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Authigenic clay formation following Fe-oxide reduction in a Fe-Si-C rich lake sediment

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Authigenic Fe minerals are ubiquitous and important in the turnover of organic matter, nutrients and pollutants, making the iron cycle intrinsic to the water quality of lakes, coastal waters and groundwater.

Surprisingly large gaps still remain in our understanding of the redox transformation reactions of iron oxides and especially the subsequent Fe containing phases formed.

Many studies have looked at the speciation and partitioning of reactive Fe-oxides in lake sediment, however few studies have looked at the conditions and formation mechanisms for the Fe minerals resulting from Fe-oxide reduction.

We are currently investigating a natural Fe-Si-C rich lake sediment (total concentrations are app. 2500, 5000, and 10000 $\mu\text{mole/g}$, respectively), with only minor influx of detrital minerals. The lake sediment is characterised by a high fraction of Fe-oxides in the top samples, and high relative concentrations of Fe (II) in the lower sediments. In a series of experiments we are tracking the changes in Fe pool reactivity with sediment depth and correlating the findings with mineralogical analysis. The results demonstrate vivianite formation at an early stage, but the bulk of the Fe is found to react with Si from diatom frustules forming a poorly crystalline clay mineral within 50 years of sedimentation.

U-series evidence for a brief but widespread interval of coral reef development during MIS 5e, Cape Range, Western Australia

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A series of 4 constructional/erosional and laterally continuous marine terraces (paleoshorelines) extend for ~100 km along the western flank of Cape Range, WA. The lowest terrace, known as the Tantabiddi Member (TM), is a broad (up to 5 km wide) constructional reef-lagoon terrace; a laterally continuous palaeo-scarp along the adjacent Jurabi Terrace marks the inner shoreface. The TM was deposited during MIS 5e (Stirling *et al.* 1998) and considered a direct geomorphic analogue of the modern Ningaloo reef-lagoon system. The TM has a maximum terrace elevation of between +1.5 and +2.5 m above MSL, which is consistent with other MIS 5e reef sites from tectonically stable margins. Corrected U-series coral ages (N=31) collected from 5 shoreface localities along a 20 km coastal stretch of Cape Range were found to increase in age from 119.1 ± 2.1 ka (N=7) in the south to 121.7 ± 1.6 (N=7) in the north. This age trend is consistent with a northward narrowing in terrace width, as modern bioerosive processes expose progressively older sections of the TM. A distinct modal age peak between 120-122 ka is observed (14 out of 31 corals). Without knowing the full geomorphic (lateral) or stratigraphic (vertical) extent of TM (i. e. a complete record of reef development), but considering the laterally expansive number of sample localities, this age cluster might suggest a brief but extensive interval of reef development at Cape Range during late MIS 5e.

Effects of structural phosphate on the microbial reduction of iron oxide and secondary mineralization product formation and reactivity

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The bioreduction of Fe (III) oxides may result in the production of a suite of Fe (II)-bearing secondary mineralization products, including magnetite, siderite, ferrous hydroxy carbonate, vivianite, and green rusts. To better understand the effects of iron oxide structure and composition on the formation of particular secondary mineralization products of Fe (III) oxide bioreduction, we examined the effects of phosphate doping on the bioreduction of lepidocrocite (γ -FeOOH) by the dissimilatory iron-reducing bacterium *Shewanella putrefaciens* CN32 and the reactivity of the secondary mineralization products with U (VI).

Anoxic defined mineral medium containing 75 mM formate and 80 mM Fe (III), in the form of phosphate doped (0 – 0.7 mass % P) lepidocrocite, was inoculated with *S. putrefaciens* CN32. Samples were collected for measurement of Fe (II) and characterization of the secondary mineralization products by X-ray diffractions, scanning electron microscopy, and ⁵⁷Fe Mössbauer spectroscopy. Aqueous suspensions of secondary mineralization products were spiked with U (VI) and subsequent U speciation was measured by U L_{III}-edge X-ray absorption fine structure spectroscopy (XAFS).

In the absence of structural phosphate, lepidocrocite was rapidly and stoichiometrically reduced to magnetite, which over time was partially transformed to ferrous hydroxy carbonate. Doping with between 0.2 – 0.7 mass % P significantly inhibited the initial reduction of lepidocrocite but ultimately resulted in greater overall Fe (II) production and the formation of carbonate green rust as the dominant secondary mineralization product; doping with 3.0 % P resulted in the formation of green rust and vivianite. In the presence of green rust, U (VI) was completely reduced to nanoparticulate uraninite; however, U (VI) was only partially reduced to U (IV) by magnetite.

Geochemical and isotopic characteristics of the Nuvvuagittuq belt: Implications for Earth's early crust formation

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The first 500 million years of the Earth's history are unrepresented in the rock record. As a result, the nature of the Earth's early crust and the processes responsible for its formation are largely conjecture. However, recent ¹⁴²Nd studies of the Nuvvuagittuq faux-amphibolites suggest that this greenstone belt formed nearly 4.3 billion years ago, making it the only known remnant of Hadean crust preserved on Earth. Moreover, the faux-amphibolites are mafic in composition and likely were produced directly by melting of the primordial mantle, unlike the granitic sources of Hadean zircons. The faux-amphibolite can be divided into three distinct chemical groups mainly based on the abundance of high field strength and rare earth elements. These groups are stratigraphically superimposed and have compositional analogues in three types of ultramafic sills following the same stratigraphic succession that appears to record an evolution from 'tholeiitic to 'calc-alkaline' magmatism.

A new series of faux-amphibolite were analysed for ¹⁴²Nd isotopic composition. The new data confirm previously reported deficits in ¹⁴²Nd. The ¹⁴²Nd/¹⁴⁴Nd ratios for the faux-amphibolite correlate positively with their Sm/Nd ratios producing a slope corresponding to an age of 4276⁺⁶¹-.104 Ma for all faux-amphibolite. The lowest ¹⁴²Nd/¹⁴⁴Nd ratios were found in the enriched low-Ti faux-amphibolites. Line fitting only these sample corresponds to an age of 4263⁺⁴¹-.64 Ma. When including the corresponding cogenetic ultramafic sills we obtain a ¹⁴⁶Sm-¹⁴²Nd age of 4310⁺⁴³-.61 Ma.

The composition of the faux-amphibolite is consistent with its protolith being Hadean basaltic to andesitic hydrothermally altered volcanic rocks with a geochemical evolution typical of the volcanic successions of many younger Archean greenstone belts. Regardless of the exact tectonic setting, this volcanic succession suggests that the geological processes responsible for the formation and evolution of Archean greenstone belts were active as early as 4.3 Ga.

