Unravelling Plio-Pleistocene sea surface temperature signals: a multi-proxy latitudinal approach from the South China Sea

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The tropical oceans are thought to have played a major role in the evolution of the Earth’s climate since the Pliocene, such that accurately reconstructing tropical sea surface temperatures (SSTs) is an essential part of investigating how the global climate system has evolved over the past 5 Ma. Marine sediments from the tropical South China Sea (SCS) have yielded numerous paleotemperature records, however disagreement among different proxies and the potential causes of these differences may be hindering our understanding of the climate system. Using sediments from ODP Sites 1148 and 1143 located in the northern and southern SCS, respectively, we have applied three independent palaeo-proxy techniques to examine variations in SST for the past 5 Ma. Specifically, we have generated comparable SST records using the alkenone U'K', TEX86 indices and Mg/Ca ratios in planktic foraminifer, G. sacculifer.

Our Pliocene TEX86-derived temperatures for both sites indicate SSTs continuously higher than 27°C, exceeding modern mean annual SSTs. The southern SCS is generally warmer (28.0-32.5°C) than the northern SCS (27.0-31.0°C), with ODP Site 1143 displaying both greater variability (4.5°C) and a long-term decrease from 4 to 2 Ma. In contrast, the northern ODP Site 1148 exhibits lower variability (3.5°C) and no apparent trend such that the two records converge to similar values in the Pleistocene. Our Mg/Ca-SSTs show a similar trend to Mg/Ca SSTs at ODP Site 806 in the western equatorial Pacific [1], remaining generally stable (25.5-31.5°C) throughout the last 5 Ma with no indication of any global cooling. Alkenones are abundant in our samples. However, during the Pliocene, concentrations of tri-unsaturated alkenones are below detection limits indicating that SSTs in the SCS were above the limits of the U'K' proxy (27.0-29.0°C) during this time.

The high U'K' indices are consistent with the high SSTs in our TEX86 records, implying that SSTs in the Pliocene and early Pleistocene exceeded modern mean annual SSTs. In contrast, our Mg/Ca-SSTs (25.5-30.5°C) during this same period are offset from our TEX86-SSTs (27.0-32.5°C) by, on average, >2°C at both SCS sites. Furthermore, our alkenone SSTs for ODP Site 1148 show that the northern SCS has cooled over the last 2 Ma, but this cooling is not seen in our Mg/Ca records. Higher TEX86-derived temperatures may be in part due to TEX86-SST estimates corresponding to warm season SSTs, as reported for a SCS core top sample [2], but it is unclear if such a bias can explain the high U'K'-derived SSTs. With these data we shall discuss reconstructing past tropical warmth and the application of various SST proxies in the Pliocene.


Gahnite-bearing rocks (ZnAl2O4) are volumetrically abundant throughout the Proterozoic Broken Hill Domain, New South Wales, Australia, where they are associated with Broken Hill-type (BHT) Pb-Zn-Ag mineralization (including the supergiant, 200 Mt, Broken Hill deposit). Historically, the presence of gahnite has been utilized as an exploration guide for ores of this type, but has led to relatively limited sulfide discoveries. Major element chemistry has been used successfully to define a compositional range of gahnite associated with metamorphosed massive sulphides deposits, but it fails to distinguish sulfide-rich from sulfide-poor occurrences.

Major and trace element data from LA-ICP-MS and electron microprobe analyses provide valuable insight both into the origin of gahnite at Broken Hill, and its use as an exploration guide. Samples from 12 BHT deposits were analysed to determine whether or not prospective BHT deposits can be compositionally distinguished from non-prospective occurrences based on trace element content. Data were discriminated using a Principal Component Analysis to distinguish gahnite associated with the main ore lode from that associated with unmineralized lode pegmatites and sillimanite gneiss. Gahnite from the main ore bodies at Broken Hill have a relatively restricted compositional range that, based on a series of bivariate plot with density ellipses, overlap with the compositions of gahnite from several minor BHT occurrences. Based on contour maps of ore grade (wt. % Pb + Zn) associated with each gahnite locality, gahnite associated with the highest grades from the minor BHT deposits, have compositions that plot within the field for gahnite from the main ore bodies suggesting that trace element chemistry (e.g., Co: 60-80 ppm, and Cr+V+Mn+Ga: 1,100-2,200 ppm) may be used as an exploration guide for high-grade ore.
Spatial distribution of As(V) in cell-mineral aggregates formed by NO₃⁻-reducing Fe(II)-oxidizing bacteria

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Ground water contamination with As is an environmental problem affecting human health [1]. Sorption of As to Fe(III)-(oxyhydr)oxides, is one of the most efficient mechanisms for immobilizing As in the environment. Fe(II)-oxidizing bacteria have recently been identified as possible contributors to As immobilization [2]. The objective of this study was to map the partitioning of As at various stages of precipitation [3] and to clarify the detoxification mechanisms.

The nitrate-reducing, Fe(II)-oxidizing Acidovorax strain BoFeN1 was cultured in presence of 0.2-1 mM arsenate. Samples were prepared anoxically for spectromicroscopic identification and mapping of the of cell-mineral aggregates formed during biogenic Fe(II) oxidation. Chemical speciation of As was measured at sub-100 nm spatial resolution by scanning transmission (soft) X-ray microscopy (STXM) using X-ray fluorescence (XRF) detection at beamline 11.0.2, Advanced Light Source (ALS), Berkeley USA.

Biogenic Fe-precipitates formed at different stages of microbial Fe(II) oxidation were found to vary significantly in their affinity for arsenate sorption/coprecipitation. The cytoplasm and the periplasmatic Fe(III) precipitates formed when cultivated with Fe(II) were highly depleted in As(V). No reduction of arsenate to arsenite was detected, which would be an essential step in the conventional As-detoxification systems. These results together indicate a yet unknown, efficient mechanism of either hindering As(V) from entering the cytoplasm through the phosphate transport mechanisms, or an arsenate-specific efflux pump. Although present in the genome of BoFeN1, the ArsC, ArsA and the ARR3 genes which are involved in the conventional detoxification, seemed not to play a role in the As depletion of the cells. In contrast, cell-associated extracellular precipitates of mineral-filled cell-residues of late stages of Fe(II) oxidation were enriched in their As(V)-content.

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Origin of Anomalous Isotope Effects in Photo- and Thermo-chemical Reactions of Organosulfur Compounds

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15F. Organic sulfur in the Earth System

There is overwhelming hypothesis about the importance of sulfur mass-independent isotopic (MIF) signatures Δ34S, Δ33S, and Δ36S observed in the early Earth’s history[1]. The accumulation of MIF signals in ancient rocks has been linked to UV photolysis of SO2 that penetrated deep in the Earth’s atmosphere during the Archean[2]. Recently, it has been argued that thermochemical sulfate reduction (TSR) produce anomalous sulfur-33 compositions[3], but the source of this anomalous isotope signature have been suggested to result from a magnetic isotope effects (MIE) and the anomaly is limited to the magnetic isotope 15S and not on 34S[4].

In order to elucidate the mechanisms and differentiate between the sulfur isotope anomalies produced by photochemical and thermochemical reactions. We carried out a series of UV photolysis experiments of SO2 with methane (CH4), acetylene (C2H2), and ethylene (C2H4). The photolysis produced a number of methylated sulfoxide aerosol species (such as dimethylsulfone - DSO and methanesulfonic acids -MSA). The different isotope patterns are observed for the radiation under 190 to 220 and 250 to 330 nm UV absorption bands. But all shows anomaly in both S-33 and S-36. New thermochemical experiments of model organosulfur compounds demonstrate that thermolysis of terminal thiyl (such as glutathionine) and aromatic thiane (1,3,5-trithiane) compounds can also produce significant Δ33S anomalies. These Δ33S enrichments are attributed to a magnetic isotope effect (MIE) that affects only odd isotopes via the formation of thyl-disulfide ion-radical pairs.

The findings in this thermal experiment are not consistent with multiple sulfur isotope trends of extracted methylated sulfoxide compounds observed in SO2-CH4-C2H2-C2H4 photochemical experiments, which exhibit significant 34S anomalies and further the assertion that the early Archean record does not reflect this thermally induced radical sulfur chemistry. Detailed reaction mechanisms and processes leading to photochemical and thermochemical S-MIF signals will be presented.

References:
Direct evidence for isotopic fractionation during congruent dissolution, precipitation and at equilibrium

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This study provides direct experimental evidence of magnesium (Mg) isotope fractionation between an aqueous fluid and magnesite during its congruent dissolution, precipitation, and at equilibrium. Closed-system batch reactor experiments were performed at temperatures from 120 to 200 °C and at 15 to 30 bars CO2 pressure. During congruent magnesite dissolution the fluid became enriched in isotopically heavy Mg, with a steady state δ26Mg/24Mg fractionation factor (εeqm) for the were found to be 0.99881 at 150 °C and 0.99912 at 200 °C, close to those predicted by density-functional electronic structure models. Magnesite precipitation was provoked by increasing the reactor temperature after equilibrium had been attained via dissolution. Kinetic isotope fractionation effects consistent with Rayleigh fractionation were observed immediately after the reactor temperature was increased and rapid magnesite precipitation occurred. However, isotopic exchange continued as the system equilibrated, eradicating the kinetic signal in the precipitated solid. As most natural systems fail to sustain rapid precipitation rates long-term, this observation suggests that kinetic fractionation effects in precipitated minerals will not be preserved in most geological systems.

