

**Geochemistry Group
Research in Progress Meeting**

**New developments and
novel applications in
isotope geochemistry**

Monday 3rd March 2008

The Geological Society, Burlington House, Piccadilly,
London

The logo for nu instruments features a blue checkmark on the left, followed by the text "nu instruments" in a blue, italicized serif font.

IsotopThe logo for Isotop X consists of the word "Isotop" in a bold, black sans-serif font, followed by a large, stylized "X" that is blue with horizontal white stripes.

The logo for Isoprime features a stylized, multi-colored circular emblem composed of overlapping loops in green, yellow, blue, and red, followed by the word "Isoprime" in a grey sans-serif font.

New developments and novel applications in isotope geochemistry

Oral program

- 09.30 am** Registration, Poster set up and Tea/Coffee
- 10.25 am** Welcome address
- 10.30 am** **Invited Lecture:** Stable isotopes in sedimentary carbonates: 60 years young and still a lot to learn
Julian Andrews, University of East Anglia
- 11.00 am** Diatoms and stable isotopes from Lake Challa, Kilimanjaro.
Elizabeth Turner, Lancaster University
- 11.15 am** Selenium isotope ratios over the last 500 ka from the Cariaco Basin, Venezuela
Andrew Shore, Leicester University
- 11.30 am** Dust Flux to the Eastern Mediterranean over the Last Glacial Maximum
Matthew Box, Leeds University
- 11.45 am** The marine Pb isotope response to ice sheet growth and decay at the last glacial maximum
Kirsty Crocket, Bristol University
- 12.00 pm** The behaviour of lithium isotopes in glacial rivers
Josh Wimpenny, Open University
- 12.15 pm** Understanding growth controls in colloform sphalerite using combined chemical, crystallographic and S isotope analysis
Craig Barrie, Liverpool University
- 12.30 pm** Geochemistry Group AGM
- 12.40 pm** Lunch and Poster Session
- 1.30 pm** **Invited Lecture:** Mass independent Ni isotopic fractionation in bulk meteorites
Tim Elliott, Bristol University
- 2.00 pm** The Cadmium Isotope Composition of Ferromanganese Crusts
Tristan Horner, Imperial College
- 2.15 pm** Volcanic Outgassing and the TI Isotope Composition of the Oceans
Richard Baker, Imperial College
- 2.30 pm** Determination of Ce isotopes by thermal ionisation mass spectrometry
Matthias Willbold, Bristol University
- 2.45 pm** Laser ablation MC-ICP-MS Pt-Re-Os isotope study of platinum-group alloys: exploiting the Pt-Os chronometer
Jude Coggon, Durham University
- 3.00 pm** Origin of Cr-diopside in peridotite xenoliths: Recent metasomatic addition revealed by a micro-sampling, trace element and Sr isotopic study of on-craton and off-craton peridotites
Jacqueline Malarkey, Durham University
- 3.15 pm** Afternoon Tea and Poster Session

- 3.45 pm** Age resolution of polymetamorphic events in the Scottish Northern Highlands using Lu-Hf methods
Anna Bird, Royal Holloway University of London
- 4.00 pm** The age of isotopic enrichment on Snæfellsnes
Christina Manning, Royal Holloway University of London
- 4.15 pm** Melt productivity of ocean island basalt sources: Evidence from U-series
Julie Prytulak, Bristol University
- 4.30 pm** Zinc Isotopes in the Soil-Plant Interface
Tim Arnold, Imperial College
- 4.45 pm** Calcium and potassium isotope analysis in solution and laser ablation mode on an IsoProbe MC-ICP-MS
Matthew Thirlwall, Royal Holloway University of London
- 5:00 pm** Closing remarks & prizes
- 5:05 pm** Wine, nibbles and posters
- 6:00 pm** *Exeunt omnes*

Poster Session

- P1** Fe isotope fractionation and diagenetic pyrite formation.
Romain Guilbad, Edinburgh University
- P2** Post-glacial evidence for the future of the Icelandic Western Rift Zone
Robert Steele, Bristol University
- P3** A noble gas approach to fluid origin in mesothermal gold deposits, Otago and Alpine Schists, New Zealand.
Nicholas Goodwin, Manchester University
- P4** The origin of high $^3\text{He}/^4\text{He}$, high-temperature mantle in the initial eruptions of the Iceland plume
Natalie Starkey, Edinburgh University
- P5** Testing the bipolar seesaw with Pa and Th isotopes in the SW Atlantic
James Rae, Oxford University
- P6** Geochemical proxies in vent mussel shells as indicators of environmental conditions at hydrothermal vents
Jitka Libertinova, University of Wales, Bangor
- P7** Micro solution ICP-MS as applied to ordinary chondrites.
Sarah Gordon, Imperial College, London
- P8** Chemical separation and isotope analysis of nickel in geological and meteoritic samples
Marcel Regelous, Royal Holloway, London
- P9** Lithium and magnesium isotopes in the mantle: mantle heterogeneity or diffusion?
Philip Pogge von Strandmann, Bristol University
- P10** Glacial weathering intensity recorded in the authigenic Hf isotope composition of deep North Atlantic sediments
Marcus Gutjahr, Bristol University
- P11** TOF-SIMS and its application to cosmochemistry
Ashley King, Manchester University
- P12** Possible vital effects in diatom oxygen isotopes
George Swann, NIGL
- P13** Experimental determination of Fe isotope fractionation between liquid metal, silicate and sulfide at high pressures and temperatures
Helen M. Williams, Oxford University
- P14** Isotopic Tracers and Optimised Solutions for High-Precision U-Pb ID-TIMS Geochronology
Dan Condon, NIGL
- P15** New model calculations for the production rates of cosmogenic nuclides in iron meteorites
Katja Ammon, Edinburgh University
- P16** The discussion of using Jurassic belemnites as palaeotemperature indicators
Q. Li, University College, London

- P17** Field, geochemical and age studies of Rhyolite Glaciovolcanism at Oraefajokull Volcano, S.E. *Iceland* – A Window On Quaternary Climate Change
A.J. Walker, Manchester University
- P18** Tracing micrometeorite delivery to Earth with He isotopes in FeMn crusts
Sudeshna Basu, SUERC
- P19** Improving throughput by using sequential multi-element approaches for stable isotopic analyses *Michael Seed, GV Instruments*
- P20** Mesoproterozoic crustal evolution of southwest Norway
Nick Roberts, Leicester University
- P21** An improved method for TIMS high precision Nd isotopic analysis of very small aliquots (1- 10ng) with example application in garnet Sm/Nd geochronology.
Jason Harvey, Birkbeck College, London
- P22** Isotopic fractionation of Fe and S during sulphide-promoted reductive dissolution of Fe oxides *Alison McAnena, Newcastle University*
- P23** Seawater $^{87}\text{Sr}/^{87}\text{Sr}$ ratios and two Late Devonian episodes of perturbations in carbon cycling *Eleanor John, Leeds University*

Oral program abstracts

Stable isotopes in sedimentary carbonates: 60 years young and still a lot to learn

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Stable isotopes of carbon and oxygen in sedimentary carbonate minerals are today a 'standard technique' for environmental and earth scientists curious to learn more about how Earth surface processes work. Much of Quaternary science and palaeo-oceanography is based on stable isotope stratigraphies: without this backbone it is doubtful these disciplines would be where they are today. Much of our understanding of palaeoclimatology is similarly based on stable isotope data, locked up in the crystal lattice of that most humble (or is it infuriating) mineral, calcite (or its polymorph aragonite). This presentation will touch briefly on how our knowledge has progressed from the early years, mentioning a few of the highlights and glossing over the failures.

But mainly we will be looking forward. A lot has changed in the last decade or so. Hardware has improved immeasurably and most of it is proven: we can now sample μg quantities of carbonate, either physically with a mill, or directly with an ion beam. We can run many samples automatically and generate vast data sets of many thousands of analyses. This has particularly advanced the analysis of, for example, terrestrial palaeoclimate records in speleothems where high resolution time-series data probably do require 'more to be better'.

New ideas in the fundamental science often lead to a paradigm shift, and we are probably right at that point now with stable isotopes in sedimentary carbonates. It has recently become possible to examine the ordering or 'clumping' of ^{13}C and ^{18}O into bonds with each other in the calcite lattice. This isotope effect is temperature dependent: more important the temperature dependency is not related to the isotopic composition of the fluid from which the calcite precipitated. This means we no longer have to assume compositions of palaeowaters. Will palaeoclimatologists be released from the 'straight jacket of assumptions' that have limited them in inferring absolute temperature records from archives like speleothems? We can also return to older problems in deep time: were the Phanerozoic oceans warmer or oxygen isotopically depleted in the Palaeozoic? Does atmospheric carbon dioxide concentration drive global temperature in deep time? We might soon know for sure. The next decade looks exciting, but just as John Hudson cautioned 30 years ago in his classic isotope review paper, be prepared for some surprises!

Ghosh *et al.*, 2006. ^{13}C - ^{18}O bonds in carbonate minerals: a new kind of palaeothermometer. *Geochim. Cosmochim. Acta.*, **70**, 1439-1456.

Diatoms and stable isotopes from Lake Challa, Kilimanjaro

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Tropical mountain lake ecosystems are sensitive barometers of CO₂ change on glacial – interglacial timescales due to the slow diffusion rates of CO₂ in water and decreasing atmospheric CO₂ concentrations with elevation. Previous analysis of lake sediments from East Africa have focused on stable carbon isotopes of bulk organic matter ($\delta^{13}\text{C}_{\text{bulk}}$) whose interpretation is complicated by source effects. To refine these existing analyses, a methodology has been developed utilising organic inclusions within fossil diatoms as hosts for carbon isotope analysis. Diatoms respire using dissolved carbon within lakes, thus stable carbon isotopes of diatoms ($\delta^{13}\text{C}_{\text{diatom}}$) should reflect changes in biogenic dissolved carbon flux in response to climate or environmental change. A 25ka (21m) sediment core taken from Lake Challa, 880m altitude on the foothills of Kilimanjaro, forms the backdrop to this study. Presented here are preliminary results of $\delta^{13}\text{C}_{\text{diatom}}$ and the oxygen isotopes of diatoms ($\delta^{18}\text{O}_{\text{diatom}}$) alongside other palaeoenvironmental proxies collected on Lake Challa in connection with the ESF funded CHALLACEA project. Initial results show a clear negative correlation between $\delta^{18}\text{O}_{\text{diatom}}$ and $\delta^{13}\text{C}_{\text{diatom}}$ and a suggestion that $\delta^{13}\text{C}_{\text{diatom}}$ could be a new palaeoproductivity indicator. A positive correlation is found with $\delta^{13}\text{C}_{\text{bulk}}$, reflecting the diatomaceous nature of these sediments, although $\delta^{13}\text{C}_{\text{diatom}}$ is 3 per mille more negative suggesting the frustule proteins are enriched in ¹²C. We also observe a correlation with $\delta^{13}\text{C}_{\text{carb}}$ (C.Wolff pers.com), although the lack of carbonate in sediments older than 6ka and diagenetic effects limit the use of this isotopic host. In developing a new proxy we add to the arsenal of isotopic techniques provided by biogenic silica and enable new insights into lacustrine biogeochemical cycling to be made.

Selenium isotope ratios over the last 500 ka from the Cariaco Basin, Venezuela

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Due to their redox-sensitive nature, and the tendency for mass-dependent fractionation to be induced by redox reactions, some authors have begun investigating whether the isotopes of elements such as Mo, Fe and Se can be used in palaeoredox studies (e.g. Mo [Siebert et al., 2003]). This study presents the first report of selenium isotope ratios as a possible palaeoredox proxy for palaeoceanography.

A record of seawater selenium isotope ratios ($^{82}\text{Se}/^{76}\text{Se}$) has been produced using organic-rich shales from the Cariaco Basin, Venezuela (ODP Leg 165, Hole 1002) spanning the last 500 ka (Marine Isotope Stages 1 – 12). A high sedimentation rate and an alternating laminated – bioturbated sediment sequence has made the Cariaco Basin an ideal natural laboratory for studies of this kind. Previous studies have related the alternating laminated (anoxic) – bioturbated (oxic) sediments to the larger-scale interglacial – glacial changes which characterise this time period (Peterson et al., 1991). We propose differences in the cycling of Se due to variations in water column oxygen content will affect seawater selenium isotope ratios and sediment components deposited from the seawater. In turn this will vary with known interglacial – glacial patterns.

