementar UK Ltd.) It's been a busy few years at Elementar UK
16:45	17:00	Philip Dunn (LGC Ltd.) Application of Metrological Principles to Isotope Ratio Analysis
17:00	17:30	Group photo and depart for conference dinner

**Conference Dinner National Justice Museum, High Pavement, Nottingham, NG1 1HN**

18:00	18:30	Arrival and drinks
18:30	19:45	History tour (staggered start times in groups of 25)
19:45	21:00	Dinner
21:00	23:00	Optional walking tour of Nottingham and drinks at Canalhouse Pub

**Friday 7th July 2017**

09:00 09:30 Arrival at British Geological Survey

**Session 5 – Palaeodiet and Provenance**

Chair: Angela Lamb

09:30 10:30 Tamsin O'Connell (University of Cambridge)  
**KEYNOTE:** The real "Palaeodiet": isotopic approaches to past human subsistence

10:30 10:45 Jamie Lewis (University of Bristol)  
A tale of Swine and Strontium; Strontium concentration, radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) and stable ( $\delta^{88}\text{Sr}$ ) strontium isotope systematics in a controlled feeding study

10:45 11:00 Helen Whelton (University of Bristol)  
A multi-proxy approach to diet and animal management in the Neolithic of northern Greece

11:00 11:30 Posters and refreshments

**Session 6 – Isotopes in the Marine Realm**

Chair: Melanie Leng

11:30 11:45 Isabel Seguro (University of East Anglia)  
Seasonal net and gross biological oxygen production in a temperate shelf sea from oxygen-argon-ratio and oxygen triple isotopes

11:45 12:00 Harold Bradbury (University of Cambridge)  
Using calcium isotopes to constrain the precipitation of authigenic carbonate in marine sediments

12:00 12:15 Babette Hoogakker (Heriot Watt University)  
Using stable isotopes methods to assess ocean oxygenation in the past; examples from the Atlantic ocean

12:15 12:30 Andy Johnson (University of Derby)  
Seasonally resolved isotopic temperature data as a tool for identifying the cause of marine climate change in the Pliocene

12:30 13:00 Closing remarks, prizes, and next meeting

13:00 15:00 Lunch and discussion

15:00 - Meeting end

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## Abstracts – Oral Presentations

(In alphabetical order of presenting author)



## Improvements in sensitivity in IRMS measurements

Helen Atkinson, Paul Dennis, Steve Welsh, Simon Moseley

Sercon Limited, Unit 3B Crewe Trade Park, Gateway, Crewe, Cheshire, CW1 6JT, UK

An increase in the sensitivity of isotope ratio mass spectrometers is required to meet the demands of researchers for (i) smaller sample sizes associated with higher resolution sampling, and (ii) new developments in clumped isotope ratio analysis where high precision is required for multiply substituted isotopologues which are present at low natural abundances on the order of tens of ppm or lower.

Following an analysis of the electron and ion optics of the Sercon 20-22 Nier type electron impact ion source we have made modifications to the source optics. The improvements in sensitivity resulting from the modifications are significant. For CO<sub>2</sub> and N<sub>2</sub> a near factor of two improvement in sensitivity in both continuous flow and dual inlet modes is observed, whilst the improvement for H<sub>2</sub> is lower. Using this source modification in a large radius magnetic sector dual inlet IRMS we report a sensitivity of <450 molecules per CO<sub>2</sub> ion. This is the highest sensitivity yet reported for any IRMS instrument.



## Using calcium isotopes to constrain the precipitation of authigenic carbonate in marine sediments

H. Bradbury<sup>1\*</sup>, A.V. Turchyn<sup>1</sup>

<sup>1</sup> *Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, UK*

*\* hjb62@cam.ac.uk*

The removal of carbon from the surface through deposition and burial of carbon-minerals in the ocean is a critical component of the global carbon cycle. However the material deposited on the seafloor is not representative of the material buried due to a dynamic chemical and microbial reactor, which exists beneath the seafloor. The reduction of sulfate oxidises organic carbon in anoxic sediments and generates subsurface alkalinity as does the anaerobic oxidation of methane. The alkalinity produced can lead to authigenic carbonate formation when combined with the calcium ions from the porewater.

Calcium isotopes in carbonate minerals are enriched in the lighter <sup>40</sup>Ca relative to the fluid from which they precipitate. As such the remaining fluid, during precipitation, becomes depleted in <sup>40</sup>Ca leading to a heavier  $\delta^{44/40}\text{Ca}$  signature. The  $\delta^{44}\text{Ca}$  of the pore fluid along with the calcium concentration allows for the identification of the zones of precipitation. We present high-resolution pore fluid calcium isotope data for Ocean Drilling Project Sites 1081 and 1086, as well as a steady-state model of the isotopic composition of the porefluid with varying dissolution and precipitation rates. The knowledge gained from these sites allows for the classification of two major processes controlling the authigenic formation of carbonate and the carbon isotope composition of the carbonate formed. The IODP/ODP pore fluid database is then classified using this approach to discuss the carbon isotopic composition of the globally deposited authigenic carbonate.



## Pushing research boundaries: Benefits of temperature ramped gas chromatography in EA-IRMS

C. Brodie<sup>1\*</sup>, O. Kracht<sup>1</sup>, A. Hilker<sup>1</sup>, C. Douthitt<sup>2</sup>

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

<sup>2</sup> Thermo Fisher Scientific, USA

\* [chris.brodie@thermofisher.com](mailto:chris.brodie@thermofisher.com)

The Thermo Scientific™ EA IsoLink™ IRMS System has fundamentally improved analysis by EA-IRMS using temperature ramped gas chromatography with a single GC column and a patented helium management system that reduces cost per analysis. These innovative features open doors to push research boundaries at new levels, especially for the analysis of very small concentrations and on very high C/N and C/S ratio samples.

This presentation will principally focus on the advantages of using temperature ramped gas chromatography. Traditionally, gas chromatography in EA-IRMS employed a GC column held at an isothermal temperature as the gases eluted. However, using temperature ramped gas chromatography in the EA IsoLink IRMS System, a feature common in GC-MS and GC-IRMS, the temperature of the GC column can be quickly changed as analyte gases are eluting, improving peak separation, peak fidelity, analysis of very small sample amounts and precision of replicate measurements.

We will discuss these improvements in peak separation, background determination, troubleshooting of the combustion, pyrolysis and chromatographic processes, blank determination and analysis of very small sample concentrations. Complete baseline separation of each analyte is achieved with sound background correction and peak fidelity, including for very large (7000 µg C) and very small (11 µg N and 1 µg S) analyte amounts. For 5 replicate measurements on wood,  $\delta^{13}\text{C} = -24.10 \pm 0.06\text{‰}$ ;  $\delta^{15}\text{N} = 3.20 \pm 0.23\text{‰}$  and  $\delta^{34}\text{S} = 5.92 \pm 0.26\text{‰}$ .



## Using stable isotope analysis of stromatolites from a lake in Ethiopia to investigate the African Humid Period termination

J. Dean<sup>1,2\*</sup>, T. Raub<sup>3</sup>, M. Leng<sup>2</sup>

<sup>1</sup> University of Hull, Hull, HU6 7RX, UK

<sup>2</sup> British Geological Survey, Keyworth, NG12 5GG, UK

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At numerous times through the Pleistocene, north and east Africa became substantially more humid than they are in the present. The most recent African Humid Period (AHP) occurred ~15 to 6/5ka BP. While the extent of this AHP is now clear, one issue that is yet to be settled is how rapid or gradual the termination was, which goes to the heart of the question of why it ended: was it a linear response to orbital changes or did non-linear feedback mechanisms lead to rapid change? Sediment cores taken from lake Chew Bahir in Ethiopia contain too little carbonate for a thorough investigation of the termination of the AHP using stable isotopes. However, we discovered stromatolites along former lake shorelines. Here we will discuss the development of stable isotopes from stromatolites as a proxy for hydroclimate change and the application of this relatively novel method to establishing the nature of the AHP termination at Chew Bahir. Stromatolites are sedimentary structures formed by trapping, binding and carbonate precipitation induced by microorganisms. They continue to grow upwards from their base to form a new layer every year. SEM and probe analysis has been carried out on all stromatolites and has shown they are composed of calcite with some silicates. Taken together, our stromatolites extend from >9 to ~4.5ka. The older samples were collected from the AHP highstand at 534 m.a.s.l. and the youngest samples from 502 m.a.s.l. Assuming the stromatolites have remained in situ since formation (which is a fair assumption since the lake level has only fallen since then and they are too heavy to be carried by the wind), this >30 m drop in lake level demonstrates the significance of the AHP termination at Chew Bahir. We believe the oxygen ( $\delta^{18}\text{O}$ ) and carbon ( $\delta^{13}\text{C}$ ) isotopes of stromatolite carbonates reflect changes in the composition of the water in which they grew. Using  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  from the overlapping chronologies of the stromatolites, we have produced a near continuous, ~25-year resolution record of the changes in hydroclimate over this time.