Efficient bromine-induced mercury oxidation observed under temperate conditions at the Dead Sea

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We measured massive conversion of Hg⁰ to Hg²⁺ in the presence of halogens at the Dead Sea producing among the highest observed levels of Hg²⁺ in the Earth's atmosphere, levels as high as 136 ppqv. High Hg²⁺ concentrations were accompanied by strong depletions of Hg⁰, down to 22 ppqv, or below 10% of the global tropospheric background concentration. Most observed Hg²⁺ occurred in gaseous form (≥96%) with only minor contributions of Hg²⁺ bound to particulates. Inverse correlations of Hg⁰ to Hg²⁺ showed that only two-thirds (summer) and three-quarter (winter) of depleted Hg⁰ was recovered as Hg²⁺, an indication of substantial and immediate deposition of converted Hg²⁺.

Hg²⁺ production and Hg⁰ depletion temporally coincided with high BrO levels and depletion of O₃ with no apparent time lags between species. Our observations show faster Hg²⁺ oxidation than current lifetimes suggest, and indicate that bromine-induced mercury oxidation is very efficient under warm conditions. Enhanced Hg²⁺ started at BrO levels below 6 pptv, and Hg²⁺ levels increased substantially at BrO levels above 6 pptv up to 50–60 pptv, above which Hg²⁺ levels stabilized. These data provide direct evidence of frequent Hg²⁺ formation by bromine species in the temperate zone under both moderate and high temperatures. Fast oxidation rates and low thresholds of bromine species needed to initiate oxidation suggest that this mechanism is important across temperate and tropical oceans when low levels of gaseous BrO are present.

Ca-isotope fractionation during interaction with clay minerals

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Ca-isotope ratios of marine organic and inorganic mineral precipitates have been used as a proxy for multiple purposes in marine geochemistry, e.g. monitoring the oceanic Ca-budget or recording changes in paleo-temperature. However, only little is known about diagenetic processes involving Ca, which have the potential to alter the proxy archives.

Findings in porewaters from the Cascadia margin suggest a relationship between Ca-isotopy and ammonium concentration, which might be due to fractionation of Ca-isotopes during desorption from marine clay minerals [1]. In order to determine if Ca-isotope fractionation happens during adsorption and desorption of Ca onto clay minerals laboratory experiments on well characterized montmorillonite were carried out.

Adsorption of Ca onto montmorillonite at 21 °C and total desorption of Ca at different temperatures showed no evidence for Ca-isotope fractionation. However, during partial desorption Ca-isotope fractionation was observed. The degree of Ca-isotope fractionation during partial desorption depends on the amount of released Ca as well as on temperature.

Processes observed in the lab experiments will contribute to a better understanding of natural occurring processes. Therefore, we analyzed porewaters from 3 different sites of IODP Exp. 303 from the North Atlantic with different dominating lithologies (siliciclastic vs. calcareous) and different Ca-concentration trends with depth. The results show that a strong correlation between ammonium and δ^{44/40}Ca can be observed at siliciclastic clay-bearing sites while this correlation is missing at carbonate-dominated sites. This indicates that ammonium which is produced during organic matter remineralization, displaces isotopically light Ca from clay minerals. Our new findings suggest that the release of light Ca into the porewater is a general diagenetic process in siliclastic, organic-bearing sediments.

[1] Teichert *et al.* (2009) *EPSL* **279**, 373–382.

Multiple Sulfur isotope constraint of environmental VOSCs and related Sulfur compounds: Implication for organosulfur production and cycling in natural systems

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We report results from a study to examine volatile organic sulfur compounds. We have developed methods to convert volatile organic sulfur compounds (VOSCs) into a form that can be analyzed for the four sulfur isotopic compositions. Compounds studied include dimethylsulfide (DMS), methanethiol (MT), carbonylsulfide (OCS), dimethyl disulfide (DMDS), and carbon disulfide (CS₂).

Results will also be reported for analysis of multiple sulfur isotopes of VOSCs and their precursor (DMSP) from three different field sites – the York River Estuary in Virginia, Fayetteville Green Lake in New York, and the Delaware Great Marsh near Lewes Delaware.

DMSP extracted from the York River Estuary was identified by electrospray mass spectrometry and analyzed for its sulfur isotope composition, using cell extracts isolated by standard methods. This DMSP had $\delta^{34}\text{S}$ values of +18.5 ‰ to +19.2 ‰, and $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ similar to seawater sulfate. The DMSP is slightly ³⁴S-depleted relative to seawater sulfate. This observation is consistent with the origin of sulfur in DMSP being related to assimilatory pathways of sulfate.

Analyses of VOSC extracts from Fayetteville Green Lake, a stratified sulfidic freshwater system and the Delaware Great Marsh yield strikingly different $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ values of total VOSCs (inferred to be mostly MT and DMS) that are similar to but slightly ³⁴S-enriched relative to the compositions of coexisting sulfide (negative $\delta^{34}\text{S}$ and $\Delta^{36}\text{S}$, and positive $\Delta^{33}\text{S}$). These differences are interpreted to reflect different pathways for VOSC production.

The analytical methods and the implications of the isotopic results for interpreting the pathways for formation of VOSCs in these three systems will be discussed.

Biological diversity in the Archean: New results from NanoSIMS

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NanoSIMS carbon (C⁻), nitrogen (CN⁻), sulphur (S⁻), silicon (Si⁻) and oxygen (O⁻) compositions of fossil spheroids and spindles in the ~3 Ga Farrel Quartzite (FQ) of Australia have been assessed to gain insight to their biogenicity and syngeneity.

Results show that the spheroids and spindles have parallel C⁻, CN⁻, and S⁻ distributions as well as a 1:1 correspondence of C⁻ and CN⁻ to microstructures imaged by optical microscopy. These features suggest biogenicity [1]. NanoSIMS maps further demonstrate an internal, organic network in the spindles that is difficult to reconcile with possibilities that the spindles might be aggregates of organic particles on crystal surfaces. The FQ microstructures have Si⁻ and O⁻ distributions that mimic the C⁻ and CN⁻ distributions, suggesting an intimate association between organic matter and silica that likely reflects syngeneity [2].

Thus, the FQ assemblage joins a host of other examples of probable Archean microfossils and organic biosignatures. Moreover, the spindles demonstrate an architecture that is remarkable for ~3 Ga organisms. Our results align with those of Waldbauer *et al.* [3] which suggest that the Archean was a time of evolutionary innovation and diversification.