Sediments deposited under an anoxic water column (interglacial) are dominated by organically - bound Se which has little fractionation with the water. In contrast, samples deposited under an oxic water column (glacial) have an increased proportion of authigenic Se which should be enriched in light isotopes relative to the water. However, the data show small differences between glacial and interglacial samples. Furthermore, and counter-intuitively, the measured whole rock $^{82}\text{Se}/^{76}\text{Se}$ ratios display slight enrichment in heavier isotopes during oxic (glacial) periods compared with those from anoxic (interglacial) periods. This can be interpreted as representing a decrease in global anoxic sedimentation which shifts the seawater Se isotope ratio towards a heavier value. Se concentrations correlate with other redox indicators such as Mo and total organic C concentrations. The variations in these proxies represent changes in the productivity and organic matter preservation of the basin.

Peterson, L.C., Overpeck, J.T., Kipp, N.G., and Imbrie, J., (1991) A high-resolution late Quaternary upwelling record from the anoxic Cariaco Basin, Venezuela. *Paleoceanography* 6 (#1), p. 99 – 119.

Siebert, C., Nägler, T.F., von Blanckenburg, F., & Kramers, J.D., (2003) Molybdenum isotope records as a potential new proxy for paleoceanography. *Earth and Planetary Science Letters* 211, p. 159 – 171.

Dust Flux to the Eastern Mediterranean over the Last Glacial Maximum

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Recent studies have increasingly recognised the importance of aeolian dust within the climate system. The available marine and terrestrial records from the Last Glacial Maximum (LGM, 21 ky BP) imply that the increase in atmospheric dust loading was not spatially uniform. No detailed long-term dust record exists for the Eastern Mediterranean (EM) despite its proximal position under the Saharan dust (SD) plume to Europe and western Asia.

Detrital sediments in the Eastern Levantine basin of the EM are derived principally from two sources: the River Nile with its Blue and White Nile tributaries - and SD. These sources are characterised by distinct $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios (Blue Nile (BN) ~ 0.705 , White Nile (WN) ~ 0.710 and SD ~ 0.720).

In this study a ca. 21 ky SD record in the EM has been developed based on a well-characterised marine core situated S.E. of Cyprus (marine core 9501). This core is well dated both by radiocarbon and through correlation with U/Th dated continental speleothem records.

Through Sr isotope analysis we construct a semi-quantitative Saharan dust flux curve for the Levantine basin for the past ca. 21 ky. The results show a decrease in dust flux during the African Humid period 5-9 ky BP compared to both the Holocene and prior to 12 ky BP.

The marine Pb isotope response to ice sheet growth and decay at the last glacial maximum

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Northern hemisphere ice sheet growth during glacial periods caused intense physical erosion over large areal extents, at times as much as 30% of the current global land surface. The contribution of weathering products from the continents to the ocean associated with high latitude glaciation is poorly constrained and hampers efforts to model their impact on glacial/interglacial CO₂ cycles. During the Quaternary, early stage weathering of U+Th rich accessory phases that were freshly exposed during glacial periods is likely to have preferentially released radiogenic Pb to the sub-glacial, pro-glacial, and eventually, marine system. Thus, the seawater Pb isotopic composition might act as a regional proxy for the riverine alkalinity flux to the oceans. Here we discuss the potential of this proxy at high temporal resolution for the last 45 ka at two sites from the NE and NW Atlantic; Feni Drift (ODP Site 980) and Orphan Knoll (IODP Site U1303), respectively.

Pb isotope data from ferromanganese crusts have been used to postulate greater weathering intensity during interglacial periods, but low temporal resolution precluded investigation of the detailed structure of the record at glacial inception and termination. We have applied a tested method of Pb extraction from authigenic Fe-Mn oxyhydroxide phases in marine sediments to obtain higher resolution data from the two ocean cores. Results from both sites exhibit abrupt shifts in Pb isotope ratios to values significantly more radiogenic than obtained from Fe-Mn crust data.

At both ocean sites, ²⁰⁶Pb/²⁰⁴Pb values gradually decrease from elevated values at the beginning of the Holocene period, attributed to enhanced chemical weathering of terrestrial glacial deposits on initial exposure to a warmer, more humid climate. However, significant differences in the data occur during the glacial and deglacial portions of each record reflecting the instability of the Laurentide and British Ice sheets and the related delivery of ice rafted debris to the North Atlantic. The pathway of the Pb signal (pre-formed or authigenic coatings) has yet to be determined and is the subject of ongoing work, however, we consider that the data will eventually offer useful constraints on the magnitude of chemical weathering during the Quaternary.

The behaviour of lithium isotopes in glacial rivers

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Lithium readily fractionates during weathering due to the large relative mass difference between its two isotopes. For this reason Li has been used as a tracer of weathering processes; studies have shown that during weathering the light isotope ^6Li is preferentially taken up by clays and secondary minerals while the heavy isotope ^7Li is enriched in solution.

On geological timescales, weathering of Ca-Mg silicates is the most important climate moderating process. For this reason, understanding of weathering processes is crucial. It is clear that the presence of glaciers in river catchments can affect the weathering process; for example, cation fluxes are higher while silica fluxes are lower compared to non-glacial catchments of the same rock type. In this study, we have investigated the effects of glaciated areas on the behaviour of Li isotopes in rivers from Greenland.

Two types of catchments were studied. These were catchments that received water directly from the ice sheet (glacial), and catchments that had no direct link to the ice sheet (non glacial). The glacial rivers are characteristically dilute and sediment-rich, and have high flow rates and discharge. The intensity of chemical weathering in these rivers is low, because there is little time for the water to interact with the rock. On the other hand, non glacial rivers have much higher total dissolved solids, weathering intensity is high and the rivers are generally supersaturated with respect to secondary minerals.

The Li isotopic composition of the glacial rivers is $\sim 25\text{‰}$; for non glacial rivers it is $\sim 29\text{‰}$. These values are higher than the average $\delta^7\text{Li}$ value of global rivers (23‰). This suggests that although chemical weathering intensity in the glacial rivers is low, Li is still being taken up in to secondary minerals with preferential uptake of ^6Li . Saturation state modelling indicates that there is a positive relationship between $\delta^7\text{Li}$ and the saturation state of Fe-oxide minerals, but there is no relationship between $\delta^7\text{Li}$ and the saturation state of Al-silicates.

The $\delta^7\text{Li}$ value of seawater appears to have increased over the past 8 Ma. Our data suggest that the Li isotopic composition of glacial rivers is not significantly different from non-glacial rivers, so it is unlikely that the onset of Northern Hemisphere glaciation could have been responsible for this rise in seawater $\delta^7\text{Li}$.

Understanding growth controls in 'colloform' sphalerite using combined chemical, crystallographic and S isotope analysis

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Colloform textures are common in sulfide ore deposits and involve the formation of texturally distinct microcrystalline layers. Here we present the results of a detailed study of samples of colloform sphalerite from the Galmoy ore body in Ireland. Detailed petrographic, crystallographic, chemical and *in situ* laser S isotope data reveal a series of layers which can be explained in terms of a 7 stage development history. *In situ* laser S-isotope analysis reveals dramatic variations in the $\delta^{34}\text{S}$ signature from -25‰ to +10‰, indicating the colloforms developed from two distinct sources of sulphur. Values lighter than around -5‰ suggest a bacteriogenic S source, whereas heavier values suggest a hydrothermal source.

Stage 1 in the samples development is characterised by a $\delta^{34}\text{S}$ of -25‰, a strongly bacteriogenic signature. Stage 2 which represents the initial phase of sphalerite precipitation though is characterised by a $\delta^{34}\text{S}$ of between 0 and +5‰ indicating hydrothermal S input. Although these results suggest that bacteriogenic S is still present and these layers have formed through mixing of the two sources. Stages 3-4 show a variable $\delta^{34}\text{S}$ of between -13‰ and -2‰ which is indicative of a prevailing bacteriogenic source with decreasing hydrothermal input. By stage 5 the principal S source is a hydrothermal one and characterised by a $\delta^{34}\text{S}$ of ~+9‰. This suggests that by stage 5 the bacteriogenic S source which was prevalent in most of the previous stages has most likely become exhausted or at least restricted. Stage 6 has a variable $\delta^{34}\text{S}$ of between -2 and -8‰ and suggests that the hydrothermal S source is diminishing and by stages 7 the S source is almost end-member bacteriogenic with a $\delta^{34}\text{S}$ of between -13‰ to -18‰.

Crystallographic analysis using electron backscatter diffraction (EBSD) indicates that discrete layers within the samples show variation in sphalerite crystallographic preferred orientation (CPO). This occurs either in a <100>, <110> or <111> orientation, or in some cases layers have a random orientation of crystals. While there is some correlation between changes in CPO and S source, it is remarkable that the dramatic changes recorded only indicate that the CPO may switch, not what orientation will subsequently develop. This suggests that while S source may play a role in CPO development it is not a primary control. Therefore, other factors such as growth rate, temperature, degree of supersaturation and trace element availability must be controlling the crystallographic orientation within discrete colloform layers.

Mass independent Ni isotopic fractionation in bulk meteorites

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The advent of multi-collector plasma mass-spectrometry (MC-ICPMS) provides the opportunity to investigate large portions of the periodic table previously unamenable to isotopic study. Attractive targets span from the light isotopic systems (Li and B) to U series nuclides. Improved control of mass bias, enhanced sensitivity and throughput have enabled significant advances, even on systems previously accessible TIMS analysis. Coupling the MC-ICPMS with a laser gives rise to further attractive options, not least high resolution isotopic records in ferro-manganese crusts and in-situ hafnium isotopic measurements on zircons. Perhaps the most surprising success of the MC-ICPMS, however, has been its application to work that requires very high accuracy (<5ppm). Here we report the results of such a study on mass-independent fractionation of the Ni isotopic system in extra-terrestrial material.

The Ni isotopic system is a tempting target for studying processes occurring in the early solar system. Ni has 5 stable isotopes of which one (⁶⁰Ni) is the daughter of the short lived ⁶⁰Fe ($t_{1/2} \sim 1.5$ My). Thus Ni isotopic studies can potentially be used to investigate the timing of early Fe-Ni fractionation via measurements of $\epsilon^{60}\text{Ni}$ and heterogeneity in neutron rich, iron-group nuclides (as has previously been identified in ⁵⁴Cr) via $\epsilon^{62}\text{Ni}$.

We separated Ni from bulk meteorites using a three column procedure and analysed the separated samples on a Finnigan Neptune MC-ICPMS, internally normalising to ⁵⁸Ni/⁶¹Ni and externally normalising to bracketing NIST SRM986 standards. Analytical details are presented in an accompanying contribution by Regelous et al. The two standard errors of our analyses are typically ± 0.03 on $\epsilon^{60}\text{Ni}$ and ± 0.06 on $\epsilon^{62}\text{Ni}$. Terrestrial peridotite, basalt and metal separates are within error of NIST SRM986 passed through the same chemistry. We find small (<30ppm), but significant Ni isotopic variability in both $\epsilon^{60}\text{Ni}$ and $\epsilon^{62}\text{Ni}$ magmatic iron and chondritic meteorites. Only the enstatite chondrites have Ni isotopic ratios that are the same as the Earth. The clear $\epsilon^{62}\text{Ni}$ heterogeneity shows imperfect mixing of different nebular nucleosynthetic components between the precursor materials of different meteorite groups. This variability poses difficulties in using variations in $\epsilon^{60}\text{Ni}$ for chronology. However, Ni isotopic variability yields a valuable tool for tracking the provenance of the precursor material of different meteorites and thus genetically linking chondritic and iron groups. Ni is a major, moderately refractory element, present in sufficient abundance for analysis in most meteorites. Significantly, the Ni isotopic similarity of enstatite chondrites and the Earth further supports the common heritage of material that comprises these two bodies. Deriving modern silicate Earth from an enstatite chondrite protolith places important constraints on the processes that occurred on the early Earth.