## How pure is pure? A cautionary tale for clumped isotope ratio measurements

P.F. Dennis<sup>1\*</sup>, A.D. Marca<sup>1</sup>, L. Clarke<sup>2</sup>, S.Umbo<sup>1</sup>, R.Kirk<sup>1</sup>, S. Crook<sup>1</sup>

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<sup>2</sup> Division of Chemistry and Environmental Science, Manchester Metropolitan University, Manchester

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Multiply substituted isotopologues are molecules, formula units and other moieties in which there are two, or more isotopic substitutions by rare heavy isotopes. They are more commonly referred to as clumped isotopes and over the past 13 years there has been considerable progress in development of analytical techniques that can measure with sufficient accuracy and precision their variability in naturally occurring gases and minerals. The most widely developed application has been clumped isotope thermometry of carbonate minerals.

Not-with-standing this progress there are a number of unresolved issues relating to both sample preparation and mass spectrometer analytical techniques. A major consideration is the effect contamination of the analyte gas has on the measured clumped isotope composition. For carbonates the major multiply substituted isotopologue that is of interest in the analyte CO<sub>2</sub> is <sup>18</sup>O<sup>13</sup>C<sup>16</sup>O that is present at a nominal concentration of approximately  $45 \times 10^{-6}$ . A contaminant species at the same nominal mass of 47 need only be present at a relative partial pressure with respect to the analyte CO<sub>2</sub> of just  $4.4 \times 10^{-10}$  to cause systematic offsets in the data of 0.01‰. Such offsets are at the measurement precision required for clumped isotope thermometry and therefore are significant. Contamination is usually minimised by the use of either porapak-Q capillary GC columns, or a static porapak-Q trap during sample preparation with the effectiveness of removal of contaminants evaluated by monitoring the mass 48 signal. In this presentation we show, using high precision measurement of  $\Delta_{47}$  ( $\pm 0.01\text{‰}$ ),  $\Delta_{48}$  ( $\pm 0.03\text{‰}$ ) and  $\Delta_{49}$  ( $\pm 3\text{‰}$ ) that many naturally occurring carbonate sample types, including biogenic carbonates, speleothem carbonate and natural travertine/tufas contain a component of contamination even after purification. The contamination is revealed in a linear covariation of measured  $\Delta_{47}$  values with both  $\Delta_{48}$  and  $\Delta_{49}$  values. The gradients of the  $\Delta_{48}$  versus  $\Delta_{47}$  plot is 4.2, whilst that of the  $\Delta_{49}$  versus  $\Delta_{47}$  plot is 692. These gradients are independent of the sample type.

It is not possible unambiguously to identify the contaminant species though the pattern of covariation is consistent with chloro-carbon contaminant species in the ion source. The resolution and peak quality of the MIRA mass spectrometer is not sufficient to separate the contaminant and analyte gas peaks but is good enough to characterise the mass difference between the CO<sub>2</sub> and the contaminant species. Careful measurement of the mass difference between the CO<sub>2</sub> isotopologues and the contaminant species at masses 48 and 49 shows a mass difference of approximately 1 part in 1300. The contaminant occurs at a lower mass than the CO<sub>2</sub> isotopologues. This observation excludes hydrocarbon contamination due to the positive mass defect associated with hydrogen. The small negative mass difference is consistent with CCl and CHCl contaminant species.

As yet we have not been able to identify the precursor molecule or the source of the contamination. The fragmentation pattern is not dissimilar to that of dichloromethane and may indicate the presence of cleaning solvents. However, we have not been able to rule out that a further potential source is the phosphoric acid and samples used for analysis. We believe the bulk of extant data for  $\Delta_{48}$  and  $\Delta_{49}$  in published studies are not of sufficient quality to rule out contamination as an important feature of published data sets.



## Application of Metrological Principles to Isotope Ratio Analysis

P. J. H. Dunn<sup>1\*</sup>, D. Malinovsky<sup>1</sup>, H. Goenaga-Infante<sup>1</sup>

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The application of isotope ratio mass spectrometry (IRMS) in forensic contexts has been increasing, particularly its use as a tool for identifying the source of a material [Gentile 2015]. Methods that are used to provide forensic evidence or intelligence must be capable of providing data of sufficient quality to meet the needs of stakeholders and to avoid miscarriages of justice. Several metrological principles can be applied to stable isotope analyses to ensure that measurement results are of high quality. These include ensuring traceability of results, correct estimation of measurement uncertainty and method validation.

Traceability for IRMS measurements involves correct scale calibration of measured results to the internationally agreed reporting scales (e.g. VSMOW-SLAP) using the correct number of reference materials, as well as reporting the assigned delta values for all within the traceability chain. Method validation involves the determination of various performance characteristics for a specific method which provides objective evidence that the method is suitable for its intended use. Finally estimation of measurement uncertainty results in a range of values within which can be found the true value for the measured result with some degree of probability (often approximately 96 % for an expanded uncertainty).

While there has been much focus on traceability for isotope ratio measurements [e.g. Coplen 2006, Coleman 2014], the awareness over why method validation and correct estimation measurement uncertainty are important and how to go about them appears to be more limited. This paper will provide guidance to end-users about these aspects. A ten point plan for method validation covering the essential aspects for stable isotope analysis will be discussed. The various factors which can contribute to the overall measurement uncertainty for IRMS-derived delta will also be presented, including a discussion about the effect of various corrections, commonly applied to raw instrumental data, on the overall measurement uncertainty. Examples of different approaches to uncertainty estimation, as used in an inter-laboratory comparison on bulk honey carbon isotope ratio measurements, will be presented and compared.

### References:

- Gentile, N. *et al*, (2015). Isotope ratio mass spectrometry as a tool for source inference in forensic science: a review. *For. Sci. Int*, 251 (), pp139-158.
- Coplen, T.B. *et al* (2006). New Guidelines for  $\delta^{13}\text{C}$  Measurements. *Anal. Chem.*, 78 (7), pp2439-2441.
- Coleman, M. & Meier-Augenstein W.M. (2014) Ignoring IUPAC guidelines for measurement and reporting of stable isotope abundance values affects us all. *Rapid Commun. Mass Spec.*, 28 (17), pp1953-1955.



## Using stable isotopes methods to assess ocean oxygenation in the past; examples from the Atlantic ocean

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Past reconstructions of ocean oxygenation are important to understand the natural oxygen cycle. Such datasets are valuable for the wider scientific community to validate climate models, and improve predictions of future oxygen changes. Novel datasets of oxygen usage in addition are important to define the role of biological processes in sequestering carbon in the oceans.

During my presentation I will discuss a recently developed proxy method, using the gradient between carbon isotopes measured on specific benthic foraminifera, to quantitatively reconstruct oxygen concentrations in sea-water (Hoogakker et al., 2015). I will provide examples of its application from several Atlantic Ocean sites.

### References:

Hoogakker, B.A.A., Elderfield, H., Schmiedl, G., McCave, I.N., Rickaby, R.E.M. (2015). Glacial-interglacial changes in bottom-water oxygen content on the Portuguese margin. *Nature Geoscience* **8**, 40-43 (2015).



## Seasonally resolved isotopic temperature data as a tool for identifying the cause of marine climate change in the Pliocene

A.L.A. Johnson<sup>1\*</sup>, A. Valentine<sup>2</sup>, M.J. Leng<sup>3</sup>, H.J. Sloane<sup>3</sup>, B.R. Schöne<sup>4</sup>, D. Surge<sup>5</sup>

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<sup>2</sup> Student Advice and Support Services, Loughborough University, Loughborough LE11 3TU, UK

<sup>3</sup> Isotope Geoscience Facilities, British Geological Survey, Keyworth NG12 5GG, UK

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Alteration in the pattern and vigour of ocean currents has often been invoked as the principal driver of changes in regional climate, including cases in the recent past (Pliocene, Pleistocene and Holocene) and instances predicted in the near future. The theory behind such interpretations is, however, suspect (e.g. Crowley, 1996; Seager et al., 2002), and it may be that other regional or global drivers are more important. The present cool temperate marine climate on the US eastern seaboard north of Cape Hatteras (northernmost North Carolina and Virginia) reflects the influence of cool southward-flowing currents, and a similar influence can be inferred in the Early Pliocene (Johnson et al., 2017). Change to a warm temperate (or marginally subtropical) marine climate in the Late Pliocene has been ascribed to the impingement on the area of warm, northward-flowing currents, assisted by the absence of a barrier equivalent to Cape Hatteras (e.g. Williams et al., 2009). Seasonally resolved oxygen isotope ( $\delta^{18}\text{O}$ ) data from bivalve shells reveals, however, that seasonal temperature range was often in excess of that characteristic of the area south of Cape Hatteras (influenced by warm currents), and indicates the continuing influence of cold currents from the north (Johnson et al., 2017). Some isotopic evidence of seasonal temperature range from bivalves is consistent with warm-current influence (Winkelstern et al., 2013), but otherwise the evidence points to a different control (probably global climatic change) on the Late Pliocene warming of marine climate on the US eastern seaboard that is shown by isotopic data for annual average temperature.