[1] Oehler *et al.* (2006) *Astrobiology* **6**, 838–850. [2] Oehler *et al.* (2009) *Prec. Res.* **173**, 70–78. [3] Waldbauer *et al.* (2009) *Prec. Res.* **169**, 28–47.

How can geochemistry save the world?

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The world faces numerous challenges going forward. The resources of many essential elements will be depleted over the next 10 to 100 years. Many of the remaining deposits are located in environmentally sensitive locations. The carbon concentration of the atmosphere has been increasing dramatically over the past few decades; this increase has been linked to global warming [1]. The combination of limited petroleum resources and higher energy demand lead to an oil price spike in 2008. The twin concerns of global warming and increasing oil prices lead to an explosion of bio-fuel production using land that could otherwise have been used for food production. Land pressure and a large increase in the cost of phosphate resulted in a dramatic rise in food prices and increased starvation worldwide [2]. As an alternative to expensive and environmentally damaging petroleum, nuclear energy has again become a popular option, reopening the question of nuclear waste storage.

These global challenges form the greatest opportunity for geochemistry since its development as a distinct discipline. Our field holds the key to finding and exploiting our remaining resources in an environmentally secure manner, and managing pollution, water, carbon, etc. The key to playing our vital role in addressing these challenges lies in properly communicating to the public their severity and how we can help address them. An excellent example of the role of public awareness is global warming. Public concern forced our governments to provide grant funding, oblige industry to collaborate with academic researchers, and motivate many in our community to orient their research programs towards generating new innovative solutions for carbon capture and storage on a global-scale.

It is critical that our community, in part through our scientific societies, better reach out to the public and government decision makers to inform them of 1) the consequences of the limited global resources and 2) how use geochemistry to make improved decisions on how to manage our planet.

[1] Oelkers & Cole (2008) *Elements*, **4**, 305-310. [2] Oelkers & Valsami-Jones (2008) *Min. Mag.*, **72**, 337-340.

The weathering of basaltic rocks and their effect on global chemical cycles

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The chemical and mechanical weathering rates of 8 basaltic catchments in NE Iceland have been determined for the past 44 years from elemental riverine fluxes [1]. Weathering rates increased dramatically over this time period, which coincides with the recent global climate change [2]. Detailed analysis of these data demonstrates that increased temperature is the major cause of the feedback between climate and basalt weathering rates [3]. Of the riverine fluxes to the oceans, the transport of suspended material is far more affected by climate than the transport of dissolved species.

The fate of suspended material in the oceans was evaluated by dissolving both riverine suspended material and sediments collected from Icelantic estuaries in both natural and Si-free artificial seawater. Estimates of the overall dissolution rates of the basaltic material suggest from 1 to 10% will dissolve annually, though the major element chemistry of the ocean water is little changed due to secondary mineral precipitation. In contrast, REE distributions, and Nd and Sr isotope ratios of sea water are found to be strongly influenced by basaltic sediment-seawater interaction. Corresponding experiments performed using Amazon River estuary sediments agree previous experimental results [4] confirming that Si-rich sediments have a far lower effect on ocean chemistry than basaltic sediments.

Taken together these observations demonstrate 1) the strong link between basaltic rock weathering and global chemical cycles, and 2) that past basalt weathering rate variations can be evidenced by seawater isotopic composition.

[1] Gislason *et al.* (2006) *Geology*, **34**, 49–52. [2] Gislason *et al.* (2009) *Earth. Planet. Sci. Let.* **277**, 213–222. [3] Eiriksdottir *et al.* (2009) *GCA*, **73**, A323. [4] Wolff-Boenisch *et al.* (2006) *GCA*, **70**, 838–870.

Lipid biomarkers in methanogenic sediments of the alpine Lake Bled (SW Slovenia)

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Combined molecular, biogeochemical and organic geochemical data are presented that enable determination of the methanogenic pathway in sediments of dimictic Lake Bled (NW Slovenia), which has a developed anoxic hypolimnion most of the year. Methane concentrations in sediment pore waters were rather low, averaging 114 μM . The average $\delta^{13}\text{C}$ value of methane was $-69.5 \pm 1.2\%$ indicating that methane was predominantly formed hydrogenotrophically. Methanogenic archaea are shown to constitute 73% of the total population of archaea at the surface, where fresher organic matter accumulates, and hydrogenotrophs, mostly *Methanomicorbiaceae*, were dominant (56%). Deeper in sediments, there were 27% of *Euryarchaeota* archaea with unknown affiliation, 24% of *Thermoplasmatales* and related linkages and only 21% of hydrogenotrophic methanogenic archaea. A similar percentages (about 17%) of sequences representing acetotrophic archaea (*Methanosaetaceae*) were present in both layers. Lipid biomarkers, comprising aliphatic hydrocarbons, aliphatic alcohols, sterols and fatty acids, decreased nearly exponentially with depth. Lipids of bacterial origin constitute 5% of total lipids and do not change significantly with depth. Diploptene, which is an unsaturated terpene, was also identified with isotopic composition of -67.5% inferred a methanotrophic bacterial source. C_{27} sterols were the dominant sterols in the surface sediments, and the presence of cholesterol, as the major sterol indicated the important contribution of aquatic algae to sedimentary organic carbon. It was noteworthy that the $\text{C}_{29}\Delta^5$ sterol (24-ethylcholest-5-en-3 β -ol), which has been commonly associated with terrestrial sources, showed $\delta^{13}\text{C}$ values similar to those of other planktonic sterols confirming their autochthonous origin. The longer chain n-alkanes, $n\text{-C}_{25}$ to $n\text{-C}_{33}$, showed $\delta^{13}\text{C}$ values between -34.0 and -37.0% , confirming their terrestrial origin. Similar to the n-alkanes, the longer chain n-alcohols exhibited $\delta^{13}\text{C}$ between -35.0 and -36.0% indicating terrestrial sources.

