The chemistry of sulfur in volcanic geothermal fluids

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Sulfur compounds are among the major components in volcanic geothermal systems, playing an important role in the transport and precipitation of many metals. Aquifer geothermal fluids are reduced with hydrogen sulfide (H2S) and sulfate (SO4) predominating. Sulfur dioxide (SO2) may also be degassed from a magma source into the geothermal system. Upon ascending to the surface the composition of the deep geothermal fluid may change due to cooling, boiling and mixing with shallow ground- and surface waters. These processes result in steam fumaroles, alkaline hot springs and acid-sulfate springs and mud pots at the surface and oxidation of hydrogen sulfide to sulfate via series of complex reactions and formations of metastable sulfur species including thiosulfate (S2O32-) and polythionates (SxO62-).

Samples of volcanic and non-volcanic geothermal waters were collected from several locations in Iceland and analyzed for sulfur species concentration on site and major and trace elemental content. The waters include samples of well discharges, alkaline hot springs, acid-sulfate mud pots and springs. The measured surface temperature were 7-100°C and the pH was 1.83-9.71 (at 25°C). The waters are of NaCl and acid sulfate type with molal SO4/Cl ratio between 0.05 and 2813. The concentration of the main sulfur species were SO4 = 0.02-106 mM, S2O3 = 1.7-394 µM and H2S = 0.3-2160 µM. Metastable sulfur species were only detected in surface geothermal waters whereas H2S and SO4 are the only forms found in well waters discharging aquifer fluids. The formation of thiosulfate and polythionates is considered to result from oxidation of hydrogen sulfide and hydrolysis of sulfur. The associated major and trace elemental chemistry in the geothermal waters is largely influenced by the sulfur chemistry, both due to changes in water pH and redox state and by complexing the metal cations. Acid-sulfate waters are often enriched in trace metals, these being transported as free ions and sulfate complexes, whereas alkaline NaCl waters have very low metal concentrations with ions, hydroxo and carbonate complexes predominating.

Isotopic systematic of the In’Teria lithospheric mantle (Hoggar, SE Algeria)

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The Hoggar massif (SE Algeria) is located above an E-W trending belt of anomalously high heat flow [1]. The maximum heat flow (100-120 mW.m-2) has been recorded at the northern margin of the Hoggar swell, near In’Teria district. The volcanic In’Teria district is composed of melilite pipe, which contains xenoliths of spinel and garnet peridotite, pyroxenite, and mega-crystals of pyroxene and amphibole. Spinel peridotites record two metasomatism events before their entrainment by melilitic magmas: (1) injection of alkali silicated magmas (basaltic or kimberlitic); (2) carbonatitic metasomatism possibly related to the partial melting of a volatile enriched garnet bearing peridotite.

Nd and Pb isotope analyses were performed on all lithologies. The Pb isotopic ratios range from 18.4 to 19.9, 15.60 to 15.68, and 38.2 to 39.5 for 206Pb/204Pb, 207Pb/204Pb and 208Pb/204Pb, respectively. In the 207Pb/204Pb- 206Pb/204Pb space the samples report into two distinct domains. A first one carried by spinel peridotites and pyroxenites shows a clear himu affinity, signature which seems to be characteristic of the rejuvenated North African lithosphere [2]. This composition is also expressed in the melilitites from In’Teria and from recent alkali magmatism [3]. The Garnet bearing peridotites (± spinel peridotites) show high 207Pb/204Pb (15.6) for a given 206Pb/204Pb (18.5) and form a second domain close to the EM1 pole.

The data suggest (1) an isotopic stratification of the Lithosphere, (2) an evolution through time of the source of magmatism and (3) intricate interaction between those reservoirs via melting and metasomatism reactions. The In’Teria peridotites sample thus a more complex possibly more ancient (or preserved) lithosphere than in the central Hoggar. This is suggested by the “persistence” of EM1 signature not registered in the Central Hoggar.

Near-infrared spectroscopic determination of salinity and internal pressure of fluid inclusions in cuboid diamonds

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Diamonds are physically and chemically stable capsules that can carry hydrous components directly from the mantle. Studies of infrared spectra of diamonds with numerous micro-inclusions have shown the presence of water, carbonates and other minerals [1, 2]. Some inclusions preserve high internal pressures indicating that the original fluids and minerals were trapped during growth of host diamonds in the mantle [3, 4]. Infrared absorption spectra and Raman spectra of fluid and mineral inclusions are sensitive to the residual pressure. In principle, infrared absorption spectra of liquid water have potential to serve as a sensitive barometer for the residual pressures in fluid inclusions in diamonds. However, the extremely high absorption coefficient of water has avoided the application of infrared absorption spectroscopy to the pressure estimation of fluid inclusions in diamonds. In addition to the pressure estimation, vibrational spectroscopy is sensitive to the salinity of fluid and can give information on chemical composition of fluids in diamonds [5].

Recently, we have proposed a near-infrared (NIR) spectroscopic method to achieve the simultaneous determination of salinity and internal pressure of fluid inclusions in natural minerals including diamonds [6]. The use of NIR provides several advantages; NIR is transparent to various minerals including opaque minerals, no spectroscopic interference arises from minerals on the NIR absorption of hydrous fluid, etc.

In this study, a combination band between bending and stretching vibrations of molecular water at 5180 cm⁻¹ was observed for fluid inclusions in diamonds. Effects of salinity and fluid pressure on the spectral profiles were quantitatively investigated through laboratory calibrations. This method has been applied to fluid inclusions in natural diamonds with cubic growth habit (cuboid). The salinity and residual pressures were determined non-destructively.


Prebiotic polymerization of amino acids on the early Earth: Chemical evolution in the Hadean oceanic crusts

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Prebiotic polymerization of amino acids is the most fundamental reaction to promote the chemical evolution for origin of life. Many previous experiments favour high-pressure environments (>20 MPa) for polymerization of amino acids [1]. This leads to a new hypothesis that the first peptide may have formed in the Hadean oceanic crusts. Therefore, experiments simulating the crustal conditions were performed with various pressures (1~175 MPa) and temperatures (100~200°C) using autoclaves. Purified amino acid powders (100mg) of alanine, glycine, valine and aspartic acid were used in the present experiments without activating each amino acid or mixing with catalysts. The products were analyzed using HPLC and LC-MS.

Results indicate that: (1) glycine was polymerized up to 11-mer, which was not formed by previous experiments without catalyses; (2) valine was polymerized up to 3-mer; and (3) aspartic acid was polymerized up to 4-mer, accompanied with production of other amino acids. It is noteworthy that all examined polymerization reactions were promoted under high-pressure and water-poor conditions. Formation of by-products, such as melanoidines, was also controlled by pressure, increasing the effectiveness of polymerization of amino acids. Such situations would have happened inside of deep oceanic crusts of the early Earth.

**The formation and oxidation of green rust: Mechanisms, kinetics and trace element speciation**

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Green rust (GR, Fe$^{2+}_4$Fe$^{3+}_{12}$(OH)$_{12}·$SO$_4·x$H$_2$O) nanoparticles have the potential to provide effective solutions for contaminated groundwater remediation (e.g., permeable reactive barriers). Structural Fe$^{2+}$ within GR can reduce adsorbed trace elements (e.g., Se$^{6+}$) and significantly lower their solubility and bioavailability. GR forms in suboxic environments and when exposed to oxic conditions rapidly transforms (minutes) to various iron (oxyhydr)oxide phases. The kinetics and mechanisms of these reactions and the fate of associated trace elements are poorly understood.

Synchrotron-based *in situ* time-resolved Small/Wide Angle X-ray Scattering (SAXS/WAXS) and Energy Dispersive X-ray Diffraction (EDXRD) were used to characterise the crystallisation and oxidative transformation of GR nanoparticles via the oxidation of a Fe$^{2+}$-sulphate solution, utilizing advanced environmental cells. The speciation of associated trace elements (i.e., Zn and Se) were analyzed by X-ray Absorption Spectroscopy (XAS). Results showed that initially Fe(OH)$_2$ formed which then transformed to GR-sulphate (GRII). With continued oxidation GRII transformed to lepidocrocite (L) and goethite (G) (Fig. 1).

![Time-resolved WAXS data showing GR formation and transformation](image)

Figure 1: Time-resolved WAXS data showing GR formation and transformation.

The EDXRD showed that with increasing pH (pH 7, 8, 9) the rate of GRII transformation and the final L/G ratio increased. Zn$^{2+}$ replaces Fe$^{2+}$ in the structure of GRII, and retards the oxidative transformation by ~50%. XAS data indicates that Se$^{6+}$ is reduced during GR formation, but only partially reoxidised when transformation to lepidocrocite/goethite occur.

**Librational dynamics of nano-confined water: Neutron spectroscopy and molecular dynamics computer simulations for hydrocalumite**

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Molecular-scale understanding of the structure, dynamics, and energetics of nano-confined water in mineral interlayers and nano-pores is essential for many geochemical, environmental and technological applications. Layered double hydroxides (LDHs) are excellent model systems for such molecular-level studies, because their interlayers have a well-defined structures and can contain H$_2$O molecules and various anions in well-defined structural positions.

Here we report the first results of a comprehensive investigation of the H$_2$O structure and dynamics in the interlayers of hydrocalumite – an LDH phase with the composition of [Ca$_2$Al(OH)$_6$]Cl·2H$_2$O. One fully hydrated and one dehydrated sample were studied by the inelastic and quasielastic neutron scattering techniques using several complementary instruments (HFBS, DCS and FANS at NCNR; HRMECS and QENS at IPNS) at temperatures above and below the previously discovered phase transition.

Together the experimental and molecular modeling results capture the important details of the dynamics of nano-confined water and the effects of the orientational ordering of H$_2$O molecules above and below the phase transition. They provide otherwise unobtainable experimental information about the transformation of H$_2$O librational and diffusional modes across the order-disorder phase transition and significantly add to our current understanding of the structure and dynamics of water in LDH phases based on the earlier NMR, IR, X-ray, and calorimetric measurements.
Fluid-mobile elements in evolved Archean magmas: Implications for Archean subduction processes

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The role of subduction zone melting in the formation of Archean continental crust is highly debated. In the study of modern mantle-derived magmas, fluid-mobile elements are the most powerful discriminants between subduction zone and other types of magmas. Indeed, the relative abundance of these elements can also be used to differentiate between various types of subduction environments (‘hot’ vs. ‘cold’) and fluid and metal sources (sediment, serpentinite, direct eclogite melt). However, surprisingly little coherent data are available for fluid-mobile element systematics in Archean felsic magmas. The main reason for this shortfall appears to be the widely held view that the systematics of these lithophile, relatively large ions are too easily disturbed by later geologic overprint to be of much use.

Here we report a systematic dataset of fluid-mobile and other trace elements in 60 felsic Archean granitoids, 3.8-2.5 Ga in age and representing several cratons. The data-set includes Li, Be, B and As, widely viewed as some of the most useful discriminants for and against subduction processes.

Comparison of some of the most lithophile elements (e.g. Tl and Rb) between modern arc-derived rocks and the Archean granitoids gives no indication that at least the relative abundance of these elements should be disturbed in the Archean samples. Indeed, the majority of Archean granitoids show a remarkable similarity in all fluid-mobile element features with modern arc derived magmas, strongly suggesting that subduction zone magmatism was operational as far back as 3.6-3.7 Ga.

B/Be and As/Pr and compatible element systematics clearly discriminate between direct Archean slab melts (i.e. adakites) and the much more fluid-mobile element-rich wedge melts. In between these extremes are TTG that share some characteristics with each end-member. They could have formed by melting of underplated basaltic eclogite at the base of the crust, in mantle above (hot) subduction zones where B and As were lost at too shallow depth, or they could represent differentiates from very hydrous basaltic precursors in which garnet and amphibole replace olivine and pyroxene as the earliest crystallizing phases. Geochemical data suggest that TTG formed in different geodynamic environments.

The merits of “recycled oceanic crust-eclogite” lineage in the mantle source of group-I kimberlite melts

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The source of group-I kimberlites, located deep within the upper mantle, remains controversial. Primary melt compositions, so crucial in tracking compositions and melting conditions of possible mantle sources, tend to be obscured by contamination and alteration of kimberlite rocks. At present, group-I kimberlites are thought by many to have a source in “plume”-type, OIB-like mantle. Recently, another type of magma source, recycled oceanic crust (eclogite) has regained favor. Such a source is supported by “dry” carbonate-chloride composition of the primary magma for the unaltered Udachnaya-East kimberlite [1, 2], and by low 87Sr/86Sr in magmatic perovskite for this (0.7030 [3]) and other kimberlites (0.7023-0.7033 [4]).

Recycled oceanic crust (eclogite) should be a common component in the deeper mantle as a result of subduction processes. It contains generally unradiogenic Sr (as recorded in kimberlitic perovskite), and, after suitable ageing, would be expected to develop the unique Hf-Nd isotope signatures of many group-I kimberlites. Lithophile trace element contents are ≈10x higher than in peridotite, providing the oft-quoted ‘pre-enriched’ source required for kimberlites. Carbon and chlorine, prominent in unaltered kimberlites, could be inherited from the altered portion of oceanic crust. Volatile-fluxed melting of such a source can proceed at relatively low temperatures to relatively high melt fractions, favorable for melt segregation and ascent. Eclogite garnet remains residual even at high degrees of melting, thus explaining the garnet-signature in kimberlites. Eclogite is olivine-free and must produce melts undersaturated in olivine, as is the case for the primary melts inferred for the Udachnaya-East kimberlite. Finally, the density contrast between primary kimberlitic melt and an eclogite source are greater than for a peridotite source, consistent with inferred high ascent rates of kimberlite magmas and preservation of diamonds.

Combined xenolith and receiver function study, western Bohemian Massif, central Europe

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The occurrence of strong negative phases at 7.5s Ps delay, may indicate body of partial melt at ca. 65 km depth beneath western Bohemian Massif (see Figure below).

To test the hypothesis, we studied 2 suites of lithospheric mantle xenoliths, different in age (P-T-fO2, petrophysical, geochemical and isotope [Sr, Nd, Pb] constraints). The xenoliths from 25 Ma old volcanics are spinel lherzolithes. The suite from 0.3 Ma old volcanics represent cumulates, porous fragments of magmatic veins or porous wehrlites. These samples are strongly altered by mantle metasomatism (changes of fO2, geochemical constraints, density/porosity).

Sulfide oxidation intermediates in anoxic sediments of Black and Baltic seas: Differences and similarities

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Sulfide Oxidation Intermediates (SOI): elemental sulfur (S0), polysulfides (S2n+), and their protonated forms, thiosulfate (S2O32−), sulfite (SO32−) and polythionates (S4O62−) may be produced by oxidation of hydrogen sulfide by abiotic and biologically catalyzed processes, utilizing wide variety of electron acceptors (O2, Fe(III), Mn(IV) and NO3−). SOI may serve also as substrate for bacteria [1]. SOI also play important role in a variety of geochemically and environmentally important processes (e.g. pyrite formation by polysulfide pathway).

Zero-valent sulfur (ZVS) in samples was analysed by the protocol that consists of 4 procedures: 1) detection of inorganic polysulfides by methylation with methyl trifluoromethanesulfonate followed by HPLC-UV detection of dimethylpolysulfanes [2]; 2) detection of colloidal elemental sulfur, polysulfide and polythionate by reaction with hydrogen cyanide followed by HPLC-UV detection of thiocyanate; 3) pre-treatment with zinc chloride solution followed by chloroform extraction and HPLC-UV detection of elemental sulfur; 4) analysis of individual polythionates by HPLC-UV. Detection limit of each procedure was ≤2 µM. Thiosulfate, sulfite and solid phase S0 concentrations were studied by the methods from [1].

In sediments from both Black and Baltic seas thiosulfate prevails over sulfite in pore-waters. The main zero-valent sulfur pools in sediments are solid sulfur in sediments and dissolved polysulfidic zero-valent sulfur in pore-waters. Close to the pyritization front particulate sulfur content in sediments sharply increases, and becomes the main zero-valent sulfur pool.

The main difference between two systems is that in the Black Sea polysulfides are not in the equilibrium with particulate elemental sulfur, S2−4 is the most abundant polysulfide species. In the Baltic Sea polysulfides are close to the equilibrium with particulate elemental sulfur, S2−4 is the most abundant polysulfide species. Possible thermodynamic and kinetic factors, which can result in this difference will be discussed.