The results of this study confirm the concept of dynamic equilibrium during water-mineral processes. Dynamic equilibrium also means that minerals and fluids will continue to equilibrate isotopically long after equilibrium is attained. This conclusion has significant consequences for the use of mineral isotopic compositions to illuminate chemical weathering processes, water-rock interaction in the crust, and past environmental conditions.

On the competition between kinetic and equilibrium isotope fractionation during low-T silica precipitation

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Formation of Si-bearing phases due to precipitation or adsorption always favors incorporation of light isotopes (apparent fractionation factor Δsolid-fluid < 0‰), which is usually explained by kinetic isotope fractionation. We challenge this assumption by conducting two sets of laboratory experiments.

First, Si-adsorption experiments (exp. #1) onto suspended gibbsite were performed at different initial monosilicic acid concentrations ([Si]aq= 10, 20 and 40 ppm) at pH 7. Adsorption of silicic acid results in an increase of δ30Si values and a chemical steady state is reached after ~300 h of experimental runtime. These experiments confirm that Δsolid-fluid < 0‰ but also show that the magnitude of Δsolid-fluid depends on the initial Si concentration. We show that Si concentrations affect the precipitation rate, but there is no obvious reason why isotope fractionation should depend on precipitation rate in a well-mixed system where no isotope fractionation due to diffusion in the solution should occur.

However, according to DePaolo [1], the fractionation of isotopes between solution and forming solids depends on the ratio of net precipitation rate Rp to the backward reaction rate Rb. When Rp ≈ Rb, a competition between equilibrium and kinetic fractionation is expected. To test this hypothesis, a second set of experiments (exp. #2) were conducted, where solutions were frozen and thawed within 24 hours up to 130 days and sampled at regular intervals, during which amorphous silica was repeatedly precipitated/adsorbed and redissolved. In this special setup, Rp << Rb might be achieved, a condition for isotope fractionation to reflect equilibrium[1]. Several sets of these experiments were performed at pH 4.5 and 7, with solutions initially containing [Si]aq = 45 ppm and [Al]aq = 2.7 or 27 ppm. We suggest precipitation of an Al-O-OH phase and subsequent precipitation or adsorption to Si-bearing phases due to precipitation or adsorption is not necessarily dominated by kinetic isotope fractionation.

In the first set of adsorption experiments (exp. #1), we suggest precipitation of an Al-O-OH phase and subsequent adsorption of Si and Al. Experiments with high initial Al concentration show changing δ30Si values with experimental runtime. The δ30Si values increased during the first 20 days to up to 2.4‰ and then shows a decline to almost starting values of 0‰ after 130 days. This setup allows that Rp shifts from values >> Rb, to values Rp ≈ Rb, which results in a change from kinetically- to equilibrium-dominated isotope fractionation.

In the first set of adsorption experiments (exp. #1), where Rp > Rb, kinetic isotope fractionation is assumed as Si rarely exchanges with the solution.

To conclude, the withdrawal of Si in natural systems due to precipitation or adsorption is not necessarily dominated by kinetic isotope fractionation. Instead, isotope fractionation might approach Δsolid-fluid ≥ 0 if Rp << Rb, which can then be interpreted as equilibrium isotope fractionation.

Mercury speciation in deep-sea waters of the Mediterranean Sea

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This communication presents results of the investigation of the distribution and speciation of mercury (Hg) in deep-sea waters of the Mediterranean Sea during oceanographic cruise on board the Italian research vessel URANIA as a part of GIMOS project. The study includes deep water profiles of dissolved gaseous Hg (DGM), reactive Hg (RHg), total (THg), monomethyl Hg (MeHg) and dimethyl Hg (DMeHg) in open ocean waters. A special attention is paid on the distribution of DGM, which plays the major role in the exchange of Hg between water and atmosphere. Average concentrations of measured Hg species were characterized by seasonal and spatial variations. Overall average THg concentrations ranged between 0.41 to 2.65 pM (1.32 ± 0.48 pM) and were comparable to those obtained in previous studies for the Mediterranean Sea [1,2]. Generally, average THg concentration was higher in W and E Mediterranean Deep Waters (WMDW and EMDW) and Levantine Intermediate Water (LIW) than overlaying Modified Atlantic Water (MAW). High concentrations and portions of DGM and MeHg indicate high reactivity of Hg in open ocean waters. DGM was present in surface waters mainly as Hg²⁺ as no DMHg was detected at the surface, while towards the bottom a noticeable, but relatively small portion of DMeHg is present. DGM represents a considerable proportion of total Hg (average 20%, 0.23 ± 0.11 pM). The portion of DGM typically increased towards the bottom, especially in areas with strong tectonic activity (Alboran Sea, Strait of Sicily, Tyrrhenian Sea), indicating its bacterial and/or geotectonic origin. This is also confirmed by the fact that average DGM concentration was the highest in deep water masses (WMDW and EMDW). The percentage of MeHg (0.22 ± 0.12 pM) was on average approximately the same as for DGM. The observed increase of MeHg towards the bottom could be the consequence of photochemical degradation and/or microbial actions in surface and microbially mediated methylation in deeper waters [3,4]. Results will be also compared to the results obtained in the last GEOTRACES Atlantic Ocean cruise.

Evidence for the $O_2$ and $CO_2$ rich Archean atmosphere

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In the oxygenated world, the $CO_2$ and $O_2$ contents of the atmosphere and oceans are regulated at steady-state levels by the balance between the forward and backward reactions of: $CO_2 + H_2O = CH_2O + O_2$. Today, ~100% of the $CH_2O$ formed on land and ~99.7% of the $CH_2O$ formed in the oceans by oxygen photosynthesis are recycled back to $CO_2$ in <10 yrs by aerobic oxidation. Burial of the ~0.3% of organic matter as kerogen in sediments has been responsible for the long-term (~10,000 yrs) production of $O_2$ in the atmosphere and oceans. Oxidation of the kerogen during soil formation has been the main pathway for the long-term consumption of $O_2$.

In the anaerobic world, such as the one postulated by many for the Archean, organic synthesis is carried out by anoxicogenic photosynthesis (e.g., $CO_2 + 2H_2O = CH_2O + H_2O$). Fresh organic matter decomposes by fermentation (e.g., $CH_2O + H_2O = CH_4 + H_2$, c.f., Hoeler et al., 2001), but kerogen is not decomposed. In such a world, the atmospheric $CO_2$ is continuously converted to reduced C compounds ($CH_2O, CO, CH_4$ and $C_2H_5OH$) and not completely recycled back to $CO_2$. Thus, the atmospheric $CO_2$ continuously decreases, even with continuous supplies of $CO_2$ by volcanic gas and weathering of carbonates, and disappears in ~100 Ma since the emergence of photoautotrophs, creating an icy, dead planet (Ohmoto and Lasaga, 2001). However, the abundances of carbonates and organic C-rich shales, and their $\delta^{13}C$ values, in Archean sedimentary rocks are essentially the same as those in younger ones (Ohmoto, 2004), suggesting that since ~3.8 Ga, the atmosphere and oceans have remained $O_2$ and $CO_2$ rich and the modern-styled redox cycle of $C$ has operated.

Black shales with high pyrite contents, which positively correlate with organic C contents, and sulfate-rich sediments are not uncommon in Archean rocks (Ohmoto, 2004). $\delta^{34}S$ values of the pyrites and sulfates show large variations, from -20 to +35‰ and from +2 to +27‰, respectively (Ohmoto, 1992, 2004; Kiyokawa et al., in prep.). The common $\delta^{15}N$ values for kerogen in Archean shales (0 to +15‰) are essentially the same as those in Phanerozoic ones (Yamaguchi, 2004; Kerrich et al., 2006). These data suggest that since >3.5 Ga, the oceans have been rich in $SO_4^{2-}$ and $NO_3^-$. Researchers have interpreted the isotopic records of S, Fe, Mo and Cr in sedimentary rocks based on anoxic Archean atmosphere models. However, we can better explain these isotopic data, as well as the Pb isotope data and the variations in the $Fe^{III}$, $Mo$, $Cc$, and $U$ contents, of Archean rocks with the model of a fully-oxygenated Archean world. The isotopic variations in the 2.7-2.5 Ga Hamersley sediments can be explained by combinations of biological-, diageneric- and hydrothermal processes in a nearly-closed euxinic basin, which episodically hosted matalliferous brine pools and/or opened to the $O_2$, $S_2$, $Mo$- and $U$-rich oceans.

Many researchers have cited the presence of AIF-S (or MIF-S) and detrital grains of uraninite and pyrite in some Archean-aged sedimentary rocks as strong evidence for an anoxic Archean atmosphere. But such arguments are invalid, as AIF-S and these detrital minerals have also been found in much younger-aged materials (Ohmoto, 2004; Watanabe et al., Goldschmidt 2012).