Surface-catalyzed peptide formation on sulfide minerals

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The formation of peptide from amino acids in dilute solutions on the early Earth remains an enigma for the origins of life. Hypotheses by Wächtershäuser [1, 2] and Russell and Hall [3] propose that sulfide minerals could catalyze the production of the first peptides. It has been shown that dipeptides form in the presence of a (Ni, Fe)S precipitate with CO and H₂S (or CH₃SH) at 100°C [4]. However, the formation of COS, has been shown to be a condensation agent for peptide formation [5]. Consequently, a special role of sulfide minerals for peptide formation has not been demonstrated. We present results that show that peptide formation is significantly enhanced in the presence of pyrite (FeS₂), chalcocopyrite (CuFeS₂) or sphalerite (ZnS) and in the absence of condensation reagents. That the peptization reaction is surface catalyzed is supported by the fact that the yield of peptides strongly correlates with mineral surface area. Metal sulfides in aqueous solution are expected to develop four different functional groups ($\equiv\text{Me-OH}$, $\equiv\text{Me-OH}_2^+$, $\equiv\text{S-H}$ and $\equiv\text{S}^-$) [6]. Amino acids exist as unreactive zwitterions in neutral solution. The pair of acidic ($\equiv\text{Me-OH}_2^+$) and basic ($\equiv\text{S}^-$) sites of metal sulfides could activate the carboxyl ($-\text{CO}_2^-$) and amino ($-\text{NH}_3^+$) groups of amino acid zwitterions. The yield of peptides with sphalerite was much higher than with pyrite or chalcocopyrite under the same surface-area condition. It is known that the oxidation of surface iron and reaction with water forms hydroxyl radicals ($\cdot\text{OH}$) [7]. Zinc is incapable of oxidation and, thus peptides formed on the surface of ZnS would not be subjected to decomposition by $\cdot\text{OH}$. Sphalerite may have been a useful catalyst for the promotion of prebiotic peptide formation.

- [1] Wächtershäuser (1988) *System. Appl. Microbiol.* **10**, 207–210. [2] Wächtershäuser (1990) *Proc. Natl. Acad. Sci. USA* **87**, 200–204. [3] Russell & Hall (1997) *J. Geol. Soc.* **154**, 377–402. [4] Huber & Wächtershäuser (1998) *Science* **281**, 670–672. [5] Leman *et al.* (2004) *Science* **306**, 283–286. [6] Rönngren *et al.* (1991) *J. Colloid Interface Sci.* **145**, 396–404. [7] Cohn *et al.* (2004) *EPSL* **225**, 271–278.

Geochemical cycles of Fe, Mo, U, Cu, Cr, REEs, and S during the period 3.5 - 3.2 Ga ago

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To understand the geochemical cycles of redox-sensitive elements in the Archean, we have carried out systematic investigations of a variety of rocks (mostly from drill cores) in the Pilbara Craton, Western Australia, including: (a) the ~3.46 Ga Marble Bar Chert/Jasper Formation that deposited in a deep sea; (b) submarine basalts of the 3.46-3.43 Ga Duffer and Apex Formations that were altered by deep-sea hydrothermal fluids; (c) footwall alteration zones of the ~3.25 Ga massive sulfide deposits in the Panorama district; and (d) ~3.43 Ga paleosols that developed in a >50x200 km area.

Hematite crystals are abundant in many of these rocks. Mineralogical and geochemical characteristics of the hematites and their host rocks suggest the following processes for the formation of hematite (and its precursors) in these rocks: mixing of Fe²⁺-rich hydrothermal fluids and O₂-rich deep-sea water for hematite in (a); reactions between ferrous-rich minerals and O₂-rich deep-sea water for hematite in (b) and (c); high temperature reactions between ferrous-rich minerals and seawater SO₄²⁻ for hematite in (c); and mixing of Fe²⁺-rich soil/groundwater and atmospheric O₂ for hematite in (d). The hematite-rich rocks are characteristically enriched in U, Mo, Cu, Cr, and REEs, much like modern goethite/hematite-rich submarine rocks and laterites. Depletions/enrichments of these redox-sensitive elements are also common in rocks below and above the hematite-rich zones in (a) – (d), much like those observed in altered modern submarine volcanic rocks and soils.

Results of our investigations suggest that, during the ~3.5–3.2 Ga period: (1) the atmosphere and oceans were fully oxygenated, because higher than 50% of the present atmospheric pO₂ level was required for deep oceans to be oxygenated; (2) the land surface was fully colonized by microbes to generate abundant organic acids; (3) U, Mo, Cu, Cr, REEs, and S were leached from rocks by O₂- and organic acid-rich soil water and transported to the oceans; and (4) the normal seawater was rich in SO₄²⁻, U, Mo, Cu and Cr, but poor in Fe and Ce. These characteristics are essentially the same as those of the modern systems, suggesting that the modern-day geochemical cycles of redox-sensitive elements were already established ~3.5 Ga ago.

Importance of post-adsorption on the long-term migration of actinides

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Long-term migration of actinides should be elucidated to estimate the impact of geological disposal. In the estimation by mathematical model, retardation of the migration is assumed to be caused by the adsorption of actinides on microorganisms and minerals. If the adsorbed actinides change its chemical states after adsorption, it should affect the long-term migration of actinides. We have conducted the research on the mineralization and fixation of actinides after the adsorption by microorganisms and minerals.

In the study of uranium ore deposit at Koongarra, Australia, U (VI) is mineralized to be formed saleeite on apatite, and torbernite in Fe minerals in the downstream of the secondary ore deposit [1]. These mineralization gave larger retardation factor by 100 times than that estimated adsorption of U (VI) by the soils at Koongarra. We confirmed the fixation of U (VI) by the laboratory experiments. U (VI) is changed its chemical state to more insoluble species than adsorbed one during the crystallization of amorphous iron minerals to hematite [2]. U (VI) is also mineralized as autunite on the surface of apatite during the dissolution of apatite [3].

In the accumulation experiments of U (VI) by *Saccharomyces cerevisiae*, the adsorbed U (VI) is mineralized to H-autunite on the cell surface [4]. Cerium (III), analogue of Am and Cm, is adsorbed by Mn oxidizing bacteria. The adsorbed Ce is moved to MnO₂ formed by the bacteria, and is oxidized to Ce (IV) [5]. Pu (VI) is adsorbed by *Bacillus subtilis*, and then is reduced to insoluble species of Pu (IV) after the adsorption [6].

These results indicate that post-adsorption is one of the important phenomena to retard the migration of actinides in environment.

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Application of *in situ* X-ray observations to melting and melt properties at high pressure

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In situ X-ray observation is useful for studying melting and the melt properties at high pressure. Here, I will present our recent developments for the *in situ* X-ray absorption, imaging, and diffraction methods. We use both large volume press and the diamond anvil cell to conduct the above *in situ* X-ray observations. The density and viscosity of silicate and metallic melts are measured by the X-ray absorption and imaging using a large volume press at SPring-8 and Photon Factory. The X-ray absorption method is based on the Lambert-Beer's law. We developed the cell assembly using diamond or corundum capsules for measuring the density of the silicate melt or metallic melt. The X-ray intensity was measured by the two ion chambers placed in front and rear of the press. We measured the density of the dry and wet peridotite and basaltic magmas up to 4 GPa by this method.