δ¹³C and δD of Archaeal lipids in gas hydrate-bearing deep sediments

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Archaeal ecology associated with methanogenesis is poorly understood in deep marine sediments, although methane consuming process in aerobic/anaerobic conditions has been clarified at sub-surface sediments. Recently, we have found much archaeal isoprenoids in gas hydrate-bearing sediments at Cascadia margin (IODP exp 311). In this study, the archaeal lipid distributions with their carbon (δ¹³C) and hydrogen (δD) isotopic compositions are reported to evaluate the archaeal activities with their metabolisms.

A variety of archaeal biomarkers including crocetenes, 2,6,10,15,19-pentamethylicosane (PMI), and acyclic and tricyclic biphytane diols (BP[0] and [3]) are abundant between 100 and 200 mbsf. Ether-bound cleavage of alcohol lipids gives isoprenoid hydrocarbons from membrane lipids. Concentrations of the resulting biphytanes (BP[0] to [3]) are about 100 times higher (e.g. BP[0]: 458 µg/gCorg at 173 mbsf.) than those of crocetenes and PMI (up to ~5 µg/gCorg). These biomarkers are isotopically divided into two distinctive groups (Fig 1). One group consists of BP[0], [2] and [3] with their isotopic compositions of ~ –20‰ in δ¹³C and ~280 to –222‰ in δD. As the δ¹³C value is comparable with that of bulk organic carbon, these biomarkers could be derived from heterotrophic archaea. Another group consists of phytane and BP[1] with ~ –40‰ in δ¹³C and ~204 and ~172‰ in δD. The carbon isotopic composition indicates activity of chemoautotrophic archaea, probably methanogens.

High ³He/⁴He reservoir – Highly depleted source?

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Many ocean island basalts (OIBs) show variable ³He/⁴He ratios higher than those of MORBs (Mid-ocean ridge basalts) which are uniform of around 8Ra. OIB sources are generally regarded to be non- or less-degassed compared to those of MORBs. However, since high ³He/⁴He ratios up to 50Ra have been found in Baffin island with MORB-like Sr and Nd isotope signatures [1], the high ³He/⁴He reservoir has often been attributed to a highly depleted one [2] and a refractory phase such as olivine or dunite is raised as a candidate to retain such He due to its higher He/U ratio than the source material [3]. Since both He and U are highly incompatible elements with their partition coefficients of less than 10⁻³ between crystal and a melt, He concentration in a refractory phase should be much lower than in the primary source.

Although OIBs from Hawaii and Iceland show high ³He/⁴He of more than 20Ra and depleted characteristics for solid element isotopes (Sr, Nd, Pb, Hf), depleted characteristics can be explained by mixing with MORB-like asthenospheric components. ³He/⁴He ratios higher than 20Ra can be also found in OIBs from Samoa, which are not highly depleted in solid element isotope signatures. To explain the observed isotope signatures, ³He concentration in the primary source should be > 10⁻¹⁰ccSTP/g, which seems much higher than the expected value in a refractory phase (<<10⁻¹²ccSTP/g).

 Kimberlites also show high ³He/⁴He ratios up to 26Ra [4] and their solid element isotope signatures tightly cluster close to BSE. Since such signatures are common for Group I kimberlites in quite different space and time, those characteristics would be attributed to that of the source. In the kimberlite source, the effect of ancient E-MORBs stored in the non-convective mantle for more than 2 b.y. has been suggested [5]. By taking account of such signatures, ³He concentration in the kimberlite source is estimated to be in the order of 10⁻⁵–10⁻⁶ ccSTP/g. Thus, high ³He/⁴He reservoir is not limited in a highly depleted source and at least should retain significant amount of ³He.

Microbial controls on contaminant metal transport in porous media

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Toxic heavy metals in aquifers, which may arise from either natural geologic processes or anthropogenic activities, pose risks to human health as well as to other life forms. Previous laboratory experiments have demonstrated that bacteria commonly found in geologic settings are likely to adsorb metal contaminants, a fact suggesting that their presence can attenuate metal migration. However, as bacteria are also likely to migrate through the groundwater system a better understanding of the combined effect of these two processes is required.

The aim of our laboratory study is to explore a) the affinity bacteria exhibit towards metals b) the effect that bacterial shape and surface chemistry have on the bacterial filtration and c) use the above data to develop predictive models of the impact of microbes on metal mobility in porous media.

We make use of Micrococcus Luteus (spherical shape) and Pantoea Agglomerans (rod shape) species, grown in the same medium to mimic the nutrient uniformity of the subsurface environment and a range of metals. Potentiometric titrations and spectroscopic measurements are conducted in order to identify the type and concentration of sites present on the bacterial wall. The stability constants for the adsorption of metals onto these sites are determined through batch absorption experiments.

Titration and Zn adsorption experiments confirm that by using the same growth medium, the two microbes acquire the same surface chemistry in terms of site pKa, site concentrations and Zn stability constants. We envisage that the use of a set of thermodynamic metal stability constants will improve the accuracy of the reactive transport model used to simulate our data.

Immobilisation of Arsenic in paddy soil by Iron(II)-oxidizing bacteria

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Arsenic-contaminated groundwater is an environmental problem with about 1-2% of the world’s population affected. As arsenic-contaminated water is also used for irrigating rice fields, the uptake of arsenic via rice is in some cases even higher than via drinking water. Arsenic is oftentimes of geogenic origin, in many cases bound to iron(III) minerals. Microbial iron(III) reduction leads to dissolution of Fe(III) minerals and thus the arsenic bound to these minerals is released to the environment. In turn, iron(II)-oxidizing bacteria have the potential to co-precipitate or sorb arsenic during iron(II) oxidation followed by iron(III) mineral formation.

We are currently investigating arsenic co-precipitation and immobilization by anaerobic and aerobic iron(II)-oxidizing bacteria. Co-precipitation batch experiments with pure cultures of nitrate-dependent, phototrophic, and microaerophilic Fe(II)-oxidizing bacteria are used to quantify the amount of arsenic that can be immobilized during microbial iron mineral precipitation. Iron and arsenic speciation and redox state are determined by synchrotron-based methods (EXAFS, XANES). Microcosm experiments are set-up either with liquid media or with rice paddy soil amended with arsenic. Rice paddy soil from Vercelli (Italy) including a natural population of Fe(II)-oxidizing microorganisms is used as inoculum. Dissolved and solid-phase arsenic and iron are quantified, As speciation is determined and the iron minerals are identified. Additionally, As uptake into the rice plant is quantified and a gene expression pattern in rice (Oryza sativa cv Gladia) is determined by microarrays as response to the presence and stimulation of aerobic and anaerobic Fe(II) oxidizing bacteria.
Constraining the role of anoxygenic phototrophic Fe(II)-oxidizing bacteria in the deposition of Banded Iron Formations

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Banded Iron Formations (BIFs) are Precambrian sedimentary deposits of alternating iron and silica mineral layers. The mechanism of BIF deposition is still unclear. Early BIFs were likely deposited in an O2-free environment, for which there have been two formation processes suggested. The first mechanism is the photooxidation of Fe(II) via UV light, which was recently found to have likely offered a negligible contribution to BIF formation. Here we focus on constraining the second anoxic mechanism; the biological oxidation of Fe(II) via anoxygenic Fe(II)-oxidizing photoautotrophs.

In order to find the limitations of photoferrotrophic BIF deposition, we take a holistic approach, investigating the oxidation of Fe(II) by modern Fe(II)-oxidizing phototrophs, the precipitation of Fe(III) (hydr)oxides, and the fate of the cell-mineral aggregates at the basin floor. Specifically, physiology experiments with Fe(II)-oxidizing phototrophs under various conditions of light intensity, pH, Fe(II) concentration and temperature allow us to determine the environmental limits of such a metabolism. We carry out precipitation experiments to characterize the sedimentation rates, composition and aggregate size. Finally, we simulate the diagenetic fate of these aggregates on the basin floor by placing them in gold capsules under temperature and pressure conditions relevant for the Transvaal Supergroup BIFs of South Africa. Recently, we have developed a tank simulating the Archean ocean in which the strains grow in continuous culture and collect the aggregates formed under various geochemical conditions.

Numerical modeling of Ca-enrichment on authigenic carbonate formation at mud volcanoes: A case study off Costa Rica

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The Costa Rican forearc is characterized by active fluid venting related to mud diapirism and volcanism. The peculiar situation at the latter sites is that Ca concentrations in the upward migrating fluids are well above seawater levels. In turn, these Ca-enriched fluids could offer a potential reason for widespread carbonate caps on top of the mounds. The main objective of our study is to better constrain the impact of Ca-enrichment from fluid venting on calcium carbonate precipitation rates. Here, the numerical model is applied to investigate this relationship by application of a number of systematical variations. In addition we provide comprehensive results of turnover of methane, AOM-related authigenic carbonate formation and velocity of the rising fluids at six different stations off Costa Rica continental margin. Fluids of 3 of 5 sites (Quepos Slide, Culebra Fault, Mudpie) are enriched in calcium. In contrast, fluids of the other two sites (Mounds 11 and 12) are low in calcium.

Simulations with varying fluid flow rate and increased Ca concentrations in the ascending fluid demonstrate that the impact of Ca-enrichment on carbonate precipitation rate is significant. This effect is more pronounced at lower advection rates. Saturation state of upward migrating fluids is a sensitive parameter affecting calcium carbonate precipitation in surface sediments. At the active vent locations of Mounds 11 and 12 about 98% of the CH4 is released into the bottom waters due to high advection rates (100-200 cm a\(^{-1}\)). The lower CH4 turnover by AOM at Mound 11 and 12 also causes reduced alkalinity production hence retarded formation of authigenic carbonates. In comparison, moderate flow rates (0.1-40 cm a\(^{-1}\)) at Culebra Fault, Quepos Slide and Mudpie lead to reduced CH4 output. Here, higher efficiency of AOM and Ca fluxes increase the calcium carbonate precipitation rates, thus higher Ca fluxes from below induce more precipitation of calcium carbonate.
The effect of mica on pressure solution of single crystal calcite

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Clays and micas are known to accelerate the rate of pressure solution in various geomaterials. It is not clear however whether clays exert merely a mechanical effect (i.e., maintaining a thick conduit for fluids at the contact) or whether their surface chemistry plays a critical role. A case in point is the insoluble clay filling of stylolites, which are thought by some to be merely an inert byproduct of dissolution, while others consider it to be a necessary feature for the propagation of the seam.

To study the “clay effect” on pressure solution, we polished the corner of a cleaved calcite single crystal rhomb into a triangular face (edge length \textasciitilde 200\textmu m) and pressed it against either muscovite or quartz discs to yield nominal contact stresses of 10-20MPa. Immersing the contact in pre-saturated (with respect to microcrystalline calcite) solutions of distilled water or 0.25M NH\textsubscript{4}Cl caused axial shortening of the crystal, which was measured with a capacitance sensor (<0.5nm/h resolution). Contact morphology was imaged \textit{in situ} with a confocal microscope (~3\textmu m spatial resolution).

In pre-saturated water solution the axial shortening of calcite loaded against muscovite is \textasciitilde 1nm/h, and no significant changes in contact morphology are detected. In pre-saturated NH\textsubscript{4}Cl solution however, both calcite-quartz and calcite-muscovite contacts evolve in two stages: the first stage is characterized by low axial strain rates (<5nm/h) during which the original contact area inside the triangle (as determined by interference fringes) shrinks and its perimeter roughens. The second stage is distinguished by high axial strain rates (~40nm/h) and changes in the size and spatial position of isolated contacts (diameter< 10 microns) in a dynamic channel-island morphology covering the entire triangular region. Post-experiment SEM analysis suggests dissolution in this region and precipitation on the free faces adjacent to it. At this point we see no significant difference between the calcite quartz and calcite muscovite experiments under similar load conditions.

Trace element and Nd-isotopic compositions of the Neoproterozoic clastic sedimentary rocks of the Ikorongo Group, NE Tanzania: Implications for provenance, palaeoweathering, mineral sorting and post-depositional processes

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The north-eastern part of the Archaean Tanzania craton is unconformably overlain by a Neoproterozoic clastic sedimentary cover, namely the Ikorongo Group. The Ikorongo Group is comprised of conglomerates, quartzites, shales, siltstones, red sandstones with rare flagstones and gritstones and is regionally subdivided into four litho-stratigraphic units: the Makobo, Kinenge, Sumuji and Masati Formations.

Geochemical data from the mudrock samples (i.e., shales and siltstones; \textit{N} = 54) indicate derivation from cratonic sources that formed by intra-crustal differentiation. Initial $\epsilon_{\text{Nd}}$ values of \textasciitilde 27.4 to \textasciitilde 38.1 and T\textsubscript{DM} ages (2.2 – 2.9Ga) for the mudrock samples (\textit{N} = 10) confirm derivation from the Musoma-Mara Greenstone Belt (MMGB) of the Archaean Tanzania craton. The ranges in T\textsubscript{DM} ages, however, provide insight into the participation of a relatively juvenile crust and/or progressive younger periods of magmatism in the source terrains.

The similarity in the Nd-isotopic compositions between the source rocks and the Ikorongo mudrocks indicate that Nd signatures of the sediment sources are unaffected by factors such as weathering, heavy mineral sorting and post-depositional processes.
Neoproterozoic carbonates: An isotopic archive of ocean acidification?

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The Neoproterozoic is a period of exceptional Earth System change marked by extreme fluctuations from icehouse to greenhouse climatic conditions. These severe environmental changes are preserved in the geological record of warm water carbonates sharply overlying glaciogenic strata. In concert with the environmental changes, the carbonate rocks display large and stratigraphically systematic amplitude fluctuations in their stable isotopic composition (Li, B, C, O, Ca). The most intriguing isotopic signal is a characteristic negative C-isotopic excursion. This signal has been used to assess atmospheric \( p\text{CO}_2 \), organic productivity and carbon cycling during the extreme Earth System changes. Because of the relationship between carbonate \( \delta^{13}\text{C} \), \( p\text{CO}_2 \), ocean acidification and B isotopic composition of marine carbonates, we analysed Neoproterozoic carbonate rocks to obtain their B-isotopic signature and reconstruct ocean pH variation. We collected a C-B-Li-Ca isotopic dataset on postglacial cap carbonates from two discrete glacial intervals in Namibia; these glaciations occurred during the ca. 750-630 Ma time slice. The cap carbonates represent palaeo-geographically and palaeo-environmentally different settings and thus can be used to determine and assess the lateral uniformity and/or variability of these isotopes. Systematic B-isotope excursions (up to 9%e) in the postglacial carbonates appear to be associated with fluctuations in atmospheric \( p\text{CO}_2 \) and changing weathering rates and can be interpreted as directly reflecting periods of acidification of the surface ocean. Changes in the weathering input are reflected in systematic Li- and Ca-isotope (12%e and 0.8%e, respectively) excursions. These data provide new insights into the nature of the initiation and termination of Neoproterozoic glaciations and into the isotopic composition of ancient oceans.

A comparative analysis of gas hydrates occurrence and origin in three Indian Ocean regions

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To establish the structural and lithological controls on gas hydrate distribution and to assess the potential energy resource and environmental hazards in the Indian Ocean, cores were recovered from the Krishna-Godavari (KG) and Mahanadi deepwater Basins offshore southeast India, and from an Andaman Sea site. The pore fluids were analyzed for: Cl, SO₄, carbonate alkalinity, ammonium, Na, K, Ca, Mg, Sr, Ba, Li concentrations, \( \delta^{18}\text{O} \), \( \delta^{13}\text{C-DIC} \), \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratios, and DOC; together with infra-red imaging they provided important constraints on the presence and distribution of gas hydrates, thus on the subsurface hydrology. Evidence for gas hydrates was obtained at each of the sites. The presence and distribution of gas hydrates were inferred from infra-red imaging and pore fluid chloride concentrations and/or salinity, and occasionally mousse-like textures. Chloride concentrations and salinity anomalies, suggest pore volume occupancies from <1% to ~61% at two of the sites in the KG Basin, and from <1% to ~76% at the site in the Andaman Sea. In the KG Basin, the highest methane hydrate concentrations were associated with fracture zones in clay/silt sediments or in some coarser grained horizons, in Andaman Sea higher concentrations were associated with volcanic ash.