The Cadmium Isotope Composition of Ferromanganese Crusts

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The geochemistry of Cd in seawater has attracted significant attention over the past 30 years. This interest is based on the nutrient-type marine distribution of Cd, which closely resembles the distribution of phosphate. The origin of this similarity is still disputed, but a number of studies have suggested that Cd is a micronutrient with an important biological function in the oceans. This interpretation is supported by recent Cd isotope data obtained for seawater and cultured phytoplankton. In particular, Ripperger et al. found that Cd-depleted surface seawater typically exhibits fractionated Cd isotope compositions, with $\epsilon^{114/110}\text{Cd}$ values of up to $+38 \pm 6$. This fractionation was interpreted to reflect uptake of dissolved seawater Cd by phytoplankton. Despite Cd concentrations that display the expected increase along the global deep-water pathway, seawater samples from ≥ 900 m depth have uniform isotope compositions of $\epsilon^{114/110}\text{Cd} = +3.3 \pm 0.5$ (1sd, $n = 8$). This constancy indicates that the Cd distribution in surface waters is primarily governed by near-quantitative closed system uptake of dissolved seawater Cd.

The objective of the present study is to investigate whether ferromanganese (Fe-Mn) crusts are useful archives of deep-water Cd isotope compositions. To this end, we have acquired Cd isotope data for the recent growth surfaces of 15 Fe-Mn crusts from the Atlantic, Southern, Indian and Pacific Oceans. These samples were previously characterized for both radiogenic (Nd, Hf, Pb) and stable (Mo, Ti) isotope compositions in a number of studies. The analyses were conducted by multiple collector inductively coupled plasma mass spectrometry using a ^{111}Cd - ^{113}Cd double spike.

All but two of the Fe-Mn crusts display Cd isotope compositions that are identical within uncertainty (about $\pm 1 \epsilon^{114/110}\text{Cd}$) and these samples yield a mean $\epsilon^{114/110}\text{Cd}$ of $+3.1 \pm 0.7$ (1sd) that is indistinguishable from the deep-water Cd isotope value reported by Ripperger et al. This indicates that Fe-Mn crusts record seawater Cd isotope compositions without significant isotope fractionation, and hence they may also reliably archive time-resolved Cd isotope data. Two samples from the South Atlantic and Southern Ocean, however, have slightly lighter Cd isotope composition of $\epsilon^{114/110}\text{Cd} \approx 0$ to $+1$. The origin of this distinct signature is presently unclear but it may be due to remineralization of organic material that records incomplete biological uptake of Cd from surface waters.

Volcanic Outgassing and the Tl Isotope Composition of the Oceans

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Thallium is a conservative element in seawater with a marine residence time of ~20 kyr [1]. It is thus unsurprising that the present oceans have a nearly constant Tl isotope composition of $\epsilon^{205}\text{Tl} = -6 \pm 1$ [2-4]. This uniformity is also expressed in the recent growth surfaces of hydrogenetic ferromanganese (Fe-Mn) crusts, which incorporate seawater-derived Tl by adsorption and display $\epsilon^{205}\text{Tl} = +13 \pm 1$ [2]. While time-series analyses of six Fe-Mn crusts reveal nearly constant Tl isotope compositions over the last 30 Myr, a dramatic change from about +6 at 60 Ma to +13 is observed at about 30 Ma [5]. This change has been confirmed by a recent high-resolution time-series study of the Pacific Fe-Mn crust CD29-2 [6].

Given these systematics, it is not unreasonable to assume that the time-series data reflect a change in the Tl isotope composition of seawater. Of particular interest is the possibility that the trend was generated by larger fluxes of Tl derived from subaerial volcanism in the early Cenozoic. This interpretation is in accord with observations that (i) volcanic emissions presently provide ~30% of the global input flux of Tl into the oceans [1], and (ii) such emissions may display low $\epsilon^{205}\text{Tl}$ due to isotope fractionation by partial degassing. The increase of $\epsilon^{205}\text{Tl}$ from 60 to 30 Ma may furthermore be essentially synchronous with the decrease of atmospheric CO₂, as inferred from B isotope data [7], and a 5‰ shift in the S isotope composition of seawater sulfate [8]. It has been proposed that both of these changes could reflect decreasing rates of volcanic outgassing during the early Cenozoic [7, 8].

Our Tl isotope data from a suite of volcanoes demonstrate that while some volcanic gases have $\epsilon^{205}\text{Tl}$ -values as low as -16, the majority of samples record an isotopic signature much closer to that of the mantle ($\epsilon^{205}\text{Tl} = -2 \pm 1$). Incorporating these values into an ocean model indicate that changes in volcanic Tl flux are unlikely to alter the Tl isotope composition of the oceans. More likely, a change in the relative sizes of the output fluxes (pelagic clays vs. hydrothermally altered ocean crust) can produce the observed variation.

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Determination of Ce isotopes by thermal ionisation mass spectrometry

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Radiogenic $^{138}\text{Ce}/^{136}\text{Ce}$ ratios in geological and cosmological materials are a valuable tracer and dating tool in geo- and cosmochemistry. However, the variation in global $^{138}\text{Ce}/^{136}\text{Ce}$ ratios is small (e.g., 0.03% in ocean island basalts). In addition, the isobaric interference of ^{138}Ba and the influence of the dominant ^{140}Ce ion beam (88.5%) on ^{138}Ce (ca. 0.251%) during mass spectrometric analysis present an analytical challenge. Here, a new technique is reported that achieves a more than two-fold improvement in reproducibility (0.002%; 2RSD) compared to reported methods. The results show that only the measurement of Ce as an oxide species using thermal ionization mass spectrometry (TIMS) combined with the accurate monitoring and correction of the background between the acquired ion intensities can yield accurate and reproducible $^{138}\text{Ce}/^{136}\text{Ce}$ ratios. A comparison of published data for the Ce reference material JMC 304 reveals its isotopic heterogeneity. Therefore, a new reference material has been prepared from ultra-pure Ce metal (Ames Laboratory). It is now available for distribution. An initial characterization of the new reference material yielded a $^{138}\text{Ce}/^{136}\text{Ce}$ ratio of 1.33738 ± 0.000004 ($2s_{\text{mean}}$; $N = 35$) as a working value.

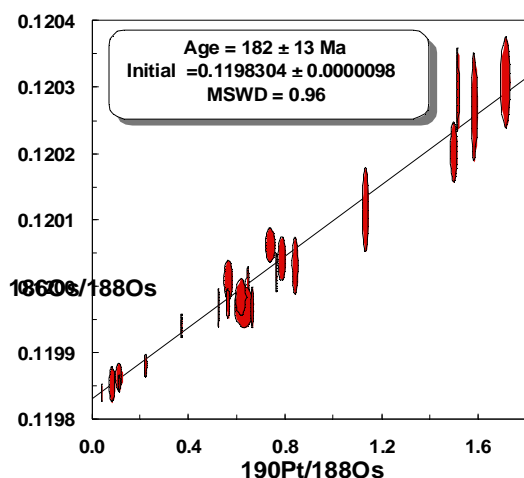
Laser ablation MC-ICP-MS Pt-Re-Os isotope study of platinum-group alloys: exploiting the Pt-Os chronometer

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The origins of detrital accumulations of platinum group element alloys have long been debated. Genetic models range from the result of serpentinisation of peridotites, supergene enrichment, through magmatic crystallisation products to the residual products of mantle melting. Os isotopes are a powerful tool for constraining the origins of such grains, especially when coupled to detailed petrological studies. Since Os is the daughter isotope in two radioactive decay systems, ^{190}Pt - ^{186}Os ($t_{1/2} = 469.3$ Gy) and ^{187}Re - ^{187}Os ($t_{1/2} = 41.6 \pm 0.4$ Gy) it can be used as both a tracer and geochronometer. We have developed a method for the rapid simultaneous acquisition (40s) of Re-Os and Pt-Os isotope data on PGA grains down to $40\ \mu\text{m}$ diameter by laser ablation MC-ICP-MS (Nowell *et al.*, in press). During laser ablation the Re-Os chronometer is analytically non-robust and reliable age information can not at present be retrieved. In contrast, we will show for the first time that the Pt-Os chronometer can be exploited by laser ablation MC-ICP-MS and appears to provide reliable ages (Nowell *et al.*, in press).



We have exploited this Pt-Os chronometer to date ophiolite complexes, which hitherto have been extremely difficult to date, through the analysis of associated detrital PGA grains. Preliminary Pt-Os isotope data for detrital grains from California and Borneo yield Pt-Os isochron ages of 202 ± 8.1 Ma and 182 ± 13 Ma (fig.1) which are close to the best estimates for the Josephine and Meratus ophiolites respectively. Calculated initial $^{186}\text{Os}/^{188}\text{Os}$ ratios are entirely consistent with mantle values.

Figure 1. Multi-grain isochron for Borneo PGAs

Clearly caution must be exercised when interpreting isochron ages based on multiple detrital PGAs which may be unrelated and derived from multiple parent bodies of varying ages. This ambiguity could be avoided by dating individual grains and we will also present both multi-grain and single-grain Pt-Os ages for PGA grains associated with the Central Lapland Greenstone Belt (CLGB). The multi-grain isochron gives an approximate 'average' age for the CLGB whereas the single grain ages provide the age spectrum of parent bodies in the CLGB.

Nowell, G.M., Pearson, D.G., Parman, S.W., Luguet, A., and Hanski, E. 2007. Precise and accurate $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ measurements by Multi-Collector Plasma Ionisation Mass Spectrometry, part II: The application of laser ablation MC-ICPMS to single-grain Pt-Os and Re-Os geochronology. *Chemical Geology* (in press).

Origin of Cr-diopside in peridotite xenoliths: Recent metasomatic addition revealed by a micro-sampling, trace element and Sr isotopic study of on-craton and off-craton peridotites

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The modal abundance of clinopyroxene (cpx), and garnet, in mantle peridotite is a dominant factor in controlling the lithophile trace element budget of the lithospheric mantle. The abundance of cpx, along with garnet, also strongly influences physical properties such as density. It is therefore critical to understand the origin and timing of cpx formation within mantle samples if we are to understand the potential temporal controls on the chemical and physical evolution of the continental lithosphere. Recent work indicates that cpx and garnet may have a young metasomatic origin. This is supported by melting experiments and close examination of natural assemblages that indicate that above approximately Fo_{92} , cpx should be exhausted from the melting assemblage. However, cratonic peridotite xenoliths, with average olivine Fo content of 92.6, contain widely varying cpx contents.

We have investigated the possible origins of cpx within mantle xenoliths from both cratonic and non-cratonic settings via detailed in-situ Sr isotope studies (Micromill and TIMS) coupled with major and trace element measurements. Previously Sr isotopes in cpx have been dominantly analysed using bulk mineral separates. This study is the first to use TIMS to analyse Sr isotope variation between cpx crystals within an individual xenolith. Micro-drilling generally yields between 2 and 10 ng Sr. Purification of this Sr enables accurate interference-free runs via TIMS while aliquotting the dissolved sample enables full trace element analyses to be obtained for all samples.

We present results from two localities: spinel lherzolites from an alkali basalt in the Middle Atlas of Morocco plus a kimberlite-hosted garnet lherzolite from Kimberley, S. Africa, a location with a strongly metasomatised mantle xenolith suite. Cpx from the Atlas samples show a very limited range of $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70342 to 0.70368), coincident with the mode for lithospheric cpx globally, and indicative of a recent, convecting mantle origin. In contrast to this isotopic homogeneity, the samples exhibit a large range in trace element concentrations, with Sr varying in one thin section between 340 ppm and 134 ppm. Cpx are LREE enriched, consistent with a recent, metasomatic addition. This variation does not correlate with the spatial distribution of cpx or with the limited isotope variation. The cpx from Kimberley are much more radiogenic and heterogeneous in $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70587 to 0.70412) but there is no isochronous relationship despite variation in Rb/Sr. These cpx are also uniformly LREE enriched. In general, cratonic peridotite cpx analysed in bulk are less radiogenic than the cpx in the single sample from Kimberley studied in detail. The large range of Sr isotopes recorded by this sample reflects interaction of a melt, originating in the convecting mantle, with a more enriched lithospheric component. The bulk analyses indicate that the convecting mantle derived melt dominates in most cpx formation events but our spatial discrimination shows that this melt is clearly interacting with older lithospherically derived Sr in some instances.