X-ray imaging is also applied for the measuring the melt density and viscosity. A composite density marker, composed of metal and corundum, was developed for the density standards for metallic melts. The movement of the density marker can be monitored by the CCD camera with a YAG fluorescence screen. Viscosity of basaltic and peridotite magmas and the Fe-Si melts are measured by this method.

X-ray diffraction is used to detect melting at high pressure. We determined the solidus temperatures of Fe (Ni)-S and Fe (Ni)-Si alloys to the core pressures by the diamond anvil cell, whereas we applied a multianvil press (SPEED-Mk II) to determine the melting temperature of Fe (Ni)-H and FeS-H systems. I will show the procedure and some results on determination of the melting temperature using the X-ray diffraction method at high pressure.

In situ analyses of Sr isotopes and REE of phosphate minerals in the Ediacaran phosphorite of Weng'an region, South China

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The Ediacaran is one of the most important ages through the history of the life because of the multicellular animal appeared for the first time. Especially, the Ediacaran sections in Weng'an region, are relatively continuous, and contain various fossils like the oldest animal embryo fossil and multicellular algae fossil [1]. The Sr in the ocean is derived from the hydrothermal and continental sources, and the former has a low Sr isotope ratio and the latter has the high ratio [2]. So the elucidation of Sr isotope variation of seawater through the time allows us to estimate variation in the continental influx. Sawaki and colleagues showed the change in Sr isotope ratios from the Ediacaran to early Cambrian [3]. However, the whole rock composition of carbonate rocks is susceptible to secondary alteration and involvement of detrital materials. This study presents the *in situ* Sr isotope analyses of phosphate and carbonate minerals in the phosphorite with nano-SIMS to evaluate the Sr isotope signatures in the Ediacaran, and *in situ* REE analyses of those with LA-ICP-MS to estimate the redox condition during the precipitation of the phosphate minerals

The Sr isotope ratios of phosphate minerals are consistent with those of the whole rock within the errors. The REE patterns of the phosphate minerals in the Upper Phosphorite Member, where the animal and multicellular algal fossils occur, have different REE patterns from those in the Lower Phosphorite Member. The former has a faint negative Ce anomaly whereas the anomaly lacks in the latter. The appearance of its in the upper indicates that the phosphate deposition occurred under the oxic condition. In addition, the change from lack of Ce anomaly in the lower to its appearance in the upper, concomitant with the first occurrence of multicellular algae and metazoans, implies oxygenation of seawater due to more active photosynthetic activity by algae, and foundation of a new niche for the multicellular animals.

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Delineating Primary and Secondary Organic Carbon in Neoproterozoic Glacial Sediments

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Extractable biomarkers are often used to elucidate the environment and biota of ancient sediments, including those of the so-called Snowball Earth. However, recent research has shown that the method must be applied with care when analyzing these glacial sediments, as, like all glacial sediments, they have a potential for incorporation of older detrital carbon [1]. In Phanerozoic glacial sediments, the distinct elemental, molecular and isotopic compositions of the terrestrial and marine biomass allow discrimination between primary marine and redeposited terrestrial organic matter [2-4]. In contrast, the Proterozoic biosphere was largely microbial and marine, thus biomarker and isotopic analyses are insufficient for distinguishing primary organic matter from secondary reworked organic matter.

New High-Resolution Analytical Approaches

Although traditional bulk methods are not sufficient to discern separate sources of organic matter within Precambrian glacial sediments, the novel combination of Raman spectroscopy and biomarker analysis allows discrimination between mixed pools of organic carbon. Together, these methods reveal that sediments deposited in São Francisco craton in Brazil contain at least two generations of kerogen, one of low maturity and aliphatic character, and thus presumably syn-sedimentary, and the other more structurally ordered, of high maturity, and thus potentially older redeposited material. These conclusions are supported by the extractable biomarker data, as hopane and sterane abundance is highly correlated with rocks showing Raman spectra indicative of low maturity. This discovery has important ramifications for examining life during Snowball Earth, but also for the application of bulk analytical techniques to Precambrian glacial sediments. Finally, this combination of techniques provides a promising new high-resolution methodology not only for examining the preservation of microbes, but for separating them from their environment.

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A predictive model for silicate mineral dissolution rates

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We are developing a predictive model that can approximate silicate mineral dissolution rates as a function of pH, rate of water exchange around a dissolved cation, ratio of metal cations to silicon in the mineral structure, and temperature. Our approach allows estimation of dissolution rates for minerals for which we do not have experimental data. Furthermore, our approach highlights inconsistencies in published mineral dissolution kinetics data, and places constraints on possible reaction mechanisms. Numerous studies have examined the effect of pH and temperature on mineral dissolution kinetics. Casey and Westrich [1] showed that the rate of water exchange around an octahedral cation is correlated to the mineral dissolution rates in orthosilicates. It has also been suggested that minerals with a lower connectedness (the number of bridging oxygen atoms per silica tetrahedron) dissolve more quickly than minerals with a higher degree of polymerization.

Approximately 800 data from 39 studies have been compiled; using nonlinear multivariate regression, we produced the model

$$\log r = -9.41 + \frac{24200}{RT} + 0.25pH + 1.0 \log k_{\text{solv}} + 3.0 \frac{X}{Si}$$

where R is the gas constant, T is temperature, k_{solv} is the rate of water exchange around a dissolved cation, and X/Si is the ratio of metal cations to silicon per tetrahedral unit in the mineral structure. This model reasonably predicts dissolution rates for all orthosilicates, as well as chrysotile, diopside, tremolite, wollastonite, augite, and hornblende. Conversely, it does not provide estimated rates that match experimental data for enstatite, anthophyllite, epidote, and talc. This model also estimates an activation energy of 57 kJ/mol, which is similar to the average E_a of 56 kJ/mol calculated by Wood and Walther [2].

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Evaluation of calcium binding and carbonate precipitation by cyanobacteria in aquatic and terrestrial habitats by XAFS

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Bacteria are known to play a major role in geochemical cycling of metals and biosorption of metals, however there is little understanding of these processes in the context of cyanobacteria. Prokaryotic phototrophs are widespread in terrestrial and aquatic habitats, and contribute significantly to primary production in all ecosystems. An interesting aspect for autotrophic metabolism is the presence of CO₂ concentrating mechanisms (CCMs) to maintain high rates of CO₂ fixation for photosynthesis under conditions of low [CO₂], which enables them to survive under a wide range of environmental conditions [1]. CCMs consist of active transport systems to accumulate inorganic carbon (Ci) within the cell, with Ci uptake as either HCO₃⁻ or CO₂ by transporters. Activation of HCO₃⁻ transporters leads to production of OH⁻ that is expelled from the cell, leading to cyanobacterial biomineralization observed as whitening events [2], and may also be instrumental in the formation of carbonate microbialites in habitats such as Pavilion Lake, Canada [3].