A comparative analysis with the Gulf of Mexico and convergent margin gas hydrate occurrences as well as the implications for global change and slope stability will be discussed.
Modeling biogeochemistry in an Early Ocean Analogue

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In the 590 m deep Lake Matano, Indonesia, a persistent pycnocline at 100 m depth separates the oxic epilimnion from anoxic deep waters. The resulting redox gradient drives the biogeochemical cycling of iron, manganese, methane, and other elements, producing vertical distributions that are remarkably close to being at steady state. Given the low sulfate concentrations, this lake is an excellent modern analogue of the sulfate-poor oceans of the early Earth and is therefore useful for characterizing anaerobic reactions that dominated these oceans. To quantify the rates of these reactions and vertical elemental fluxes, a geochemical model needs to be coupled to a model of physical mixing. Our previous work [1] has shown that a 1-dimensional mixing model may be insufficient. We therefore combine 3D and 1D hydrodynamic models with a geochemical reaction-diffusion model, which we use to characterize the biogeochemical transformations within the redox gradient. In particular, we test the possibility, suggested by the C isotope data and microbial ecology, that anaerobic oxidation of methane takes place in the absence of sulfate.


Mantle heterogeneity and crustal production in magma-dynamics simulations of mid-ocean ridges

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Simulations of coupled magma/mantle flow and thermal structure have great promise as a tool for connecting surface observations of lava flux, chemistry and chemical heterogeneity with physical processes of melt transport at depth. I report on progress in solving the 2D equations of magma dynamics (McKenzie 1984) coupled with two-component equilibrium thermo-chemistry via the Enthalpy Method (e.g. Alexiades & Solomon 1993). The simulations are configured to model a mid-ocean ridge. I have investigated the relationship between mantle material properties (permeability and rheology) and the efficiency of melt focusing and crustal production. The models predict the distance over which magma is focused to the ridge (Sparks & Parmentier 1991) and quantify the variation of focusing distance with key material parameters. Melting of a chemically heterogeneous mantle is also considered, with particular attention to the effect of variations in mantle fertility.
Temperature dependent $V^{3+/4+/5+}$ substitution(s) in goethite ($\alpha$-FeOOH)

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Temperature is likely to affect V-substitution in goethite due to the redox-sensitive nature of V. To assess the effect of temperature on V substitution in goethite, a series of V-substituted goethite were prepared under varying temperature regimes, and analysed using wet chemical and multi-spectroscopic techniques. Increasing temperature enhanced the proportions of $V^{4+/5+}/V^{3+}$ incorporated in goethite as indicated by X-ray absorption near edge spectroscopy (XANES, see figure).

The oxidation state of V dictates the symmetry of the V polyhedron, with octahedral symmetry being preserved better for $V^{5+} > V^{4+} > V^{3+}$. The total vanadium substitution ($V^{5+} + V^{4+} + V^{3+}$) dropped by 94% with increase in initial aging temperature from 25 to 70°C suggesting that higher temperatures favour the oxidation of $V^{3+}$ to $V^{4+}$ and $V^{5+}$. The results show that low nucleation temperatures preserved the oxidation state of $V^{3+}$, which has a similar ionic radius, hydrolytic properties and octahedral symmetry as $Fe^{3+}$ leading to 13.3 mol per cent substitution. This work provides information about the interaction between temperature, V oxidation and incorporation into the goethite structure. These aspects are important for sequestration strategies of V.

Accurate chronology of Antarctic climate and greenhouse gas changes over the past 470 ky

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In order to evaluate the roles of orbital and greenhouse-gas forcings on global climate (glacial cycles in particular), one needs a paleoclimate chronology with accuracy better than 2 ky (~1/10 of precession cycle). Kawamura et al. (2007, Nature) established such an Antarctic ice-core chronology for the past 360 ky through orbital tuning of $O_2/N_2$ ratio of trapped air in the Dome Fuji and Vostok ice cores, which records the local summer solstice insolation without lag.

Here we extend the Dome Fuji $O_2/N_2$ chronology back to 470 ky ago, which covers MIS 11 and Termination V. The onset of Antarctic warming for the last five Terminations is found to occur within the rising phase of summer insolation at high northern latitudes. Furthermore, null hypotheses that the last five Terminations are not linked with precession can be rejected at 5% significance level, while the null hypothesis for obliquity cannot be rejected with high statistical power. Antarctic cooling at the last four glacial inceptions appears to be in phase with the decline of northern summer insolation and obliquity, but earlier than atmospheric CO$_2$ decrease by a few millennia. These results are consistent with the classic Milankovitch theory that high northern latitude summer insolation is the primary pacemaker of the late Pleistocene glacial cycles.
The effect of BSA on the dissolution rates of amorphous silica in solution at different pH

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Dissolution experiments of amorphous silica in solutions containing various concentrations of bovine serum albumin (BSA) were performed to evaluate the effects of proteins on the dissolution rates. The dissolution experiments were carried out using Pyrex glass flasks containing 0.1 g of amorphous silica (5-100um in size) and 100 ml of 0.1 mM NaCl solutions with 0.05, 0.1, 0.2, 0.5, 1.0 mg/ml of BSA. Three sets of these flasks were prepared, and solution pH of each set was initially adjusted to pH4, 5, and 6 by HCl or NaOH, and then dissolution reactions were conducted at 25°C for 10 days. During the reaction, solution pH and concentrations of Si and BSA were measured every two days with a glass electrode, HPLC equipped with ion exclusive column, and UV-VIS spectrometer, respectively. Similar experiments using 0.1, 1.0, and 10.0 mM NaCl solutions without BSA were also carried out for inorganic controls. The dissolution rates of amorphous silica in these reaction systems were obtained using the Si concentrations for the reaction period of 2 to 10 days. Results of the experiments demonstrated that BSA showed strong rate-enhancement effects on the dissolution of amorphous silica depending on its concentrations and also on solution pH. The dissolution rates were increased successively about 4, 7, and 13 times relative to those of inorganic controls with increasing concentrations of BSA up to 1.0 mg/ml at pH6, 5, and 4, respectively. These values of increasing rates at pH 6 to 4 are consistent with increase in positive charge of BSA originated from protonation of amino group. Therefore, surface complexation of the positively charged sites of BSA (NH₃⁺) with the negatively charged sites (SiO⁻) of amorphous silica is likely to be an important factor enhancing the dissolution rates of amorphous silica.

The Armstrong Unit (AU=km³/yr) and processes of crust-mantle mass flux

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In his years at UBC, Richard Lee Armstrong pioneered concepts of the co-evolution of crust and mantle. He held that for most of earth history, crustal mass has been constant. Referring to processes, for him this required equality of subduction flux of crust-derived sediment to the mantle, and mantle-derived magmas to continental crust. Utilization of processes briefly noted as “on the horizon” by Armstrong (1991)—his last paper—has proliferated in the literature on the destruction side: lower crustal delamination events at Andean margins and as a consequence of continental collisions, slab-breakoff events, and subduction erosion events. Although calling on these processes is increasingly commonplace (for 2007, Citation Index lists over 1600 citations to crustal delamination alone), criteria for their identification are evolving. Remember that Dick thought that the geochemical community was not inclined to accept the volumetric importance of even sediment subduction. Here “important” is taken to be one whose global rate exceeds on the order of 1 km³ a year. This is called an Armstrong Unit (AU). The criteria for identifying candidate processes differ for events occurring at present, which can be studied using geophysical tools, and those that occurred in the past, where processes must be inferred from geochemically distinctive magmatic rocks, spatially changing magmatic patterns and abrupt thermal events in short-duration orogenies. Also, there are “missing crustal parts” to many orogens: accretionary prisms and forearcs in general, and lowermost mafic crust. It is inferred that these parts have low survival probability and may be returned to the mantle, over the lifetime of an orogeny. Examples in British Columbia and the Adirondacks show the challenge of applying this train of thought to crust/mantle evolution.
Implications of chemical and isotopic variations in Neogene Puna Plateau Ignimbrites for Central Andean crustal evolution

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Voluminous dacitic ignimbrites have erupted in a subduction zone setting along the compressional Central Andean margin in the last 11 Ma. A compilation of some 600 published and new analyses allows a view of the spatial-temporal crustal evolution of the ignimbrite complexes that erupted through the thickened crust of the Puna plateau between 22°S and 27°S latitude. Their variable chemistry reflects the conditions that generate large crustal magma systems. AFC modeling largely based on 87Sr/86Sr ratios and δ18O/16O shows that the large volume ignimbrites (>500 km3) are best modeled as approximately 50-50 mixtures of mantle-wedge derived basalt and variable composition crustal contaminants. Erupted mafic magmas show the mantle basalt is isotopically enriched (εNd ~ -2.0, ε18O ~ 6), most likely by crustal recycling due to forearc subduction erosion and delamination. An estimated volume of 8200 km3 for the erupted ignimbrites with a 90 km3/km/Ma arc magma production rate produces a plutonic/volcanic ratio of 4:1 and a 5.4 km thickness of new crust distributed across the plateau. Crustal contaminants in the ignimbrites are spatially and temporally variable with 87Sr/86Sr ratios from about 0.715 to 0.735 at 300 to 125 ppm Sr and δ18O/16O shows that the large volume ignimbrites (>500 km3) are best modeled as approximately 50-50 mixtures of mantle-wedge derived basalt and variable composition crustal contaminants. Erupted mafic magmas show the mantle basalt is isotopically enriched (εNd ~ -2), most likely by crustal recycling due to forearc subduction erosion and delamination. An estimated volume of 8200 km3 for the erupted ignimbrites with a 90 km3/km/Ma arc magma production rate produces a plutonic/volcanic ratio of 4:1 and a 5.4 km thickness of new crust distributed across the plateau. Crustal contaminants in the ignimbrites are spatially and temporally variable with 87Sr/86Sr ratios from about 0.715 to 0.735 at 300 to 125 ppm Sr and δ18O/16O shows that shows the large volume ignimbrites (>500 km3) are best modeled as approximately 50-50 mixtures of mantle-wedge derived basalt and variable composition crustal contaminants. Erupted mafic magmas show the mantle basalt is isotopically enriched (εNd ~ -2), most likely by crustal recycling due to forearc subduction erosion and delamination. An estimated volume of 8200 km3 for the erupted ignimbrites with a 90 km3/km/Ma arc magma production rate produces a plutonic/volcanic ratio of 4:1 and a 5.4 km thickness of new crust distributed across the plateau. Crustal contaminants in the ignimbrites are spatially and temporally variable with 87Sr/86Sr ratios from about 0.715 to 0.735 at 300 to 125 ppm Sr and δ18O/16O shows that shows the large volume ignimbrites (>500 km3) are best modeled as approximately 50-50 mixtures of mantle-wedge derived basalt and variable composition crustal contaminants. Erupted mafic magmas show the mantle basalt is isotopically enriched (εNd ~ -2), most likely by crustal recycling due to forearc subduction erosion and delamination.
Application of infra-red spectral and multi-element analyses in the gold exploration in North Mara mines, Tanzania

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A combination of Short Wavelength Infra red (SWIR) spectral and multielement analyses was used to characterize certain hydrothermal alteration, pathfinder elements and their distribution within gold deposits in the Archean Musoma-Mara greenstone belt in Tanzania. The aim was to fingerprint hydrothermal systems responsible for the formation of major gold deposits in the belt. The SWIR spectra of white mica and chlorite from the samples revealed compositional zoning which reflects pH changes associated with hydrothermal fluid-rock interaction during mineralization. White mica crystallinity is variable in the deposits reflecting thermal gradient during hydrothermal alteration. On the other hand, gold pathfinder elements distribution showed extension of pathfinder element signature beyond a distance of 600 m width from the ore zone with either As and Sb association or Ag and Bi association. This suggests that different redox conditions have affected the deposits. This study confirms that a combination of SWIR spectral and multielement data is a cost-effective method in generating mineralization targets and can be applicable in areas with similar styles of mineralization.

Calibrating U-series tools for weathering rate and duration on a soil sequence of known ages

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The U-series isotopes provide a range of potential tools with which to assess the timing and rate of chemical weathering. Using such tools commonly involves making assumptions about the leaching coefficients of the nuclides from the soil, for instance that leaching is first order with respect to U concentration [1]. No study has yet tested these assumptions or the general applicability of U-series tools to weathering questions, on a soil sequence with known ages.

In this study we have measured U and Th isotopes on a set of 24 samples taken from four soil profiles from the Merced chronosequence in the Central Valley (California) [2]. These soils are formed from granitic to dioritic sands deposited on river terraces with ages of 40, 250, 600 and 3000 kyrs. This chronosequence has been extensively studied for trace element, mineralogical and textural variables and so makes an ideal test bed for U-series tools for weathering. We have augmented our new U-series data with bulk chemical analysis from which loss of U and Th in the soil profiles can be assessed.

The U-series data show few clear patterns within each soil profile but show a clear trend in average (230Th/238U) values for each soil profile from an original high value of 1.37 at 40 kyr to lower values with increasing duration of weathering (1.16, 1.07 and 1.04 respectively). These values are not consistent with a uniform leaching constant for 238U, but suggest early rapid leaching followed by slower leaching at a rate more comparable to that of Th. This can be modelled as a two stage leaching process (which would require rapid early release of U from easily weathered mineral phases early in soil formation) or by using non-linear leaching constants. Such variable weathering rates are consistent with losses of U and Th normalised to Ti.

This and future chronosequence work will allow more accurate use of U-series nuclides to assess weathering rates and durations in settings where the timescales of weathering are not independently known.

Aleutian primitive andesites: From the mantle, but how?
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Primitive andesites (Mg#>0.6) are an important end-member in forming high Mg# (>0.5) andesites virtually identical to continental crust. In the western Aleutians, high Mg# andesites contain little or no older, recycled continental material, so unless the chemical similarity is a coincidence, they are juvenile continental crust, and are crucial to understanding continental genesis.

The most primitive Aleutian andesites have the highest La/Yb, Dy/Yb, and Sr/Y in the arc, and the most depleted Pb, Sr and Nd isotopes in global arc magmas. High Ni, Cr and Mg# indicate mantle-derived liquids. High H2O and alkalies stabilize high SiO2 melts with olivine. In the Aleutians, there is no evidence for evolved components which, mixed with basalt, could form primitive andesite. Thus, Aleutian primitive andesite passes into arc crust from the mantle.

This said, the ultimate origin of primitive andesite remains uncertain. Hydrous melt of subducting oceanic crust in eclogite facies may react with peridotite to form primitive andesite, but then how can primitive andesite erupt in close proximity with primitive basalts recording higher mantle temperature? Also, why are Sr isotopes in Aleutian primitive andesite so low?

Alternative and supplementary hypotheses abound (e.g., Kelemen et al. ToG 2003, Fig. 16). Cold diapirs may rise into the mantle, but why would mafic eclogites be buoyant? Basalt may react with cold, shallow mantle at ~ 1.5 GPa to yield andesites but why would they be isotopically different from basalt? Dense lower crustal cumulates may founder into underlying mantle, but then what is the source for the abundant H2O, K2O, etc? Subduction erosion, or imbrication of the subduction zone, may cycle oceanic fragments into the mantle wedge where they are heated by conduction, but again low Sr isotopes pose a puzzle.

Decoupling of plant-driven weathering from leaching in the critical zone
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The root systems of vascular plants acquire mineral-derived nutrients by chemical weathering. These processes have been assumed to load soil and ground waters with leachable weathering products. We isolated the effects of red-pine root systems on concentrations of mineral-derived Ca and Mg in shallow soil waters of the 60 m3 Hubbard Brook “sandbox” mesocosms growing 15-20 yr old trees, and in replicated 0.0002 m3 columns growing 6-12 month old seedlings. At both scales, tree-system soil waters had 20-60% lower concentrations than controls without trees, and the tree systems showed correspondingly smaller leaching losses. Increased mineral weathering fluxes in these systems were largely diverted into soil and biomass pools (Figure 1), perhaps by localization of mass transfers within the biofilms observed to blanket and attach rootlets and microbes to mineral surfaces. This may maximize return on resources devoted to weathering by vascular plants, and decouple nutrient uptake from leaching losses under certain conditions in nature.

Figure 1: Partitioning of weathered (W) Ca and Mg mass in experimental ecosystems, in mol m-2 yr-1 [1]. Upper (green) values are sandbox fluxes over 15 yr; lower (blue) values are column fluxes over 6 to 12 months.