Age resolution of polymetamorphic events in the Scottish Northern Highlands using Lu-Hf methods

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Trace and major element data for garnets from the Northern Highland terrane have been determined using the new RHUL LA-ICPMS system and the Natural History Museum electron microprobe. Garnets show wide variation between the Moine stratigraphic divisions and basement rocks. Morar Division garnets show marked MnO zoning, changing from 0.1 wt% at the rim to 5.8 wt% in the core. Fe and Mg show the opposite trend, with FeO decreasing from 34.7 to 30.8 wt% in the core. Garnet cores are quite homogeneous in samples from southern Morar rocks near Polish and Genuig; the rim is much more heterogeneous and has several inclusions of zircon, apatite and monazite. HREE show a general decrease from core to rim. The chemical differences correlate to textural changes within the garnets. In thin section the garnets form idio to xenoblastic crystals with three different textural zones, with an orange core and the outer two zones being purple or pink in colour. In some garnets there is a planar inclusion fabric which represents a pre garnet fabric, which in some cases is preserved as a smoothly curving inclusion trails. Preservation of these trails is probably the result of garnet growth during continuous deformation. The inclusions in the garnets are smaller than crystals of the same mineral in the matrix, which could indicate that substantial matrix recrystallisation has taken place. Vance et al, (1998) have previously dated garnets from south Morar using Sm-Nd, and achieved 788-823 Ma ages providing strong evidence for Proterozoic (Knoydartian) amphibolite facies metamorphism. We will present new Lu-Hf ages from these garnets. The Lu-Hf ratios from these rocks are much higher than the Sm-Nd ratios; this means they have the potential to yield more precise ages than Sm-Nd. Sm and Nd concentrations are strongly controlled by inclusions in the garnets, whereas Lu and Hf are not, this is another advantage of Lu-Hf dating.

Garnets from a pelitic gneiss from the Glenfinnan Group also show MnO zoning, but to a much lesser extent than the Morar garnets. These garnets have a Ca- and HREE- rich core with many inclusions including apatite, monazite, quartz, and zircon. The zoning is much less obvious in thin section. We have determined Rb-Sr ages from muscovite and biotite of 444.4 ± 1.9 Ma and 414.4 ± 3.9 Ma respectively from this sample, and will present an Lu-Hf age, as the garnet has $^{176}\text{Lu}/^{177}\text{Hf}$ ratios >30 . This indicates the muscovite from this rock was not affected by the Scandian event, however the biotite could in principle reflect post-Scandian cooling, but could equally be post-Grampian.

Vance et al (1998). Extensional versus compressional settings for metamorphism: Garnet chronometry and pressure-temperature-time histories in the Moine Supergroup, northwest Scotland, *Geology*

The age of isotopic enrichment on Snæfellsnes

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The range of isotopic and chemical compositions in Icelandic lavas is commonly interpreted as a product of mixing between isotopically depleted and enriched components, thought to originate from melting an entire section of recycled oceanic crust [1, 2]. In these models the gabbroic section forms the depleted end member and the crustal layer forms the enriched component. Lead isotopic data has shown the mixing relationships to be more complicated than simple binary mixing, indicating that at least 5 separate components are needed to account for the compositional range [3].

The lavas most enriched in incompatible elements in Iceland, representing the closest approach to an enriched end-member, are found on the Snæfellsnes peninsula (SNP) and in the central volcanoes of southern Iceland (SI). We present new Nd-Hf-Pb isotopic data from these areas. The SNP and SI show $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 0.283077–0.283192 and 0.283076–0.283149 respectively. Nd-Hf ratios correlate with incompatible element enrichment, as elsewhere in Iceland, and thus also with Sm/Nd and Lu/Hf ratios.

Samples from the SNP exhibit higher $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ for a given $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ than those from SI forming 2 sub-parallel trends on Hf-Nd isotope and the equivalent parent/daughter diagrams. These correlations are interpreted as resulting from the perturbation of a mantle isochron by recent melting possibly related to the generation of the recycled component beneath Iceland. If this is the case then Lu/Hf and Sm/Nd will have been fractionated during this event and so the Lu/Hf and Sm/Nd isochron ages of $448 \pm 65\text{Ma}$ and $300 \pm 72\text{Ma}$ respectively could indicate the age of the recycled crust. However it is possible that these ages have been reduced by subsequent partial melting. We have developed a method for correcting for the effects of partial melting by quantifying the effects of melting on parent/daughter fractionation. Applying this to our data yields a corrected age of $\sim 450\text{Ma}$ for the recycled component beneath Iceland, consistent with Pb isotope ages [3].

1. Chauvel and Hemond (2000). G3. 1, 1525-2027
2. Kokfelt et al. (2006). J. Pet. 47(9), 1705-1749
3. Thirlwall et al. (2004). GCA. 68(2), 361-386

Melt productivity of ocean island basalt sources: Evidence from U-series

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If fragments of recycled mafic oceanic crust exist and melt as lithologically distinct bodies in the source of ocean island basalts (OIB), then their presence should be discernable by much higher melt productivity at the inception of melting compared to peridotite. Measurements of U-series disequilibrium in young, mafic lavas offers a unique opportunity to investigate physical properties such as melting rate, which we highlight in most cases is primarily dependent on melt productivity. We explore solutions to a simple dynamic melting model using combined ^{238}U - ^{230}Th and ^{235}U - ^{231}Pa disequilibria on lavas from Pico Island, Azores. We find that for the plausible range of partition coefficients, the maximum melt productivity beneath Pico ranges from 0.6 to 6%/GPa (average maximum productivity is 3%/GPa). This is consistent with a garnet peridotite source but not with direct contributions of discrete, highly productive eclogitic lithologies. The low melt productivity does not necessarily rule out the involvement of mafic lithologies in the source of OIB, but instead requires time for these melts to chemically interact with the surrounding peridotite. Subsequent melting of such trace element enriched peridotite carries a geochemical signature of the mafic lithologies but not a record of their high melt productivity. Such a multi-stage melting process may thus help reconcile the systematic melting behaviour of OIB and lithospheric thickness with the wide trace element and isotopic heterogeneity that does not share the same systematic co-variation.

Zinc Isotopes in the Soil-Plant Interface

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From the geosphere/biosphere system as a whole down to the organism and cellular level, naturally occurring isotopes have the potential capability to uniquely understand the mechanisms controlling inorganic element flux. This is exemplified in our work on zinc (Zn) isotopes in plants. The use of multicollector ICP-MS, together with complete sample digestion and anion exchange chromatography, has allowed the measurement of Zn isotopes to be made precisely and accurately in the geological and biological matrices studied. Precision on $\delta^{66}\text{Zn}$ was below $\pm 0.1\text{‰}$ (2 S.D., $n=4$ typically) on analyses and the accuracy of mass bias correction was tested using a combined standard sample bracketing and external empirical normalisation procedure.

Zinc deficiency is the most widespread micronutrient disorder in rice (*Oryza sativa*) and differences between genotypes render some genotypes more susceptible to deficiency than others. Hence rice was chosen as a model species in our uptake and isotope fractionation studies. A previous hydroponic study in our laboratory showed Zn uptake by tomato, lettuce and rice all produced an enrichment of the light Zn isotopes in plant shoots [1]. A study of vegetation in a watershed, however, revealed a more complex picture, and plant shoots and roots were generally enriched in heavy isotopes relative to the litter and superficial soils [2].

In the results presented here, rice grown under field conditions showed only heavy or insignificant fractionations relative to the soil matrix (in contrast to the hydroponic study). A genotype tolerant to Zn soil deficiency (RIL46) and a genotype intolerant to deficiency (IR74) were grown in both zinc fertilised and unfertilised (Zn deficient) plots as part of a larger study. On the zinc fertilised plots, shoot samples of both genotypes showed a negligible difference in $\delta^{66}\text{Zn}$ compared to the growth soil. On unfertilised plots, however, genotype RIL46 preferentially absorbs heavy Zn ($\delta^{66}\text{Zn}_{\text{plant shoot-soil}} \sim 0.2\text{‰}$). This heavy isotopic enrichment corresponds with research on iron isotopes in grasses ($\Delta^{56}\text{Fe}_{\text{plant-soil}} \sim 0.2\text{‰}$) [3], which use a siderophore chelated uptake mechanism. Subsequent laboratory root exudation rate measurements for siderophores show a three fold increase for RIL46 over IR74. Using an uptake model that includes soil solubilisation effects, this experimental exudation rate can explain real Zn uptake rates in the field. All evidence therefore supports a Zn-siderophore absorption mechanism by genotype RIL46 in Zn-deficient soil.

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Calcium and potassium isotope analysis in solution and laser ablation mode on an IsoProbe MC-ICP-MS

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Calcium and potassium isotope ratio determinations have several potential applications including K-Ca geochronology, stable Ca isotope fractionation in palaeothermometry, the search for extinct ^{41}Ca in meteoritic K, and metabolism studies. Precise determination of these ratios by TIMS is challenging, particularly for K, where large mass fractionation occurs during ionization that cannot easily be corrected as ^{40}K abundance is too low. The use of H_2 in the hexapole collision cell of the GV instruments IsoProbe MC-ICP-MS reduces ^{40}Ar to undetectable levels relative to the ^{40}Ca solution blank signal of 1mV (equivalent to ~80ppt Ca), and leaves only a small (~2mV) stable ^{40}ArH (?) signal at mass 41.

Mixed K-Ca solution standards yield $^{42}\text{Ca}/^{40}\text{Ca}$ and $^{43}\text{Ca}/^{40}\text{Ca}$ internally normalized to $^{44}\text{Ca}/^{40}\text{Ca} = 0.021504$ that are within error of high-precision TIMS measurements¹, a prerequisite for the use of double-spike for mass bias correction. Over a day, preliminary $^{41}\text{K}/^{39}\text{K}$ ratios normalized to $^{44}\text{Ca}/^{40}\text{Ca}$ yield 0.4‰ 2s reproducibility, comparable to the 0.5‰ achieved by the most precise TIMS study². Clearly, Ca isotope ratios normalized to K yield similar reproducibility, and double spike normalization is expected to improve this by a factor of at least 3-4, as external reproducibility of $^{42}\text{Ca}/^{40}\text{Ca}_\text{N}$ is the same as the 0.2‰ internal precision. Ca-normalized $^{41}\text{K}/^{39}\text{K}$ ratios change slightly with solution Ca/K ratios, in part possibly the consequence of ^{40}CaH interference on ^{41}K . Identical Ca-normalized K and $^{44}\text{Ca}/^{40}\text{Ca}$ -normalized Ca ratios are measured on Ca-spiked column-processed K solutions, and this has been used to obtain <0.3% precision on the very low (<100ppm) K contents of some Icelandic picrites.

We have also analysed a modern *Tridacna* calcite using these methods, and obtained Ca-normalized K and $^{44}\text{Ca}/^{40}\text{Ca}$ -normalized Ca ratios within error of the standard solutions, despite no chemical separation, after minor correction for Sr^{++} isobars monitored at mass 43.5. The same *Tridacna* has been analysed on the IsoProbe following ablation using the new RHUL laser ablation facility, and we again observe $^{44}\text{Ca}/^{40}\text{Ca}$ -normalized Ca ratios within error of the solution standard.