Trace element composition of size-fractionated particulates in the North Atlantic U.S. GEOTRACES section

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Sinking (>51 µm) and suspended (<51 µm) marine particulates were collected via in situ filtration during the US GEOTRACES North Atlantic Zonal Transect cruises on the R/V Knorr in 2010 and 2011. Total and acetic acid-leachable compositional profiles for key trace elements and isotopes (TEIs—$Fe$, $Al$, $Zn$, $Mn$, $Cd$, $Cu$) and other TEIs of interest (Co, Ti, Ba, V, Ni, Mo) are presented, allowing a first look at particulate composition for a full ocean transect, in sixteen-point depth resolution.

This transect explores a diverse array of sites—the Saharan African and North American continental margins, a mid-ocean ridge hydrothermal plume, several benthic boundary layers, as well as open-ocean sites—which significantly expands our knowledge of the highly-variable and dynamic marine particulate world. Common behaviors are observed for several groups of elements, highlighting differences between lithogenic and biogenic particulate pools, and the dynamics that exchange material between different size-fractions. Acetic acid-leachable particulate data furthermore provides constraints on exchangeable and/or bioavailable elemental pools, and also explores the behaviors of redox-sensitive metals in oxygen minimum zones, benthic boundary layers, and in surface waters. Combination of this dataset with other, forthcoming GEOTRACES results (e.g., $^{234}$Th export, dissolved TEI parameters) will be an exciting product of the worldwide GEOTRACES program.
Bio-mineralization of rare earth elements

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Geochemical behaviors of rare earth elements (REEs) are important to understand the migration of trivalent actinides and fission genic REEs from nuclear power plants and high level radioactive waste. When REEs migrates in environments, their chemical states may change by the interaction with inorganic and organic materials. Many researchers have studied the interaction of REEs with inorganic materials. However, the biotransformation of REEs have not fully understood. We have conducted the research on the effects of microorganisms on chemical states change of REEs.

We found that Sm(III) phosphate minerals were formed on the cells surface of gram negative bacterium Pseudomonas fluorescens after exposure of Sm(III) solution with the resting cells, even though no phosphate is added. TEM-SAED analysis showed that Sm-monazite was developed directly from the surface of cells. Sm(III) ions were first adsorbed by the functional groups of cells surface, followed by the chemical states change by the reaction with phosphate ions released from inside the yeast cells.

When phosphate is provided in the solution as glycerol phosphate-Ca, Yb concentration decreased abruptly with time after P. fluorescens exposed to the solution containing Yb(III) and lactic acid. TEM and XAFS analyses showed that the precipitates containing Yb and P were formed directly from the cells surface. Interestingly, precipitates containing Ca and P, but no Yb were observed on the cells. On the contrary, without glycerol phosphate, Yb concentration in the solution slightly decreased with time by the formation of Yb-lactate complex in the solution.

These findings strongly indicate that Yb phosphate mineralization was occurred on the cells surface, even when P was provided from inside and outside cells. Thus, cell surface of microorganisms functions as specific reaction environment for biotransportation of REEs.

Speciation study of copper in stream sediments and soils

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A sequential extraction method has been used widely to elucidate its chemical binding forms in sediments including soil. However, the method might give misleading results due to alteration of the samples during the individual steps of the extraction [1]. We applied a X-ray absorption fine structure (XAFS) spectroscopy to identify the Cu species in the residues after each step of the sequential extraction. The Cu in 7 geo-standard materials (JSd-1~5; stream sediments, JSO-1 and 3; soils) was extracted using a modified three-step extraction developed by the Community Bureau of Reference (BCR) [2]. The steps and extractants are as follows;

1. Step 1: CH3COOH (0.11 mol/L).
2. Step 2: NH2OH·HCl (0.5 mol/L).
3. Step 3: H2O2 (8.8 mol/L) and CH3COONH4 (1 mol/L).

The residues after each step of extraction were filtrated by a membrane filter. The Cu3+, Cu(NO3)2, Cu doped FeOOH (or MnO2), Cu doped humic materials, and JCu-1 (a geochemical reference material of CuS ores) were prepared as a reference compounds. The Cu K-edge XANES spectra were recorded in a fluorescence mode at the BL-12C of KEK-PF. The fluorescence X-ray was measured by a 19 element pure-Ge SSD.

Figure 1 shows the Cu K-edge XANES spectra of JSd-2 and reference materials and its fitting results. The JSd-2 is a stream sediment reference material collected from the drainage basin having Cu mine. The speciation of Cu in JSd-2 is expected to be a mixture of Cu weakly adsorbed on materials (step 1), Cu bound to Fe-Mn hydroxides (step 2), chalcopyrite (step 3) and silicate materials (residue). The linear fitting result was roughly comparable to the results from the BCR scheme, although the relative amount of Cu extracted at step 3 is underestimated. Thus, the method using XAFS spectroscopy combined with BCR scheme is effective to accurately identify and quantify Cu species in sediment samples.

Figure 1. The Cu K-edge XANES spectra of JSd-2 and the residue of JSd-2 after third step in the BCR scheme, and reference materials.

Iron isotopic signature of Fe-Ni metals in ordinary chondrites using LAL-MC-ICPMS technique

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Introduction

The ordinary chondrite is the most abundant and primitive meteorite in the solar system. It is widely believed that the formation sequence of the ordinary chondrites tell us details of the early solar system history. Among the various minerals or components found in the ordinary chondrites, the Fe-Ni metal is one of the characteristic materials of ordinary chondrite. Despite the major components, the formation processes of Fe-Ni metals have still been veiled. The Fe isotopic signature is one of the key information to derive the formation processes of Fe-Ni metals in the ordinary chondrites, because (a) Fe is ubiquitously distributed in various minerals or phases in the meteorites, and (b) Fe isotope composition can vary through the formation processes. In this study, the Fe isotopic ratios of Fe-Ni grains in ordinary chondrites were measured. In order to derive inherent and reliable Fe isotopic data from complex Fe-Ni phases, we have developed a new sampling technique described below.

Experimental

In this study, Fe-Ni metals in ordinary chondrites were collected using laser ablation in liquid (LAL) technique [1, 2]. The sample surface was polished and the metal phase was ablated in the deionized water using the femtosecond laser (λ=780 nm). Unlike with the conventional micro-drilling technique, the LAL technique can provide minimum risk of contamination of Fe from equipments. After the LAL sampling procedure, the resulting sample suspension was collected using micropipette and was then subsidized to acid digestion using conc. HCl and conc. H2O2. The sample solution was heated until dryness and the resulting sample cake was re-dissolved in 0.1% HCl, and then used for the isotopic analysis of Fe using MC-ICPMS connected to the desolvating nebulizer system.

Results and Conclusion

Total 15 ordinary chondrite metals were analyzed in this study. The δ⁵⁶Fe data for L chondrites did not vary with the δ⁵⁶Fe data for LL chondrites. In contrast, Fe in the H chondrites was isotopically lighter than those for L or LL chondrites. These Fe isotopic variations between H, L and LL chondrites are consistent with the data obtained by Theis et al. (2008) [3]. However, these Fe isotopic ratios within the metallic phase in the H, L and LL chondrites cannot be explained by the simple redox reaction suggested by Theis et al. (2008). Possible cause of the present variation of Fe isotopic ratios will be discussed in this presentation.

References


Vertical distributions of ¹²³⁰Th in the Pacific Ocean and their relation to advection and diffusion

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In the central Pacific Ocean, which is remote from all the continents, the distributions of trace elements especially show the typical vertical profiles of open oceans.

Vertical distributions of ¹²³⁰Th in the Pacific Ocean have been well-described by the reversible scavenging model [1]-[5]. On the basis of the assumption of no lateral ¹²³⁰Th transport in this model, in-situ produced ¹²³⁰Th is scavenged within the basin. In contrast, the effect of lateral advection on Th distribution have been shown in the Southern Ocean and Atlantic Ocean[6]-[8] and using a model calculation the effect of isotopical diffusion have been discussed [9].

We investigated the vertical distribution of total ¹²³⁰Th in mid-latitudes of the Pacific Ocean. Because of low biogenic particle flux, high ¹²³⁰Th activity in deep water is exhibited in the central gyre. The west–east section (20°N) of ¹²³⁰Th shows a strong gradient in the deep waters around 170°E and 110°W. At depths of 2000–4000 m and 4000 m–bottom, within the time-scale of scavenging residence time of ¹²³⁰Th, the horizontal eddy diffusion could reach 1100–1400 km and 400–700 km, respectively. The horizontal eddy diffusion transport is too weak to affect Th distribution in the deep layers between each station in this study area. We observed the depletion of total ¹²³⁰Th compared with a reversible scavenging model prediction for the deep layers in the mid-latitudes of the North Pacific Ocean. The observed depletion is partly explained by lateral advection, adopting the scavenging-mixing model. Additionally, a bottom scavenging process above the seafloor and a diffusion process are considered to explain the ¹²³⁰Th deficit.

In the Eastern Subtropical Pacific, advection and diffusion of low-¹²³⁰Th water in the high particle flux region could affect the distributions of ¹²³⁰Th. At the station on the East Pacific Rise, we observed exceptionally depleted ¹²³⁰Th in deep layers. The ¹²³⁰Th depletion would be attributed to the active hydro-thermal activity in this area.