Mineralogy and chemistry of stardust samples

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Comets are primitive bodies that likely preserve the fundamental building blocks of the solar system. The return of samples from comet Wild-2 by the Stardust mission provides an opportunity to study some of the earliest solar system solids in detail. We report here transmission electron microscopy observations of several Stardust particles.

Terminal particles were extracted from aerogel keystones of an ~2 mm long "carrot-shaped" track (C2067 T112), and an ~2 mm long "ginseng-shaped" track (C2061 T113). The single terminal particle from T112 consists of an ~10 µm rounded grain of forsteritic olivine. Energy-dispersive x-ray spectra show that the core of the grain is Fo99 - x-ray mapping reveals a slight enhancement in Fe towards the rim of the grain to Fo97. The forsterite is strained and shows a high density (2x10¹⁰/cm²) of oriented planar defects along (100). One small inclusion of chromite was observed.

Multiple terminal particles have been extracted and analyzed from T113. The mineralogy of these particles is similar and is dominated by coarse-grained enstatite (En90) that is largely orthoenstatite with numerous clinoenstatite lamellae. One particle (TP1) contains minor forsterite (Fo88). The enstatite also contains small inclusions of diopside with % levels of Al, Cr and Fe. The diopside has Cr/Fe at. ~3. Two of the terminal particles (TP1,TP3) contain nepheline intergrown with the enstatite. Diffraction analysis and dark-field imaging show that the nepheline is polycrystalline and EDX analyses show no detectable K. Some of the nepheline grains are partly vesiculated.

Nepheline is a rare phase in primitive meteorites and its petrogenesis is generally attributed to Na metasomatism of aluminosilicate glass or crystalline feldspar, and we infer a similar origin for the nepheline in the Stardust particles. The planar defects in the forsteritic terminal particle and some of the pyroxene microstructures likely result from shock. It is unknown whether the shock effects resulted from processes that occurred on Wild-2 or if they formed in response to the capture event.

Extraction of grain and phase boundary material properties from zoned garnets

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In recent studies, we used the repository potential of garnet in combination with high-resolution analytical techniques (i.e. EBSD, FE-EMPA and TEM/FIB) and numerical simulations in order to gain new knowledge about the nature of chemical pathways in terms of geometrical (e.g. boundary width) and physical properties (e.g. diffusivities and solubilities), which is fundamental in understanding reaction kinetics and mass transfer in the Earth’s deep crust and upper mantle.

Reactions of type A + plagioclase (Pl) → garnet (Grt) + C often form Grt rims (~20 µm wide) along reactant boundaries and we found that the necessary mass transfer across reaction rims is amplified by the formation of subgrains perpendicular to the reaction fronts, which allows for short-circuit diffusion. Information about the contribution of grain boundary diffusion to bulk material flow in Grt is stored during the formation of asymmetric growth zonings and micron-scale compositional variations along grain and phase boundaries. Our evaluation of these compositional patterns by diffusion modelling allows for the derivation of $D^{gb}/D^{vol}$ ratios and rim growth rates. Reaction progress needs the transfer of material through the interior of reacting Pl towards the reaction fronts. About 100 nm wide pores in Pl and Grt-Pl phase boundaries, which both are filled with a non-crystalline material, suggest that a coupled diffusion and dissolution/precipitation process, during which internal and surface dissolution/precipitation formed new nano-scale pathways and a non-crystalline transport medium, likely enhanced mass transfer in Pl and along Grt-Pl phase boundaries.

Information about phase boundary material properties is also stored in the zoning of Grt porphyroblasts, which formed during the retrograde Fe-Mg exchange between Grt and biotite. If temperature falls below a limiting value during cooling, non-equilibrated rim compositions start to develop along Grt-Qtz phase boundaries due to insufficient chemical transport rates. Because the extent of non-equilibrated rim compositions reflects the transport capacity of the present intergranular medium, our simulations by diffusion modelling of observed compositional patterns formed during cooling at Grt-Bt-Qtz triple junctions allows for the extraction of boundary material properties.
Lost City: Serpentinization and life

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The ultramafic-hosted Lost City Hydrothermal Field (LCHF) at 30°N on the Mid-Atlantic Ridge is characterized by a combination of extreme conditions never before seen in the marine environment. These conditions include venting of basic, 40-91°C, metal-poor hydrothermal fluids with high concentrations of dissolved H₂ (1-15 mmol/kg), CH₄ (1-2 mmol/kg), and other low molecular weight hydrocarbons[1-3].

The fluid chemistry is driven by fluid-rock reactions in the underlying ultramafic basement at temperatures up to 200°C. Hydrothermal activity has been ongoing for >30,000 years [3]. Egress and mixing of warm, pH 9-11 fluids with cold seawater forms carbonate chimneys that tower up to 60 m above the surrounding seafloor. Radiocarbon measurements of CH₄ show that the carbon source cannot be modern seawater bicarbonate [2]. Stable carbon and hydrogen isotopic compositions of short-chained hydrocarbons are compatible with production through serpentinization and Fisher-Tropsch type reactions and carbon being leached from the underlying mantle rocks during alteration processes [2].

The porous interiors of the vents, bathed in CO₂-absent fluids, provide novel niches dominated by a single phylotype of Lost City Methanosarcinales (LCMS) [4]. These organisms grow under significantly hotter and more extreme pH conditions than known to support any other methanogen or methanotroph. In chimneys with little or no venting, the LCMS group is replaced by a single phylotype of anaerobic methanotrophic Archaea (ANME-1) [4]. The ultramafic underpinnings of LCHF are compositionally similar to early Earth lavas erupted into primordial oceans. Resulting high pH vents may have been important prerequisites for life [5].


Two diffusion mechanisms for Argon in K-feldspar?

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New argon diffusion data generated by laser depth profiling of laboratory experiments on gem quality K-feldspar, demonstrate two diffusion pathways, confirming earlier work on quartz (Watson and Cherniak 2003), and other minerals (Jay Thomas ref). Earlier noble gas depth profiling analyses have used 213nm and 266nm lasers capable of measuring profiles greater than 1 micron deep, but it was notable that the surface analysis always contained anomalously high Ar concentrations, and spatial resolution better than 1 micron proved elusive. Combined RBS and laser analyses of quartz demonstrate that the surface layer may contain a second shallow diffusion profile and this experiment was intended to test for a similar effect in K-feldspar.

The application of a 193nm Eximer laser to noble gas extraction has enabled us to analyse the upper micron of samples previously exposed to Ar at high pressure, and has the capability of measuring noble gas diffusion profiles at a spatial resolution approaching 0.1 microns. The new data shows that the surface layer which appeared as one or at most two anomalous points in earlier work is in fact a diffusion profile with a shape approximating to that expected for Fickian diffusion in a mineral lattice. The measurement of such profiles in K-feldspar allows us to compare the diffusion constants with empirically derived natural samples and laboratory stepped heating experiments used for Ar-Ar dating.

The argon diffusion parameters derived from the near surface in K-feldspar, like the diffusion parameters derived for quartz, have low activation energies and very low pre-exponential factor. This combination of parameters implies relatively slow diffusion rates under magmatic conditions, but diffusion rates which exceed those generally derived from stepped heating experiments close to the conventional closure temperature. The implications for thermochronology will be explored by comparing the variation of the two diffusion mechanisms with temperature.
Mantle mixing and the origin and persistence of geochemical reservoirs

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A variety of mechanisms have been proposed for the origin of mantle heterogeneity as observed in mid-ocean ridges and oceanic islands. One source is related to plate motion and recycling: heterogeneity is introduced into the mantle by processes associated with melting, alteration, and subduction, while heterogeneity is destroyed by the stirring action of convection, the stretching and folding common to all kinematic mixing processes. Thus the rate and efficacy of mantle mixing partially constrains the origin and fate of the isotopic heterogeneity seen in mid-ocean ridges and oceanic islands. Mantle mixing is influenced by a variety of factors, including time-varying flow, plate motion, viscosity variations, and phase transitions. Chaotic mixing can be observed in calculations of time-varying 2-D flows, but the rate of mixing in 3-D has been poorly constrained. We present a method for assessing mixing in 3-D, using dispersal and stretching of ellipsoidal tracers, with applications geochemical reservoirs in the mantle. Stirring may be rapid on a regional scale (resulting in fairly uniform mid-ocean ridge basalts on length-scales up to thousands of km) while heterogeneities at the global scale of the Dupal anomaly are retained for billions of years because of isolation across long-wavelength cells. Essentially, the regions that exhibit high rates of stretching and thinning have the most important influence on mixing, and packets of material that are stirred rapidly in regions of high strain rate are carried wholesale into regions of more sluggish convection. The analysis of mixing is complicated by the fact that structures created by passive tracers in 3D exhibit different characteristics than structures observed in 2D models. Nevertheless, it remains difficult to account for mantle isotope systematics and for the Earth's overall heat flow budget without invoking some barriers to flow in the mantle's interior, such as would be provided by mantle layering.

Climate correlations across the MIS 5/4 boundary based on a stalagmite record from Dongge Cave, China

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We present the δ18O record of stalagmite D11 from Dongge Cave (southern China) on an updated timescale based on twenty-four U/Th ages obtained on a Finnigan-MAT Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). Stalagmite D11 grew between ~97 and 49 ky BP. 2σ errors associated with U/Th ages average ~3‰, and are as small as 1.8‰. The growth rate was moderate, between ~5 to 28 µm/yr. The oxygen isotope record consists of 878 isotope measurements with an average temporal resolution 55 years, ranging from 11 to 115 years. In accordance with previous interpretations [1, 2], the δ18O record of stalagmite D11 can be considered a reflection of Asian Monsoon intensity.

The D11 oxygen record is punctuated by millennial scale intervals of strong monsoon intensity, which have a one-to-one correspondence with Dansgaard-Oeschger (D/O) warm events 17 through 22, continuing the trend previously seen at Hulu Cave [1]. We can therefore assign absolute ages to these events, with a precision averaging less than ±300 years. The time interval covered by stalagmite D11 is also important in terms of climate because it includes the onset of major glaciation at the MIS 5/4 transition. Previously, we have made critical correlations between Asian Monsoon intensity, atmospheric methane concentration [3], and Heinrich events in the North Atlantic [1, 4], which have enabled us to determine a sequence of events surrounding the last two glacial terminations. By examining the relationships between the Asian Monsoon, sea level, δ18Oatm, and atmospheric methane over the timescale recorded by stalagmite D11, we can determine if these different aspects of climate relate to each other in a similar way during major glacial buildup.

Multi-stage zircon growth during a single partial melting event – Insights from REE partitioning

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Zircon crystallisation in migmatites and associated leucogneisses is commonly interpreted to occur during terrain-wide cooling following the peak of metamorphism. However, detailed study of zircon zoning in both absolute REE concentrations and partitioning behaviour with associated garnet, has revealed a more complex history of zircon growth. Metapelite underwent biotite-controlled vapour-absent partial melting at ~6 kbar and ~860°C, with production of sillimanite-spinel-garnet melanosome and segregation of quartzofeldspathic leucosome. REE distribution data from texturally constrained zircon and garnet indicate that early-crystallised zircon in metapelitic gneiss grew in equilibrium with peritectic garnet during partial melting. Later-crystallised zircon is REE-depleted and probably grew during crystallisation of trapped melts. In leucogneisses zircon cores grew prior to substantial garnet growth, but the main phase of zircon grew in equilibrium with peritectic garnet prior to entrainment. Late, HREE-depleted zircon crystallised with the leucogennite. Late pegmatites contain garnet that is intensely HREE-depleted relative to entrained zircon, which grew in equilibrium with metapelite garnet.

The data indicate that zircon growth does not solely occur at a single stage of a P-T path during terrain-scale crystallisation of melts, but at various stages during melt generation, transport and crystallisation. Zircon growth is accounted for by local domain-scale compositional and physical parameters that lead to multiple zircon growth events occurring across a terrain at different times and in different textural sites. Continued melting and melt extraction allows for entrainment of previously formed zircon into melts that crystallise later in the P-T evolution of the terrain. As such, prediction of the timing of zircon growth during the P-T evolution of a terrain and linking of U/Pb ages to specific stages on a P-T path, may not be accurately described by generic P-T-X models. Instead, detailed domain specific modelling is required, underpinned by textural and geochemical criteria that describe locations of zircon growth and timing relative to associated metamorphic assemblages.

Monitoring Uranium transformations

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Researchers have commonly assumed that reduction of U(VI) to U(IV) under anaerobic conditions would sequester uranium in the subsurface as uraninite, which has low solubility and is easily formed in the laboratory. Using X-ray absorption spectroscopy (XAS), however, our group and others have shown that products of biostimulation are more complicated than previously thought. As the complexity of a system increases, the nature of the products becomes increasingly difficult to predict. A useful research method in complex natural sediments is measurement on length scales smaller than the scale of natural heterogeneity. We have used X-ray-based techniques to monitor contaminant transformations in the local atomic distribution around U during biogeochemical evolution of highly heterogeneous subsurface material from the Integrated Field Challenge Site at Oak Ridge National Laboratory. We have applied X-ray fluorescence (XRF) to map the spatial distribution of key elements and XAS to monitor changes in U valence state and U speciation as they occur in intact, undisturbed microcosms for >1 yr. We have also taken subsamples for microbial analysis and monitored aqueous-phase parameters to link the U transformations to biogeochemical processes. These results will be presented.
Crustal versus hydrothermal sources to 2.7-2.3 Ga seawater: Constraints from Os isotopes and Re, Mo abundances in black shales

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Re-Os geochronology and redox-sensitive metal abundances (e.g., Re, Mo) in black shales have great potential to constrain Early Earth marine geochemical cycles and the chronology of atmosphere and ocean oxygenation. Seawater \(^{187}\text{Os}/^{188}\text{Os}\) (as recorded by the initial \(^{187}\text{Os}/^{188}\text{Os}\) \([I_{\text{Os}}]\) of Re-Os isochron regressions) reflects a balance between the riverine flux of radiogenic Os from oxidative weathering of upper continental crust (present-day value of \(\sim 1.0-1.5\)) and the flux of unradiogenic Os from hydrothermal alteration of oceanic crust and peridotites, and cosmic dust (\(\sim 0.11-0.13\)). Chondritic \(I_{\text{Os}}\) obtained from the 2.70 Ga Joy Lake Sequence (Superior Province, Minnesota, USA) [1], 2.50 Ga Mt. McRae Shale (Hamersley Group, western Australia) [2], and 2.32 Ga Rooihoogte and Timeball Hill Formations (Transvaal Supergroup, South Africa) [3] are consistent with dominance of the Late Archean to Early Paleoproterozoic marine Os budget by hydrothermal and extraterrestrial inputs. However, an interval of elevated Re and Mo abundances in the Mt. McRae Shale together with elevated Re abundances in the Joy Lake sequence may record mild shallow water oxygenation (whether local or global) prior to the 2.45-2.32 Ga Great Oxidation Event [2]. Thus, oxidative weathering of crustal sulfides may represent a measurable, albeit minor source of Re and Mo to Late Archean seawater relative to the hydrothermal and extraterrestrial fluxes. New high-resolution chemostratigraphic profiles through black shale intervals in the 2.6-2.5 Ga Ghaap Group (Transvaal Supergroup, South Africa) are consistent with this hypothesis.


Cell-mineral surface origins of the biogeophysical response

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Successful bioremediation schemes rely on effective monitoring of subsurface biogeochemical processes and cell transport. Recent laboratory results show induced polarization (IP) geophysical measurements are sensitive to microbial activity in porous media. This presents the potential for high-resolution, non-invasive, long term monitoring of biogeochemical conditions over large subsurface volumes using low-frequency electrical techniques. Critical to future field-scale implementation, however, is a fundamental understanding of the bioelectric IP effect, which we believe is rooted in cell-mineral surface processes. Key parameters are surface ion mobility, local dielectric, and surface potential, which we probe using polarization force microscopy. Polarization forces over a bacterium are higher than those over a mica surface at low relative humidities. This is suggestive of differential water retention and increased surface ion mobility at the cell interface, both of which represent possible polarization mechanisms (viz. IP effects), at least for partially saturated conditions. Moreover, low-frequency dispersions of the local permittivity inferred from polarization force data collected over cells correspond to dispersions modeled for a bacterium in aqueous conditions. Specifically, frequency cut-off values increase with increasing ion mobility in a pattern that is consistent with the modeled values. Further polarization force measurements and nanoscale mapping of the heterogeneous electrical layout at the mineral-microbe interface should provide much needed molecular-level insight into column and field-scale bio-IP phenomena.
A seismological perspective on mantle lengthscales

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Although many seismological images are oriented towards the definition of larger scale features in the mantle, the distribution of sources and receivers allows reasonably high resolution for about half the mantle. In such images the best resolution is of high velocity anomalies, mostly likely associated with past subduction; yet some anomalies appear in regions without subduction in the last 150 Myr. This suggests that some fragments of subducted material display significant resistance to thermal assimilation into the surrounding mantle. A typical dimension of these high wavespeed features is of the order of 500 km, which is interestingly a typical dimension of a coherent segment of slabs entering a subduction zone. For smaller bodies surface processes are likely to be more important than volumetric and this may require some reassessment of the types of diffusion parameters employed in thermochemical convection calculations.