### References:

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## Approaching proxy data – climate model comparison using lake isotope Proxy System Models

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Proxy System Models (PSMs) allow the quantification of palaeo-climate data and the forward modeling of geological proxies from climate models, providing a crucial link for the comparison of proxy data and climate models and improved understanding of archive systematics. Here we present results of forward modeled lake carbonate isotope values for the last millennium, from the output of two climate models, SPEEDY-IER and CSIRO Mk3L, using a Proxy System Model of intermediate complexity. These results are compared to validation exercises, comparing more complex, tuned, site-specific versions of the PSM to monitored lake sites in Turkey and the UK. Although the PSMs work well for individual lakes, driven by local meteorological data, they struggle to produce time series with similar amplitude and low frequency variability to long-term core records of  $\delta^{18}\text{O}$  change when driven by climate model output. Spatially, however, global gradients of lake carbonate  $\delta^{18}\text{O}$  are reconstructed reasonable well by the forward model. We show the importance of understanding present day isotope hydrology, from the monitoring of local and regional water vapour, precipitation and lake waters, to improving our PSMs and allowing better comparison between climate models and lake sediment isotope records.



## The oxygen-17 excess of stratospheric and oceanic nitrous oxide

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Tropospheric nitrous oxide (N<sub>2</sub>O) displays an oxygen-17 excess of  $\Delta(^{17}\text{O}) = (0.9 \pm 0.1) \text{‰}$  (relative to VSMOW). The origin of this oxygen-17 excess is under debate: Tropospheric and stratospheric in-situ N<sub>2</sub>O sources as well as isotope fractionation and exchange during biological N<sub>2</sub>O production are all considered to make a contribution, as might the stratospheric photolysis sink. More measurements are required to constrain the relative contributions of the different processes and to improve our understanding of the underlying atmospheric chemical and microbial processes.

Here, we report measurements of the oxygen-17 excess of N<sub>2</sub>O in mid-latitude stratospheric samples, from altitudes between 8 and 26 km. N<sub>2</sub>O was extracted cryogenically at 77 K, separated from other condensable gases using a PoraPlotQ pre-column and then thermally decomposed in a gold furnace at 900 °C (Kaiser et al., 2007). The standard uncertainty of the oxygen-17 excess for repeat analysis of a 5 nmol N<sub>2</sub>O aliquot was 0.3 ‰.

This new dataset significantly enhances the altitude range of oxygen triple isotope measurements in stratospheric air. Previous results were limited to the lower stratosphere between 8 and 12 km (Cliff et al., 1999). The average  $\Delta(^{17}\text{O})$  value of the stratospheric samples analysed here is  $(-0.19 \pm 0.46) \text{‰}$  relative to tropospheric N<sub>2</sub>O. Since the  $\Delta(^{17}\text{O})$  of stratospheric N<sub>2</sub>O is not significantly different to tropospheric N<sub>2</sub>O, these data suggest that the tropospheric oxygen-17 excess is not due to the stratospheric return flux. This rules out stratospheric photolysis or reaction with electronically excited oxygen atoms as source of the oxygen-17 excess in N<sub>2</sub>O. It confirms that the  $\Delta(^{17}\text{O})$  value may be related to tropospheric in situ sources, e.g. NH<sub>2</sub>+NO<sub>2</sub> (Röckmann et al., 2001), or to microbial nitrogen conversion reactions (Kaiser & Röckmann, 2005; Kaiser et al., 2004).

To investigate the latter hypothesis, we have measured the oxygen-17 excess of oceanic N<sub>2</sub>O.  $\Delta(^{17}\text{O})$  values between 0.1 and 4.6 ‰ (relative to VSMOW) were observed during three field campaigns in the temperate, subtropical and tropical Atlantic Ocean, the Scotia Sea and the Weddell Sea. This shows that the  $\Delta(^{17}\text{O})$  of oceanic N<sub>2</sub>O was not in equilibrium with the atmosphere, indicating a potential biological source for the oxygen-17 excess.

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## Fractionation of inorganic phosphate oxygen isotopes during mineral dissolution by microbially produced organic and inorganic acids

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Inorganic phosphorus (Pi) is an essential macronutrient for all organisms playing an integral role in the structure and function of key biomolecules. The dominant source of Pi to the environment comes from minerals such as apatite. The release of Pi depends heavily on pH and the concentration of soluble Pi in soil is usually very low. However, some bacteria are able to solubilise relatively insoluble inorganic phosphate compounds through the production of organic and inorganic acids. The oxygen isotope compositions of phosphates ( $\delta^{18}\text{OPO}_4$ ) have been used to track Pi sources and investigate Pi biogeochemical cycles. During biological processing, oxygen isotope exchange occurs between phosphate and water resulting in a temperature dependant equilibrium  $\delta^{18}\text{OPO}_4$  composition. In the natural environment, phosphate is only completely cycled when present at low concentrations and as a limiting nutrient. At high phosphate concentrations,  $\delta^{18}\text{OPO}_4$  values fall between the source material and equilibrium values. It is not known whether this is a two component mixing between source and equilibrium  $\delta^{18}\text{OPO}_4$  values or whether other processes are fractionating the source material. It is also unclear what isotope fractionation (if any) occurs during partial dissolution of minerals by organic acids, and what effect different organic acids have (recent studies suggest that phosphate release is highly dependent on the type of organic acid). The aim of this study was to determine the stepwise fractionation of phosphate oxygen isotopes during microbial dissolution of a pure apatite mineral by examining a range of organic and inorganic acids and the effects of two different phosphate solubilizing bacteria. The experiments were as follows: 1) A Burkholderia sp. and a Bacillus sp. were grown in a minimal growth media with apatite as the sole source of Pi; 2) The minimal growth medium with apatite and the addition of a) acetate b) oxalate, both to a final concentration of 1 mM and c) HCl to a final pH of 2. For the biological experiments, the media were sampled during the lag, log and stationary phase of growth. The abiotic experiments were sampled to obtain a Pi concentration equivalent to the biological samples. Analyses included cell counts, pH, temperature and  $\text{PO}_4$  concentrations, and samples were taken for  $\delta^{18}\text{OPO}_4$  and  $\delta^{18}\text{OH}_2\text{O}$ . Initial results show that bacterial uptake and fractionation is likely to be species specific and that abiotic and organic acid dissolution is small but variable. Future research will focus on expanding the range of organic acids and phosphate solubilizing bacteria used to further define the fractionation effects from abiotic and organic acid dissolution. These data will aid understanding of Pi  $\delta^{18}\text{OPO}_4$  fractionation effects and improve our understanding of soil Pi biogeochemistry.



# The isotopic characterisation of tetraether lipids (GDGTs) by high temperature GC-IRMS

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Large polar compounds such as glycerol dibiphytanyl glycerol tetraether lipids (GDGT) are widely used as biomarkers for organisms or biogeochemical processes (Schouten et al., 2013) and, similar to other lipids such as leaf waxes, their stable carbon and hydrogen isotopic composition bear the potential to provide large amounts of information about source organisms, provenance, hydrology and biogeochemistry. However, due to their high molecular weight, intact GDGTs are not amenable to conventional compound specific isotope ratio mass spectrometry (GC-IRMS) which routinely only allows oven temperatures up to 320°C. High temperature GC-methods (HTGC, up to 430°C) on specialised equipment, on the other hand, has been applied to the analysis of GDGTs in biomass (Nichols et al., 1993; Sutton and Rowland, 2012) and environmental samples (Lengger et al., in prep), but there are no reports of HTGC-IRMS systems, most likely due to their enhanced complexity. Here, we present the development of HTGC-IRMS, and the stable hydrogen isotopic composition of GDGTs in environmental samples.

HTGC-IRMS employed elevated temperatures (400°C), a short, HT-stable column, and a modified interface. The system allowed the use of an *n*-alkane standard mixture for normalisation onto the V-SMOW-SLAP line (Mix B, A. Schimmelmann, University of Indiana), as well as the accurate determination of the  $\delta^2\text{H}$  values of high molecular weight standards: a C<sub>40</sub>, C<sub>50</sub> and C<sub>60</sub> *n*-alkane, and of triacylglycerides (C<sub>45</sub>-C<sub>69</sub>, 10 ‰ precision, comparison to bulk EA-IRMS). GDGTs from a sample from a Black Sea methane seep microbial mat, and polar fractions obtained from a mixture of marine sediments, and an ombrotrophic peat bog, were analysed. The GDGTs from the methane seep showed, as expected,  $\delta^2\text{H}$  values very close to those of other lipids from the same source organisms. GDGTs in the marine sediment sample differed from GDGTs in terrestrial samples, and from bacterial tetraether lipids, indicating that these values are related to both source water  $\delta^2\text{H}$  values and microbial metabolism, and warrant further investigation.

HTGC-IRMS, for the first time, revealed the stable hydrogen isotopic composition of GDGTs. Better knowledge of isotopic distributions of GDGTs and other large, polar biomarkers will enable their application to provenance and source determinations, and hydrological and biogeochemical paleoreconstructions.

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# A tale of Swine and Strontium; Strontium concentration, radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) and stable ( $\delta^{88}\text{Sr}$ ) strontium isotope systematics in a controlled feeding study

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Non-traditional stable isotope systems utilising mass independent (radiogenic) and mass dependent fractionation are being increasingly used for both modern ecological niche estimation and archaeological provenance and palaeodietary reconstruction employing dental enamel. The expansion of these novel systems is growing with recent studies using Ca, Mg, Fe, Cu, Zn and Sr isotope systems (Jaouen et al., 2013; Knudson et al., 2010; Martin et al., 2015; Reynard et al., 2010). However, the ability of biogeochemists and archaeologists to make effective use of these isotopic proxies is reliant on both a detailed understanding of the biogeochemical behaviour of the element in question and, most crucially, the isotopic discrimination that might occur between diet and consumer tissues, i.e. the trophic level effect.