Characterization of microbial activity by petroleum compositional changes using ultra-high resolution mass spectrometry techniques (FT-ICR-MS)

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Introduction & Methods

Most of the world petroleum reserves are biodegraded with the largest oil reserves being found on the flanks of foreland basins in Canada and Venezuela. Coal as another essential energy source is also known to being partially biodegraded yielding to biogenic gas.

In this study, the compositional changes of fossil fuels during biodegradation in lab experiments and in natural reservoir profiles under aerobic and anaerobic conditions will be shown as well as indicators of microbiological activity.

The fossil fuel compositions were analyzed using an ultra-high resolution Fourier Transform-Ion Cyclotron Resonance-Mass Spectrometry (Bruker12T FT-ICR-MS) and GC-MS techniques. For FT-ICR-MS the ionization methods used include Electrospray (ESI) and Photoionization (APPI) in positive ion mode.

Results & Discussion

One example of compositional changes during biodegradation of bitumen and assessment of microbial activity is shown in Fig. 1.

Figure 1: Changes in oxygen compound systematics of aerobic biodegradation lab experiments of oil sands bitumen: a. alcohols, b. carboxylic acids, c. hydroxy-carboxylic acids, d. dicarboxylic acids. All oxygen compound classes (O1-4) are becoming strongly enriched in the absence of light whereas under light no or only minor changes are observed.

Thermodynamic properties of carbonate liquids: required for models of carbonate stability in the mantle

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Not only is mantle carbonate an important reservoir in the global carbon cycle, it also plays a key role in mantle melting processes. Mantle carbonate, of which MgCO3 and CaCO3 are the most important components, has been shown to have a major effect on both the depth of melting and the resultant magma composition (e.g., Dasgupta et al., 2006). In order to fully explore under what T-P conditions mantle carbonate can be subducted into the lower mantle, as well as to examine all possible temperature, pressure, and composition conditions where mantle carbonate influences melting, the number of phase equilibrium experiments needed is prohibitive. Therefore, thermodynamic models of mantle melting that incorporate carbonate are of considerable interest. In order to achieve this, thermodynamic data on CaCO3 and MgCO3 liquids are needed, including their heat capacity, enthalpy, volume, and compressibility. By mixing the alkaline earth carbonates with the alkali carbonates, liquidus temperatures are lowered to those below decomposition (< 1300K), permitting measurement of various thermodynamic properties to be made. This method also tests whether the molar volume, compressibility, and heat capacity of carbonate liquids mix ideally with respect to composition, allowing the partial molar properties for CaCO3 and MgCO3 to be derived. Previous work in the system Li2CO3-Na2CO3-K2CO3-CaCO3 by Liu and Lange (2003) has shown that the volume and thermal expansion mix ideally. In this study, we show that the compressibility and heat capacity of Li2CO3-Na2CO3-K2CO3-CaCO3 liquids also mix ideally with respect to composition at one bar. Compressibility measurements were made on eleven liquids (four containing ≤ 50 mol% CaCO3) using frequency-sweep acoustic interferometry at one bar between 800 and 1300 K. When the ideal mixing model for compressibility is applied, the fitted partial molar compressibilities are acquired (Table 1).

<table>
<thead>
<tr>
<th>Carbonate Component</th>
<th>βCaCO3 (10^5 GPa⁻¹)</th>
<th>∂βCaCO3/∂T at 1100 K (10^5 GPa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO3</td>
<td>5.36 ± 0.13</td>
<td>0.0061 ± 0.0010</td>
</tr>
<tr>
<td>Li2CO3</td>
<td>8.09 ± 0.06</td>
<td>0.0044 ± 0.0008</td>
</tr>
<tr>
<td>Na2CO3</td>
<td>10.62 ± 0.07</td>
<td>0.0103 ± 0.0006</td>
</tr>
<tr>
<td>K2CO3</td>
<td>14.09 ± 0.06</td>
<td>0.0135 ± 0.0004</td>
</tr>
</tbody>
</table>

Table 1. Partial molar compressibilities for the carbonates.

A Perkin-Elmer Diamond differential scanning calorimeter is being used to measure liquid heat capacities. We have applied our results to a thermodynamic analysis of the fusion curve of CaCO3 in order to constrain its one-bar enthalpy and entropy of fusion in addition to the pressure dependence of the compressibility (bulk modulus) of CaCO3 liquid (K’0), using a 3rd-order Birch-Murnaghan equation of state. Currently, our best estimate for the K’0 of CaCO3 liquid is 4.5 ± 0.5. Though DSC measurements are ongoing, our preliminary estimate for the enthalpy of fusion for CaCO3 at one bar is 67.5 ± 0.5 kJ/mol for a one-bar metastable melting temperature of 1295°C.
Fossil Corals as an archive of Phanerozoic seawater chemistry

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Numerous observations indicate that the composition of seawater has not remained constant through time. It has been hypothesized that such variability is linked to changes in geologic processes such as continental weathering, sea-floor spreading, and continental onlap. Fossil corals may be suitable candidates for studying seawater chemistry. Although there is evidence that incorporation of some elements into the coral skeleton is biologically mediated, other elements seem to accurately record certain chemical properties of the seawater from which the corals grow.

We studied a suite of ~12 well-preserved fossil corals dating back to the Triassic. The primary objective of this work was to assemble a collection of fossil corals that have been meticulously tested and shown to be diagenetically unaltered with respect to their original structure and mineralogy. X-ray diffraction, micro-Raman spectroscopy, and cathodoluminescence analyses suggest that these specimens contain little to no secondary calcite. Electron and optical microscopy studies reveal crystal structures consistent with modern coral aragonite. Clogged isotope data for 6 specimens give ratios. In fossils with low Mn/Ca, we observe a positive correlation between Na/Ca and S/Ca, as in modern corals. We sometimes observe a negative relation between Sr/Ca and Mg/Ca, similar to some modern corals. However, secondary ion mass spectrometry (SIMS) analyses suggest there is some micro-scale alteration indicated by high Mn/Ca, high Mg/Ca, and low Sr/Ca ratios. In fossils with low Mn/Ca, we observe a positive correlation between Na/Ca and Sr/Ca, and as in modern corals. We sometimes observe a negative relation between Sr/Ca and Mg/Ca, also similar to some modern corals.

The second objective of this study is to analyse properties such as Sr/Ca and Mg/Ca in corals to supplement existing records of global seawater chemistry since the Triassic. Initial results from SIMS measurements of Sr/Ca ratios are consistent with some existing records of Sr/Ca in seawater through time; Sr/Ca is relatively constant from the modern to the Triassic. These results are supportive of using corals as archives of paleo-seawater chemistry. Additionally, we find that Mg/Ca ratios in fossil corals decrease with age, but because of possible vital effects, the implications for seawater chemistry are uncertain.


Transport and deposition of engineered nanoparticles (NPs) in saturated porous media (schist): role of interactions between NPs and the rock matrix

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The increasing use of engineered nanoparticles for industrial and household purposes (cosmetics, clothing, electronic, automotive, medical products...) will inevitably lead to their introduction into different environmental compartments, including groundwater. Assessing the risk of groundwater contamination by nanoparticles is worth studying but requires the knowledge of their mobility and environmental reactivity. How far these nanoparticles will travel in waters? A number of studies addressed the processes driving mobility of nanoparticles in simple waters and conditions (clean Quartz sand, bare silica surfaces, uniform and spherical glass beads...). They highlight nanoparticles dispersion in water is highly dependent on physical and chemical key parameters of nanoparticles (solubility, pHtotal, which may vary with chemical composition, crystallinity, size and eventual coating...), and on the overall groundwater composition (pH, ionic strength, major element concentration, e.g. Ca or Na, organic matter contents...). The present study conducted in the frame of the AquaNano project aims at characterising metal oxide nanoparticles (TiO2 and CeO2) behaviour and reactivity during transport in schist (heterogeneous medium). Transport (flushing) experiments of nanoparticles suspension through 10 cm long rock column under pressure (up to 5 bars) have been conducted in laboratory. After the experiments, NPs retained in column have been mapped using scanning electron microscopy (SEM). Chemical and physical interactions between NPs and the rock matrix have been constrained using Raman spectroscopy associated with SEM. Results show that NPs deposition and aggregation occurred during their transfer while favorable (repulsive and low ionic strength) transfer conditions were applied in column. Also, it appears a more rapid transfer of NPs concomitant with an increase of NPs retention (by a factor 40) by rock matrix after successive NPs inputs in the column separated by NPs-free water circulation. Experiments conclusively demonstrate that physical and chemical properties of NPs and rock matrix (biotite, quartz...) govern the mobility of NPs. We suggest a rearrangement of NPs (adsorption/desorption processes) in column during NPs-free water circulation and modifications to preferential pathways for NPs circulation while aggregation enhanced NPs deposition.
Dissimilatory iron reduction and the redox cycling of green rust

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Introduction

Green rusts (mixed FeII/FeIII layered double hydroxides) have been identified in FeIII/FeII transition zones in a variety of natural and engineered subsurface environments including groundwater, soils, and sediments, and among corrosion products in zero valent iron permeable reactive barriers. Many of these environments are characterized by periodic or seasonal cycling of redox conditions (e.g., redoximorphic soils in areas with seasonal flooding) that create the opportunity for cycling of Fe between oxidized and reduced forms. In recent years evidence has been building that suggests the green rust mineral fougerite plays a central role in Fe redox cycling in these environments.