Cyanobacteria associated with Pavilion Lake microbialites as well as from a range of terrestrial habitats were examined for evidence of calcium binding and carbonate precipitation by XAFS. Preliminary examination of the Ca K-edge of these cyanobacteria exposed to high dissolved calcium concentrations revealed immediate binding to cell surfaces in all cases. In addition, cyanobacterial cultures exposed to high [Ca²⁺] for ~6 months produced carbonate precipitates and distinct XAFS spectra: cultures isolated from Pavilion Lake are similar to that of calcite, whereas those from terrestrial habitats appear unrelated to carbonate mineral standards examined in this study. This suggests that calcium bound to cyanobacterial cell surfaces can produce distinctive XAFS spectra that may or may not relate to observed carbonate precipitates.

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Multiple sulfur isotope evidence for deep biosphere in altered oceanic basalt and peridotite basement rocks

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We present new high-precision multiple sulfur isotope data of altered oceanic basaltic and serpentinized ultramafic basement rocks. Bulk-rock sulfur analyses yield a wide range of δ³⁴S_{CDT} values (–44 to +15 ‰) but yield distinct Δ³³S* values depending upon their host rock types; sulfides from serpentinite sites (ODP sites 897 and 895) are characterized by excess ³³S relative to seawater sulfate (Δ³³S +0.16 to +0.05 ‰, analytical precision ± 0.01 ‰), whereas sulfides from basaltic basement sites (801C and 1301B) are depleted in ³³S (Δ³³S - 0.06 to 0.05 ‰). We propose that enriched Δ³³S values in serpentinites are linked to the formation of secondary sulfide through closed-system microbial sulfate reduction, where 10 to 90 % of sea-water sulfate are reduced with a large isotope fractionation factor of 40 - 70 ‰. In contrast, the depleted Δ³³S values for secondary sulfides from basaltic sites suggest open-system sulfate reduction, also with a large fractionation factor of up to 80 ‰ consistent with microbial sulfate reduction. These large isotope fractionation factors are required to account for the measured range of Δ³³S values. A group of samples from 1301B and 895 shows near-zero Δ³³S values (± 0.02 ‰), suggesting these could have been formed by high temperature water-rock reactions during the early stages of oceanic crust alteration. The closed- versus open-system behavior of sulfur alteration is related to the higher H₂ production capacity of ultramafic compared to basaltic basement rocks. These new multiple sulfur isotope data add a new dimension that is critically needed to constrain the temperature, water-rock ratios as well as the extent and mechanisms of sulfate reduction during high to low temperature alteration of oceanic basement rocks, thus offering a unique tool to trace the extent and activity of the putative deep sulfur biosphere in the oceanic lithosphere.

* Δ³³S = ln (δ³³S+1) – 0.515 × ln (δ³⁴S+1)

Life in young ocean crust: Insights from subsurface microbial observatories

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Oceanic crust comprises the largest hydrogeologic reservoir on Earth, containing fluids in thermodynamic disequilibrium with the basaltic crust, yet we know little about microbial ecosystems that inhabit this vast realm and exploit chemically favorable conditions for metabolic activities. Samples recovered from ocean drilling operations are often compromised for microbiological assays, hampering efforts to resolve the extent and functioning of a subsurface biosphere. Here, we report results from the first *in situ* experimental observatory systems that have been used to study seafloor life. Experiments that were deployed for four years in young (3.5 Ma) basaltic crust on the eastern flank of the Juan de Fuca Ridge record a dynamic, post-drilling response of crustal microbial ecosystems to changing physical and chemical conditions. Twisted stalk particles exhibiting a biogenic iron oxyhydroxide signature coated the surface of mineral substrates in the observatories - biosignatures indicating colonization by iron oxidizing bacteria during an initial phase of cool, oxic, iron-rich conditions following observatory installation. Following thermal and chemical recovery to warmer, reducing conditions, the *in situ* microbial structure in the observatory shifted, becoming more representative of natural conditions in regional crustal fluids. Notably, the microbial community in the post-rebound phase was dominated by *Firmicutes* bacteria, whose metabolic potential is unknown but may involve N or S cycling. The recorded transition of the subsurface ocean crust borehole microbial community confirms that observatory experiments are powerful tools for exploring the subsurface ocean basement biosphere, the largest but most poorly understood biotope on Earth.

Coal and human health

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Coal is an important resource, but contains inorganic and organic substances that may pose health and environmental concerns. Impacts may occur when the toxic substances in coal are mobilized into the air through combustion processes or into water supplies through leaching, thus leading to potential exposures. A recent study suggests that areas with high levels of coal production have worse overall adjusted health status, including higher rates of lung and kidney disease [1].

We are conducting studies that integrate epidemiology, toxicology, and geochemistry to examine the health and environmental impacts of coal. In studies of coal and water supplies, we have identified a possible link between the occurrence of coal and kidney nephropathy and renal/pelvic cancer [2]. One disease, Balkan endemic nephropathy (BEN) may have a multifactorial etiology, but with one key factor being the leaching of toxic organic substances from low rank coal into drinking water supplies. A high proportion of BEN patients also have renal/pelvic cancers, possibly from the same factors causing the kidney nephropathy in BEN itself. Interestingly, states in the USA with the highest incidence of renal/pelvic cancer also have large rural populations using untreated well water associated with low rank coal. Preliminary studies in two of these states (Wyoming and Louisiana) reveal the presence of significant levels of potentially toxic, coal-derived organic substances in the drinking water supplies. Epidemiology and toxicology studies are consistent with a role for coal-derived organics in drinking water in an increased risk for kidney disease.

Indoor coal combustion and inhalation of particulates containing toxic substances may also be linked to lung disease. Studies in the Navajo Nation, New Mexico are intended to investigate this link. Studies of coal fires will examine links (if any) between the emission of particulates and respiratory illness in people living downwind of these fires.

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Ion microprobe analysis of $\delta^{18}\text{O}$ in speleothems as a source of sub-annual-resolution climate records

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High-temporal-resolution climate proxy records are imperative for studies of abrupt climate change or related shifts in seasonality [1]. Ion microprobe analysis of $\delta^{18}\text{O}$ in speleothems provides new information about abrupt climate events and seasonality changes that would not be resolved with standard drill-sampling. We use the WiscSIMS CAMECA 1280 ion microprobe to measure $\delta^{18}\text{O}$ at sub-annual resolution (10 μm) with a spot-to-spot precision of $\sim 0.3\%$ (2 s. d.) and a confocal laser fluorescence microscope (CLFM) to image growth bands.