We present the results of a study to investigate the strontium concentration ([Sr]), radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) and stable strontium ( $\delta^{88}\text{Sr}$ ) isotope systematics in a controlled feeding experiment on domestic pigs designed to simulate terrestrial versus marine protein consumption. We find that, in line with other workers, [Sr] of tissues and diet increases with marine protein consumption, consistent with the marine realm being enriched in Sr. The results of the radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) analysis offer a validation of the use of strontium isotopes for provenance studies. We confirm that the radiogenic strontium isotope composition of dental enamel does represent the radiogenic strontium isotope composition of the diet, modified only marginally by drinking water. The results of the  $\delta^{88}\text{Sr}$  analysis have revealed a distinct shift of  $0.322 \pm 0.060$  ‰ towards isotopically light Sr with trophic level. The magnitude of this shift is consistent with the predictions from the analogous shift observed in calcium isotopes. This is the first time that trophic level fractionation in  $\delta^{88}\text{Sr}$  has been identified in a controlled setting.

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## Catchment-scale lake Nitrogen isotopes from sediments of headwaters to terminal basins and their relationship to algal community change

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The Windermere catchment, English Lake District comprises 11 upland tarns (>100 m.a.s.l.) and lowland (<100 m.a.s.l.) lakes which feed into Windermere, England's largest and longest lake. Fossilised algal pigments (light-absorbing compounds found in all photosynthesisers) which are taxonomically specific were quantified for five lowland and two upland lake sediment cores and were used alongside bulk sediment nitrogen ( $\delta^{15}\text{N}$ ) isotopes to help validate N sources and cycling within the Windermere catchment since the 19<sup>th</sup> century. Lacustrine sedimentary algal communities derived from algal pigments revealed catchment-wide increases in autochthonous production over the last ~200 years and is supported by reductions in the Carbon/Nitrogen (C/N) ratios, driven predominantly by wastewater treatment as determined by regression tree analyses. However, this source of lake fertilisation was restricted to lowland lakes which received treated and untreated effluent. Stable  $\delta^{15}\text{N}$  and C/N ratios revealed that atmospheric reactive nitrogen (Nr) deposition which is high in this region, could have been another important nutrient source across the catchment. This was indicated by declines in  $\delta^{15}\text{N}$  beginning ~1900 in the upland tarns, which corresponded to declines in the C/N ratio and increases in chlorophyll a, a pigment found in all algae. Interestingly stable carotenoids derived from different algal groups mainly decrease at this time which could be a result of recovery from Industrial Revolution derived acidification. Further investigations are currently been undertaken to help determine if indeed there has been a fertilisation effect of Nr on these oligotrophic uplands by looking at species changes of diatoms. Diatoms are algae which have siliceous cell walls and so, are well-preserved in sediments. Different diatom species also have different environmental tolerances to for example nutrients and pH, thus making them ideal to track historical changes in these conditions. Further down the catchment, lowland lakes had typically heavier and asynchronous  $\delta^{15}\text{N}$  signatures attributed to their multiple confounding N sources including heavy  $\delta^{15}\text{N}$  inputs of sewage and agricultural runoff, which in some basins may have masked the relative importance of the lighter Nr deposition signatures. Further, different lake characteristics such as depth, water retention time and catchment to lake area ratio will have also influenced the extent and nature of N cycling both in the catchment and the lake itself. This project offers a unique synthesis into N cycling across a catchment and its influence to lake ecological communities.



## The real “Palaeodiet”: isotopic approaches to past human subsistence

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The analysis of human diet in prehistory tells us much more than just the foods consumed by past populations, since diet reflects the interaction between demography, economy, environment and food production technology.

Over the last three decades, stable isotopic analyses of archaeological remains of humans, animal and plants has transformed our understanding of past human subsistence. This talk will describe the contribution that isotopic analyses have made to the study of palaeodiet, from the Palaeolithic to the recent past, as well as the potential for future developments.



## Effects of cleaning methods upon preservation of isotopes and trace elements in ostracods

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The trace element (Sr/Ca and Mg/Ca) and stable isotope ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) geochemistry of fossil ostracod valves provide valuable information, particularly in lacustrine settings, on palaeo-water composition and palaeotemperature. The removal of sedimentary and organic contamination prior to geochemical analysis is essential to avoid serious bias of the results. Previous isotopic and trace element work on ostracod shells has, however, employed different treatments for the removal of contamination. Beyond simple 'manual' cleaning using a paint brush and methanol under a low-power binocular microscope; for isotopic work pre-treatments include chemical oxidation, vacuum roasting and plasma ashing, and for trace element work sonication, chemical oxidation and reductive cleaning. These studies have shown that the impact of different treatments may vary, depending on species and sedimentary settings. Here, a systematic investigation of the cleaning methods is undertaken using specimens of the ubiquitous euryhaline species, *Cyprideis torosa*. Cleaning methods are evaluated by undertaking paired analyses on a single carapace (comprising two valves); in unaltered individuals the two valves have identical geochemical and isotopic composition. Hence, one valve is subjected to the chosen treatment and the other to simple manual cleaning: any differences in composition can confidently be assigned to the treatment method. We show that certain cleaning methods have the potential to cause serious alteration to the geochemical signal, and hence have implications for palaeo-water or palaeotemperature reconstructions. We propose a recommended valve cleaning approach for trace element and isotopic studies which combines the removal of contamination, and maintains the geochemical signal.



## **It's been a busy few years at Elementar UK**

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A lot has happened at Elementar UK since the last SIMSUG. For starters, we weren't even called Elementar! That changed in January this year but since 2011 we have been working hard creating two exciting new mass specs, a range of innovative new inlet systems and powerful new software packages aimed at significantly improving the tools available to the stable isotope community.

This presentation will take a (very) brief tour through our new technologies and demonstrate how they will help bring about novel insight into new and existing application areas.



## Seasonal net and gross biological oxygen production in a temperate shelf sea from oxygen-argon-ratio and oxygen triple isotopes

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Temperate shelf seas are major carbon sink areas. Quantifying accurately primary production is therefore essential to understand the shelf sea carbon pump and its role in the uptake of anthropogenic CO<sub>2</sub> emissions.

Here we use high-resolution dissolved oxygen-to-argon (O<sub>2</sub>/Ar) ratios and oxygen triple isotopes (<sup>16</sup>O, <sup>17</sup>O and <sup>18</sup>O) to derive estimates of net and gross biological oxygen production in the Celtic Sea during the most productive seasons (spring, summer and autumn) in 2014-2015. O<sub>2</sub>/Ar ratios were measured continuously using a shipboard membrane inlet mass spectrometer (MIMS). Additional discrete water samples obtained from CTD hydrocasts were used to measure O<sub>2</sub>/Ar depth profiles and the  $\delta(^{17}\text{O})$  and  $\delta(^{18}\text{O})$  values of dissolved O<sub>2</sub>.

Calculations of net ( $N(\text{O}_2/\text{Ar})$ ) and gross ( $G(^{17}\text{O})$ ) oxygen fluxes showed higher values during the spring bloom and lowest during the autumn bloom. Continuous  $N(\text{O}_2/\text{Ar})$  underway measurement was on average  $(58 \pm 38)$  mmol m<sup>-2</sup> d<sup>-1</sup> and discrete  $G(^{17}\text{O})$  measurements was average  $(170 \pm 161)$  mmol m<sup>-2</sup> d<sup>-1</sup> during the spring bloom. Results from the summer cruise showed a peak in production just below the mixed layer. These peaks are not detectable by high coverage ocean colour satellite systems, typically used to calculate total annual production. Our results show primary production values at unprecedentedly high resolution in the shelf sea.



# Oxygen isotope values of freshwater gastropod carbonate in temperate fluvial systems; implications for palaeoenvironmental studies in fluvial sequences

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Stable isotopic analysis of freshwater gastropod aragonite and calcite has been used to infer past environmental and climatic conditions, based on the principle that the  $\delta^{18}\text{O}$  value of gastropod carbonate ( $\delta^{18}\text{O}_{\text{carb}}$ ) is controlled by the temperature of mineralisation and the  $\delta^{18}\text{O}$  of the host water ( $\delta^{18}\text{O}_{\text{water}}$ ; Fritz and Poplawski, 1974; Leng and Marshall, 2004). In temperate mid-latitude regions, such as northwest Europe,  $\delta^{18}\text{O}_{\text{water}}$  in freshwater environments is derived from the  $\delta^{18}\text{O}$  of meteoric water, controlled largely by the  $\delta^{18}\text{O}$  of precipitation, which, in turn is strongly related to prevailing air temperature (Darling *et al.*, 2003; Andrews, 2006). Consequently, the  $\delta^{18}\text{O}_{\text{carb}}$  values of carbonate mineralised in these systems is closely related to prevailing air and water temperatures.