Experimental Methodology

Carbonate green rust was produced in anoxic defined mineral medium containing 75 mM formate and 80 mM FeIII, in the form of phosphate doped (0.7 mass % P) lepidocrocite, inoculated with Shewanella putrefaciens CN32. The green rust was then oxidized by introducing sterile air into the headspace. After 24 h the suspensions were sparged with sterile Ar and re-inoculated with S. putrefaciens CN32. Samples were collected for measurement of FeIII and characterization of the secondary mineralization products by powder X-ray diffraction, scanning electron microscopy, and 57Fe Mössbauer spectroscopy.

Discussion of Results

Results of the analysis of the product of green rust oxidation were consistent with ferric green rust. In our experiment, the oxidation of green rust by O2 to ferric green rust occurred over a period of 24 h without the formation of other FeIII oxide phases. However, the initial green rust was formed in the presence of phosphate and sorption of phosphate or silicate by green rust has been shown to promote oxidation of green rust to ferric green rust by suppressing the dissolution of green rust, a prerequisite for the formation of other ferric phases such as lepidocrocite or goethite. After re-inoculation, total FeIII concentrations rebounded to pre-oxidation concentrations and green rust was observed as the dominant secondary mineralization product. Since phosphate and silicate are typically available in soils and sediments, similar conditions may be encountered in-situ. Thus, our results indicate the potential for cycling of green rust between reduced and oxidized forms under redox dynamics similar to those encountered in environments that alternate between iron-reducing and oxic conditions and are consistent with the identification of green rust in soils/sediments with seasonal redox cycling.


Using laboratory-derived mineral dissolution rates to test biogeochemical weathering in the field

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Chemical weathering controls the long-term carbon cycle over million year timescales. Accurate modeling of atmospheric CO2 requires an understanding of the feedbacks between weathering and CO2 in natural waters and the atmosphere. However, field-based chemical weathering rates are notoriously hard to measure. Conversely, laboratory-derived mineral dissolution rates are generally two to five orders of magnitude faster than those measured in the field (see [1] and cited references). Additionally, biology plays a critical role in weathering that is very difficult to simulate in the lab or measure in natural environments.

We measured serpentine dissolution in both laboratory dissolution experiments and in field weathering experiments and modeled our results using the reactive transport code CrunchFlow to try to quantitatively interpret field weathering of serpentine at two recently glaciated sites in Maine and California. Serpentinites exert a strong control on the ecosystems that form on them due to the bulk chemistry of serpentine rocks, high in Mg and trace elements, and low in nutrients such as Ca, K, P, and N, which causes an extreme and stressful environment for biota. Laboratory dissolution studies showed that lizardite dissolves six times times faster in the presence of oxalate, a biological exudate, than in inorganic acids at pH 5. Field samples of a deep profile of the Pine Hill Serpentinite on Little Deer Isle, Maine, show that Ca and other major elements are depleted from the bedrock at depths of up to 1 m, most likely due to the weathering of Ca-rich pyroxene. Conversely, some trace metals including Cu and Zn show enrichment in the upper meter of the profile. Ongoing reactive transport modeling will allow us to quantitatively interpret the processes contributing to these observed profiles.

Experimental study of stibnite solubility and antimony complexation in aqueous sulfide solutions from 20 to 95°C

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Modeling antimony transport and mobility in natural hydrothermal systems and mitigation of stibnite (Sb2S3) scaling in geothermal power stations require precise data on changes in stibnite solubility in response to small changes in pH, sulfide concentration, pressure and temperatures between 20°C and 350°C. There is some uncertainty in stability and stoichiometry of antimony(III) sulfide and hydrosulfide species (i.e. thioantimonites and oxythoantimonites) at 25°C and at higher temperatures, the nature of the thioantimony(III) stoichiometry is poorly constrained.

We have conducted flow-through solubility experiments with natural stibnite to determine the solubility of stibnite in aqueous sulfide solutions from pH 6.1 to 12.7 and sulfide contents from 0.01 to 0.06 molar Stotal at 22°C. Higher temperature experiments up to 60°C have been completed at pH 11.1 and 0.006 molar Stotal and experiments up to 95°C and at variable pH are on-going. Our experimental results are similar to the solubilities found at 25°C by [1]. Krupp(1988) concluded that HxSb2S42-x species are dominant between pH 3 to 12. We note that for arsenic(III)-sulfide/hydrosulfide interactions, the dominant thioarsenite stoichiometry is apparently as the As(HS)3 moiety [2], [3], [4]. At 60°C, our solubilities are also similar to solubilities extrapolated to higher pH and temperature from [1] but predict lower solubilities at 90°C. Our measurements will provide a complete set of stibnite solubility data from 22°C to 95°C in reduced, sulfide-containing fluids and permit a new evaluation of the stoichiometry and stability of thioantimonite species over this temperature range.

References

Regional Erosion Surfaces and Climatic Readjustments, Midwest USA: Clues from late Pleistocene loess and paleosols (OIS 5e-2)

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Background
In the Midwestern, USA, early Wisconsinan time was marked by a series of events that until recently were not clearly linked to post-glacial climatic readjustments on a regional scale. Areas outside the Wisconsinan glacial border and adjacent to major river divides in several Midwestern states were examined in an attempt to locate similar adjacent regions on a scale comparable to continental glaciations.

Studies in the early 20th Century in northeastern Iowa identified an extensive erosion surface [1]. Buried by late Wisconsinan loess, this surface cut the entire stratigraphic section from the Wisconsin till to the pre-Illinoian till and thus established its relative age as younger than Wisconsinan till and older than late Wisconsinan loess deposition. Radiocarbon dates for basal Wisconsinan soils, the uppermost unit truncated by the erosion surface, indicated an age of generally greater than 18000 BP. That age indicates its development was a direct response to shifts in climate associated with glacial retreat.

Wisconsinan glaciation extended through much of the upper Midwest but at that time, there was no evidence that the surface in Iowa had parallels in adjacent regions. In the 1980’s, we began studies of the Ohio/Wabash stream divides in southeastern Indiana traditionally known as “Illinoian till plain’ stratigraphically, late Wisconsinan loess overlying Illinoian till. From the investigations, it was determined that although the loess was present in a uniformly continuous blanket across these areas, there was little or no Illinoian till beneath. The late Wisconsinan loess lay directly on bedrock, pedimentation, or older tills. Borings on subdued hills revealed that these erosion surfaces contained complete stratigraphic sections that had been sequentially truncated by an erosion surface [2, 3]. Hidden beneath loess, this erosion surface had cut the slopes that descend in all directions from the remnant outliers to form the floor of the ‘till’ plain.

Recent Regional Evidence
The Mississippi/Ohio divide in southern Illinois within the Illinoian drift border and well south of the Wisconsinan drift border were examined most recently. Multiple coring sites and soil pits were located near the divides of tributaries to the Big Muddy River drainage. Here, as in Indiana and Iowa, undisturbed thicknesses of late Wisconsinan loess directly overlie bedrock, pedimentation or older drift revealing erosional surfaces. Illinoian till is present only in protected coves of the subsurface landscape.

Conclusions
During the waning phases of the last glaciation in North America, a period of significant subaerial erosion occurred that remained largely unknown and undocumented, in part because of a lack of exposures and the difficulty in developing subsurface stratigraphic landscapes. The relative synchronicity, extent, and number of erosion surfaces outside the Wisconsinan drift border suggest a subaerial response to shifts in climatic events occurring during and immediately following the withdrawal of the last glacial ice sheet.

Nacre as a proxy for water-temperature and hydrostatic-pressure

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Many proxies of chemistry, temperature, salinity and pH are based on chemical measurement of mollusk shells, including elemental ratios, and isotopic ratios. These are chemical proxies. Here we present the first evidence of a structural proxy: mollusk shell nacre, or mother-of-pearl, and specifically the angle spread and thickness of aragonite (CaCO3) tablets in modern nacre.

With 20-nm resolution, Polarization-dependent Imaging Contrast (PIC)-mapping [1-4] displays in grayscale the orientation of the aragonite crystal axes in mollusk shell nacre, and it also shows the tablet layer thickness (Fig. 1). Both parameters are species-specific [5]. Furthermore, we found a strong correlation between nacre crystal mis-orientations and environmental temperature, and between nacre tablet thickness and hydrostatic pressure [5]. These observations have far-reaching implications: Nacre tablet thickness may provide insight into the depth at which extinct mollusk species lived, whereas crystal orientations may be used as a paleothermometer of ancient climate, spanning 450 Myr of Earth history.

Thus far we only tested the “nacre as a proxy” hypothesis on modern nacre. Once validated on fossil nacre, e.g. from ammonites, this hypothesis will be put to a test.

Figure 1: Polarization-dependent Imaging Contrast (PIC) maps of nacre from the fresh-water mussel shell of Lasmigona complanata. Different aragonite tablet crystal orientations are shown as different gray levels.