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Poster program abstracts

Fe isotope fractionation and diagenetic pyrite formation

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Novel analytical capability has permitted transition metal isotopes to be developed as a potentially powerful new tool for tracing biogeochemical processes [1]. In anoxic sedimentary environments, the behaviour of transition metals and especially that of Fe is controlled by their sulphur chemistry. Fe isotope measurements of sedimentary Fe-S species show evidence of significant Fe isotope fractionation processes in both modern and ancient environments (up to a range of ~5‰ for $\delta^{56/54}\text{Fe}$) [2]. Experiments and measurements of natural samples indicate that Fe isotope fractionation can be the product of both biological [3] and inorganic processes [4]. The problem at the present is in our lack of basic understanding of the geochemical processes responsible for the measured fractionations. First experimental investigations on FeS formation show evidence for kinetic fractionation [5]. The remaining question is which inorganic processes are responsible for the observed fractionations, and whether equilibrium or kinetic processes are involved. No experimental data currently exists for Fe isotope fractionation during pyrite formation, although pyrite is the most common iron sulfide mineral in the Earth's subsurface. The aim of this research is to understand the mechanisms by which Fe isotopes fractionate abiotically during pyrite formation. This work is necessary in order to: 1) characterise the Fe isotopic signature of pyrite and other Fe-S minerals, 2) contribute to a better understanding of natural data and 3) investigate the future application of the isotopic signature of pyrite as a biogeochemical tracer.

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Post-glacial evidence for the future of the Icelandic Western Rift Zone

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It has been suggested in the literature that the Icelandic Western Rift Zone (WRZ) is failing in the north, as the Eastern Rift Zone (ERZ) increasingly accommodates tectonic spreading. This suggestion is supported by depletion in incompatible trace elements (ICTE) in the northern WRZ relative to the southern WRZ (Sinton et al., 2005). An alternative view is that this trace element trend could be due to a long wavelength mantle source change, which should be accompanied by enriched radiogenic isotopic signatures in the northern WRZ, relative to the southern WRZ (Sinton et al., 2005).

While the north of the WRZ is a large plateau, forming the Langjökull ice cap, the south is much lower and contains the Þingvellir graben, the deepest on Iceland (Saemundsson, 1992). This implies that the north of the WRZ, the place that should be failing, is a region where volcanism is dominating tectonics. While the south of the WRZ, where magmatism should be the strongest, is an area where tectonics is dominating volcanism. These observations are inconsistent with the belief held in the literature that the ERZ is propagating to the south, at the expense of the WRZ.

A study of O-Sr-Nd-Pb data from 44 new samples from the WRZ and the last glacial central volcano Hengill, finds no evidence for WRZ shutdown in the north. The geomorphological evidence suggests WRZ shutdown is more likely to occur in the south. This brings into question the validity of the assumption in the literature, that the ERZ is propagating to the south and that the WRZ is failing in the north. There is a very slight isotopic and trace element enrichment in the south relative to the north. This can be explained by a change in melting regime between last-glacial and post-glacial time, due to glacial unloading. This causes varying degrees of sampling of two mingled sources with different volume, fertility and enrichment, the plum pudding mantle model (Phipps-Morgan and Morgan, 1999).

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A noble gas approach to fluid origin in mesothermal gold deposits, Otago and Alpine Schists, New Zealand.

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Despite their economic importance around the globe, the origins of gold and mineralizing fluids in mesothermal gold systems remain poorly understood. The mineralization process may involve complex fluid evolution, mixing and unmixing and differing contributions from meteoric, magmatic or metamorphic fluid sources.

Noble gases are excellent tracers of fluid origin in terrestrial processes due to their inertness and occurrence in low abundance in a wide variety of crustal materials. The main terrestrial reservoirs of noble gases including the atmosphere, mantle and crust have unique resolvable noble gas isotope fingerprints. The relative noble gas contributions from these potential fluid sources are resolvable. Magmatic fluids are identifiable by primordial ³He and crustal fluids by radiogenic isotopes, such as ⁴He and ⁴⁰Ar. The presence of a diluted dissolved atmospheric signature may indicate the mixing of meteoric and metamorphic fluids and the degree of elemental fractionation can identify unmixing processes such as boiling.

Economically significant Mesozoic gold deposits are hosted by the Otago Schists on the South Island of New Zealand and Pliocene-recent gold bearing quartz veins occur in the Alpine Schists of the Southern Alps. Uplift along the Alpine fault has exposed quartz veins of varying depth of formation down to the brittle-ductile transition providing samples to permit assessment of meteoric fluid penetration versus crustal fluid buoyancy. The lack of a significant ³He signal displayed by initial results confirms the predicted absence of a magmatic fluid component. Argon isotopes counter intuitively display a more radiogenic signature in samples from the young system than the ancient system, potentially due to more extensive fluid-rock interaction in the recent system. Non-radiogenic Ar, Kr and Xe are atmospheric in value while elemental Xe/Ar and Xe/Kr show xenon excess, possibly sourced from the source sediments.

Preliminary halogen data has been acquired from the same suite of samples by irradiation converting the halogens to noble gases. By combining this halogen data with salinity measurements from fluid inclusion microthermometry we should be able to determine noble gas concentrations in water. Fluid inclusion salinities typically range from 3-6 wt% NaCl. Br/Cl show ratios from seawater values and above, while I/Cl are all orders of magnitude greater than seawater typical of I excess from organic sediment contributions. This is consistent with the observed excess Xe.

The origin of high $^3\text{He}/^4\text{He}$, high-temperature mantle in the initial eruptions of the Iceland plume

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Recent studies have shown an apparent link between high $^3\text{He}/^4\text{He}$ ratios and depleted mantle. This is inconsistent with the prevailing view that the preservation of a mantle domain with high concentration of primordial ^3He must reflect a lack of depletion and degassing, and apparently removes the need for the survival large portions of pristine mantle. The high Mg-basalts from Baffin Island and West Greenland are amongst the earliest basalts erupted by the Iceland plume, and their major element composition is consistent with their derivation from partial melts of mantle that is up to 200°C hotter than normal. Some of these rocks have the highest recorded terrestrial magmatic $^3\text{He}/^4\text{He}$ ratios (up to 50 R_a). In a detailed study of the geochemistry of a new suite of early Iceland plume picrites from Baffin Island and West Greenland we show that the extreme $^3\text{He}/^4\text{He}$ ratios are found in basalts with a range of trace element and lithophile radiogenic isotopic compositions. The majority of samples are compositionally indistinguishable from mid-ocean ridge basalts, but several have compositions indicative of an Iceland-type source. This observation is inconsistent with a unique, discrete mantle reservoir with high $^3\text{He}/^4\text{He}$ that is a residue of ancient mantle depletion. The simplest explanation is that the early Iceland plume sampled an anomalously hot mantle reservoir that had a sufficiently high concentration of high- $^3\text{He}/^4\text{He}$ helium to dominate subsequent mixtures with other mantle reservoirs. Seismic evidence for the source of the Iceland plume is the subject of debate, but it is clear that the starting Iceland plume sampled a hot, He-rich reservoir that is not available to steady-state mantle plumes.

Testing the Bipolar Seesaw with Pa and Th isotopes in the SW Atlantic

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The use of sedimentary $^{231}\text{Pa}/^{230}\text{Th}$ ratios as a proxy for ocean circulation has provided evidence for a strong link between climate and North Atlantic overturning rate over the last deglaciation. First results from the Southern Hemisphere suggest that the proxy should also provide information about rates of flow of southern component waters. In this study, we have applied Pa/Th to intermediate depths in the South Atlantic, to investigate the relationship between Antarctic Intermediate Water (AAIW) flow rates, northern water masses, and climate. Measured $^{231}\text{Pa}/^{230}\text{Th}$ ratios are slightly below the isotope production ratio during the Last Glacial Maximum (LGM), increase to values significantly above the production ratio in the early Holocene and then decrease to just below the production ratio at the present day. Nd isotopes are used to confirm the presence of AAIW at this site since the LGM. Compared to the deep North Atlantic, $^{231}\text{Pa}/^{230}\text{Th}$ ratios in this region are affected by a greater range of processes, including changing source water composition, boundary scavenging at the core site and upstream, variations in opal content, and circulation rates. Box modelling is used to help understand these various influences, and suggests that AAIW circulation may have been faster during the LGM and early deglacial, slowed over the late deglacial and early Holocene and increased again to the present day. These results support the idea that AAIW may play a dynamic role in climate change and the bipolar seesaw through salinity feedbacks with Glacial North Atlantic Intermediate Water (GNAIW), and also suggest that AAIW circulation may respond to orbitally-forced changes in high southern latitude temperature and sea ice during the Holocene.

Geochemical proxies in vent mussel shells as indicators of environmental conditions at hydrothermal vents

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The shells of many bivalve species have been shown to contain high resolution seasonal records of shell growth and environmental conditions across different geographical locations stretching from estuaries to coastal waters and to the deep oceans. Utility of bivalve shells would tell us about environmental settings in more novel environment such as deep-sea hydrothermal vent fields. Vent mussels *Bathymodiolus* sp. live under conditions of continuous darkness, close to vents discharging hot (≤ 10 - 350°C) vent fluid enriched in various metals, dissolved methane and sulphide. The mussels have been shown to live in hydrothermal settings where temperatures rarely exceed 10 - 15°C and experience rapid temperature fluctuations on the timescale of seconds to days. This temporal variability in the environment has the potential to be recorded in the geochemical composition of the shell, whilst fluctuations in shell geochemistry may reflect changes in the shell growth rates and formation of internal shell growth bands.

In this study we present data on the periodicity of the growth banding and data on the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ composition in the shells of *B. azoricus* and *B. puteoserpentis* from Menez Gwen and four other vent fields along the Mid-Atlantic Ridge (MAR) which could provide high resolution records of changes in their growth and environmental settings.

No apparent periodicity was observed in the formation of the microgrowth increments (5 - $40\ \mu\text{m}$) in suitably prepared polished and etched shell sections of *B. azoricus*. The shell $\delta^{18}\text{O}$ values range from 1.3‰ to 4.3‰ , which correspond to temperatures from 1.2°C to 11.7°C and predominantly increase (about $>1\text{‰}$) with distance from the umbo and thus the temperature decrease throughout their life. One interpretation of these patterns would be that through ontogeny the animal's proximity to the vents decreased as they migrated to the regions with cooler temperatures. Such a geochemical proxy-based interpretation of variable *Bathymodiolus* habitat during ontogeny is interesting, since submersible observations have indicated that at Lucky Strike small mussels ($<3\ \text{cm}$) occupy settings with lower temperatures than large mussels ($>6\ \text{cm}$). The shell $\delta^{13}\text{C}$ values range from 1.2‰ to 6.5‰ and their profiles, throughout outer calcite shell layer, show predominantly an increasing trend (about 1‰). Statistical analysis show significant difference in $\delta^{13}\text{C}$ between two species *B. azoricus* and *B. puteoserpentis*. The shell $\delta^{13}\text{C}$ of vent mussels is significantly higher ($+4\text{‰}$) than that of shallow water species (varying between $\pm 2\text{‰}$), and may be due to the presence of sulphide-oxidising symbiotic bacteria.

Micro solution ICP-MS as applied to ordinary chondrites.

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Inductively coupled plasma mass spectrometry (ICP-MS) is a destructive technique commonly used within geochemistry to obtain bulk chemical analyses for relatively large sample sizes (mg). Here we present a method with the ability to obtain absolute abundances for ~52 trace and minor elements from 100µg accurately extracted, non-contaminated separates. This is applicable to rare samples which are too precious to be completely destroyed and/or are heterogeneous causing separate extraction to be notoriously difficult e.g. chondritic meteorites.

100µg of sample are extracted from a pre-characterised thick section using a micromill. The non-destructive characterisation is carried out via scanning electron microscopy (SEM) and electron probe microanalysis (EPMA), allowing a comprehensive 2D model of the sample to be constructed. Individual drill pits (50µm deep, 30µm in diameter) are accurately excavated using the model as a guide. The separate is collected in a droplet of milliQ water which is pipetted from the sample surface and deposited on a pre-weighed and cleaned section of fine mesh filter paper. This, complete with sample is re-weighed to find the precise separate mass (+/- 0.5µg), allowing the absolute abundance of elements to be calculated post-ICP-MS analysis. The sample plus filter paper is then subjected to typical HF:HNO₃ digestion, diluted to an appropriate level (~2 x 10⁴) with 2% HNO₃ and passed through an Agilent 7500s ICP-MS. These data are standardised to a set of multi-element standards of CI abundances. The combination of a PFA and Babington nebuliser allow the ICP-MS analyses to be less susceptible to residual drift and more sensitive with regards higher mass elements (>Rb) than typical ICP-MS. Oxide interferences are maintained at <0.5% CeO⁺/Ce⁺, with doubly charged species interference being <1.2% Ce⁺⁺/Ce⁺.