Detailed characterization of cave hydrology, regional climate and U-Th-dated speleothems [2, 3] make Soreq Cave (Israel) ideal for high-resolution analysis. Combined $\delta^{18}\text{O}$ and CLFM analysis shows that the couplets of bright and dark fluorescent calcite observed in Soreq speleothems are annual growth bands. A quantitative measure of seasonality ($\Delta^{18}\text{O}$ (dark-bright) = gradient of $\delta^{18}\text{O}$ between dark and bright fluorescent calcite in a single annual band [4]) reveals abrupt changes from year-to-year and longer-term trends. Analysis of $\delta^{18}\text{O}$ along a radial traverse (>1100 spots) of Soreq stalactite sample 2N, which grew from $\sim 34\text{--}4\text{ ka}$, reveals significant Eastern Mediterranean climate changes across the last glacial-interglacial transition with sub-annual resolution.

The maximum magnitude of $\Delta^{18}\text{O}$ (dark-bright) in sample 2N decreases from $\sim 2.0\%$ prior to the termination of the Younger Dryas (YD) to $\sim 1.5\%$ for the rest of the Holocene, suggesting a shift in regional seasonality. The change in $\Delta^{18}\text{O}$ correlates with CLFM imaging. The fluorescence of calcite prior to the YD is consistently reversed within an annual band (dark before bright) relative to Holocene bands (bright before dark). We propose that the coupled shift in $\Delta^{18}\text{O}$ (dark-bright) values and fluorescent banding indicates a change in the local seasonal rainfall pattern, which could change the growing season of predominant vegetation and cause a reversal of fluorescent banding.

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Providing solar system water and high planetary angular momentum, using a return to Ringwood's core formation model, supported by the behavioural evolution of the mantle

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Longstanding problems of the Solar System are:- the mean specific angular momentum (a. m.) of SS planetary materials is $>10^5$ times the Sun's, and the origin of SS water. I have shown [1] that during a cool secondary stage of SS formation the nebular flow would be outward and could sufficiently build up each protoplanet's a. m. as it grew, moving outward too, in the flow. So attaining the high a. m. requires completion of growth during nebular presence, ruling out the post-nebula growth in cores-by-percolation models.

Those models do nothing for the origin of SS water, which is low in star-forming clouds. Ringwood's model (1960-1978) uses the nebula to reduce hot FeO erupted at the protoplanet's surface; the Fe is then 'subducted' to form the core. For Earth this would generate >400 ocean volumes of reaction water, a SS benefit foreseen by Ringwood. The heat required is internal (accretion, gravitation, radiogenic) so orbital distance is immaterial; important for the cores in the Galilean moons. The inferred outward nebular motion implies the close-in nucleation of protoplanets, shielded from stellar heat by nebular dust opacity. Many exoplanets are close-in too.

Asteroids being too small for convective overturn, meteoritic irons must come from unsubducted positions, not cores. Ringwood-mode core formation made the early-Earth's mantle as wet as it could hold, seen in its behaviour and petrology. But at $\sim 2.5\text{Ga}$, its drying-out by ocean production reached a critical loss of water-weakening in the presence of interstitial melt [2], halting convective motion for $\sim 270\text{Ma}$ [3, 4], during which oxygenic life won its battle against MOR effusions, depositing BIF and oxygenating the atmosphere, which is why we are here [3, 5]. The restart was in the 2-layer mantle mode that prevails today, with deep-keeled cratonic tectospheres of stiffened mantle [5].

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Reassessing reaction rates for TSR by experiments and modelling

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The large uncertainties in published kinetic rate data for the thermochemical reduction of sulfate (TSR) hamper the development of detailed geochemical modelling approaches to be included in e.g. basin modeling software for risk assessment. The scatter in of the reported activation energies or rate constants for TSR has several reasons:

Many experimental approaches suffer from a lack of control of crucial system parameters, such as pH and hydrogen fugacity during the experiment. In most studies the temperatures are above 320°C, which allows additional parallel reactions as e.g. thermal cracking of hydrocarbons. In addition, ignoring disproportionation reactions of initially added elemental sulfur in parts some published reaction rates based on sulphate concentrations.

In molecular modeling studies the calculated kinetic rate constants mainly depend on the choice of the interacting molecules, e.g. sulfate or bisulfate or contact-ion pairs of sulfate with different organic molecules.

We performed geochemical modeling, using Geochemist's Workbench® with a modified thermodynamic database and published kinetic data for several relevant sulfate-reducing reactions. Published experimental studies have been reinvestigated for the aforementioned effects (e.g. initial S).

Additionally, experiments in Dickson-type flexible gold bags and sealed gold capsules have been carried out to test some commonly made assumptions about the order of the reaction with regard to hydrogen, sulfate, elemental sulfur and different organic compounds.

We find that the following parameter are critical in controlling the rate of TSR in addition to pH: levels of dissolved molecular hydrogen, presence of CH₃^{*} radicals produced during cracking, and the presence of S^{*} radicals.

A key question is whether there is one initial step of the TSR reaction – as assumed in the modeling studies – or whether there are several possible reducing agents for the hexavalent sulfur that are important in natural settings and hence have to be included in the geochemical modeling.

Isotopologue data reveal denitrification as the primary source of nitrous oxide at nitrogen fertilization gradient in a temperate agricultural field

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The microbial origin of nitrous oxide (N₂O) production in terrestrial ecosystems has long been debated. Both nitrification and denitrification produce N₂O but their relative importance remains uncertain. Here we apply site preference (SP – the difference in δ¹⁵N between the central and outer nitrogen [N] atoms in N₂O), to estimate the proportion of N₂O from bacterial denitrification. Soil flux chambers were deployed at a N fertility gradient planted to winter wheat in a corn–soybean–winter wheat rotation at the Kellogg Biological Station Long-term Ecological Research site in SW Michigan. Fertilizer (28% urea ammonium nitrate) was applied to plots along the gradient in the spring of 2007 to obtain levels of 0, 134, and 246 kg N ha⁻¹. The average flux weighted δ¹⁵N-N₂O increased with increasing N fertilizer rate (-14.7, -12.3 and -9.1 ‰, for the 0, 134, and 246 kg N ha⁻¹ treatments, respectively), whereas the δ¹⁸O values decreased (33.2, 28.7 and 25.3 ‰, respectively). Weighted SP values for N₂O were low at all N rates (0.7, 4.0, and 3.8 ‰, respectively), which is consistent with a source of N₂O predominantly from denitrification. Consequently, we find that denitrification was the principal pathway of N₂O production in row-crop agricultural fields, irrespective of the rate of N fertilizer applied.