This relationship has important implications for the understanding of the climatic regime of many important Pleistocene fluvio-lacustrine interglacial and interstadial deposits. Many of these have important stratigraphic and archaeological significance, for example the MIS 11-aged sequence of Swanscombe, Kent (Bridgland, 1994). These are rich in fossil mollusc remains; however, they frequently lack the biological material used for traditional climate reconstruction. Stable isotopic analysis of fossil gastropod remains from these sequences provides a mean to derive a palaeoclimatic record; however, the application of this technique is limited, due to the paucity of modern analogue studies that allow the relationship between  $\delta^{18}\text{O}_{\text{carb}}$  values and temperature in freshwater gastropod carbonate to be fully understood.

Considering this, this talk will present the results of the first systematic investigation of  $\delta^{18}\text{O}_{\text{carb}}$  values of three gastropod taxa *Bithynia tentaculata* (L), *Radix balthica* (L), and *Valvata piscinalis*; Müller, 1774) in three lowland fluvial systems in southern Britain (River Thames, R. Wey and R. Colne). These results indicate that the  $\delta^{18}\text{O}_{\text{carb}}$  values of carbonate in modern assemblages of gastropod species are consistent with mineralisation in isotopic equilibrium with  $\delta^{18}\text{O}_{\text{water}}$  values, and through several stages can be robustly correlated to prevailing air temperature. Furthermore, interspecies differences in  $\delta^{18}\text{O}_{\text{carb}}$  values are observed in these modern systems, which can be related to differences in the growth patterns of individual taxa. The presentation will conclude by discussing the significance of these results in regards to measured  $\delta^{18}\text{O}_{\text{carb}}$  values from fossil molluscan assemblages in Pleistocene fluvial sequences in southern Britain, and highlighting future areas of refinement to this technique.

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# Source Water Isotope Identification Toolkit (SWIIT) for detecting historical water use by forest trees

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Hydrological regimes are being perturbed globally under climate change, with many regions forecast to become warmer and drier. Given that water availability is a primary determinant of vegetative health and productivity, alterations in the spatial and temporal distribution of this critical resource are expected to significantly impact forest ecosystems. The hydrological limitations on vegetative health are particularly complex in environments where multiple sources of water are potentially available to trees in lowland riparian zones. To anticipate how subsurface hydrological partitioning may evolve in the future, the dynamics of tree water source usage and the potential impacts to overlying vegetation, we require a robust, quantitative framework that is constrained by historical data. Here, we outline a toolkit (SWIIT- 'Source Water Isotope Identification Toolkit') to retrospectively investigate the dynamics of tree water uptake. SWIIT utilises tree-ring isotopes ( $\delta^{18}\text{O}$ ) in combination with a biomechanistic fractionation model to predict the isotopic signature of water utilised during any particular period of growth (seasonal/annual). Through comparisons with measured  $\delta^{18}\text{O}$  in local endmember water sources, and climatic and hydrological variables, this methodology can be used to reconstruct and inform on past ecohydrological interactions. We provide a comprehensive overview of the theoretical basis behind the modelling component and assess the data requirements to constrain its predictions. The toolkit's utility is demonstrated for several riparian field studies characterised by differences in climate, geomorphic and hydrological complexity. Whilst our examples are for riparian areas, we suggest that SWIIT can be applied to a range of forested environments where distinct isotopic endmembers exist. To aid application of SWIIT for data-poor environments, we present a set of tool groups that enable SWIIT's application over a range of data availability and output resolution.

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## Extracting the $\delta^{18}\text{O-PO}_4$ record from carbonate speleothems – methods development and potential applications

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Increases in the application of key nutrients such as phosphate in fertilisers has led to a requirement to understand how these nutrients interact with and leach from soil systems under different environmental conditions. Studies aiming to understand historical pollution and the impact of modern agricultural systems on nutrient losses require long term records of pollution dynamics. Cave speleothem deposits are one of the best potential archives for understanding changing nutrient dynamics, offering high resolution, accurately dated, multi proxy archives of environmental change<sup>1</sup>. Currently, work on speleothem P focuses on changes in P concentration as a proxy for vegetation decay and rainfall intensity. However, phosphate oxygen isotopes ( $\delta^{18}\text{O-PO}_4$ ) have the potential to record changes in the extent of P cycling within overlying soil systems and whether applied fertiliser P is leached rapidly out of the agricultural system. This projects' objective is to develop a method for the extraction and analysis of  $\delta^{18}\text{O-PO}_4$  from speleothems, with a final goal of targeting samples which may help us understand changes P dynamics through recent history. Due to the low concentrations of P in speleothem carbonate (frequently <100ppm) and the finite amount of carbonate material available, we are working to optimise existing methods<sup>2</sup> to work with small volumes of carbonate material (200 to 500 mg). Advances using this technique will allow us to address the following key areas: 1) In  $\text{PO}_4$  rich environments,  $\delta^{18}\text{O-PO}_4$  can inform how the source of  $\text{PO}_4$  may have changed over time, potentially identifying the historical application of fertilisers, 2) In  $\text{PO}_4$  limited systems where biological cycling of P has occurred within the soil zone, speleothem  $\delta^{18}\text{O-PO}_4$  should reflect the  $\delta^{18}\text{O}$  of soil waters. This should help us to understand isotope fractionation between karst water and speleothem carbonate, a critically unresolved question when interpreting traditional carbonate  $\delta^{18}\text{O}$  palaeorecords from speleothems.

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## Stable carbon and nitrogen isotopes of invertebrate remains: a glimpse of food web structure change?

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Assemblages of microscopic remains in sediment records provide a wealth of information about past environments. A further step can be taken by analysing stable carbon and nitrogen isotopes ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) of plant and invertebrate remains. Offsets in  $\delta^{15}\text{N}$  (trophic position) and  $\delta^{13}\text{C}$  (energy source) between organisms gives insights in food web structure and energy flow. Here we present a pilot study from Loch nam Fear in the Flow Country, Scotland. The assemblage composition of macrophytes and invertebrates indicated a distinct change in aquatic community around 1990 reflecting the 1986-9 establishment of a conifer plantation 500m from the lake. A 1-3 permille decrease in  $\delta^{15}\text{N}$  of plant and zooplankton remains suggest that the conifer plantation had a strong impact on nitrogen cycling and possibly led to reduced aquatic food chain length.



## A multi-proxy approach to diet and animal management in the Neolithic of northern Greece

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Palaeodietary and zooarchaeological proxies are widely used to investigate the interaction of humans with their animals and provide insights into economy, diet and herd management practices. Complementary multi-disciplinary techniques are used to bring together multiple lines of evidence to refine interpretations regarding the processing and consumption of commodities [1, 2]. Here, biomolecular and isotopic analyses of lipid residues from ceramic vessels are combined with zooarchaeological studies and stable isotope analyses of human and animal skeletal collagen  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values from Neolithic northern Greece. Lipid residues absorbed in pottery vessels provide a direct reflection of contents of the vessel during use [3]. Fatty acid  $\delta^{13}\text{C}$  values are a reflection of the isotopic composition of diet and an indication of the environment from which they derived [4]. Bulk stable isotope  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values from skeletal collagen represent a long-term dietary average [5]. Results demonstrate the fatty acid  $\delta^{13}\text{C}$  values of lipid residues are consistent with the high abundance of pig and sheep/goat in faunal assemblages. Dairy farming does not appear to have been intensively practised. Animal bulk collagen  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values reflect a largely terrestrial diet, with the exception of cattle, where relatively enriched  $\delta^{13}\text{C}$  values infer consumption of  $\text{C}_4$  or drought-stressed  $\text{C}_3$  vegetation. This suggests different animal management strategies for cattle, sheep/goat and pigs were practised. Enriched  $\delta^{13}\text{C}$  values observed in cattle are not reflected in  $\delta^{13}\text{C}$  values of ruminant adipose lipids in the pottery or human collagen  $\delta^{13}\text{C}$  values inferring they were not consumed on a regular basis. Differences in animal management are revealed through dietary isotopic variation of ruminant domesticates. Significantly, this would not be apparent in regions where such isotopic differences do not exist. Integration of zooarchaeological and lipid analyses has refined interpretations regarding the species being processed and consumed, revealing the cultural and economic importance of different animals.

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## Subglacial methane sources and sinks – an isotopic approach

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Glaciers and ice sheets have been postulated to serve as an impermeable ‘cap’ on the Earth’s surface, beneath which conditions of pressure, temperature and the presence of organic matter form the perfect cocktail for the production and entrapment of methane from biogenic and geological sources. During disintegration of the overburden ice mass through climatic warming, instability of sub-cap methane reserves are suggested to control the release of natural methane emissions to the atmosphere. However, progress in understanding the role of glaciers and ice sheets in methane generation is currently based solely on pressure-temperature relationships, biological rates of methane production from laboratory investigations and observations of seeps beyond the ice margin. There is a lack of direct field based evidence from contemporary ice masses, and therefore a lack of scientific consensus regarding the role of glaciers and ice sheets in contributing to the methane budget. Here, we present direct field based evidence of methane release from beneath a contemporary Icelandic glacier. Despite Icelandic glaciers typically overlying active geothermal zones, isotopic signatures suggest methane production is predominantly biogenic. The estimated annual flux of methane from beneath this single glacier (10,000 to 20,000 tonnes per year) is sufficient to rival the methane output obtained through total European subaerial geothermal and volcanic degassing. This raises the distinct possibility that other valley glaciers containing ice at the pressure melting point may generate biogenic methane in-situ at the ice bed interface. Providing conditions of low redox status enable the transport of methane to the glacier snout, ice of temperate or polythermal regime may be able to contribute significant quantities of methane to the bottom-up inventory. We discuss techniques associated with field sampling of methane gases, including development of a mobile methane laboratory and the possibility of using clumped isotope analysis to distinguish between methane sourced under differing thermal conditions.