This technique has been applied to a number of chondritic meteorites. Most recently the chondrules (rapidly quenched droplets) within Semarkona (a relatively unaltered ordinary chondrite (LL3)) have been analysed. The chondrules were fully characterised and classified by state of oxidation and petrology [e.g. 1] and grain size [2]. A selection of each group was extracted whilst ensuring that no surrounding components were incorporated into the separates. Data shows that distinct patterns can be seen in bulk composition within these groups. Differences in abundances of the more volatile elements between categories of grain size, yet similarities between chondrules classified by state of oxidation and petrology are highlighted. This has many implications regarding the formation method of chondrules and early Solar System solid bodies.

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Chemical separation and isotope analysis of nickel in geological and meteoritic samples

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We have developed new methods for isotope analysis of Ni in iron and silicate meteorites. The initial objective of this work was to look for mass independent Ni isotope variations in iron and silicate meteorites, and evaluate the potential of extinct ^{60}Fe (decays to ^{60}Ni with half-life of 1.5 Ma) as a chronometer for dating early Solar System processes. However, mass dependent Ni isotope variations in terrestrial samples also have important applications in biogeochemistry.

Ni is separated from the sample matrix using a 3 stage ion-exchange procedure. Samples are dissolved in 6M HCl, and loaded in 10% HCl-90% acetone onto a column containing 2 ml AG50W-X4 cationic resin. After rinsing with 10% HCl-90% acetone to remove the bulk of matrix elements (including Fe and Zn which interfere on Ni masses) Ni can be selectively eluted with HCl-acetone containing 0.1 M dimethylglyoxime (DMG). After evaporation, the DMG is decomposed with 15M HNO_3 , and the sample passed through 0.1 ml TRU spec resin in 7M HNO_3 in order to remove any remaining Fe and Ti (TiO^+ species may interfere on ^{62}Ni , ^{64}Ni). A final ion exchange column containing 0.1 ml AG50-X8 is used to remove residual organic material and P from breakdown of the TRU spec resin. Blanks for the entire process are between 5 and 15ng, and the yield is >98%. Scans of the final Ni fraction found no other element abundance significantly above wash solution blank; for example chemically similar Co is reduced by more than four orders of magnitude. However, so far we have been unable to obtain accurate ^{64}Ni data due to ^{64}Zn interference on this minor (0.9%) Ni isotope, but replacing the second column step with anionic resin in HF-HCl may provide a better separation of Zn, Fe and Ti from Ni.

Ni isotope measurements are carried out on a ThermoFinnigan Neptune MC-ICPMS. Samples are dissolved in 0.3M HNO_3 and introduced into the mass spectrometer via a Cetac Aridus desolvator. Measurements are carried out in 'medium resolution' mode ($M/\Delta M > 6000$ peak edge width from 5-95% full peak height), in order to resolve a minor interference from ^{62}Ni , and $^{16}\text{O}^{40}\text{Ar}$ from ^{56}Fe , allowing correction of any ^{58}Fe interference on mass 58 (<5 ppm). ^{58}Ni is approximately 68% of Ni, and so mass 58 was detected on a Faraday cup connected to a $10^{10} \Omega$ feedback resistor, enabling ^{58}Ni beams of ~900 pA to be measured. An internal mass bias correction is applied to $^{60}\text{Ni}/^{61}\text{Ni}$ and $^{62}\text{Ni}/^{61}\text{Ni}$, using the measured $^{58}\text{Ni}/^{61}\text{Ni}$ ratio. Sample data are further normalised to bracketing measurements of the SRM986 Ni isotope standard, to remove the effect of variable within-run NiH^+ production. 2σ standard errors of repeat sample measurements is typically 0.03 and 0.06 \square units for the $^{60}\text{Ni}/^{61}\text{Ni}$ and $^{62}\text{Ni}/^{61}\text{Ni}$ ratios, respectively. Our poster will describe the method in more detail, and present new Ni isotope data for a suite of 24 iron and chondritic meteorites.

Lithium and magnesium isotopes in the mantle: mantle heterogeneity or diffusion?

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One of the most important current tasks for high-temperature geochemistry is understanding and tracing crustal recycling through subduction, which has been invoked as a cause of upper mantle heterogeneity. The Li isotope system was thought to be a key to understanding these processes, because subducted oceanic crust has a Li isotope ratio significantly heavier than MORB. Additional fractionation is thought to occur due to fluid mobilisation during slab dehydration. Hence Li isotope signatures in MORB and OIB may reflect crustal recycling. However, recent studies have shown that high temperature Li isotope fractionation may occur during diffusion, and therefore interpretations of magmatic Li isotope signals are ambiguous. Clearly an additional tracer is needed to resolve this. The vast Mg reservoir of the mantle is unlikely to be affected by recycling of low Mg crustal material, although Mg isotopes are probably susceptible to high temperature diffusive effects. Thus a coupled multi-proxy approach of Li and Mg isotopes may resolve crustal recycling.

However, in order to understand the behaviour of Mg isotopes in the silicate Earth, we need data on Mg isotope ratios in the mantle. The few studies thus far undertaken on Mg isotopes in silicates provide conflicting information of the composition of the Bulk Silicate Earth (BSE) and heterogeneity in the mantle. Currently, data from Wiechert and Halliday (EPSL, 2007) suggest that the BSE is slightly heavier than most chondrites, which has been interpreted as due to sorting of solid materials in the proto-planetary disc. However, Teng et al. (EPSL, 2007) reported that MORB have a similar composition to chondrites.

This study has analysed over 40 whole-rock peridotites and abyssal peridotites from several global settings, as well as a suite of EPR MORB, for Li and Mg isotopes. This provides the first large scale consistent data of the Mg isotope composition of the mantle. The Li isotope data show a wider range than generally observed in unaltered peridotites, which is likely due to kinetic diffusion processes during metasomatism. As with Li isotopes, the smallest range of Mg isotopes is in the least metasomatised samples. However, the total range of peridotites measured in this study is just greater than the high precision external uncertainty, possibly suggesting Mg isotope heterogeneity in the mantle. However, co-variations between Li and Mg isotopes in the peridotites suggest that both systems may be affected by similar processes. Light $\delta^7\text{Li}$ in metasomatised peridotites ($<-3\text{‰}$) is associated with light $\delta^{26}\text{Mg}$, which may indicate that Mg isotopes in the mantle are affected by diffusional processes. This is a surprising and important result, considering the buffering capacity of the mantle.

Glacial weathering intensity recorded in the authigenic Hf isotope composition of deep North Atlantic sediments

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It has been suggested that during intense glacial weathering zircons should break down more easily thereby releasing a very unradiogenic Hf isotope signal to the oceans (Piotrowski et al., 2000; van de Flierdt et al., 2002). To date, however, this suggested mechanism could not be ultimately proven due to the lack of a substrate allowing for the required sub-millennial resolution. Here we present the first systematic attempt to extract the authigenic seawater Hf isotope signature from Fe-Mn oxyhydroxide fractions in sediments from the deep western North Atlantic. Although leaching of terrigenous minerals apparently obscured the original authigenic Hf isotope composition in some samples, the vast majority of our data seem to reflect a pure authigenic Hf isotope signal. Unfortunately no ultimate proof for its seawater-origin can be offered at present due to missing seawater data from the core locations in the western North Atlantic. The obtained authigenic Hf isotope records show a systematic change from unradiogenic glacial compositions with ϵ_{Hf} as low as -3.1 in 4250 m water depth and -1.7 in 1790 m water depth to more radiogenic ϵ_{Hf} today. Strikingly, in both intermediate and deep core sites, the authigenic Hf isotope signal becomes significantly more radiogenic during or shortly after the end of the Last Glacial Maximum. The Younger Dryas, a short-lived return to near-glacial conditions, is marked by an apparent drop in ϵ_{Hf} . Today the authigenic Fe-Mn oxyhydroxide fraction in sediments along the deeper Blake Ridge yields an ϵ_{Hf} of 1.5, whereas the data from intermediate depths are in the range of 2.8 ± 0.5 . The Hf isotope trends presented here support earlier suggestions of intense mechanical grinding of bulk rock during northern hemisphere glacial weathering influencing the Hf isotope composition of seawater during glacial times, demonstrated here at yet unprecedented temporal resolution. We suggest that the glacial Hf isotope budget in the western North Atlantic was indeed significantly modulated by minor contributions from chemical dissolution of zircon towards a more congruent release of Hf to the oceans during glacials (cf. van de Flierdt et al. 2007). The authigenic Hf isotope compositions as recorded in Fe-Mn oxyhydroxides possibly yield essential paleoclimatic information for the reconstruction of ice sheet growth throughout the Pleistocene.

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TOF-SIMS and its application to cosmochemistry

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Secondary ion mass spectrometry (SIMS) uses high energy (typically 10-30 keV) ions to sputter secondary ions from near-surface layers. SIMS instruments equipped with magnetic mass spectrometers have been widely used in geo- and cosmochemistry to obtain isotopic ratios and trace element abundances from micron-sized samples. The ion beam can be focused to give high spatial resolution. Since the early 1990's, time-of-flight SIMS has also become an established technique for acquiring both high mass and high spatial resolution analyses (see [1] for review).

The major advantage of TOF-SIMS over magnetic sector SIMS is the parallel detection of all secondary ions, providing a more efficient use of the secondary ions. A pulsed primary ion beam results in a low duty cycle, minimizing sample destruction and enabling depth-profiling at high depth resolution.

In Manchester, we have built and developed two TOF-SIMS instruments [2,3] for the analysis of extra-terrestrial samples. The instruments are equipped with a 40kV C₆₀ ion gun and a 25kV Au LMIS, along with a low energy duoplasmatron source (Ionoptika, Southampton, U.K.). As approximately 99% of sputtered species are neutral one instrument has also been adapted for laser post-ionization of secondary neutrals.

This range of primary ion sources allows us to efficiently analyse a wide range of samples including material from the comet Wild 2 returned to Earth by the Stardust spacecraft [4,5], solar wind captured by the Genesis mission [6] and interstellar grains - micron sized particles which formed around giant stars before arriving in the presolar nebula and becoming preserved within primitive meteorites [7,8].

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Possible vital effects in diatom oxygen isotopes

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Measurements of diatom oxygen isotopes ($\delta^{18}\text{O}_{\text{diatom}}$) are increasingly being utilised as a palaeoclimatic tool in lacustrine and marine sequences depleted in carbonates. In particular, records of $\delta^{18}\text{O}_{\text{diatom}}$ hold significant potential in aiding palaeoceanographic reconstructions in the Southern Ocean. However, due to the difficulty in purifying and separating individual taxa, measurements of $\delta^{18}\text{O}_{\text{diatom}}$ are commonly made on bulk mixed species assemblages. Accordingly, it is essential to fully understand the processes which may lead to isotope offsets in $\delta^{18}\text{O}_{\text{diatom}}$. Here, by using data from ODP site 882 in the North West Pacific Ocean, the evidence pointing towards a possible size or species effect in $\delta^{18}\text{O}_{\text{diatom}}$ is reviewed. The detection of large isotope offsets between different size fractions of diatoms imposes significant constraints upon the future use of $\delta^{18}\text{O}_{\text{diatom}}$ and reiterates the need to extract and analyse only species and size specific diatom samples for $\delta^{18}\text{O}$ analysis.