Temporal and spatial isotopic and genetic variation reveal the ecological history of an endangered seabird

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Since the arrival of humans, the Hawaiian Islands have lost at least 59 species of native birds, a number roughly equal to the N. American Pleistocene mammal extinctions. The Hawaiian Petrel offers an important proxy for understanding the fate of Pacific seabirds as it dominates the ancient Hawaiian sub-fossil record, yet declined in numbers until near extinction by the mid 20th century. We explored temporal and spatial trends in isotopic and genetic data from tissues of this endangered and poorly studied seabird. While there is only one stomach content study, at sea sightings indicate that the Hawaiian Petrel is concentrated SE of the Hawaiian Islands in fall. Among islands there is little variation in the $\delta^{13}\text{C}$ of modern birds. There is a large departure in $\delta^{15}\text{N}$ of birds from Hawaii (≤ 3 ‰) relative to birds from other islands. In the absence of elevated $\delta^{13}\text{C}$, the uniquely high $\delta^{15}\text{N}$ is not simply related to trophic level but is characteristic of a zone of denitrification in the Eastern Tropical North Pacific. The $\delta^{15}\text{N}$ of > 500 year old bones from Hawaii is also elevated relative to other islands. Thus, foraging habits are a temporally persistent phenomenon. A decline in $\delta^{15}\text{N}$ between ancient and modern individuals reflects declining trophic level. Such shifts signify wide-spread alteration to the NE Pacific marine ecosystems.

Investigating the petrogenesis of the Apollo 12 pigeonite suite basalts

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In this study we examine the petrogenetic history of the Apollo 12 pigeonite suite basalts 12007, 12011, 12017, 12019, 12039, 12043, 12052, 12053, and 12055. We use a combination of Crystal Size Distributions (CSDs), major element data via electron microprobe (EM), and laser ablation inductively coupled mass spectrometry (LA-ICPMS) on multiple phases. CSDs are a statistical analysis of the number, size, and shape of a particular phase within a thin section [1, 2]. They are plotted as the crystal size versus the natural log of the population density. A concave up CSD will indicate crystal accumulation within the magma chamber, concave down will indicate crystal fractionation, a linear CSD indicates a simple history, and a kinked CSD indicates magma mixing [1, 2].

We first perform CSDs on pyroxene, plagioclase, and olivine (when present) to allow for the identification of possible multiple crystal populations. Thin sections are photographed and crystals are traced in Adobe Photoshop. They are then analyzed using ImageTool [3], CSDslice [4], and CSDcorrections [3]. Major elements are obtained for crystal cores and rims using EM, and trace elements using LA-ICPMS.

CSDs have been calculated for 12021 and 12031 (Figure 1). The pyroxene CSD is linear, indicating simple history. However, both plagioclase CSDs are concave up, indicating crystal accumulation. CSDs of the rest of the suite, along with EM and LA-ICPMS, will be completed by the conference.

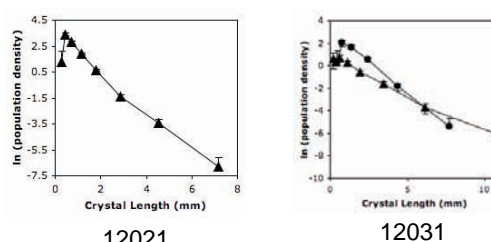


Figure 1: CSDs of plagioclase (triangles) and pyroxene (circles) for 12021 and 12031.

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Stability of amino acids and peptides during diagenesis on the early Earth

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We hypothesize that sub-seafloor sedimentary environments, where sediments are dehydrated at moderate temperature and pressure (e.g. 150°C, 200 MPa) during diagenesis, are much more feasible locations for the polymerization of amino acids [1], rather than sea-floor hydrothermal environments (e.g. [2]). This is because pressure applied in sub-seafloor environments could have stabilized amino acids and peptides even at high temperature conditions. To test the hypothesis, we conducted a series of amino acid polymerization experiments using a belt-type press. In each experiment, ~150 mg of amino acid powders (glycine, alanine, or valine) were placed under high pressure (1 – 5.5 GPa) and temperature (180 – 400°C) conditions for 2 – 24 hours. After the experiments, we analyzed yields of residual amino acids and produced peptides and elemental ratios of the experimental products.

The results showed that all three amino acids were polymerized up to 5-mer without any catalysts under the experimental conditions. At a fixed temperature (e.g. 250°C), increasing pressure increased the yields of peptides as well as residual amino acids. This indicates that amino acids and peptides were prevented from decomposing to gaseous species (e.g. CO₂, NH₃) at higher pressures. However, increasing temperature from 250 to 400°C at a fixed pressure and elapsed time (e.g. 2.5 GPa, 2 hours) significantly decreased the yield of amino acids and peptides, indicating that peptide and amino acids may not persist under such high temperature conditions, even when high pressures were applied. Elemental analyses of the experimental products showed that products with a low yield of the residual amino acid had significantly decreased N/C ratios, suggesting that NH₃ was released during the decomposition of amino acids. Thus, deamination may be a key process when determining the stability of amino acids and peptides.

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Xenon: Some unsolved problems

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Isotopes in earth science are often compared to DNA in biological sciences because both are used as tracers. Noble gases are ideal for use as tracers due to their chemical inertness and rarity. The heaviest noble gas, xenon, is a particularly excellent tracer due to its nine isotopes, five of which contain radiogenic components. The extrasolar isotope was first identified in xenon in a meteorite by Reynolds (1), which opened a new discipline named Xenology. Here, I discuss some topics in which I have been interested for decades. I hope that some of you may contribute to solving these fascinating unanswered problems.

Xe in carbonado: Some polycrystalline diamond carbonado contains enormous amounts of U-derived spontaneous fission Xe (¹³⁶Xe_{sf} = 2.5 × 10⁻⁸ cc/g) (2), which indicates that the carbonados originated in highly U-enriched environment, likely in the crust (3).

Xe in the Earth: Very early atmospheric evolution has been suggested on the basis of Xe isotopes, but in order to quantify this precisely it is essential to identify the pristine mantle isotopic composition, which is still not well understood.

Xe in the solar system: Because of multiple isotopic composition, xenon offers fundamental constraints in resolving solar evolution. The question on primordial Xe in the solar system that was first raised independently by Takaoka (4) and Pepin (5) is still unsettled.

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