## Abstracts – Poster Presentations

(In alphabetical order of presenting author)



# Stable carbon isotope analysis of Atlas cedar (*Cedrus atlantica*) pollen; an indicator of moisture availability, and its potential for climate reconstruction

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Stable carbon isotope analysis on plant tissue can be used for a range of applications, including climate reconstruction of past environments (Dawson et al., 2002) due to the strong relationship between the carbon isotopic composition of plant tissues and moisture availability (Farquhar et al., 1989). Equally, pollen exhibits a similar relationship, and due to its highly resistant nature, preserving in geological archives for millions of years (Traverse, 2007), allows for very long-term climate reconstruction. The Atlas cedar is a mountain conifer endemic to Morocco and Algeria, growing across the Rif, Middle and High Atlas mountain ranges at elevations of 1400–2600 m (Farjon, 1990). Atlas cedar is sensitive to climate, particularly moisture availability (Rhanem, 2011; Linares et al., 2013) and is threatened by future climate change. It has been present in Morocco since at least the last glacial maximum, with evidence of a southern European presence millions of years ago (Magri et al., 2017). We analysed the stable carbon isotope composition of modern pollen samples from 93 Atlas cedar trees across the Middle Atlas, Morocco and a wider environmental gradient including Europe and USA. We find a strong relationship with summer precipitation ( $r^2 = 0.63$ ,  $p < 0.0001$ ) and aridity ( $r^2 = 0.86$ ,  $p < 0.001$ ), measured using the self-calibrating Palmer Drought Severity Index (scPDSI), suggesting that pollen records the climate signal during its summer development period. These relationships suggest that fossil pollen could be used for quantitative climate reconstructions in the region, and work has started on two case studies to test the application of this technique. Pollen from a cedar-rich terrestrial sediment archive located at Col Du Zad (Campbell et al. *in draft*), and a lake archive from Sidi Ali (Zielhofer et al., 2017) will be analysed to understand the shifting climate in Morocco of the past 10,000 years, with a view to improve our understanding of climate change impacts.

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## The fate of plant wax derived hydrocarbons in a leaf-cutter ant colony

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The distribution and  $\delta^{13}\text{C}$  values of hydrocarbons may be used as proxies for palaeoenvironmental vegetation recorded most commonly within marine, lacustrine and cave deposits (e.g. Rommerskirchen et al., 2003). In the case of dry caves, bat and bird guano deposits, produced after ingesting insects external to the cave, sustain a whole community of fungi, bacteria, and invertebrate detritivores. Hydrocarbons in these guano piles may be used to provide a historical record of primary photosynthetic producers at the beginning of the food chain such that large shifts in vegetation type, e.g. forest to grassland, may be determined (e.g. Wurster et al., 2010). A colony of leaf cutter ants represents a relatively simpler ecosystem in which the carbon flow from the original vegetation may be investigated. Of particular interest is the preservation of any qualitative information conferred by *n*-alkane homologues constituting the primary proportion of plant wax from the originating vegetation.

Hydrocarbon distributions and  $\delta^{13}\text{C}$  values were determined for the various stages of processing of the vegetation harvested by an experimental colony of leaf-cutter ants (*Acromyrmex octospinosus*). Samples, representative of four stages of organic matter transformation in the colony: leaf tissue, fungal garden upper-layer, fungal garden lower-layer and a waste dump were analysed. The hydrocarbon content of the ants was also characterised at various time points in a resource-switch experiment, conducted over four months, between privet (*Ligustrum vulgare*), a  $\text{C}_3$  photosynthesiser, and maize (*Zea mays*), a  $\text{C}_4$  photosynthesiser. *n*-alkanes derived from each stage revealed the preservation of a molecular distribution indicative of the original vegetation resource. Conversely, hydrocarbons isolated from the ants exhibited no such preservation of a resource derived *n*-alkane signature and were dominated by a series of  $\text{C}_{39}$ - $\text{C}_{47}$  dienes and trienes. Determination of  $\delta^{13}\text{C}$  values for individual ant hydrocarbons, sampled over the course of the resource-switch experiment, revealed an initial lag in the assimilation of new carbon which lasted about 15 days. Subsequent,  $\delta^{13}\text{C}$  values became less depleted indicating incorporation of new  $\text{C}_4$  derived carbon and, after 4 months, all hydrocarbons had either reached or were very nearly at equilibrium with carbon from the new resource. This study demonstrates that whilst molecular distributional information may be lost due to uptake and processing of organic matter by insects, i.e. cave deposits, compound specific stable isotope analyses may still provide useful information about previous environments.

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## Silicon isotopes measurement by MC-ICP-MS, a new approach for low concentration

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Silicon isotopes are a powerful tool for the study of the biological consumption of silicic acid by key organisms such as diatoms, since the lighter isotopes of silicon are preferentially uptaken up. However, the exact fractionation of silicon isotopes during biomineralization, and the biochemical pathway responsible for the fractionation, are unknown. In order to investigate the fractionation during the active uptake of silicon, field or culture studies must be carried out under very low silicic acid concentration (below approximately 10 $\mu$ M) challenging existing methodologies.

Here we show the reproducible measurement of  $\delta^{29}\text{Si}$  of reference standard solutions from 0.4 to 0.1ppm Si measured by Multi-collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS, Finnigan Neptune, Bristol Isotope Group) with new analytical settings. We have used 10<sup>12</sup>  $\Omega$  resistors on Faraday cups L3 and C to measure isotopes <sup>28</sup>Si and <sup>29</sup>Si respectively, followed by a magnet jump to measure <sup>24</sup>Mg and <sup>25</sup>Mg. Instrumental mass-bias was corrected internally by doping with a magnesium isotopic standard, and externally by standard-sample bracketing. Reproducibility of a biogenic silica standard was improved by using additional gas and careful avoidance of interferences, which were isolated using peak-flatness tests. Our novel method provides a promising new avenue to measuring low Si solutions for applications such as biological culture studies and field studies in oligotrophic surface waters.



# African ivory in transit: sourcing cargo from a 16<sup>th</sup> century Portuguese shipwreck

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Humans have used ivory as a raw material for crafting objects for millennia. During the 16<sup>th</sup> century a considerable amount of elephant and hippopotamus ivory was procured and traded from Africa, and moved over long distances as part of Portuguese sea voyages around the globe.

Whilst mining for diamonds in 2008, mine workers in Oranjemund, Namibia found over 40 tons of cargo from a shipwreck buried under the sand for centuries (Werz 2009; Chirikure et al. 2010). The ship is likely the Portuguese nau *Bom Jesus* which wrecked off the coast of Namibia in 1533 AD, and the artefacts found reveal aspects of European trade and contact with the western African coast in the early 16<sup>th</sup> century (Hauptmann et al. 2016). Among gold and silver coins, copper ingots, and navigational equipment, 100 complete tusks of elephant ivory were preserved in the sands of the so-called "Skeleton Coast". One of the most intriguing questions is the source of this ivory, as the variety of artefacts found on the ship suggests several possible voyages for the acquisition of these goods. We are using a combination of ancient DNA and stable isotope analyses ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) to source the ivory to African habitats. This includes serial sampling of the larger tusks in the cargo to understand isotopic variability in the diets of individual elephants over their lifetime. We compare our shipwreck results to modern, historic, and archaeological isotope data from elephants across Africa. Whilst it was expected due to the outer morphology of the tusks and from historical documents of Portuguese trading ports that the elephants were from forest populations along the western African coast, the initial results suggest that most of the shipwreck ivory cargo came from elephants which were hunted in mixed savanna grassland and woodland habitats in inland western Africa.

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## Oxygen isotope signatures of topsoil and subsoil phosphates in historical field trials

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Historical use of phosphorus (P) fertilizers in UK agriculture has led to an accumulation of P in arable topsoils. The impact of residual topsoil P on subsoil P dynamics is poorly understood. Currently, it is difficult to determine the extent, rate and mechanisms of P fertilizer transport into the subsoil. However, the use of  $\delta^{18}\text{O}\text{-PO}_4$  measurements has the potential to discriminate between transfer pathways – for example, to identify where P leaching is rapid in comparison to biotic cycling of P. In this study we extracted reactive phosphate (Tamburini et al., 2010) from two well-characterised historical field trials in Scotland. The 'Woodlands Field' trials based at Craibstone Estate (SRUC), Aberdeen, include (i) a P fertilizer rotational trial established in 1922 (the 'Old Rotation') and (ii) a pH gradient trial (pH 4.5 – 7.5) established in 1961 ('the pH Rotation'). We show pilot data which indicates some significant differences between topsoil, subsoil and fertilizer  $\delta^{18}\text{O}\text{-PO}_4$  signatures in the Old Rotation. Soils treated with triplesuperphosphate (TSP) (21.0 ‰) showed a distinctive topsoil (20.5 ‰) and subsoil (8.1 ‰) profile. Furthermore, soils in a rock phosphate fertilizer treatment revealed that topsoils (20.1 ‰) were also distinct from the subsoil (17.9 ‰) although less so compared to the TSP treatment. The native soil phosphate under long-standing grass, without agronomic input, had similar topsoil (20.7 ‰) and subsoil (20.4 ‰) oxygen isotope signatures. The successful discrimination between topsoil, subsoil and fertilizer materials shows that the method could be a promising technique for tracing the fate of P in soils. Further work will include a full suite of oxygen isotope analysis of both historical field trials to (i) validate the results presented here and (ii) investigate the impact of soil pH control on TSP transfer mechanisms from topsoil to subsoil.