Dissolved elements released by the Grímsvötn volcanic ash, 2011

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During the evening of the 21st of May, 2011, the Grímsvötn volcano, located in southeast Iceland, began its strongest eruption in more than 100 years. The ash plume rose to 20 km and spread over Europe and the North Atlantic. The total amount of ash released was estimated by the Icelandic Meteorological Office to be more than 120 million tons and over 90% of it was released during the first 24 hours [1]. The purpose of this study was to measure the release rate of various elements during ash-water interaction and to assess the environmental impacts of the Grímsvötn ash.

Magmatic gases condense onto the surface of ash particles during a volcanic eruption. As the particles react with air and water vapour, the condensed gases form sulphuric and halogen acids and the ash surfaces dissolve [2]. The acid leaches cations from the bulk ash and secondary minerals can precipitate as a thin coating [3]. This material can be highly soluble in water, leading to rapid dispersal of possible harmful elements and/or nutrients into the environment when the ash comes into contact with rain or surface waters [e.g. 4].

In the present study, nanopure water (pH 5.9) was pumped through Teflon columns filled with ash of known surface area to monitor change in pH and the release of 70 elements, as a function of time. Initially, release rates were dominated by dissolution of surface salts, then after hours or days, by dissolution of the bulk volcanic ash. Within the first 10 minutes, the concentrations of most measured elements decreased by more than an order of magnitude, including some rare earth elements. Initially, S, Na, Ca, Mg and Cl dominated in the leachate, but after 12 hours, the most abundant element released was Si. The first water exiting the ash filled column had a pH of 7.3 and the pH gradually increased until it reached 9.7 at about 160 minutes. Over the next 4 weeks, pH slowly decreased to 6.5. The total release (mol/g ash) was determined for all harmful elements and compared with the World Health Organization (WHO) guidelines for safe drinking water [5]. The amount of Grímsvötn ash needed per litre of water, to exceed the WHO threshold values for As, Cd, Cr, F, Hg, and Pb, is 3.9, 35, 2.1, 0.10, 720, and 3.0 kg ash/l, respectively. Measured nutrients were P, Fe, V, Mo, and NO3.

Our study provides valuable information for assessing the environmental impact of ash from volcanic eruptions on vegetation, livestock, and people.

**High Arctic perennial spring activity and associated minerals: their value to Mars analogue studies**

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Saline spring discharge in cold environments is of specific relevance to ongoing interest in the search for the presence of water on other planets such as Mars [1]. Inherent to this search is the goal of finding morphological or geochemical evidence that life once existed on these planets. To better understand what these biosignatures may look like, current work aims to understand both how life survives in analogous environments on Earth and how such life interacts with their surroundings to produce biosignatures that may be preserved over geologic timescales.

Saline perennial springs in the Canadian high Arctic are a unique target for such studies. The brines emerge from the subsurface at constant temperatures and flow rates despite extremes in seasonal climate conditions. Mineral precipitates associated with spring discharge include carbonates, sulfates, and chlorides, however the majority of mineral growth occurs during winter months when cold temperatures drive freezing fractionation of salts within the waters to produce large amounts of ice and ice-rich minerals including ikaite (CaCO3·6H2O), mirabilite (Na2SO4·10H2O), and hydrohalite (NaCl·2H2O). Halotolerant bacteria inhabit springs at several sites including Gypsum Hill Diapir, Colour Peak Diapir, and Wolf Diapir, but they are restricted to spring outlets where chemical energy such as sulfide and methane are present and temperatures remain near 0°C. In contrast, it is hypothesized that a lack of energy source coupled with extremely high measured salinities in waters emanating from Stolz Diapir limits microbial colonization of this habitat.

Examination of mineral precipitates from these sites by microscopy and synchrotron radiation show variations in mineralogies due to differences in source water geochemistry. There is scant evidence of microbial colonization of mineral surfaces or creation of biosignatures at Gypsum Hill and Wolf Diapirs due to low accumulations of mineral precipitates or the soluble nature of minerals at near-freezing temperatures. At Colour Peak, however, bacterial sulfate reduction in the deep subsurface is recorded in carbonate precipitates as interbedded FeS2 laminations, which may be distantly comparable to mineral precipitation associated with a nearby inactive fossil spring adjacent to the White Glacier that formed ancient deposits. Independent data suggests the fossil spring may have been active for several million years and involved warm brines originating at depth, a habitat that could have provided restricted ecological niches for microbial evolution.


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**Lead Incorporation within Biological Apatite May Occur through a Polyphosphate Precursor**

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**Introduction**

Elevated levels of lead in seawater close to a lead and zinc mine in Greenland has been positively correlated to lead levels in seaweed, mussels, prawns, and in the liver and bone of wolf-fish and sculpin [1]. Although environmental lead is known to report to bone, the pathway between lead injection and transport to bone mineral has not been elucidated. A new bone mineral nucleation theory suggests that a precursor to biological apatite is calcium polyphosphate. Polyphosphate chelates strongly to calcium, and other divalent cations such as lead [2]. It is possible that polyphosphate chelation to lead could be one of many biological strategies to immobilize lead and prevent it from reacting with other species. A lead-calcium-polyphosphate complex could also be a precursor to biological apatite.

Alkaline phosphatase has been associated with apatite biomineralization [3]; tissue-nonspecific alkaline phosphatase was shown to break down polyphosphate ions into orthophosphate ions [4]. It is proposed that breaking down a calcium polyphosphate complex into orthophosphates increases the apatite saturation and allows for apatite nucleation.

To determine if a lead-calcium-polyphosphate complex could be transformed into biological apatite containing lead, lead-calcium complexes were formed in neutral pH solutions, and exposed to alkaline phosphatase under basic pH conditions.

Figure 1 shows the powder x-ray diffraction of the reaction products.

![Figure 1: Powder x-ray diffraction of the products of exposing calcium- or lead-calcium polyphosphate to alkaline phosphatase for 2 weeks at 37 °C.](image)

**Results and Conclusion**

Crystalline materials that have not yet been identified are the product of these in vitro experiments, however, this demonstrates that lead-calcium polyphosphate is a substrate for alkaline phosphatase. With further work on the experimental conditions, lead might be incorporated into biological apatite formed from the degradation products of lead, calcium, and polyphosphate.

ARSENIC BIOREMEDIATION BY BIOGENIC IRON OXIDES AND SULFIDES

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Millions of people globally are exposed to groundwaters that exceed the World Health Organization (WHO) safe guideline value of 10 ppb (or 0.13 μM) for arsenic in groundwater [1-3]. In this study we used microcosms containing sediment from an aquifer in Cambodia with naturally elevated levels of arsenic (As) in the associated groundwater to evaluate the effectiveness of microbiologically-mediated production of iron minerals for in situ As remediation. The microcosms were initially incubated without amendments to allow the microbial release of As, and other geogenic chemicals from the sediments into the aqueous phase. Following this period, either nitrate, or a mixture of sulfate and lactate were then added to stimulate biological Fe(II) oxidation and sulfate reduction, respectively.

Without treatment, soluble As concentrations in the microcosms reached 3.9 (±0.9) μM at the end of the 143 day experiment. However, As levels had decreased to 0.01 and 0.41 (±0.13) μM in the nitrate, and in the sulfate with lactate treated microcosms, respectively by the end of the experiment. Analyses using a range of biogeochemical and mineralogical tools, indicated that sorption onto freshly formed hydrous ferric oxide (HFO) and ferrous iron monosulfide (FeS) are the likely mechanisms for As removal in the respective treatments. Incorporation of the experimental results into a one-dimensional transport-reaction model suggests that, under conditions representative of the Cambodian aquifer, the in situ precipitation of HFO would be effective in bringing groundwaters into compliance with the World Health Organization (WHO) safe water limit for As, although soluble Mn release accompanying biogenic HFO generation presents a potential health concern. In contrast, production of biogenic iron sulfide minerals would not remediate the groundwater As concentration below the recommended WHO limit.