Experimental determination of Fe isotope fractionation between liquid metal, silicate and sulfide at high pressures and temperatures

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There is evidence for significant equilibrium Fe isotope fractionation (~ 0.26 ‰/amu) between metal and troilite (FeS) in iron meteorites¹ and a smaller fractionation (< 0.1 ‰/amu) between metal and olivine in pallasites^{2,3}. Theory suggests that differences in iron oxidation state and coordination between metal, silicate and FeS will result in stable isotope fractionation^{4,5}. However, it is not yet clear if the apparent observed fractionations can be extrapolated to the pressure and temperature conditions of planetary core formation. We have investigated Fe isotope fractionation between silicate melt and liquid Fe-S alloys and between liquid iron and basaltic melt at pressure and temperature conditions of 2-2.5 GPa and 1650-2023 K using piston-cylinder partitioning experiments from previous studies⁶⁻⁸. Metal, sulfide and silicate fractions were separated from mounted and sectioned experimental charges using a computer-controlled micromill (New Wave-Merchantek). Sample dissolution, Fe purification and isotopic analysis followed established procedures⁹. In agreement with another preliminary high-pressure experimental study¹⁰ we find no appreciable fractionation between liquid iron metal and basaltic melt. However, there is a resolvable Fe isotope fractionation between silicate melt and Fe-S alloy which ranges from 0.12 ± 0.04 to 0.15 ± 0.04 ‰/amu for separate experiments (errors are propagated based on the 2SD errors of replicate analyses). The Fe isotope compositions of coexisting phases from these experiments define a positive linear relationship with a slope that is, within error, equal to unity, implying isotopic equilibrium. No relationship between apparent fractionation factor and pressure or temperature is detectable within the range covered by the experiments. The fractionation factors determined from our experiments overlap with the average equilibrium fractionation factor obtained between silicate melt and pyrrhotite (Fe_{1-x}S) of 0.18 ± 0.02 ‰/amu at 0.5 GPa and 1114-1274 K¹¹ and are also broadly consistent with silicate-FeS fractionation factors inferred indirectly from iron meteorites and pallasites which range from ~ 0.16 to 0.24 ‰/amu. Taken together these observations suggest that resolvable stable isotope fractionation between Fe-S alloys and silicate melts can take place at extreme pressure and temperature conditions and that isotopically light Fe can be sequestered into the S-bearing parts of planetary cores.

- 1 Williams et al., EPSL (250) 2006
- 2 Zhu et al., EPSL (200) 2002
- 3 Weyer et al., EPSL (240) 2005.
- 4 Polyakov and Mineev, GCA (64) 2000
- 5 Schauble et al., GCA (65) 2001
- 6 Kilburn and Wood EPSL (152) 1997
- 7 Gessmann and Wood, EPSL (200) 2002
- 8 Wood et al., EPSL (in revision) 2007.
- 9 Williams et al., EPSL (235) 2005
- 10 Poitrasson and Roskosz, LPSC XXXVIII 2007
- 11 Schuessler et al., GCA (71) 2007

Isotopic Tracers and Optimised Solutions for High-Precision U-Pb ID-TIMS Geochronology

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U-Pb isotope-dilution thermal ionisation mass spectrometry (ID-TIMS) geochronology is often referred to as the 'gold standard' due to its dual decay scheme and the precision to which the decay constants have been determined. Lowering of common Pb contamination levels, improvements in mass spectrometry and the continued development of pre-treatment techniques for the elimination of post-crystallisation Pb-loss, have resulted in increased precision, with 2σ uncertainties on (low- n) weighted mean $^{238}\text{U}/^{206}\text{Pb}$ dates commonly $<1\%$. This increase in precision has resulted in a situation where interlaboratory biases exceed analytical uncertainties. This bias originates from tracer calibration, detector characteristics, and ion-counting protocols. In an attempt to eliminate this bias we have prepared a U-Pb tracer solution as well as a series of optimised solutions for monitoring long-term mass spectrometer performance.

As part of the EARTHTIME Initiative (www.earth-time.org) a quantity of mixed ^{205}Pb - ^{233}U - ^{235}U tracer has been prepared for community use, with the aim of effectively eliminating interlaboratory bias due to tracer calibration. This tracer solution is calibrated against three mixed U/Pb gravimetric reference solutions (high-purity metal derivatives). Interlab tracer U/Pb ratio calibration indicates agreement to $<0.5\%$, and uncertainties in the purity of the reference materials indicates the calibration is accurate to 0.5 to 1%. In addition to the tracer, synthetic U/Pb solutions have been prepared with $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ratios that yield concordant ^{206}Pb - ^{238}U and ^{207}Pb - ^{235}U ages at 100 Ma, 500 Ma and 2 Ga. We estimate that for each of the solutions there is enough for distribution to all U-Pb ID-TIMS labs and their utilisation for assessing long-term reproducibility (over many years) and inter-laboratory agreement without the complexity of sample dissolution and ion exchange chemistry. We believe the new tracer and standard solutions are essential for facilitating assessment and improvement of the accuracy and long-term reproducibility of high-precision U/Pb dates.

The discussion of using Jurassic belemnites as palaeotemperature indicators

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Well-preserved belemnites have been widely used as palaeotemperature proxies because they are assumed to record the primary stable isotope ($\delta^{18}\text{O}$) and trace element (mainly Mg and Ca) signals of the ambient seawater. We want to know just how good these palaeo-records are. One way to do so is to compare records from different belemnite species. Here, we compare the palaeo-proxies Mg/Ca, Sr/Ca, Na/Ca, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in rostrum of the belemnites *Acrocoelites subtenuis*, *Acrocoelites vulgaris*, *Simpsonibelus dorsalis* and *Youngibelus simpsoni*. Samples were collected from the Early Toarcian strata of Yorkshire, UK.

We find that *A. subtenuis* and *Y. simpsoni* specimens have lighter $\delta^{13}\text{C}$, less negative $\delta^{18}\text{O}$, and broader compositional ranges than do *S. dorsalis* or *A. vulgaris*, so the former pair occupied a wider range of habitats in the lower Toarcian oceans than did the latter pair. The limited compositional variations of *A. vulgaris* specimens suggest they had a restricted living environment. In addition, the poor correlation between Mg/Ca and $\delta^{18}\text{O}$ in all four species is puzzling, given that Mg/Ca is presumed to reflect temperature. A better correlation exists between Sr/Ca and $\delta^{18}\text{O}$ than Mg/Ca and $\delta^{18}\text{O}$, which suggests Sr/Ca is probably a better Toarcian palaeotemperature indicator.

Consequently, belemnite compositions are complex; each species shows a range of compositions and different species possess different compositions. Isotopic and elemental data of our belemnites must reflect the combined effects of biofractionation and differing habitats, which add noise to belemnite records, and should be taken account for when using belemnites as palaeoenvironment indicators.

This belemnite data shows the same compositional range and inter-element relationships that were found by McArthur et al. (2007b), to exist in belemnites from Bed 48 at Yorkshire, which were regurgitated as waste by a large predator and so represent an instant of Toarcian time during which climate had no time to change. The similarity suggests to us that the Early Toarcian environment was stable through the time period studied here: the middle *falciferum* to the lower *commune* Subzone and around 10^5 years.

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New model calculations for the production rates of cosmogenic nuclides in iron meteorites

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In contrast to stony meteorites, which usually have exposure ages of a few 10 Ma, most iron meteorites have been exposed to galactic cosmic rays (GCR) for hundreds of Ma. Consequently, they provide information about the solar system, encoded in cosmogenic nuclides, for much longer than stony meteorites. Yet, measuring noble gases in iron meteorites is not straightforward and only very few laboratories are able to do so. Therefore, in contrast to stony meteorites, to date very few noble gas studies of iron meteorites have been conducted. However, such studies are essential to understand, e.g., the internal dynamics of the asteroid belt and/or to determine if there has been any long-term variation of the GCR. The key is to determine precise and accurate production rates of cosmogenic nuclides, which are produced due to interactions of GCRs with the meteoroid. The few existing models that calculate such production rates ignored the effects of minor element chemistry and suffer from the scarce and scattering database of the cross sections for the production of cosmogenic nuclides from Fe and Ni [e.g. 1,2,3]. In this work we present a new physical model, based on the latest knowledge of the particle spectra and cross sections for the relevant nuclear reactions, to study the relationship between the meteoroid geometry and chemistry on the one hand and the production rates of cosmogenic nuclides on the other hand.

In order to validate the new model, depth profiles of He, Ne, and Ar were measured in the two iron meteorites Grant and Carbo. In addition, we measured artificially irradiated Fe and Ni targets to get a complete and consistent cross section database of the nuclear reactions. Combining these data with the results of Monte Carlo simulations for the depth and size dependent primary and secondary particle spectra, the production rates of ^{3,4}He, ^{21,22}Ne, ^{36,38}Ar, ¹⁰Be, ²⁶Al, ³⁶Cl, ^{39,40,41}K, ⁴¹Ca, ⁵³Mn, and ⁶⁰Fe were calculated for iron meteoroids with radii from 5 – 1000 cm.

Our new model enables accurate description of most of the cosmogenic nuclides in Grant and Carbo and we are able to determine exposure ages, radii, sample depths, and the sulphur content of our samples. Additionally the ⁴⁰K-⁴¹K dating method [e.g., 4], which is the most popular method to determine exposure ages of iron meteorites, was improved. Thus, the observed difference between ⁴⁰K-⁴¹K and ³⁶Cl-³⁶Ar ages, which was previously assumed to provide evidence that the GCR has been increased by 30-50% during the last few 100 Ma, disappears within uncertainties. Instead, there is a 20-50% difference between the ⁴⁰K-⁴¹K and noble gas ages, which could indicate a decrease of the GCR during the last few 100 Ma, or some residual limitations of our model.

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Field, Geochemical and age studies of Rhyolite Glaciovolcanism at Oraefajokull Volcano, S.E. Iceland – A Window On Quaternary Climate Change

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Oraefajokull Volcano is Iceland's largest stratovolcano, situated in the south east of the island. The age of this volcano is constrained by Lacustrine sediments lying unconformably at the base of the edifice dated at 0.6 to 0.89 Ma and the normal magnetic polarity of the volcanic rocks suggesting that the edifice is less than 780,000 years old (Prestvik, 1982)

A large proportion of the edifice is covered by the Vatnajokull Glacier including its 5km wide ice-filled caldera. Studies of the nearby region of Skaftafell suggest that south east Iceland has been permanently covered by ice of varying thickness since the last magnetic reversal (Helgason & Duncan, 2001).

Subglacial eruptions leave characteristic deposits enabling them to be distinguished from subaerial and subaqueous volcanic facies. At long-lived volcanoes, detailed mapping of interbedded subglacial and subaerial eruptive units allows the extent of previous ice cover to be inferred long after the ice has retreated. Ar/Ar dating and geochemical fingerprinting can then be applied to key eruptive units in order to build up a palaeoclimatic timeframe alongside an evolutionary history of the volcano.

Oraefajokull has erupted basaltic and rhyolitic lavas in historical record and field evidence suggests that eruptions at Oraefajokull have occurred during both glacial and interglacial periods (Stevenson et al., 2006). This makes Oraefajokull an ideal location to study the evolution of a stratovolcano throughout the varying climatic conditions of the mid to late quaternary.

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Tracing micrometeorite flux to Earth using He isotopes in ferromanganese crusts

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The He isotope systematics of ferromanganese crusts from the deep ocean floor can be explained by a mixture of extraterrestrial helium (implanted solar wind and galactic cosmic rays (GCR)) and terrestrial helium (radiogenic) from wind-borne continental dust grains. $^3\text{He}/^4\text{He}$ are typically in the range 10-20 R_a similar to values measured in oceanic sediments. However, we have identified one crust, 237KD, from the Central Pacific Ocean that has extremely high $^3\text{He}/^4\text{He}$ (up to 4440 R_a) that are comparable to the highest ratios measured in interplanetary dust particles (IDP) and micrometeorites (MM). The extremely high ^3He concentrations, up to 8×10^9 atoms/g, cannot be explained by the presence of undegassed IDP, but requires that the extraterrestrial He is carried by occasional, high concentration GCR-He-bearing particles. An excess of ^{60}Fe in 237KD has been hailed as the first evidence of debris from a nearby supernova explosion. But ^{60}Fe can also be produced from GCR reactions on Ni in extraterrestrial material. The maximum $^3\text{He}/^{60}\text{Fe}$ of 237KD samples (100–800) is comparable to the $(^3\text{He}/^{60}\text{Fe})_{\text{GCR}}$ (400-500) predicted for Ni-rich minerals that are common in iron meteorites. Consequently it is likely that the excess ^{60}Fe originates from infalling MMs and is not derived from a supernova.