The role of extracellular polysaccharides in the adsorption of metals onto biofilms

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Bacterial adsorption can affect the behavior of metals in the environment. There have been a considerable number of studies that examine adsorption of metals onto bacterial cells. However, but bacteria in most natural settings exist within biofilms, which are an attached growth state of bacteria where structured communities of cells are linked together in a matrix that includes secreted extracellular polysaccharides (EPS), proteins, and DNA. Experimental evidence indicates that EPS can bind significant concentrations of metal cations and protons, but the importance of EPS adsorption of metals and protons relative to cell wall adsorption is unknown.

In this study, we conducted potentiometric titrations to determine the proton binding capacities of three types of biomass samples: 1) bacterial cells with EPS material removed through an enzyme treatment; 2) untreated bacterial cells with EPS material intact; and 3) EPS material alone that was separated and isolated from the bacterial cells that secreted them. Gram-negative Pseudomonas putida biomass was used in all experiments; EPS removal was accomplished by washing the biomass in a solution that contained the enzyme glucoamylase, which cuts α-glucosidic bonds. EPS separation and isolation from the cells was done using ultracentrifugation at low temperature. Potentiometric titrations were conducted with each sample suspended in a 0.1 M NaClO\textsubscript{4} electrolyte to buffer ionic strength. The titration data were interpreted with a discrete site non-electrostatic surface complexation model so that the modeling results could be compared to those for a range of bacterial cells already studied.

The potentiometric titration data from the three different types of samples are identical to one another within experimental uncertainties. The data can be modeled successfully using 4 discrete sites, and the calculated site concentrations and acidity constants for each type of sample are within error of each other, and within error of the universal model of proton reactivity for bacteria proposed by Borrok et al. (2005). These results imply that either the EPS molecules are inert to proton binding, or that they exhibit virtually identical proton binding properties to those of the cell wall. These results could greatly simplify modeling of metal adsorption in biofilm-bearing geologic systems.
Heterogeneous melt inclusions from heterogeneous mantle: An example from Baffin Island, Canada

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Melt inclusions can be used to probe the compositional diversity present within magmatic systems, although the use of melt inclusions to study mantle heterogeneity in primitive basalts has been subordinate to studies of mantle melting. This study presents major and trace element compositions of olivine-hosted melt inclusions from picritic pillow basalts from Baffin Island Canada. Host lavas have trace element and isotopic compositions derive from two distinct mantle sources – depleted MORB mantle and an enriched composition, possibly recycled metasomatized oceanic lithosphere [1]. The influences of crustal or lithospheric contamination appear negligible and melt inclusions provide a means to study a primitive basaltic magmatic system that is demonstrably sampling two different mantle-derived components.

Melt inclusions show a large range of incompatible trace element compositions, with indices of incompatible element enrichment such as K/Ti and La/Nb in melt inclusions from individual samples varying to greater extents than evident in the entire suite of host lavas. Trace element variations rule out crustal contamination or incomplete aggregation of a polybaric melting column as the source of incompatible trace element variations. Furthermore, arrays defined by trace element compositions of melt inclusions directly overlie and extend those defined by host lavas, and strongly imply that melt inclusion compositions reflect mixtures of melts derived from the same two mantle endmembers sampled by the host lavas. This is supported by (1) near-normal distributions of K/Ti that can be reproduced by models of continued mixing and (2) the similarity of average K/Ti for melt inclusions to that of their host lava. The larger variations evident in melt inclusions are consistent with mixing samples at a smaller scale, but similarities between inclusions and hosts demonstrates that the compositions of melts trapped within inclusions have not had their trace element abundances further fractionated by diffusional exchange during mixing or by equilibration between inclusion and host or external melt subsequent to trapping. Projected compositions of mantle endmembers from mixing arrays suggests melts derived from DMM and EM1-like mantle can reproduce the observed compositional arrays.


Electron-transfer reactions at water- and cytochrome-iron oxide interfaces

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Redox reactions that take place at the mineral-water interface play a major role in many geochemical and biogeochemical processes such as metal contaminant mobility and microbial iron respiration.

For example, dissimilatory iron-reducing bacteria are capable of electron transfer to iron oxide minerals as part of their anaerobic respiration process. Although there is evidence that multiheme outer-membrane cytochromes are involved in direct electron transfer to iron oxide surfaces, the molecular-level mechanisms of this process are still unclear. In this paper, molecular computational techniques are used in the framework of Marcus theory to compute elementary electron-transfer rates from a well-defined cytochrome model to surfaces of hematite (α-Fe₂O₃). These simulations show for the first time that interfacial electron transfer distances of 10 Å or less can be achieved for the purpose of oxide reduction. In addition, we computed rates of interfacial electron transfer in good agreement with recent experimental data on comparable systems and concluded that the interfacial electron transfer step is feasible but is a potential kinetic bottleneck in the bioreduction process [1].

Another critical issue is the fate of electrons injected in the iron oxide, whether as a result of biotic or abiotic reactions. Indeed, the rate at which electrons diffuse away from the injection site is a key factor in determining the turnover of electron accepting sites at the interface and has implications in the possible formation of new phases. In this paper, we use atomistic and quantum mechanical calculations to investigate the kinetic and thermodynamic properties of electron transfer reactions between adsorbed iron(II) and hematite surfaces and at two water-hematite interfaces. Our findings indicate that diffusion of small electron polarons occurs through the lattice at an appreciable rate and that, in the case of the basal (001) plane, lateral diffusion is significantly faster than diffusion into the bulk [2, 3].

Magma generation in the Main Ethiopian Rift (MER) and Afar

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Magmatic activity in the Ethiopian volcanic province has been attributed to the activity of a mantle plume located beneath the Afar triangle ~30 Ma years ago, when large volumes of flood basalts erupted in this area. The current location of the plume and its relationship with the recent volcanism in the MER and Afar is a subject of debate.

In the present study we assess the geochemical characteristics of basaltic lavas from seven volcanic centres within the rift-valley (Ayelu, Hertali, Dofan, Fantale, Kone, Bosetti and Gedemsa from NE to SW) in order to locate the present position of the plume and to constrain source characteristics, melting depths and magma generation processes.

Trace element patterns indicate the presence of amphibole during the genesis of all samples. According to the pressure stability of amphibole this translates to a melt generation or reequilibration depth of 80 km maximum. The minimal melting depth is constrained by the crustal thickness, which decreases from 38 km in the MER to 24 km in Afar.

La/Yb ratios decline with increasing latitude of the sampling location. Low La/Yb ratios in Afar can be explained by higher degrees of melting, i.e. a reduced melt generation depth, which corresponds to the observed thin crust, whereas higher La/Yb values measured in the MER basalts result from higher melting depths and mirror the increased crustal thickness.

Basalts from Afar and the Afar-MER transition zone display εNd values above +4.8 and 87Sr/86Sr ratios between 0.70354 and 0.70383. Samples from the MER plot below εNd +4.8, their 87Sr/86Sr values range from 0.70384 to 0.70430. Assuming a plume related origin, two enriched mantle end-members similar to EM I and EM II can be identified in the MER samples, constraining the present location of the plume. Low 206Pb/204Pb ratios (19.317 to 18.484) support this finding and rule out the involvement of a HIMU component. In Afar, an additional MORB-like component is present.

To summarize, the sampled quaternary basaltic lavas were derived from a heterogeneous EM-like plume-source and subsequently modified by reequilibration within the lithospheric mantle beneath the Ethiopian rift. Incipient sea-floor spreading can be inferred from a MORB component in Afar. The MER lavas however are most probably the surface expression of ongoing mantle plume activity.

Reproducibility of apatite fission-track length inversion modeling

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Although apatite fission-track length data have long been used to derive thermal history information, there are no agreed-upon conventions for calibration of length measurements. In an effort to document variability among analysts and determine what features a length calibration protocol should include, an experiment was conducted in which eleven analysts measured approximately fifty track lengths on one or both of two grain mounts, one with unannealed induced tracks in F-apatite and another with a single large-etch-figure population featuring a broad distribution of spontaneous track lengths. Variation in the measured length distributions among analysts was considerably in excess of statistical expectation, probably reflecting differences in microscope technique.

Two thermal history scenarios were tested with inversion modeling: cooling-only, and a reheating history indicated by other data from the field area. When cooling-only inversions assumed a standard literature value for initial track length, results varied markedly. However, when track lengths were normalized using each analyst’s unannealed mount measurement, histories became much more consistent, although differences remained in the amount of time spent at high temperatures (~100°C), due in part to differential sampling of long- and short-length populations. Accounting for track angle using c-axis projection further enhanced congruence for various thermal history features, such as the onset time of fast cooling. The second scenario was primarily evaluated in terms of the predicted peak reheating temperature. Under both initial-length assumptions, predictions showed considerable variation when lengths were used without accounting for track angle, but again inversions that utilized c-axis projection were much more congruent.

Taken in sum, these results indicate that fission-track length calibration should account not only for absolute length measurement but also the relative tendencies among analysts for measuring different length populations. However, even with the minimal length calibration steps of measuring an unannealed induced population and accounting for initial length variation as a function of etch figure diameter, reproducibility of many thermal history features was good, and improved when track angle data were utilized as well.
Differentiation of high-K calcalkaline magmas at Mount Bidkhan volcano (Central Iranian Volcanic Belt)

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Mount Bidkhan is an Oligo-Miocene stratovolcano, with a caldera, located in the southeastern part of the Central Iranian Volcanic Belt (CIVB). A detailed stratigraphically-controlled sampling of deposits was performed in the proximal, medial and distal sectors of the volcanic edifice. Eight kinds of products have been recognized: 1) pyroclastic flows 2) fall-out levels; 3) lahars; 4) surges 5) lava flows; 6) brecciated lavas and lava breccias; 7) dacitic domes/plugs; 8) ring and radial dykes. Major and trace element compositions of whole rocks were obtained on selected volcanics by means of WD-XRF and ICP-MS. Analyses on mineral phases were carried out by SEM-EDS; plagioclase and clinopyroxene were analyzed in detail along core-rim profiles and through X-ray mapping for major elements. Products exhibit high-K calcalkaline affinity and can be classified as andesites and dacites. The mineral assemblage is chiefly composed of plagioclase and, subordinately, clinopyroxene, orthopyroxene, amphibole, biotite and magnetite. Quartz phenocrysts and abundant K-feldspar in the groundmass make the dacitic products peculiar. Accessory minerals are apatite, zircon and sphene. Core-rim compositional profiles in plagioclase and clinopyroxene evidence that almost all of the crystals are complexly zoned. Specifically, plagioclase and clinopyroxene commonly exhibit small-scale oscillatory zoning, which sometimes turns into significant An mol% and Mg# changes respectively. The integrated analysis of petrochemical data allows the preliminary hypothesis that the geochemical evolution of magmas might be chiefly ruled by AFC processes at shallow depth, to which repeated episodes of mixing due to inputs of less evolved magmas are superimposed. In particular, microanalytical data highlight that the most significant magma recharging episodes are recorded at the phenocryst rims, slightly prior to the eruption. Future research will be focused on possible relations between inputs of less differentiated magmas into the feeding system and the onset of violent strombolian to plinian eruptions.

Redox-linked coordination change in OmcA: Implications for dissimilatory Fe(III) reduction

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OmcA is a bis-his ligated decaheme c type cytochrome with an unknown crystal structure expressed in the outer-membrane of the metal reducing bacteria Shewenella oneidensis in response to reducing conditions. Although metal reducing bacteria play an important role in bioremediating toxic and heavy metals, their mechanism of electron transfer to solids is not yet completely understood. We hypothesized that the sorption behavior of OmcA is redox dependent due to its purported role in electron transfer to metal-oxides. Fe K-XANES and EXAFS data for the reduced and oxidized OmcA in solution, oxidized OmcA dissolved in 6 M GdnHCl (Guadininium-HCl) and oxidized OmcA sorbed to SnO2 surfaces were collected and analyzed. Our previous work with a monoheme equine cytochrome c showed based on Fe K-XANES spectroscopy that sorption and denaturant induced changes in the heme Fe coordination were similar. Fe K-XANES and EXAFS spectra for oxidized OmcA showed evidence for a sorption induced change in the coordination environment of heme Fe. Similar to our results for the equine cytochrome c, the heme Fe coordination of sorbed OmcA was similar to the denatured OmCA. Denatured oxidized OmcA however, disintegrated, based on its XANES and EXAFS spectral similarities to Fe metal foil. OmcA behavior was markedly different from the behavior of the monoheme equine cytochrome c which, on denaturation changed from its native his-met ligation to a bis-his ligation. Based on XANES and EXAFS spectral similarities of sorbed oxidized OmcA with denatured OmcA, our results indicate that oxidized OmcA is not designed to interact with metal-oxide minerals. If OmcA is indeed the electron shuttle to metal-oxide surfaces, we expect reduced OmcA to sorb readily in order to transfer electrons; similarly, the oxidized OmcA should be designed to desorb. Fe K-XANES and EXAFS spectra for dissolved OmcA showed redox linked changes, suggesting that the sorption behavior of reduced and oxidized OmcA would differ consistent with the demands of its role in dissimilatory Fe(III) reduction.
**Crustal contamination and magma mixing in basic volcanic rocks from NW Iran: Evidence from textural and chemical disequilibria in phenocrysts and glasses**

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Basic volcanic province of north western Iran consists dominantly of alkali basalts and trachyandesites. We present the results of detailed petrographic and geochemical investigations on the basaltic rocks. A variety of features suggest that the lava flows were contaminated by upper crustal materials along their way from magma chamber onto the surface. In addition, the effects of magma mixing and mingling between the end member trachybasalt and basalt composition, which ultimately resulted in the production of intermediate magmas, are discussed in the studied samples. Evidence for crustal contamination and magma mixing include the xenocrystic phases, the reversed zoning patterns in minerals, sieved textural zones in feldspars, resorption embayment. In the glassy matrix, there are some evidences for co-mingling of basic and intermediate magma such as existence of K-feldspars in matrix of basaltic samples and two different glasses adjacent together.

**Thiobarbituric-acid reactive substances (TBARS) response curves in the presence of 1:1 and 2:1 phyllosilicates**

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Clays catalyze chemical reactions including acid hydrolysis, condensations, oxidative polymerizations, etc. Here the authors propose that properties such as the content and structural distribution of structural Fe in expandable (e.g., hectorite, nontronite) or non-expandable (e.g., kaolinite) clay minerals influence the mechanism(s) and production rate of 'OH radical species in suspension, which can alter the chemical composition of biological material. The measurement of Thiobarbituric Acid Reactive Substances (TBARS) has become the method of choice for screening and monitoring lipid peroxidation, a major indicator of oxidative stress. The assay provides important information regarding free radical activity in disease states and has been used for measurement of anti-oxidant activity of several compounds and to determine lipid peroxidation. TBARS analyses for kaolinite, hectorite, and nontronites NAu-1 and NAu-2 showed variations in amounts of lipid peroxidation. The response followed the order kaolinite (0.42 nmol/mg protein), NAu-1 (1.15), hectorite (3.35), and NAu-2 (11.1). As determined by TBARS assays, clay properties including expandability, structural iron content and distribution, were found to influence the 'OH production rate. The effect of UV light incidence (λ = 540 nm) was found to be of little influence.
Apatite as a petrogenetic indicator for lamprophyres and carbonatites

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Apatite is an important host for incompatible trace elements (LREE, Sr, Th, P, F) in the mantle and plays an important role in the trace element signature of mantle-derived melts. For this study, we analysed fluorapatite from different textural settings in Palaeoproterozoic lamprophyres and carbonatites in the Fennoscandian Shield to gain information about their petrogenesis. The lamprophyre and carbonatite dykes represent low-volume partial melts derived from an enriched lithospheric mantle. Enrichment patterns (high Ba, Sr, LREE; low HFSE; [1]) are consistent with carbonatite metasomatism in the source. The P2O5 content of the lamprophyres is around 4 wt%, consistent with the apatite saturation level of high temperature, low SiO2 basic magmas [3]. This may indicate a P-rich residual phase remained in the mantle source.