Geochemical and isotopic characteristics of Earth’s early mafic crust: a comparison between Nuvvuagittuq and Isua greenstone belt metavolcanic rocks

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Investigation of Earth’s primitive crust largely has focused on felsic rocks because they are the most likely host rocks of zircons, providing robust geochronological constraints. However, these felsic rocks cannot be directly produced from melting of the mantle but instead originate by melting of an older mafic precursor. Despite the scarcity of preserved early mafic crusts, the Isua and Nuvvuagittuq greenstone belts are dominated by basaltic metavolcanic rocks. The Isua greenstone belt includes geochemically distinct subterranes dominated by tholeiites and boninite-like rocks (Garbenschiefer) interpreted to have been produced in an arc setting. Similarly, the Nuvvuagittuq belt is mainly composed of a succession of tholeiitic, boninitic and calc-alkaline rocks (Ujaraaluk unit) also sharing geochemical characteristics with suprasubduction related rocks. Both greenstone belts comprise rocks with 142Nd anomalies compared to modern terrestrial Nd. Because 142Nd anomalies can only be produced while 146Sm decay was active, i.e. before 4 Ga, both suites of rocks acquired their 142Nd isotopic composition in the Hadean. The Isua metavolcanic rocks were formed between 3.7-3.8 Ga. Therefore, their elevated 142Nd isotopic composition is consistent with their Eoarchean derivation from an incompatible-element depleted Hadean mantle source. Consequently, they show no correlation between their 142Nd/144Nd and Sm/Nd ratios. However, the Nuvvuagittuq mafic rocks display a positive correlation between their 142Nd/144Nd and Sm/Nd ratios consistent with them being formed in the Hadean, between 4.3 and 4.4 Ga, from a “normal” depleted mantle. The Nuvvuagittuq rocks with the strongest arc-like signature have larger 142Nd anomalies compared to the tholeiitic rocks. However, most Isua mafic rocks analyzed so far for their 142Nd isotopic composition are tholeiites. Here we present a 146Sm/144Nd isotopic study of the Garbenschiefer which has the strongest arc-like signature in the Isua greenstone belt, allowing comparisons between the different groups of Isua mafic rocks. The studied set of Garbenschiefer rocks covers a relatively wide range of 146Sm/144Nd ratios (0.1650–0.2610) and preliminary analyses suggest that they also yield 142Nd anomalies. The Isua and Nuvvuagittuq greenstone belts represent the oldest preserved mantle-derived suites of rocks and despite the fact that they were most likely formed ~500 million years apart, they share striking geochemical similarities. A geochemical and isotopic comparison between these greenstone belts will allow us to better understand the evolution of Earth’s early crust through time and the geological processes responsible for its formation.
Pressure effects on sulfur mass-independent fractionation during SO$_2$ photolysis and its implication to the Archean atmospheric chemistry

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Large $\Delta^{33}$S values are measured in pyrite sulfur in rocks deposited before 3.2 Ga and between 2.7 Ga and 2.4 Ga, whereas those between 3.2 and 2.7 Ga yield relatively small $\Delta^{33}$S values [1,2]. This apparent structure in the Archean $\Delta^{33}$S signal may reflect changes in the atmospheric chemistry such as an incipient, transient rise of oxygen before the great oxidation event (i.e., whiff of oxygen) [1,3], the formation of organic haze aerosols [4], or a change in the redox state of volcanic gases [5].

In order to test various hypotheses, we performed laboratory SO$_2$ photolysis experiments using a flow through photochemical reactor with a Xe arc lamp as the light source. We will report the results of experiments to test the effect of pSO$_2$ and pN$_2$ on the pattern of multiple sulfur isotope fractionation. A new experimental system allows us to experiment at lower pSO$_2$ (i.e., low SO$_2$ column density) than using static photochemical cells. The results show that SO$_2$ photolysis experiments using a flow through photochemical reactor with a Xe arc lamp as the light source. We will report the results of these experiments suggest that the change in the atmospheric chemistry such as an incremental, transient rise of oxygen before the great oxidation event (i.e., whiff of oxygen) [1,3], the formation of organic haze aerosols [4], or a change in the redox state of volcanic gases [5].

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References

Trace-element control on near IR transmittance of pyrite

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Pyrite, which commonly occurs intergrown with economic ore minerals in a variety of hydrothermal deposits, can be transparent to near-infrared (NIR) light and has been therefore studied by NIR microscopy to observe internal features, such as growth zoning or fluid inclusions. The main limitation of the NIR petrography and microthermometric studies on pyrite is the transmittance of the mineral, which depends on its trace element content, the thickness and the crystallographic orientation of the section used [1].

In this study, we investigate growth zoning in pyrites from two different localities: i) the Toromocho porphyry Cu-Mo deposit, Peru, and ii) the Butte district, USA, by NIR microscopy, electron microprobe (EMP) analysis and FTIR spectroscopy to quantify the effect of minor and trace element substitutions on the NIR light transmittance of the mineral.

Pyrite samples from Toromocho exhibit growth zoning pattern controlled by trace amounts of Co and As. Both elements were often below the detection limit of the EMP, 75 and 470 ppm, respectively. However, As reaches 0.49 wt.% in IR-opaque growth bands (no transmittance detected by FTIR spectroscopy from 0.7 to 5 μm), while the presence of Co was revealed by FTIR transmitted spectrum with its characteristic IR absorption peak at 2 μm [2]. In pyrite samples from the Leonard Mine at Butte, oscillatory growth and sector zoning, observed in NIR light, is controlled by a high Cu content, reaching up to 2500 ppm in some growth bands (Figure 1).

Figure 1 : IR transmitted-light photomicrograph of pyrite (Butte district) superposed to the electron microprobe line scan for Cu. The profile is 1800 μm long and is located along the X-axis.

Trace concentrations of As, Co and Cu decrease significantly the infrared transmittance in pyrite, which is the main limitation for a successful fluid inclusion study. Often trace element content is at the ppm level, thus requiring the use of more sensitive analytical technique, such as LA-ICP-MS, to correctly quantify trace amounts of these elements in the pyrite structure. Correlation between trace element content and quantitative FTIR transmittance spectroscopy allows preselection of samples potentially suitable for fluid inclusion studies.

Interfacial water: properties explored with an Atomic Force Microscope

The proportionality factor, \( \eta \), is the viscosity of the liquid and \( A \) is the area of the shear. With substitution, we can relate the viscosity on a wetting surface Fig. 1(a), to that of a non-wetting surface, Fig. 1(b) to solve for the slip length, \( b \) [2]

\[
\eta_{\text{eff}} = \frac{\eta_{\text{bulk}} v_{\text{shear}}}{(d + b)} \tag{2}
\]

Where \( \eta_{\text{bulk}} \) is the interfacial viscosity of water on a surface with zero slippage, and \( \eta_{\text{eff}} \) is the interfacial viscosity of water on a surface with slippage. This suggests the boundary viscosity of water strongly depends on the wetting properties of the surface.

\[ F_c / A = \eta (dv/dz) \tag{1} \]

The wetting case is conveyed in (a) and non-wetting in (b).

Figure 1. Schematic of slip length from a shearing an AFM tip. The wetting case is conveyed in (a) and non-wetting in (b).

We investigated the boundary viscosity and slip length as a function of gap size for mineral, crystalline and other carbon and carbon like surfaces. The slip length values will be discussed relative to surface properties, as well as surface wettability (contact angle), and viscosity.


The Pliocene closure of the Central American Seaway: reconstructing surface-, intermediate- and deep-water connections.

A. H. Osborne1*, M. Frank1, R. Tiedemann2

Timing of Gateway Closure

The shoaling of the Isthmus of Panama and the associated reorganisation of deep-ocean circulation have been controversially reported as contributing to both a warming and a cooling of global climate. A resulting increase in moisture supply to the northern hemisphere, through the initiation or strengthening of the Gulf Stream, may have been an important precondition for Northern Hemisphere Glaciation. A robust timeframe for the closure of this major ocean gateway is essential for understanding its direct and indirect effects on global climate.

Method

We use radiogenic isotopes of Nd and Pb to reconstruct the history of shallow, intermediate and deep water connections between the Caribbean Sea and the eastern Equatorial Pacific Ocean from 5.0 to 2.0 million years ago. Surface water exchange is characterised using the Nd isotope composition of planktonic foraminiferal calcite. The Nd and Pb isotope compositions of early diagenetic ferromanganese coatings of the same sediment samples are employed to reconstruct intermediate and deep water exchange.

Results and Conclusion

Our results indicate that Caribbean Intermediate Water composition continued to diverge from a relatively constant Pacific deepwater Nd composition from 5.0 to 2.0 Ma. Comparison with published stable isotope and Mg/Ca records from the same ODP Sites 999, 1000 and 1241 suggest that Caribbean Intermediate Water composition continued to change even after a decrease in surface water exchange with the Pacific (4.5 Ma onwards [1]). A more rapid restriction of mixing between the Pacific and Caribbean at intermediate depths from 4 to 3.5 Ma clearly preceded the major increase in ice-rafted-debris north of Iceland [2].

Reduction of jarosite by *Shewanella oneidensis* MR-1 and its geochemical implication

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Jarosite is a common mineral in acidic, sulfate-rich environments formed by the oxidation of sulfide in mining areas. Decomposition of jarosite by dissimilatory iron reducing bacteria (DIRB) under acidic conditions has been well proved previously [1], and this process influences the mobility of many heavy metals accumulated in jarosite. However, the effects of DIRB on the stability of jarosite under neutral pH conditions have been seldom studied. This study aims to evaluate these effects, and provide a more comprehensive understanding of the geochemical mechanism.

Jarosite was synthesized by microbial oxidation of ferrous ion at 30 °C. The used bacteria strain was *Shewanella oneidensis* MR-1. We designed a series of batch experiments to study the microbial reduction process of jarosite under anaerobic, aerobic, and no inoculation conditions for 20 days. Lactate was added to the solution as electron donor for MR-1. Temporal evolution of Fe(II) and total dissolved Fe in solution was monitored everyday by using o-phenanthroline method. The concentrations of sulfate, lactate and acetate were determined by ion chromatography (IC). The content of K+ was examined by inductively coupled plasma optical emission spectrometer (ICP-OES). The compositions of the secondary minerals were analyzed by X-ray diffraction and scanning electron microscopy coupled with energy dispersive spectrometer. Diffuse reflection spectroscopy was employed to investigate the component of Fe-bearing minerals. Transformations of jarosite in 40 days and 80 days were also investigated to confirm the reduction process.