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## Clumped isotope evidence for episodic, rapid flow of hydrothermal fluids in a mineralized fault system in the Peak District, UK

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We have used clumped isotope thermometry to study a fault hosted hydrothermal calcite vein associated with the Mississippi Valley Type (MVT) mineralization of the southern Pennines, UK. This is the first published data set obtained using a new high precision mass spectrometer, MIRA, optimised for clumped isotope analysis and an associated clumped isotope-temperature calibration. The study, at high spatial resolution, consists of analyses of multiple generations of vein growth in two transects across the vein. The vein grew episodically at temperatures between 40° and 100°C. The oxygen isotope composition of the precipitating fluids in equilibrium with the vein calcite range between  $\delta^{18}\text{O}$  values of -5 and +5‰ VSMOW. The fluid temperatures and isotope compositions lie on a well defined mixing line between a cool meteoric end member, and a warm hydrothermal fluid with an evolved isotopic composition.

We interpret each episode of growth as being associated with an increasing flux of basin derived formation waters and an increasing temperature of precipitation. Heat is conserved in the fluid as it ascends along the fault surface and fluid flow must have been rapid and the pulses short lived. Fluid flow could have been driven by high pore pressures associated with rapid sedimentation, hydrocarbon generation and diagenesis in basin facies of the Visean Bowland-Hodder group. Fracturing of shale units and failure of capillary seals, possibly triggered by uplift, allowed the release of fluids into aquifers within the sediment pile. Transmission of pore fluid pressures from the shales to fault zones may have resulted in fault rupture, enhanced fracture permeability and rapid fluid flow. Vein growth ceased as pore pressures dissipated. Such behaviour is closely related to a seismic valve type model for mineralization.



## Intra-site variability in late Holocene stable carbon isotope records from a tropical wetland ecosystem (Tasik Chini, Peninsular Malaysia)

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Our current understanding of carbon dynamics in the tropical regions mainly comes from studies on main channels of large river systems such as the Amazon (Pereira et al., 2014). The role tropical lakes and wetlands play remains largely unknown, despite the fact that many of these wetlands currently are undergoing rapid environmental change from the combined effects of climate change and human impact on the landscape. The flood pulse wetland ecosystem Tasik Chini (Peninsular Malaysia) is a designated UNESCO Biosphere Reserve site and heavily promoted for ecotourism. Despite this, the lake has been artificially dammed, and the catchment is heavily disturbed by bauxite mining, rubber and oil palm plantations. To investigate the effects of these different anthropogenic drivers on the carbon cycle of the lake ecosystem we retrieved sediment cores from three of the twelve interconnected basins that make up the wetland, including sites that range from pristine to heavily impacted. The cores, which have been individually dated using radiometric techniques (<sup>210</sup>Pb, <sup>14</sup>C), span from 6000 cal yr BP to the present. A comparison of the  $\delta^{13}\text{C}$  and C/N ratios of bulk lake sediment samples to plant and soil material obtained from the Tasik Chini catchment illustrates that the fossil material shows values comparable to those of lacustrine algae and C<sub>3</sub> land plants. The  $\delta^{13}\text{C}$  records of our three cores show opposing results, with trends toward less negative  $\delta^{13}\text{C}$  values in the more pristine sites, but with a trend towards more negative  $\delta^{13}\text{C}$  values in the site located next to a bauxite mine. The differences in trends as well as in observed abrupt changes illustrate the complex nature of carbon cycling in tropical wetlands such as Tasik Chini, and indicate that further research is needed to better understand spatiotemporal trends in the tropical carbon cycle.

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## SEAPORT - a new stable isotope facility at the University of Southampton Waterfront Campus

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The newly established SEAPORT Carbon Laboratories are a research and teaching facility of the University of Southampton located at the National Oceanography Centre in Southampton, UK. It is hosted within Ocean and Earth Science at the University of Southampton. The facility is available for use by staff, students and external clients.

The Stable Isotope Ratio Mass Spectrometry Laboratory (SIRMS lab) is a central part of these laboratories. It was initially established in 1998 and has been completely refurbished in 2015 by the University of Southampton. With the support from the National Environment Research Council (NERC) and the University of Southampton, new instrumentation was added to extend its capabilities in order to serve as a central stable isotope facility for the University and for external clients.

The facility's function is the measurement of light stable isotope ratios of various organic and inorganic materials, such as  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  with dedicated gas source isotope ratio mass spectrometers (IRMS) operated in dual inlet and continuous flow modes. The areas of research comprise geology, biology, chemistry, ecology, medicine and archaeology.

The lab consists of two dedicated laboratory spaces, which have the necessary technical infrastructure to operate several mass spectrometers and peripherals under optimal conditions. The SIRMS lab is permanently staffed with a full time Research Scientist and a Laboratory Technician who oversee the sample preparation, maintenance of the instrumentation, method development and quality assurance/quality control and are actively involved in student, PhD student and postdoc training and teaching.

Here we present an overview of the lab, introduce our new instrumentation and provide some examples of recent research applications.



## Anti-predation strategy, growth rate and extinction amongst Pliocene scallops of the US eastern seaboard

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*Placopecten*, *Chesapecten* and *Carolinapecten* are scallop (pectinid bivalve) genera occurring in the Pliocene of the US eastern seaboard. The first, present in the area today, is a smooth, streamlined form, adept at escaping predators by swimming ('flight' strategy). The other two, which are extinct, are plicate ('ribbed') forms. Plication facilitates a 'resistance' strategy towards predators which is benefited by large size and high shell thickness - maximally so if these states are achieved early in life. Oxygen isotope ( $\delta^{18}\text{O}$ ) profiles show that early ontogenetic extensional growth in Pliocene *Placopecten* was at the same moderate rate as in modern *Placopecten*. By contrast, in *Chesapecten* it was as fast as in the fastest-growing modern scallop (c. 80 mm/annum), and accompanied by development of an unusually thick shell, while in *Carolinapecten* it was substantially faster still (<140 mm/annum). Rapid growth in *Chesapecten* and *Carolinapecten* may have been enabled by high primary productivity, which is indicated by the abundance, diversity and large size of co-occurring vertebrates. The extinction of *Chesapecten* and *Carolinapecten*, and the survival of *Placopecten*, can be attributed to a decline in primary productivity which prevented a maximally effective 'resistance' strategy towards predators but had no deleterious impact on a 'flight' strategy.



## **‘A Pig of a Problem’.**

### **Unpicking $\delta^{15}\text{N}$ trophic systematics at the individual amino acid level**

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Stable nitrogen isotope ( $\delta^{15}\text{N}$ ) measurements in bone collagen are routinely used to assess trophic level in both modern ecological and archaeological palaeodietary contexts. The assignment of trophic level is based on the well-observed phenomena that  $\delta^{15}\text{N}$  increases by between 3 and 5 ‰ between dietary protein and bone collagen. Despite the repeated observations of this phenomena by various workers a detailed understanding of how the nitrogen trophic level effect is driven is still lacking. At a fundamental level all bulk collagen  $\delta^{15}\text{N}$  values are a weighted average (by % N) of their component amino acids and it is changes in the  $\delta^{15}\text{N}$  value of the amino acids that must drive the observed changes in bulk collagen  $\delta^{15}\text{N}$  value.

We present the results of an investigation into the nitrogen trophic level effect using samples from controlled feeding experiment conducted on two successive generations of domestic pigs. The experiment is designed to investigate the effect of marine and terrestrial protein consumption with pigs fed one of five diets of varying marine and terrestrial protein content. We have measured both bulk  $\delta^{15}\text{N}$  values and individual amino acid  $\delta^{15}\text{N}$  values in a wide range of body tissues as well as the feeds to attempt to improve the understanding of the observed increase in  $\delta^{15}\text{N}$  with trophic level.

We demonstrate that both bulk  $\delta^{15}\text{N}$  values and individual amino acids  $\delta^{15}\text{N}$  values are highly correlated with dietary marine protein content. We find that juvenile individuals who have not yet achieved a steady weight have systematically lower  $\delta^{15}\text{N}$  values in bulk tissues and individual amino acids  $\delta^{15}\text{N}$  values compared to mature individuals. Over the range of amino acids studied we find that for all amino acids except lysine, histidine and phenylalanine, the trophic level fractionation in amino acid  $\delta^{15}\text{N}$ , i.e. tissue amino acid  $\delta^{15}\text{N}$  – dietary amino acid  $\delta^{15}\text{N}$ , is not constant with marine protein consumption. This presents a problem for reconstructing trophic position using amino acid  $\delta^{15}\text{N}$  values in complex ecosystems where mixed marine and terrestrial resources may be exploited.