Apatite macrocrysts in the lamprophyres are euhedral to subhedral and appear compositionally homogeneous in BSE images. Many grains also contain submicroscopic (<3µm) inclusions of monazite. The apatites are mildly enriched in Si and LREE and have positive Eu anomalies, typical for apatites from a metasomatized lherzolite [2]. Apatite macrocrysts in the carbonatites display alteration textures characteristic of autometasomatic reactions with the magmatic fluid, however unaltered domains are also enriched in Si and LREE with positive Eu anomalies. We therefore propose that the macrocrysts are mantle-derived xenocrysts.

Matrix apatite from the lamprophyres has a skeletal texture and shows a core-to-rim decrease in Sr and LREE content. These grains lack Eu anomalies, which supports our model both in that they are not genetically related to the macrocrysts and that they crystallised from P2O5-saturated lamprophyric magma during ascent and emplacement.


Uranium isotope ratios in atmospheric deposits in Japan

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235U/238U ratios in atmospheric deposits in Japan, which had been collected with rainwater by Japan Meteorological Agency (JMA) and Meteorological Research Institute (MRI), were measured by ICP-MS after chemical separation of uranium using UTEVA resin.

The 235U/238U ratios in the atmospheric deposits collected in March between 1963 and 2000 at Fukuoka, which is located at southeast Japan (Kyushu Island) and where Kosa events are observed in spring seasons, were slightly higher than the natural 235U/238U ratio. No obvious secular change in the ratio was observed in those deposit samples through the period studied, while large amounts of anthropogenic radionuclides had deposited in the early 1960s because of nuclear test explosions.

Contrarily, the 235U/238U ratio in the Reference Fallout Material (RFM) prepared by MRI, which is a mixture of atmospheric deposits collected at 14 monitoring stations of JMA located all over the Japanese Islands between 1963 and 1979, was significantly lower than the natural ratio. We conducted the HNO3 extraction treatment for the RFM sample, and measured the 235U/238U ratios in the leachate and in the residue separately. The ratio in the leachate (extracted part) was obviously lower than the natural ratio, whereas that in the residue (silicates part) was nearly the same as the natural ratio. This result suggested that uranium having the low 235U/238U ratio, i.e., depleted uranium (DU), was not originally contained in mineral particles but was adsorbed on them secondarily. The 235U/238U ratios in Japanese atmospheric depositions may show regional variation, since the 235U/238U ratios in the Fukuoka deposits in the 1960s and 1970s were slightly higher than the natural ratio.

The present results suggest that DU had fallen in the 1960s or 1970s at some regions in Japan, and further indicate the possibility of the global fallout of DU in those times, although its origin is unknown.
Geochemical and isotopic properties of micro-metallic aggregates in the Oklo natural reactor

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The Oklo-Okelobond-Bangombé uranium deposits, the Republic of Gabon, known as natural fission reactors are useful natural analogues for radioactive waste disposal in geological media, because large-scale fission reactions occurred spontaneously 2.0 Ga ago. Our major concern is to understand the geochemical behavior of fission products generated in the reactors. Since Tc, Ru, Rh and Pd are highly produced by fission, their long-term behaviors are important for the radioactive waste disposal.

It has been known from the microscopic observation of artificial spent fuel that fissiogenic Ru, Rh and Pd formed aggregates [1]. Similar aggregates were also found in the Oklo reactors [2, 3]. We found a number of metallic aggregates sized 10 to 40 µm in the Oklo reactor zone 13. EPMA analyses showed that the aggregates consist mainly of Ru, Rh, Pd, Te, Pb, Bi, As, Sb and S. Isotopic analyses with a sensitive high resolution ion micro-probe (SHRIMP) revealed that Ru, Pd and Te in the aggregates are pure fissiogenic origin.

Figure 1: Two components diagram of metallic aggregates in SD37-S2/CD at the Oklo reactor 13.

Figure shows a correlation diagram between (Ru+Rh+Te+Pd+Bi+Sb+As+S) and (Pb+S) components of the aggregates found in SD37-S2 borehole at the Oklo reactor 13. Interestingly, almost all of the data points are plotted on a single line, suggesting that fissiogenic Ru, Rh, Te and Pd formed aggregates after mixing with microcrystal of galena in the reactor.


Effects of nanoparticle aggregation on metal sorption, desorption and speciation

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Iron oxyhydroxide nanoparticles play an important role in the mobility of aqueous metal species through both sorption and desorption processes. However, the natural and often rapid aggregation of such nanophases in aqueous systems can lead to changes in their structure, available surface area, porosity, and reactivity that may modify the mechanisms by which metal ions are retained and therefore the long-term potential of metal sequestration in the solid phase.

Batch and spectroscopic methods were used to investigate the uptake, release, and speciation of metals onto and within nanoscale iron oxyhydroxides exposed to conditions which induce nanoparticle aggregation and growth. Aqueous Cu(II) or Zn(II) was added to a suspension of synthetic 5-nm iron oxyhydroxide nanoparticles either prior to or following aggregation induced through increases in pH, ionic strength, or temperature and allowed to adsorb for a period of 24 hours. Samples were analyzed both after initial metal uptake and following a desorption step induced by lowering the pH back below the macroscopic absorption edge for the specific metal.

Analysis of filtered supernatants combined with EXAFS studies of the solid aggregates suggest that the desorption step removes the weakly-held (i.e. surface-bound) metal fraction but retains strongly-held metals that appear to be more structurally incorporated within the nanoparticle aggregates. Separate long-term desorption studies with continuous monitoring of metal concentrations were also conducted to assess the slow exchange of the strongly-bound fraction of metals from the aggregates back into solution over time.

Results show the relative effects of different aggregation methods on metal uptake and subsequent release, with temperature/time most effective at retaining metals in the solid phase and pH-based aggregation less so, while ionic strength-based aggregation had little effect relative to unaggregated particles. These findings have implications for the removal of hazardous metals from the aqueous phase and the design of remediation strategies targeting contaminated environments such as mine-impacted regions.
The use of lime (CaO) and limestone (CaCO₃) as a stabilization process applied to Arsenic contaminated soil around abandoned mines

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The main objective of stabilization process was to reduce leaching rate of heavy metals passing through soil to surface water or groundwater. Pilot scale column experiments were performed to investigate the efficiency of lime and limestone as the immobilizing amendment to reduce As leaching from the contaminated soil to the surrounding water. For As contaminated soil, surface soils were collected at around the farmland connected to the Samkwang abandoned mine, Korea and its initial As concentration was 40.99 mg/kg. For a physical model for the genuine contaminated soil leaching As, an acryl column (15 cm in diameter and 100 cm in height), which of the upper and lower part consist of dense lattice screen plates and the drain system for injection and extraction of artificial rainfall, was designed. As the mixing treatment process for the stabilization, 1 and 2 w.t.% of granulated lime or 2 and 5 w.t.% of granulated limestone were mixed with the contaminated soil and they were packed in the acryl column. From the top of the column, at every 24 hr, 1092 ml of artificial rain (50 % of average yearly rainfall) was uniformly sprayed on the top of the column at the constant rate of 100 ml/min for twenty days, representing 20 year of soil leaching in the real farmland. Leached water was drained from the bottom of the column and its As concentration was analyzed on ICP/MS (Perkin elmer, Elan 6100) to investigate the decrease of leaching amount by lime and limestone. From the result of experiments, for 1 and 2 w.t.% of lime, As concentration of leached water decreased by 95 and 96 %, respectively. For 2 and 5 w.t.% of granulated limestone, As concentration of leached water decreased by 92 and 76 %, respectively. For mixing 1 w.t.% of granulated lime and 2 w.t.% of granulated limestone, As concentration of leached water decreased by 96 %, suggesting that lime and limestone are very useful to decrease As leaching from the contaminated soil.

Pilot scale experiment for the in situ flushing coupled with high pressure air jet injection to remediate the bunker fuel oil contaminated site

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Pilot scale experiment for the in situ flushing coupled with high pressure air jet injection was performed to remediate bunker A and C- oil contaminated soil and groundwater. The contaminated site was located at Ulsan, Korea, which had been used as a roofing tile manufacturing facility area for 25 years. The average total petroleum hydrocarbon (TPH) concentration of soil in the site was 3449.95 mg/kg and it exceeded 6 times of the standard tolerance limit (500 mg/kg) regulated by Korean Soil Conservation Law. A pilot scale test site (15m x 19m x 6m) was selected in the contaminated area for the in situ flushing with high pressure air jet injection and the selected test site was mostly composed of heterogeneous sandy and gravel-sandy soils, having the 4-5m of contamination depth. Fourteen injection wells and 3 extraction wells including the trench at the right boundary of the site were built in the test site. After two percent of surfactant solution was flushed into the injection well, the high pressure air jet was injected to accelerate the mobility of flushed solution in pore spaces underground and thus to increase the removal efficiency of the in situ flushing.

The effluent solution was treated by the chemical treatment process including oil separator for its recycling. Water samples taken from injection and extraction wells were analyzed on GC/FID (Hewlett Packard, Agilent 6890) and ICP/OES (Perkin elmer, Optima 3300XL) for TPH and heavy metal concentration, calculating the removal efficiency of the in situ flushing with high pressure air injection at the test site. Total 3.6 ton of TPH (about 86% of the initial TPH) was removed from the contaminated site and TPH concentration of the residual soil was below the standard tolerance limit (500 mg/kg). The optimum surfactant solution injection rate and air jet injection rate was determined to be 1L/min and 25 kg/cm², respectively. Results from the pilot scale test suggested that the in situ flushing coupled with high pressure air jet injection has a great possibility to remediate bunker fuel oil contaminated soils.
Tracking soil organic matter export across the continent-ocean interface: A case study of the NW Mediterranean using the BIT index

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The BIT (Branched and Isoprenoid Tetraether) index has recently been introduced as a proxy for soil organic matter input and is based on the relative abundance of non-isoprenoidal glycerol dialkyl glycerol tetraethers (GDGTs) derived from organisms living in terrestrial environments versus a structurally related isoprenoid GDGT “crenarchaeol” produced by marine Crenarchaeota [1]. In this study, detailed spatial distribution patterns of BIT index were investigated in combination with other organic parameters in the continental margin of the western Mediterranean. Based on a transect sampling strategy from source (land) to sink (sea) via river, we analysed a variety of soils from the Têt Basin, suspended particulate matter in waters of the various rivers flowing into the Gulf of Lions, and marine surface sediments from the Gulf of Lions. The BIT index in soils and suspended particulate matter in river waters showed high values (>0.6), while it varies between 0.02 and 0.83 in marine sediments. Higher BIT values (>0.1) in the Gulf of Lions were distributed along the coastal zone decreasing seawards. Our results suggest that the BIT index is an appropriate proxy for tracking soil organic matter in the continental margins and especially valuable in multi-proxy studies. Furthermore, the BIT index can be used to trace past soil organic matter input where sediment deposition has been continuous.


Groundwater recharge and redox zoning in an alluvial aquifer, Cheonan, Korea

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A hydrogeochemical study of a semi-confined alluvial aquifer underneath an agricultural area in the Cheonan area, Korea, was conducted to examine the lateral redox zoning in groundwater. The aquifer consists mainly of sand-gravel alluvia locally underlying an organic-rich silt layer which is used for rice paddy fields. The redox zoning changes gradually from a ‘suboxic’ zone up-gradient to an ‘oxic zone’ near a stream along the groundwater flow path. This is caused by progressive freshening of groundwater due to changes in the infiltration mechanisms, as indicated by the isotopic composition of the groundwater. Irrigation water in paddy fields during agricultural season experiences significant evaporation during and before recharge via diffusive infiltration through an organic-rich silt layer. This results in substantial increases of solute concentrations under strong reducing conditions and a characteristic isotopic signature of the infiltration water. During the flow of suboxic groundwater toward the stream, oxic and dilute surface water infiltrates directly and mixes with the groundwater in locations where an impermeable silt layer is absent. Through this mixing, the groundwater is progressively freshened and is also contaminated by agricultural nitrate.

Reaction path modeling was performed using PHREEQC to simulate the hydrogeochemical changes across the various redox zones. The model results agree well with the observed changes of water chemistry and show that lateral redox zoning in the suboxic zone consists of denitrification, Fe/Mn reduction, and possibly sulfate reduction. In contrast, the chemistry of oxic groundwater toward the stream is characterized by precipitation of Fe/Mn hydroxides and the inputs of oxidants such as nitrate. The modeling results also suggest that the amount of reactive organic carbon originating form silty paddy soils controls the lateral extent of the interface between the suboxic and oxic zones.
Removal of toxic heavy metals by biosorption and biofilm formation of indigenous bacteria in soil

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Many studies have pointed out the problem of heavy metals - contaminated soil in Korea, but research work on clean-up technology of the contaminated soil has rarely performed. Recently the application of cost-effective and environment-friendly bioremediation technology to the heavy metals - contaminated sites has been gradually realized in Korea. The objective of this study is to remediate the sites through the reduction of heavy metal mobility by using indigenous bacteria from the soil, and to evaluate the characteristics of biosorption according to various environmental factors which can affect the sorption of toxic heavy metals.

Indigenous bacterium having a tolerance to high Pb and Cd toxicity was isolated from soil concomitantly contaminated with Pb and TPH (total petroleum hydrocarbons). The bacterium was identified as Bacillus thuringiensis and named SPb-1. As a result of batch-type biosorption experiments, the highest removal rates of aqueous Pb and Cd were observed with initial concentration of Pb and Cd less than 100 mg/L and 5 mg/L, respectively. The optimal operating conditions of Pb and Cd biosorption were as follows; culture age of over 16 hours to stationary growth phase, biomass amount of more than 2 g/L, pH 5-9, and temperature at 25°C and 35°C for Pb and Cd, respectively. Monolayer sorption to cell surface occurred for Cd biosorption, whereas the mechanisms of Pb biosorption were due to intracellular accumulation by metabolism of bacteria and precipitation with extracellular polymeric substance such as sulfide or phosphate.

Effluent volume ratio of acetate, lactate and glucose through column compared to deionized water showed 98.5 %, 97.3 %, and 94.7 %, respectively, due to the biofilm formation in pore and the flow of injected carbon source solution. The measurement of effluent volume through column could indirectly confirm the biofilm formation. Maximum removal rate of metals by biofilm depends on the carbon source solution, for example, glucose for Cr and Cd and acetate for Cu and Zn.

Copper isotopic fractionation in acid mine drainage

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Acid mine drainage (AMD) is a chronic problem that results from oxidative sulfide mineral dissolution, thereby releasing acidic, metal-rich waters into the environment. We use Cu isotope measurements to better understand the biogeochemical mechanisms contributing to Cu mobility in AMD.

The δ65Cu values (based on 65Cu/63Cu) of primary Cu sulfide minerals near an AMD-impacted stream are lower than those for stream water. In this system, the average isotopic fractionation (quantified as Δaq-min = δ65Cuaq - δ65Cum, where Cuaq is leached Cu and Cum is the mineral) is 1.43 ± 0.14‰ and 1.60 ± 0.14‰ for chalcopyrite and enargite, respectively. In addition to this field survey, we simulated sulfide leaching in batch experiments at pH 2.0 and found that, as in the field, leached Cuaq is isotopically enriched relative to chalcopyrite and enargite-bearing samples when microorganisms are absent (average Δaq-min = 1.18 ± 0.14‰ for chalcopyrite, and 0.94 ± 0.14‰ for enargite). Leaching of sulfides in the presence of Acidithiobacillus ferrooxidans results in smaller average fractionation in the opposite direction for chalcopyrite (Δaq-min = -0.61 ± 0.14‰) and no apparent fractionation for enargite (Δaq-min = -0.01 ± 0.14‰).