**Results and conclusions**

Our results indicate that jarosite can be reduced by MR-1 under anaerobic condition, and secondary mineralization accompanies the reduction process. Increases in Fe(II), K+, sulfate and acetate concentrations, and a decrease in lactate were observed for the biotic experiment. The release rate of Fe(II) was constant in the beginning period. Microscopic results demonstrated bacterial attachment to the surface of jarosite, which can be regarded as evidence of bacterial absorption. The formation of new minerals as goethite and some green rust was identified. Compared to anaerobic treatment, the concentrations of Fe(II), K+, and sulfate in aerobic treatment and no inoculation treatment were undetectable at first, and tremendously lower than anaerobic treatment after 40 days of reaction. However, reduction of jarosite in aerobic treatment and no inoculation treatment was severely limited, and secondary minerals were either not produced or undetectable.

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**Dating zircons from volcanic ash beds in sedimentary successions: magmatic crystallization vs. ash deposition**

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Detailed calibration of the Late-Middle Triassic time-scale requires precise and accurate age determinations from volcanic ash beds within biostratigraphically well dated marine sedimentary sections. High precision CA-ID-TIMS U-Pb zircon dates of volcanic ash beds have been used to quantify and calibrate the stratigraphic column across the Early-Middle Triassic boundary in South China. Despite an optimal control on the continuity of the stratigraphic record and on the accuracy of analytical procedures, some single ash-beds from the Monggan Wantuo section (Luolou Fm., NW Guangxi, S. China) yield ages that are too old and contradict the stratigraphic succession. How can we improve the confidence in the interpretation of zircon dates as proxies for the age of deposition of these ash beds?

We dated 15 samples of ash beds (four thereof with signs of sedimentary reworking) within the 15m Wantuo Morgan section, applying CA-ID-TIMS techniques on a number of single grains for each sample. In 13 out of 15 ash beds zircon dates are following the stratigraphic succession within analytical uncertainty (from the late Early Triassic Luolou Formation – 248.08 ± 0.12 Ma to the Middle Anisian Transition Beds – 246.43 ± 0.17 Ma). The zircons from two intermediate volcanic ash beds within the Transition Beds at the Early/Middle Anisian boundary yield well clustering 206Pb/238U dates at 247.10 ± 0.15 and 247.35 ± 0.11 Ma, clearly indicating that the zircons in this magma batch were crystallizing over a long period of time or remobilized from deeper levels within the same magmatic system. The problem of recurrent zircon dates in a sedimentary succession is common and can only be discovered by sufficiently dense sampling and a sufficient number of data for each ash bed.

We have to keep in mind that for the correct interpretation of dates in stratigraphic sections interlayered with fossil-bearing rocks we need: i) at least one single well preserved stratigraphic section with sufficient absolute or relative chronological control (biochronology, chemostratigraphy, astrochronology) to guarantee that the stratigraphic succession is accurately known; ii) volcanic ash beds that are as much undisturbed as possible (no volcanioclastic material, no sedimentary reworking); iii) sufficient sample and data density to be able to distinguish between magmatic and sedimentary signals coded in the crystallization ages of zircon.
Enhanced delivery of bioavailable Fe through glacial processes in Kongsfjorden, Svalbard

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Primary production in large portions of the world’s ocean is iron-limited, and the supply of bioavailable iron is not well understood. Only recently have glacially derived iron sources been considered a potential major contributor, particularly to high latitude regions. Past workers considered glacial iron to be non-bioavailable or non-reactive more generally. However, we now know that increased delivery of reactive iron to the ocean, as driven by enhanced glacial runoff, has the capacity to increase primary production and concomitant CO₂ uptake. Understanding the role of glaciers in the delivery of bioavailable iron to the ocean has become a priority, and the concentration and reactivity of glacial iron is likely controlled by chemical weathering processes tied to pyrite oxidation and bedrock type within the subglacial environment.

To better understand the factors controlling the delivery of bioavailable iron to glacial fjord environments, we sampled three proglacial streams in the Kongsfjorden region of Svalbard. The streams differed dramatically in the characteristics of their adjacent glaciers, in their suspended loads and the local bedrock. We quantified the amount of dissolved iron in the glacial meltwaters, determined the reactivity of the iron associated with the fine glacial flour of the streams, and constrained the iron properties of the source bedrock. Here, we present iron data (Fe_{Total}/Al and Fe_{Highly Reactive}/Fe_{Total}) from each sample type, along with riverine sulfate and bedrock sulfide isotope data (δ^{34}S). The average dissolved iron concentrations varied from glacier to glacier between 4 ppb and 13 ppb, which is only 2 to 3 times higher than in seawater. However, highly reactive iron was enriched in the glacial flour samples at highly variable levels. The overarching suggestion is that the Kongsfjorden glacial systems could deposit large amounts of reactive iron into the fjords via the discharge of glacial flour.

Modeling ocean acidification and de-oxygenation: Testing the linkage between large igneous province and Ocean Anoxic Event.

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Recent geochemical data and chronology enable us to explore biogeochemical dynamics in geological past. The causal linkage between ocean anoxic events and activity of large igneous provinces has been discussed based on the geochemical information, such as the rapid disturbances of osmium isotopic records or metal abundance anomalies before and during ocean anoxic events. It has been discussed that the abundance of nannoconid is rapidly decreased at the initiation of OAE1a, implying the oceanic acidification in sea surface environment. Considering the compensation mechanism of oceanic carbonate system, this must indicate drastic disturbances of Earth’s surface environment.

We developed a new atmosphere-ocean biogeochemical cycle model in order to explore the biogeochemical consequences of the activity of large igneous province, and a systematic model sensitivity study is performed with respect to an injection scenario of CO₂ into the terrestrial environment. Examined characteristic timescale of the CO₂ injection scenarios ranges from 100 year to several hundreds of thousands of years and the total amount of injection ranges in three orders of magnitude (0.01-10 EmolC).

Systematic examination shows that (1) the required CO₂ amount for the maximum carbon isotopic anomaly of +1 to 4 permil is approximately from 0.4 to 1.0 Emol (10^{18} mol), providing the theoretical requirements for the carbon isotopic anomaly accompanied with OAE2, and (2) such scenarios result in the global ocean de-oxygenation of approximately 40-80 % (depending on the degassing flux). Our simulation results also indicate that the rapid (less than 10 kyr) and drastic (greater than 100 TmolC/yr) CO₂ injection would be required to explain the strong acidification of surface waters and widespread carbonate gap. We conclude that the many characteristic features of OAEs can be explained by the short, rapid and frequent activity of large igneous province.
In-situ U-Pb dating of baddeleyite in Shergotty and a chassignite: Implications for Martian chronology

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Introduction

There is a long-standing debate on the crystallization ages of SNC meteorites, which are considered to be of Martian origin. As to shergottites, young ages of 165–475 Ma have been reported using various radiometric methods [1]. However, Bouvier et al. (2005, 2008) [2, 3] reported old Pb-Pb ages (~4.1 Ga) for basaltic shergottites Shergotty and Zagami, as well as young Rb-Sr, Sm-Nd and Lu-Hf ages (150–180 Ma) for the same meteorites. They concluded that the old ages are their crystallization ages, and the young ages correspond to the timing of shock metamorphism or aqueous alteration. Two different ages were reported for the chassignite NWA 2737. Misawa et al. (2005) [4] reported a whole rock Sm-Nd age of NWA 2737 chassignite as ~1.4 Ga, while Bogard et al. (2008) [5] obtained an 40Ar-39Ar age of 160–190 Ma for the same meteorite. We conducted in-situ U-Pb dating of baddeleyite (ZrO2) in these meteorites using SHRIMP-II and -RG in order to clarify the crystallization ages of Shergotty and NWA 2737 chassignite.

Results and Discussions

We found seven baddeleyite in Shergotty and one baddeleyite in NWA 2737, which can be used for SHRIMP analyses. Before SHRIMP analyses, each baddeleyite was carefully characterized by using FE-SEM, micro-Raman spectrometry and EPMA. The size of the baddeleyite grains range from 3×5 μm to 11×24μm. Baddeleyite usually occurs with ilmenite, titanomagnetite and pyrrhotite.

SHRIMP U-Pb measurements of the seven baddeleyite in Shergotty revealed three clusters of data points on the Concordia diagram, corresponding to ages of ~230, ~400 and older than 3000 Ma, respectively. This result could indicate an old crystallization age of this rock (in excess of 3000 Ma) and recent partial age resetting due to shock-induced melting.

Three U-Pb measurements on the one baddeleyite in NWA 2737 chassignite revealed a U-Pb age of 1640 ± 70 Ma. This is consistent with, but slightly older, than the Sm-Nd age of 1420 ± 70 Ma reported by [4]. It suggests that NWA 2737 chassignite crystallized at 1.4–1.6 Ga and experienced a thermal event, probably by impact, at 160–190 Ma.

For a better understanding of the origin and history of these baddeleyite, FIB-TEM studies are in progress.