## Isotope Ecology at the NERC LSMSF

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The NERC LSMSF provides organic and light element stable isotope mass spectrometry to the UK life sciences community, and is located at: SUERC, East Kilbride; CEH, Lancaster; and the School of Chemistry, University of Bristol.

Here at the East Kilbride node (LSMSF-EK), we concentrate most of our efforts to stable isotope ecology, principally in applications of stable isotopes to food webs and animal migration.

UK-based researchers may apply to use the Facility via standard peer-review procedures in April and September. The LSMSF-EK plays a key role in training young postgraduate scientists, and staff have been involved in organising the Principles and Practice of Stable Isotope Geochemistry in Earth and Environmental Geosciences course which will run in November 2017 at BGS, Keyworth. As a consequence, the LSMSF provides an excellent mechanism by which PhD students can gain access to the cutting-edge analytical tools and high-quality technical training essential for their research and eventual career paths.

We also carry out ongoing developmental work in anticipation of the analytical requirements of our user base and to keep our technical portfolio state-of-the-art. For instance, we are currently developing a fully-automated cryofocussing unit to measure stable isotope ratios of nanomolar quantities of N and C.

Analysis types available routinely at the LSMSF-EK include natural abundance  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ,  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  value determinations of bulk organic matter. In addition, we provide analyses of  $^{13}\text{C}$ - and  $^{15}\text{N}$  enriched samples,  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  of water samples, and  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC), and  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of carbonates.

If you have an ecology project that would benefit from stable isotope analysis, please come and speak to us.



## **A Viking Age mass burial: using Pb isotopes to further constrain the victims' origin**

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Pb isotope analysis of tooth enamel from 31 individuals recovered from a Viking Age burial pit on Ridgeway Hill (Weymouth, Dorset, England) provides further evidence for their childhood origins outside Britain. A previous study of the groups strontium and oxygen isotope compositions identify a core group of men whose origin is certainly outside of the local area and most likely from a much colder climate underlain by geologically younger rocks. These results, tantalisingly, imply that the tables were turned on a cohort of Vikings who, having launched a raiding party on the Dorset coast, were captured and executed by the local population. In an attempt to further refine the provenance of these individuals, we have extended the multi-isotope approach to include analysis of the groups Pb isotopes. Our results and conclusions are presented here.



## Effect of soil pH on the $\delta^{18}\text{O}_p$ of plant available phosphorus in soils from the Park Grass Continuous Hay experiment

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The isotopic composition of oxygen (O) associated with phosphorus ( $\delta^{18}\text{O}_p$ ) has the potential for characterizing phosphorus (P) cycling in the soil/plant system because P is mostly associated with O. Biological processes cause exchange of O between phosphate and ambient water. It is known that the inorganic pyrophosphatase (PPase) leads to a temperature-dependent equilibrium between the O in phosphate and in water. Other hydrolysing enzymes typically have a negative fractionation factor, leading to the release of phosphate depleted in  $^{18}\text{O}$  compared with the original organic P compound. The fractionation factor for the two common hydrolysing enzymes acid and alkaline phosphatase is -10 and -30 ‰, respectively. Furthermore, the uptake of phosphate by organisms can lead to isotopic fractionation, potentially depending on the organisms. However, there is still a large knowledge gap regarding the effect of soil characteristics on soil  $\delta^{18}\text{O}_p$ . In this study, we focus on the effect of soil pH on the  $\delta^{18}\text{O}_p$  of plant available P. We hypothesize that differences in the species composition and the presence/absence of certain enzymes at a low soil pH (pH  $\leq$  5) compared to a soil with a high pH (pH  $\geq$  7) will be reflected in the  $\delta^{18}\text{O}_p$  of available P.

To test our hypothesis, we analysed the  $\delta^{18}\text{O}_p$  of plant available P in soil samples taken from selected plots of the Park Grass Continuous Hay experiment, located at Rothamsted Research, Harpenden, UK. This experiment was established in 1856 to test the effects of different mineral fertilisers (nitrogen (N), P, potassium (K), sodium (Na), magnesium (Mg)) and organic manures on hay production. In 1965 the main plots were divided into four sub-plots, three of which received applications of lime to maintain a target soil pH of 7, 6 & 5, while the fourth received no lime. For this study, three fertiliser treatments were selected: a) an unfertilised control, b) N, P, Mg, K, and Na applied, and c) P, Mg, K, and Na applied. Soil samples were taken from the limed (pH 7) and unlimed sub-plots. Soil cores were divided into three depths: 0-10, 10-20, and 20-30 cm. Plant available P was extracted from fresh soil samples using anion exchange resin membranes. The extracts were purified stepwise and silver phosphate was precipitate as final analyte. The oxygen isotopic composition of the silver phosphate was determined via TC/EA-IRMS.

Regardless of the treatment or soil depth, the  $\delta^{18}\text{O}_p$  of the available P in the unlimed sub-plots was always more enriched in  $^{18}\text{O}$  compared to the limed sub-plots. We conclude that this pH effect is mainly caused by the presence/absence of certain enzymes and/or microorganisms due to the long-term differences in soil pH. Our preliminary results indicate that the  $\delta^{18}\text{O}_p$  can be a useful tool to determine the contribution of certain enzymes and/or soil microorganisms to P cycling in the soil-plant systems under field conditions. However, further studies are necessary to confirm our results under different conditions e.g. land use, management and climate.



# Magnesium isotope signature in an arable soil profile in Germany

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## Abstract

The emerging use of non-traditional stable isotopes systems in geological fields in recent years may provide an innovative tool to characterize the elemental cycles in soil-plant systems. In this study, we present for the first time magnesium (Mg) isotope signatures in soil profile from an arable field in western Germany. The soil in this field is Luvisol type and with mustard grown for years. The soils were sampled in spring 2015 before crop planting with a drilling core down to 100 cm depth. Plant available and potentially available Mg was extracted by pressurized microwave digestion (turboWAVE 1500, MILESTONE, Italy) with concentrated HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> to assess Mg nutrient levels in both topsoil (0-30 cm) and subsoil (below 30 cm). The subsoil indicated a large soil Mg pool compared with the topsoil. Soil Mg isotopic composition ( $\delta^{26}\text{Mg}$  with reference to standard material SRM 980) showed that Mg in topsoil was relatively lighter than Mg in subsoil. This may be likely due to that plants preferentially take up heavy Mg isotopes, leaving isotopically light Mg in the topsoil relative to its counterpart in the subsoil where the effect of plant uptake is much less intensive. Therefore, the Mg isotope signature can potentially yield significant information on Mg transports in soils and clarify important nutrients uptake processes by crops.

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## Antarctic Peninsula glacial discharge: exploiting the diatom stable isotope record

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The Antarctic Peninsula has undergone dramatic changes in climate over the last 50 years leading to the acceleration and retreat of 90% of marine terminating glaciers, and a loss of ice sheets that is unprecedented in the previous 11,000 years. As such, the Antarctic Peninsula accounts for 28% of the contribution of mountain glaciers and ice caps to global sea level rise ( $0.22 \text{ mm a}^{-1}$ ), and 25% of the total mass lost from Antarctica. However, the instrumental record is too short (50 years) to ascertain if these observed changes are part of a longer (centennial) natural cycle or an exceptional event, and to ascertain the mechanism forcing these changes. With this in mind, it is imperative to develop proxy records of glacial discharge to place modern observations into a longer temporal context. The novel approach of combining quantitative diatom species assemblage counts and diatom-derived oxygen isotopes from marine sediment cores can be used to develop proxy records of glacial discharge extending further back in time than instrumental records, and can elucidate the relative contributions of the atmosphere and ocean in forcing the recent mass loss.



## Reconstructing wildebeest migration routes using $\delta^{34}\text{S}$

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Movement throughout the environment is a key aspect of the ecology of migratory species, and understanding this is crucial if conservation efforts are to be successful. However, conventional methods of tracking animals in the wild are associated with a number of limitations. Intrinsic bio-marker methods, such as stable isotope analysis, offer a non-invasive solution to many of these issues.

The stable isotope signature of an animal's tissues will reflect that of its local environment at the time of tissue synthesis. Keratinous tissues, such as hair, are continuously grown and therefore contain a 'timeline' of this isotope data – this has the potential to allow reconstruction of an animal's movements as it passes through isotopically distinct environments. While hydrogen isotopes are most commonly utilised for this purpose, previous research has been largely concerned with North American and European systems. There are many complicating factors regarding the use of hydrogen isotopes in African systems, so considered here is the potential use of a different isotope – sulfur.

The analysis of sulfur isotopes has a variety of ecological applications in terrestrial systems, from identifying the source of dietary components, to indicating presence of pollution and uncovering details of plant physiology. However, the focus here will be on the use of  $\delta^{34}\text{S}$  as a further proxy for location and movement. This is possible as sulfur isotopes are influenced by local geology and vary with differing underlying bedrock and soil microbial processes. Thus, variation over the length of hair may correlate with migration between distinct geological units. Here, GPS-tagged blue wildebeest (*Connochaetes taurinus*) from the migrant population in the Serengeti are used to assess the accuracy of utilising  $\delta^{34}\text{S}$  to infer movement. In addition to this, individuals from the small population of wildebeest that remain resident in the Serengeti's western corridor year-round will be used as a control.



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## Meeting Notes