We hypothesize that the isotope effect during leaching is the same in both abiotic and biotic experiments, but additional fractionation resulting from the association of 65Cu with A. ferrooxidans likely causes the isotopic depletion of remaining Cuaq in the biotic experiments.

To investigate association of Cuaq with cells, we grew A. ferrooxidans in medium at pH 2.0 with 0, 0.1, 1, and 10 mM Cu added. We then used Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDS) to image and characterize cells grown under each condition. All cells exhibited electron dense (i.e., metal-rich) areas on cell membranes and/or within the cell. Preliminary EDS data for cells grown in 0.1 and 10 mM Cu medium shows that metal-rich areas on the outer cell membrane and in granules within the cell have slightly higher P, Fe, and Cu contents relative to the background, suggesting that cells are indeed a sink for dissolved Cu.
Slab dehydration and melting of the Philippine Sea Plate by progressive subduction beneath the SW Japan arc over the past 15 million years

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Geochemical data including 389 XRF analyses, 203 ICP-MS trace element analyses, 188 Sr-Nd, 120 Pb, and 83 Hf isotope compositions were examined to reveal the origin of the late Cenozoic magmatic activity (~15 mys) in the SW Japan arc. This activity includes OIB-type alkali basalts, IAB-type sub-alkali basalts, HMA, and adakites (ADK). Activity in the SW Japan volcanic arc commenced at ~15 Ma when the back arc basin (BAB) of the Japan Sea opened. Initiation of subduction of the young Shikoku Basin Philippine Sea plate (PHS) occurred at the same time. At ~15 Ma, OIB activity occurred in the rear arc due to upwelling of the asthenosphere by BAB opening, whereas IAB and Setouchi HMA were produced in the forearc due to dehydration and melting of the young slab. ADK and IAB activity between these two areas began at about 8-9 Ma. This ADK-IAB zone migrated to the rear arc by 2 Ma, and has remained active to the present. At the same time, OIB activity occurred in the rear arc due to upwelling of the asthenosphere by BAB opening, whereas IAB and Setouchi HMA were produced in the forearc due to dehydration and melting of the young slab. ADK and IAB activity between these two areas began at about 8-9 Ma. This ADK-IAB zone migrated to the rear arc by 2 Ma, and has remained active to the present. At the same time, OIB activity ceased in the area where ADK-IAB activity began. OIB activity does not require slab inputs and thus originates from asthenospheric mantle. In contrast, IAB, HMA, and ADK obviously require slab fluids and melts. The temporal rear arc-ward migration of the slab-related magmas indicates progressive penetration of the PHS into the anomalously hot mantle asthenosphere that was emplaced during BAB opening. Interaction of BAB opening tectonics and initiation of young PHS slab subduction combined to form the complex volcanism present in the SW Japan arc.

Oxygen isotope analysis of silicates using continuous flow isotope ratio mass spectrometry

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Oxygen is the most abundant element in the Earth’s crust and therefore 18O analysis of silicates is a routine procedure used in many geochemical applications (e.g. mineral exploration, paleoclimatology, etc.). Continuous flow isotope ratio mass spectrometry (CF-IRMS) offers an attractive alternative to the usage of hazardous fluorine or interhalogen fluoride gas vacuum lines for oxygen isotope analysis of silicates. The development of peripherals and additives for online sample processing prior to introduction in the mass spectrometer has greatly expanded the capabilities of CF-IRMS. In this study we use a modified method similar to Werner [1] to test the ability of thermal conversion elemental analysis (TC/EA) coupled with CF-IRMS to accurately analyze the oxygen-isotope composition of silicates.

Online fluorination was attempted via the use of solid fluorinated compounds which are much less hazardous to handle than fluorinated gases. At high temperatures the fluorinated additives enable the breaking of Si-O bonds in silicates liberating oxygen which is then reacted with carbon to produce CO and waste gases. Waste gases are subsequently removed before CO is analyzed using standard CF-IRMS techniques.

The results represent preliminary research into the suitability of various fluorination compounds for the accurate analysis of several internal and external silicate standards. Crushed silicate samples (e.g. NBS-28, NBS-30, and internal standards) are added to silver cups and mixed with fluorinated graphite powder, Teflon tubing, Teflon powder, potassium fluoride, or a combination of two or more additives. Cups are sealed and then heated instantaneously to 1460°C in the TC/EA. The oxygen then reacts with carbon in the furnace creating CO which is carried in a stream of helium to a chemical and cold trap. The chemical trap contains magnesium perchlorate and Ascarite II® to remove water and fluorinated compounds respectively before the gas is transported to a GC column. After gas separation in the GC column the CO is transported to the open split and then to the mass spectrometer.

With the increasing number of laboratories with CF-IRMS and TC/EA apparatus the development of this method will hopefully help to diversify their analytical capabilities.

Multiple crustal growth and recycling processes inferred from U-Pb and Lu-Hf on zircons – Evidence from the Limpopo Belt, South Africa

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The Limpopo Belt (LB) in southern Africa represents a unique example to study multiple crust-formation, -differentiation and -recycling processes in the late Archean and early Proterozoic. Magmatic events are documented at 3.2 Ga (e.g. the Sand River area) as well as at 2.6 Ga and at 2.0 Ga ([1] and references therein). The investigation of the 2.6 Ga magmatic event, which is documented all over the LB, presents a major clue to study the evolution of Archean TTG crust during subsequent magmatic activity.

The present study approaches the issue by the isotopical and geochronological study of zircons in combination with the geochemical investigation of the whole rocks. U-Pb zircon ages as well as Lu-Hf isotopes were determined by LA-ICP(MC)-MS spot analyses on 7 samples of a suite of granitic to granodioritic and minor trondhjemitic rocks from the Regina Pluton, which is located ca. 100 km west of Musina in the Central Zone of the LB. Most samples show an identical U-Pb age of ~2.65 Ga, which is considered as the intrusion age of the pluton.

The interpretation of the Hf isotope data of the studied zircons and the rare earth and trace element geochemistry of the whole rocks leads to two different models concerning the processes finally leading to the formation of the Regina Pluton.

First, the studied plutonic rocks might represent a mixture between a juvenile, depleted-mantle derived magma and Paleoarchean crust-derived material. Second, the Regina Pluton might be the result of a pure crust fractionation process taking place at 2.65 Ga, caused by partial melting of 3.28 Ga old Sand River gneiss material.

The different models have major implications on the present knowledge we have of the assembly of the Limpopo Belt and the mechanisms leading to crust formation and – recycling in the early history of the Earth.


Experimental analysis of Arsenic mobility in iron and sulfate reducing environments

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Stimulating formation of sulfide minerals in aquifers may be useful for remediating arsenic contamination. Our findings, however, suggest that mackinawite and pure arsenic-sulfide minerals such as orpiment do not provide efficient pathways for arsenic precipitation. In semi-continuous flow bioreactor experiments inoculated with natural microbial communities, we approximated a flow rate of about 28 mL·day⁻¹ with medium containing 0.80 mM acetate and 7 µM arsenic as arsenate. We examined arsenic mobility in a system containing (1) iron reducing activity, (2) sulfate reducing activity, and (3) iron and sulfate reducing activity. All of the reactors also hosted arsenic reducing activity, which reduced 70 to 90% of the arsenic flowing into the reactors to arsenite. In the iron reducing system, ferrous iron content quickly increased to 200 µM and then, at about 125 days into the experiment, started to decrease to 50 µM as methane accumulated. Arsenic concentration in the iron reducing system slowly approached the level in the inlet medium as adsorption sites were eliminated. In the sulfate reducing system, sulfide content increased quickly to about 0.4 mM where it remained for the duration of the experiment. No arsenic-sulfide minerals formed and arsenic concentration equaled inlet levels throughout the experiment. In the iron and sulfate reducing system, sulfide was undetectable and ferrous iron levels increased to about 130 µM over the first 80 days of the experiment and then slowly decreased to about 25 µM. Arsenic content ranged highest in this reactor (>7 µM) despite formation of over 6 mM mackinawite by the end of the experiment. FEG-TEM analyses show that the mackinawite contained less than 0.1 wt % arsenic. Arsenic content increased more rapidly in this reactor than in the iron reducing system because removal of ferrous iron by mackinawite increased the rate at which iron reduction could occur. These results indicate, albeit indirectly, that pyrite, rather than mackinawite, may be the primary sulfide-mineral sink for arsenic in groundwater where microbial sulfate reduction limits arsenic contamination.
Reduction of Antimony by nanoparticulate Fe$_2$O$_4$ and FeS

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Antimony finds a wide range of industrial applications, e.g. in flame retardants, brake pads and as a lead-alloy in storage batteries and ammunition and is widely distributed in the environment. Sb may occur in several oxidations states (III, 0, III, V). Under oxic conditions, Sb$^5$ oxidizes prevalently to Sb$^6$, forming the anionic species Sb(OH)$_6$$^{2-}$ which is strongly sorbed by Fe oxides [1]. In contrast, Sb$^{III}$ forms an uncharged complex Sb(OH)$_3$(aq), which is more mobile. Under anoxic conditions, Sb$^V$ and Sb$^{III}$ may be reduced by Fe$^{II}$-bearing minerals. Magnetite (Fe$^{III}$Fe$^{II}$O$_4$) and mackinawite (FeS) have been shown to reduce e.g. Se [2], As [3], and Pu [4]. We therefore investigated the reaction of Sb$^{III}$ and Sb$^V$ with these two minerals at approximately 1ppm O$_2$ (v/v) using Sb-K XAS.

When Sb$^{III}$ was reacted with magnetite at pH 4.7 to 7.6 during 1 h to 67 d, the oxidation state was stable and only one Sb species was identified by EXAFS. Sb$^{III}$ is coordinated with 4 to 5 iron atoms at a distance of 3.6 Å, FEFF Monte Carlo simulations revealed formation of a highly ordered surface complex on the{111} faces of magnetite. The trigonal pyramidal SbO$_3$ units occupy positions of Fe$^{III}$ tetrahedra, that would be ideally coordinated to six Fe$^{III}$ octahedra via corner-sharing. The experimental Fe coordination numbers below six suggest that Sb occupies positions near edges of the{111} faces. When Sb$^V$ was reacted with magnetite, reduction to Sb$^{III}$ increased linearly between pH 4.5 and 6.5, with little influence of reaction time. The Sb$^{III}$ produced by the surface reaction formed the same surface complex as after direct addition of Sb$^{III}$.

In the presence of mackinawite, Sb$^V$ was completely reduced to Sb$^{III}$ within 30 d and in the pH range 4.3 - 8.4. The local structure shows Sb$^{III}$ surrounded by three sulfur atoms at a distance of 2.5 Å as in Sb$_2$S$_3$. The lack of more distant atomic shells suggests a highly disordered structure. Again the resulting surface complex is the same as after direct addition of Sb$^{III}$. Cryo-XPS measurements of shock-frozen samples show that the S 2p spectra remain unchanged before and after Sb$^V$ reduction, while a Fe$^{III}$-shoulder emerged in the Fe 2p spectra after reduction, indicating that Sb$^V$ was reduced by Fe$^{II}$ and not by S. In no case, reduction to an oxidation state below III was observed.


Olivine morphology and the origin of main group pallasites

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Introduction

The main group pallasites (PMG) were defined by Scott [1] with later modifications by Wasson & Choi [2], who defined anomalous members with anomalous metal compositions (PMGm) and those with anomalous olivine compositions (PMG) as well as anomalous metal compositions. Shapes of olivine crystals have been investigated in detail by Scott [3] and Buseck [4] whose results are in agreement as to the morphologies of the olivine crystals of the pallasites. The shapes of macrophenocrysts range from rounded to highly angular, although microphenocrysts are rounded, with few exceptions.

Relation between Metal Composition and Olivine Morphology

Examination of the data available reveals that there are 18 PMG, 5 PMGm and 3 PMG as whose compositions and olivine morphologies are both well characterized. Of the PMG, 17 have angular olivines and 1 has rounded olivines. Of the 8 anomalous pallasites, 5 have rounded olivines and 3 angular ones. Thus, there is an apparent relationship between olivine morphology and chemical classification of PMG

Discussion

Olivine morphology clearly has a bearing on the genesis of pallasites. Wasson & Choi [2] demonstrated that the metal compositions of PMG members can be produced by a fractional crystallization model based the same system as that which produced the group IIIAB iron meteorites. This model is consistent with the hypothesis that the pallasites represent the core-mantle interface in a parent-body. Scott [5], however, has summarized some of the difficulties with this model. However, textural evidence clearly indicates that PMG have been subject to shock disruption followed by injection of metal. The rate of rounding of olivines in molten metal has been shown to be very rapid [6] indicating that the rounded olivines of the PMG members have experienced a history different from that of those with angular olivines.

Internal isochron of CAI using high precision SIMS Mg isotope analyses

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The $^{26}\text{Al} - ^{26}\text{Mg}$ decay system ($\frac{1}{2}T = 7.3 \times 10^5$ y) is a useful chronometer providing $\leq 0.1$ Ma resolution for the earliest history of our solar system. Recent estimates on the initial $^{26}\text{Al}/^{27}\text{Al}$ ratios of Ca, Al-rich inclusions (CAIs), the oldest refractory solids in the solar system are controversial, varying between “canonical” $^{26}\text{Al}/^{27}\text{Al} \sim 5 \times 10^{-5}$ and supra-canonical (6-7)$\times 10^{-5}$ [1-2], equivalent to a time period for CAI formation of less than 0.1 Ma to as long as 0.4 Ma. In order to estimate the initial $^{26}\text{Al}/^{27}\text{Al}$ ratios of individual CAIs, we developed high precision (0.1–1‰) and high spatial resolution (8-20µm) Mg isotope analytical techniques using the WiscSIMS IMS-1280, equipped with multiple Faraday cup detectors. We calibrated SIMS relative sensitivity factor (RSF) of $^{27}\text{Al}/^{24}\text{Mg}$ by using melilite and plagioclase standards that were analyzed carefully by EPMA, reducing the uncertainty of the isochron slope to be less than 1% for melilite and 5% for plagioclase.

We analyzed the Al-Mg systematics of zoned melilite mantle and interstitial anorthite in the core of a type B1 CAI, Leoville 3535-1 [3]. Melilite grains were analyzed (20 µm beam spot) in multicollection mode and anorthite grains (8 µm beam spot) in single collector mode with an electron multiplier. We applied an exponential law with ($\beta = 0.514$) for the Mg isotope fractionation correction [4]. Typical precisions for $\delta^{26}\text{Mg}$ for melilite and anorthite are 0.1‰ and 2‰, respectively. The results show a well-defined isochron with a slope of $(5.00 \pm 0.04) \times 10^{-5}$ (MSWD=1.04), indicating no evidence for multiple reheating events or any isotopic disturbance more than 40,000 years after its formation. Although the uncertainty of the anorthite RSF degrades the error of the isochron by 5%, this new result does not indicate a supracanonical value. This is inconsistent with the idea that the canonical isochron resulted from redistribution of the Al-Mg system through multiple reheating events occurring over a few kyr in the solar nebula [1].


U-Pb geochronology of apatite by high lateral resolution SIMS (NanoSIMS)

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Introduction

To determine the absolute ages using radiogenic isotopes is important for reconstruction of paleo-environments, estimate of secular changes and define the timing of geological events. U-Pb isotope geochronology for high uranium minerals such as monazite, zircon and apatite has been carried out from Hadean to Phanerozoic samples. The U-Pb dating was divided into two types: solution (TIMS) and in situ (SIMS/SHRIMP/LA-ICP-MS) analyses. In situ analyses provide isotope ages from several tens of micron in spot diameter. Recently, high lateral resolution SIMS (NanoSIMS) has been developed by Cameca, which provides submicron analysis spots. This powerful feature is advantage for analyzing the samples which have tiny mineral inclusions, chemical zonings and micro-cracks. The dating of apatite is useful because of direct dating of (micro-) fossils which are occurred as phosphate.