^3He and ^4He concentrations, and $^3\text{He}/^4\text{He}$ increase significantly from approximately 5 Ma. This is likely to be related to the increased trapping efficiency of infalling dense micrometeorites. We suggest that this is due to a decrease in the water current strength resulting from the closure of the Panama gateway. If change in $^3\text{He}/^4\text{He}$ (and ^3He) can be an efficient tracer of increase in MM flux, that maybe related to regional circulation variation, will be tested in other ferromanganese crusts.

Improving throughput by using sequential multielement approaches for stable isotopic analyses

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For many years, elemental analysis has been the workhorse in the field of stable isotope ratio mass spectrometry (SIRMS). Of the many applications available to elemental analysis, simultaneous $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ analysis has provided researchers with a rugged, high throughput system that yields results with good precision and accuracy. The analysis of $\delta^{34}\text{S}$ has, until now, been performed as a separate analysis resulting in a day's instrument down time due to reconfiguration and conditioning, increased sample consumption, and use of extra reagents. The coupling of the Elementar Vario MICRO to a SIRMS system has presented the opportunity for the simultaneous analysis of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$. We will show that the analysis of the three isotopes from one sample demonstrates no lack of precision or accuracy. Samples with a wide range of C:N:S ratios gave typical precisions of 0.03‰ $\delta^{13}\text{C}$, 0.1‰ $\delta^{15}\text{N}$ and 0.04‰ $\delta^{34}\text{S}$, which is of the same order as individual analysis of the same sample. It will be demonstrated that chromatographic integrity from the Elementar Temperature Programmed Desorption separation column is maintained for all three isotopes as compared to traditional gas chromatography through a molecular sieve.

A similar problem has been faced when researchers perform $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis of water with an elemental analyser. One isotope per sample has always been the norm. We will demonstrate that the use of the Hekatech elemental analyser coupled to a SIRMS system enables researchers to simultaneously analyse $\delta^{18}\text{O}$ and $\delta^2\text{H}$ from one sample injection. This technique is made possible due to the high operating temperature (up to 1500°C) provided by the Hekatech furnace, which results in the pyrolysis of the sample to form CO and H₂ in the presence of carbon. The pyrolysis products are then separated using a molecular sieve column resulting in well-resolved peaks ready for analysis in the SIRMS. Typical results for precision of 0.7‰ $\delta^2\text{H}$ and 0.09‰ $\delta^{18}\text{O}$ prove that the new method is reliable and that throughput is improved for simultaneous analysis

Mesoproterozoic crustal evolution of southwest Norway

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The origin of the Telemarkia terrane that comprises much of southern Norway is enigmatic, but holds pertinent information regards to the crustal evolution of the Baltic Shield and the formation of Rodinia. The terrane has been attributed to 1.52-1.48 Ga crustal growth [1], with competing tectonic models including those where Telemarkia is an accreted exotic microcontinent, or where it grew on the Baltic Shield's proto-margin and was displaced southward to its current position during the Sveconorwegian (Grenvillian) orogeny. The lack of geological data from this region hinders the testing of these models; our study aims to help resolve this.

1.52-1.48 Ga magmatism in the Suldal sector, Rogaland, comprises a plutonic-volcanic complex that has been variably deformed and metamorphosed in amphibolite facies. Whole-rock geochemistry reveals calc-alkaline and volcanic arc signatures. Field-relations, petrology, petrography and geochemistry are consistent with this complex forming in an active continental margin. This tectonic setting is compatible with a continental-rift setting [2] for the Rjukan Group supracrustals deposited on the adjacent 'inboard' terrane. Although the formation processes of continental lithosphere are still debated, it is likely that this active continental margin setting would require some form of crustal 'protolith' to have existed prior to the c. 1.5 Ga magmatism.

To date, Nd/Hf isotope studies haven't been conducted on this arc complex, however, comparable rocks within SE Norway and SW Sweden can be used as a proxy. Sveconorwegian age (c. 1.0 Ga) granites that intrude the c. 1.5 Ga arc complex have ϵ_{Nd} isotope signatures suggesting they formed from a mixture of mantle and crustal sources, with the latter representing either a 1.5-6 Ga arc complex (requiring >45% recycling), or material with an older history such as that of the Transcandinavian Igneous Belt (requiring c. 20% recycling). According to published petrogeneses of the granites, the latter is more likely; this pre-1.5 Ga isotopic reservoir may represent the crustal 'protolith' for this terrane's continental lithosphere.

An active continental margin setting, or even a mature volcanic arc is consistent with, but does not provide conclusive evidence for tectonic models that place Telemarkia on the proto-margin of Baltic Shield in a more northerly position during the Mid-Proterozoic.

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An improved method for TIMS high precision Nd isotopic analysis of very small aliquots (1- 10ng) with example application in garnet Sm/Nd geochronology.

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Technological and scientific developments have demonstrated both the attainability and the utility of very high precision (i.e. 5-20ppm 2 σ) Nd isotopic measurements with TIMS. However such high precision has been limited to relatively large aliquots of Nd, on the order of several hundred nanograms. Several potential applications of precise Nd isotopic measurements, including garnet Sm/Nd geochronology, do not always permit such large samples, instead yielding only a few nanograms of Nd. We have explored and tested an improved method for Nd isotopic analysis of such small (1-10ng) aliquots of Nd using the NdO⁺ method with a Triton TIMS at Boston University. Analyzing Nd isotopes as the oxide is a well known technique, frequently involving an oxygen bleed valve. Instead, we forego the bleed valve and load samples with a TaO slurry which provides the oxygen source. Using an in-house Nd isotopic standard solution, 4ng loads easily yield stable 2.0-2.5 volt beams resulting in internal precisions of 10ppm 2 σ RSE. Within barrel external precision of 4ng loads of the Nd standard is 13ppm 2 σ RSD (n=20). Long term (6 months, six analysts) external precision of 4ng loads of the standard is currently 23ppm 2 σ RSD (n=55) suggesting that further improvements are possible. As a further test of this method, we dissolved a natural rock sample (a metapelite), separated the Nd using TRU- spec and MLA column chemistry, and loaded nineteen 4ng loads in one barrel. Within barrel external precision was 21ppm 2 σ RSD (n=18). This precision represents a significant advance over previous NdO⁺ analyses of small samples using an oxygen bleed valve. The TaO loading method for small Nd aliquots is useful in Sm/Nd garnet geochronology as exemplified by two case studies. Garnets from eclogite facies gneisses from Norway ran very well with 2.4-18ng loads and yielded age precision as good as 0.8 million years 2 σ . Conversely, garnets from blueschist facies rocks from Sifnos, Greece, ran poorly with similarly sized 1-17ng loads and consequently yielded generally poorer age precision. Differences between the two garnet sample suites must relate to the garnets themselves (notably including much lower Nd concentration in Sifnos garnets), not the identical column chemistry nor the TaO loading method. Additional procedures may be required to cleanly separate Nd from samples where Nd concentrations are very low (\leq 1ppm). As always, clean separation and column chemistry represents an unavoidable limiting factor in achieving precise isotopic measurements.

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Isotopic fractionation of Fe and S during sulphide-promoted reductive dissolution of Fe oxides

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The use of Fe isotopes as tracers of geochemical cycling within both modern and ancient environments has been widely documented in recent years with the advance of analytical procedures for non-traditional stable isotopes (Anbar, 2004). In particular, microbial Fe reduction may be associated with significant Fe isotope fractionations (Beard *et al.*, 2003). This has led to Fe isotopes being used as evidence for the antiquity of dissimilatory Fe reduction. However, the application of Fe isotope signatures to tracing microbial Fe reduction in the rock record requires that there is no significant abiotic fractionation associated with early diagenetic processes.

There is, however, some evidence for Fe isotope fractionations occurring via abiotic pathways. Kinetic isotopic fractionations of the order of $0.85 \pm 0.3\%$ have been observed during the formation of FeS from dissolved Fe(II), a value which increases upon ageing (Butler *et al.*, 2005). Furthermore, changes in Fe oxidation state (Fe(III) \leftrightarrow Fe(II)) have been observed to fractionate Fe isotopes for different Fe-species in solution (Johnson *et al.*, 2002). A major process occurring during early diagenesis is the sulphide-promoted reductive dissolution of Fe oxides. The above observations suggest that this may also potentially fractionate Fe isotopes, but no study has yet attempted to evaluate isotopic fractionations during this process.

To further assess the use of Fe isotopes as tracers of microbial activity, a range of experiments to track the isotopic composition of synthetic Fe oxides during reductive dissolution by sulphide were performed. Analysis of these samples was carried out by MC-ICP-MS (Dauphas & Rouxel, 2006). Carefully controlled experiments covered a variety of initial starting conditions (surface area, pH, initial S²⁻ concentration), and the results considered in terms of previous claims that microbial Fe reduction can be unambiguously identified by Fe isotope fractionations in the rock record. In addition, we are also investigating the possibility that sulphide-promoted reductive dissolution of Fe oxides (which results in oxidation of sulphide to elemental sulphur) may result in S-isotope fractionations.

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Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and two Late Devonian episodes of perturbations in carbon cycling

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The Late Devonian mass extinction event, which occurred just prior to the Frasnian-Famennian boundary, has frequently been linked to the spread of anoxic bottom waters and/or elevated surface productivity in epicontinental seas due to the close association of the extinctions with two regionally (perhaps globally) extensive black shale horizons and positive $\delta^{13}\text{C}$ excursions in marine carbonates. However, other intervals during the Devonian also witnessed dramatic changes in global carbon cycling but are not associated with major extinctions. For example, recent work on early-middle Frasnian carbonate successions in Poland, Belgium and China, has revealed a prominent positive shift in $\delta^{13}\text{C}_{\text{carbonate}}$ and $\delta^{13}\text{C}_{\text{org}}$ at the base of the *Palmatolepis punctata* conodont zone (lowest middle Frasnian), which marks the beginning of a prolonged positive carbon isotope anomaly that almost lasted the entire duration of the *Pa. punctata* zone. This positive $\delta^{13}\text{C}$ anomaly is associated with evidence for transgression-related eutrophication, elevated primary productivity, oxygen-deficiency in bottom waters and faunal turnover but does not coincide with elevated extinction rates, despite the apparent intensity of the perturbations in the biosphere (Racki *et al.*, 1994; Piszczowska *et al.*, in press; Yans *et al.*, in press).

In this study, seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curves were constructed for both the Frasnian-Famennian and early-middle Frasnian boundary intervals in order to investigate any changes in the balance between the continental and hydrothermal fluxes of Sr to the oceans over these times. High resolution Sr isotope data is lacking for both intervals although many causal mechanisms for the widespread accumulation and preservation of organic-rich deposits involve changes in the continental flux of nutrients to the oceans. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured in the denticle material of apparently unaltered conodont elements collected from continuous carbonate successions in the Holy Cross Mountains of Poland. Interestingly, seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values appear to have been relatively stable at ~ 0.70805 over the Frasnian-Famennian extinction interval. This is in contrast with published data for this interval which show a major increase in oceanic $^{87}\text{Sr}/^{86}\text{Sr}$ values in the earliest Famennian but which are based on less reliable whole-rock carbonate samples. In contrast, the early-middle Frasnian data record a marked rapid rise in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the base of the *Pa. punctata* zone. Values were relatively constant during the *Pa. transitans* zone (~ 0.70794), they began to increase in the early *P. punctata* zone and reached a value of ~ 0.70814 in the late part of this zone. The most likely cause of the increase in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values is an increase in the continental (weathering) flux of Sr to the sea and this is supported by the fact that the shift in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values coincides with the reported positive shift in $\delta^{13}\text{C}$ and increase in primary productivity, which suggests an increase in nutrient influx into the shallow marine realm.

This study highlights the need for further investigation into other Devonian black shale events in order to put the Late Devonian mass extinction, and associated environmental changes, in its proper temporal context.

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