Method

We report that method and results of U-Pb dating by Cameca NanoSIMS 50 installed at Ocean Research Institute (ORI), The University of Tokyo. U-Pb dating at ORI is using $^{16}\text{O}$ primary beam and measurements are separate 2 sessions. At first, we analyzed $^{204}\text{Pb}^+, ^{206}\text{Pb}^+, ^{238}\text{U}^{16}\text{O}^+, ^{238}\text{U}^{16}\text{O}_2^+$ by magnet-static, multi-collection mode for estimating $^{238}\text{U}/^{206}\text{Pb}$ with Pb/$^{16}\text{O}^-\text{UO}_2^-/^{16}\text{O}^-$ calibration, then $^{204}\text{Pb}^+$, $^{206}\text{Pb}^+$, $^{207}\text{Pb}^+$ are measured by magnetic switching mode with single collector for $^{207}\text{Pb}^{206}\text{Pb}$. 15-20 nA primary beams were used to spatter 15-20 µm-diameter craters.

Results and Discussions

We analyzed three apatite samples (PRAP, POAP and BNCF) which were measured by SHRIMP with 30 µm-diameter craters [1]. Obtained $^{207}\text{Pb}^{206}\text{Pb}$ isochron ages of PRAP, POAP and BNCF are 1256±56 Ma (SHRIMP: 1156±45 Ma), 2790±550 Ma (2701±86 Ma) and 1224±140 Ma (918±45 Ma), respectively.

NanoSIMS provides useful apatite ages with smaller spot size than SHRIMP and a new insight to in situ geochronology.

Paragenetic types of carbonatite as indicated by the diversity and relative abundances of associated silicate rocks: Evidence from a global database

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Data on the diversity and relative abundance of igneous rock types associated with carbonatites have been compiled for 477 occurrences, which represent 90% of the 527 known occurrences. The carbonatites have been subdivided into magmatic (84%) and carbohydrothermal (16%) carbonatites. Carbohydrothermal carbonatites are defined as those precipitated at subsolidus temperatures from mixed CO₂–H₂O fluids that can be either CO₂-rich (carbothermal), or H₂O-rich (hydrothermal). The fluids can be from either alkaline silicate or carbonatite magmas but are typically associated with nepheline syenites and syenites. For the magmatic carbonatites, 24% of these localities have no associated igneous silicate rocks, while a diverse range of silicate rock types are recognized to be associated with the other 76%. Seven main silicate rock associations can be distinguished: 1. nephelinite-ijolite (28%), 2. phonolite-feldspathoidal syenite (14%), 3. trachyte-syenite (8%), 4. melilitite-melilitolite (7%), 5. lamprophyre (5%), 6. kimberlite (1%), 7. basanite-gabbro (<1%). A significant proportion of the nephelinite-ijolite and melilitite-melilitolite associations, and carbonatite-only group contain ultramafic rocks, which are interpreted as cumulates. Whereas these dunite and pyroxenite bodies might typically be considered as cumulates from silicate magmas, the possibility exists that these rocks are cumulates related to a carbonatite magma. The existence of olivine- and diopside-bearing carbonatites suggests that the potential to generate ultramafic cumulates from carbonatite magma is feasible. Thus it is possible that some carbonatite-ultramafic rock associations (10% of the magmatic localities) could be related to a carbonatite-only paragenesis.

The carbonatite only, plus some of the carbonatite-ultramafic cumulate localities are interpreted to be derived from primary mantle derived carbonatite magmas. However, most other carbonatites are considered to have been generated by differentiation from magmas represented by the associated silicate rocks that are the result of partial melting in a metasomatised lithosphere. The preferred model is that carbonatites can be generated in a number of ways, but the close spatial and temporal association with a broad spectrum of the silicate melts implies a close relationship with them.

Relationships between mantle and crust melt distribution and surficial geology and geochemistry at the 9 degrees 03’N Overlapping Spreading Center, East Pacific Rise

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A goal in the study of ocean ridges is to understand linkages in the magmatic system from the deep mantle to its surface expression at the seafloor. To explore these linkages, we undertook a geochemical, geological and hydrothermal investigation of the 9 deg 03’N OSC, EPR. Previous geophysical work provides detailed information on the distribution of melt in the upper mantle and crust. We conducted a 35-day cruise (AT15-17) to the OSC; we surveyed with DSL-120A, mapped and sampled with ROV Jason II, and mapped with the WHOI TowCam. Examination of the relationship between the spatial distribution of melt at depth and the loci of recent magmatism revealed no evidence of recent eruptions overlaying the plunging melt sill beneath the southern portion of the East Limb or that beneath the West Limb. West of the northern portion of the East Limb, where seismic studies image a wide off-axis melt sill, younger lavas with glassy buds and eruptive fissures suggests relatively recent volcanism. Lava compositions range from basalt to dacite: 33% have SiO₂ > 52 wt%. Trace elements reveal complex spatial systematics suggesting variations in source composition, extents and depths of melting, crustal evolution and assimilation. Data will be used to explore linkages between geochemical, geological, and hydrothermal variations on the seafloor and the magma supply system at depth.
Serpentine phase relations as a monitor of hydrogen production

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The distribution of iron among secondary minerals plays a key role in controlling hydrogen production during serpentinization. We examined the compositions and phase relations of oxides, sulfides, metals, alloys, silicates, and hydroxides in altered harzburgites and dunites from ODP Leg 209 to gain new insights into Fe partitioning. Thermodynamic modeling was used to investigate the influence of phase relations and Fe distribution on hydrogen production.

The samples reveal systematic trends in alteration patterns. Incipient alteration of olivine (Mg# 91) forms mesh-rims with a distinct zoning from pure brucite (Mg# 81) at the interface with olivine followed by a zone of serpentine +brucite+magnetite and finally serpentine and magnetite in the outermost mesh rims. The composition of the serpentine (Mg# 95) and brucite remain constant throughout, while the brucite abundance decreases and magnetite abundance increases from center to rim. In paragranular veins terminating the mesh texture, serpentine is even more magnesian (Mg# 97) while magnetite abundance is increased. Ni is also extremely depleted in serpentine veins (<0.03 wt.% as opposed to 0.5 wt.% Ni in the brucite halos around olivine). These relations indicate that Fe and Ni in the outer mesh rims and paragranular veins are accumulated in oxides and sulfides. Examining these relations by thermodynamic modeling suggests isothermal serpentinization (T=150-200°C) at low water-to-rock ratios as indicated by apparently steep small-scale gradients in aqueous silica activities.

Phase relations of the Fe-Ni-O-S phases along the mesh rims provide a record of the larger-scale fluid evolution. Pentlandite+awaruite+magnetite and pentlandite+heazlewoodite+magnetite assemblages indicate uniform highly reducing conditions during serpentinization. Pyrite, millerite, polydymite and violarite are found only where talc alteration is superimposed. Reaction path modeling reveals that phase assemblages in fully serpentinized and talcous rocks cannot be explained by a simple internally buffered peridotite-seawater reaction sequence. This indicates increased fO2 and fS2, possibly developing in interactions with gabbroic lithologies that are common at the sites of talc alteration. Likewise, fluids and rocks from active high-temperature vent sites also reflect interactions of seawater-derived fluids with heterogeneous basement, including gabbroic rocks.

Origins of diamond forming fluids – Constraints from a coupled Sr-Nd-Pb isotope and trace element approach

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Micro-inclusions in diamonds provide pristine information on the composition of the mantle fluids that form fibrous diamonds. While variations in the elemental composition of diamond fluids reflect mineral precipitation and fluid immiscibility their isotopic composition reflects the fluid source. We present the first ever Nd and Pb isotopic data for diamond fluids together with Sr and trace element data for a suite of diamonds from Botswana. The \(^{87}Sr/^{86}Sr\) ratios (TIMS) range between 0.70565 and 0.71817. \(^{143}Nd\) varies between -20.8 and -27.3. \(^{207}Pb/^{204}Pb\) varies between 15.61 and 15.67 and \(^{206}Pb/^{204}Pb\) varies between 17.87 and 18.26. \(^{13}C\) is typical of fibrous diamonds (-5.5 to -7.1‰). REE patterns are steep and exhibit negative \(T_{Sm}-H_{Fm}\) and \(T_{Sm}-P_{Fm}\) anomalies. Both Sr and Nd isotope ratios correlate positively with trace element contents. Clear hyperbolic trends between Sr isotope composition and element concentrations imply source mixing between 2 isotopically distinct components 1) an oxidizing fluid with highly radiogenic Sr that experienced long-term evolution within an incompatible element enriched environment; 2) a more reducing component with less radiogenic Sr, similar to the convecting mantle MORB/OIB source. This signature is different than that of carbon isotopes, which are similar to convecting mantle. We suggest that fibrous diamond precipitation was triggered by mixing of 2 fluids close to the CCO buffer enabling coexistence of carbonate and diamond. The diamonds Sr and Nd isotopic characteristics are similar to those of subcalcic garnets and glimmerites. Glimmerites could provide a source region for diamond-fluids, while the diamond forming fluids dominate the geochemical signature of subcalcic garnets.
Dating the first ~100 Ma of the solar system: From the formation of CAIs to the origin of the Moon

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Introduction

Key events in the early evolution of the solar system are the condensation of the first solids (CAIs), the formation of chondrules, and the accretion and differentiation of planetary bodies. Dating these events is key to understanding the early evolution of the solar nebula and the planet formation process. We discuss recent advances in the application of 182Hf-182W chronometry to obtain such time constraints.

Age of CAIs and Chondrules

In most meteorites, high-Ca pyroxene, the major host of radiogenic 182W/184W, is a minor component. HF-W dating of meteorites, therefore, requires low-blank methods and sensitive mass spectrometric techniques for precise and accurate W isotope ratio measurements on small quantities of W. We recently refined our techniques to meet these requirements and can now precisely determine highly radiogenic 182W/184W for as little as ~2-3 ng W. This allows resolution of time differences of less than ~1 Ma. We applied these new techniques to determine an absolute age for CAIs of 4568±0.7 Ma, which is ~1.5 Ma older than their Pb-Pb age [1]. The latter thus does not seem to date CAI formation. The HF-W age for the formation of H chondrite chondrules is 1.7±0.7 Ma, consistent with ~2 Ma Al-Mg ages for L and LL chondrules [2, 3]. In contrast, chondrules from carbonaceous chondrites formed more than ~0.5 Ma later, as constrained by differences between their Pb-Pb ages [4, 5] and the HF-W age for CAIs.

Age of the Moon

Precisely dating the Moon requires determining the purely radiogenic 182W/184W of lunar samples. This is challenging because the 182W/184W of lunar whole-rocks largely reflect the production of cosmogenic 182W. However, lunar metals contain no such cosmogenic 182W and precise 182W/184W measurements for such metals reveal that the Moon formed and differentiated >60 Ma after CAI formation. Combined with other chronological evidence this indicates that the giant Moon-forming impact probably occurred ~100 Ma after condensation of the first solids [6]. This event most likely marks termination of the major stage of terrestrial planet formation.

Hafnium-Tungsten chronometry of lunar differentiation

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Application of Hf-W chronometry to date lunar differentiation critically depends on determining whether 182W variations among lunar samples reflect 182Hf-decay within the lunar mantle. Lunar whole-rock samples are not suitable for this task due to the presence of cosmogenic 182W [1, 2]. In contrast, high-purity metal separates from lunar samples do not contain any Ta-derived cosmogenic 182W. They have constant ε182W (ε182W=0.01% deviation from terrestrial 182W/184W), indicating differentiation of the lunar mantle later than ~60 Ma after CAI formation [3]. However, mineral separates from low-Ti mare basalt 15555 were shown to have constant but elevated ε182W in spite of different Ta/W [4]. Likewise, ferroan anorthosite 60025, in spite of its young exposure age, has an 182W excess [5]. If these 182W excesses reflect 182Hf-decay in the lunar mantle, then the Moon must have formed and differentiated earlier than ~60 Ma after CAI formation, inconsistent with the result from lunar metals. To address this issue we obtained new W isotope data for the mare basalt 15555 and ferroan anorthosites 60025 and 62255.

A non-magnetic fraction of sample 15555 has ε182W=0.9±0.3 and Ta/W=4.6. For a given Ta/W, the previously reported ε182W for mineral separates from 15555 [4] seem to be shifted to higher values compared to our new data. However, the expected cosmogenic 182W as a function of Ta/W, calculated using the Sm isotopic composition of 15555 [6], is consistent with ε182W and Ta/W obtained here. Therefore, after proper correction for cosmogenic 182W, the ε182W of 15555 is identical to the other mare basalts.

Pure plagioclase separates from ferroan anorthosites 60025 and 62255 have ε182W=0.0±0.3 and -0.6±0.8, indistinguishable from ε182W values for the mare basalts and KREEP. We conclude that all lunar samples have indistinguishable ε182W values, confirming that differentiation of the lunar mantle occurred later than ~60 Ma after CAI formation, consistent with the results for lunar metals [3].


Trace element variation in young igneous zircon on the micron scale suggests shared histories

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Zircon has become an essential tool for examining the timescales of magmatic processes. Through U-Pb and U-Th analyses of zircon, we have been able to peer into long- and short-term processes such as crystallization, recycling and assimilation in magmas. However, although the zircon ages have added constraints to how we perceive these magmas, it has also opened the question of what the age distribution of zircon represents and what other information can be gleaned from the compositional variation within single zircons. This study of zircon from the 1305 A.D. Kaharoa eruption of Tarawera Volcano, New Zealand finds that the trace element variation within a single zircon can be large, but it is possible to correlate the variation between zircon grains, allowing for an examination of the processes within the magma system during the growth and storage of the zircon population.

Ages derived from $^{230}$Th-$^{238}$U analyses via SHRP-MG in the Kaharoa rhyolite show a protracted history recorded in zircon, from within error of the eruption age to greater than 300 k.y. This is in contrast to the bulk plagioclase ages from $^{226}$Ra-$^{238}$U analyses that are within error of the eruption. A closer examination of the zircon ages reveals that only a small fraction ($<10\%$) are within error of the eruption age although the rhyolite is zircon-saturated. Electron microprobe trace element analyses (Hf, Y, Yb, U, Th, Dy, Sc and Lu) of a suite of zircons from the Kaharoa Rhyolite were performed.

These zircons have a wide variation in trace element composition from the cores to the rims. Kaharoa zircon can be divided into two, age-independent populations, one with a complex trace element history, the other with simple trace element history. Certain zircons of differing age appear to have similar trace element variations, indicating that the zircons have at least seen some of the same magmatic history. Hf is especially useful in tracking the history of the zircon and can be used a proxy of temperature in the magma. Most of the zircons analyses see a marked increase in Hf content from core to rim (as much as a 20% increase), suggesting that many of the Kaharoa zircon formed in hotter magmas and the last 10 microns of zircon crystallized in cooler conditions. This implies that the young growth component in the zircon may be housed in the last few microns of zircon and thereby obscured from most ion microprobe spot analyses.

Thermodynamic modelling of Cr-bearing garnets in diamond-bearing peridotites

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A new approach is presented for modelling Cr-rich peridotite compositions and garnet-spinel compositions found in diamonds and xenoliths at conditions relevant to the deep continental Earth. Using recent experimental data (e.g., Klemme and O’Neill 1997, Girnis et al. 1999, Klemme et al. 2000, Girnis et al. 2003, Klemme 2004, Klemme et al. 2005 [1-6]), it is now possible to calculate phase relations and mineral compositions relevant to pressures, temperatures, and compositions of the deep lithospheric Earth using free energy minimization techniques. Here we present calculated phase relations in Cr-rich mantle compositions from pressures of 20-60 kbar, and temperatures 800-1400°C. The model is successful at modelling a wide range of natural mineral compositions, which are found as xenoliths in diamond-bearing Kimberlites from South Africa, and is illustrated using suites of Cr-rich xenoliths from near Kimberley, South Africa. The model can explain and quantify instances of garnet zonation in naturally occurring mantle rocks as a consequence of pressure-temperature re-equilibration without the need for metasomatic processes. This sheds further light on peridotitic diamond inclusions and their abundances, and allows further quantitative constraints to be applied to diamond-indicator mineral chemistry.

Experimental constraints on the behaviour of High Field Strength Elements in melts and fluids

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High field strength elements are important geochemical indicators in many geological settings. Mineral phases, which are known to incorporate the high field strength elements are rutile, ilmenite, Fe-Ti spinels, and other Ti-rich phases such as pyroxenes or amphiboles. A number of recent studies investigated the partitioning of HFSE between accessory phases and silicate melts [1-5]. In this talk I will give a general overview about experimental constraints on the behaviour of the high field strength elements in various magmatic and metamorphic systems. Whilst the behaviour of Zr, Hf, Nb, Ta in magmatic systems seems to be relatively well understood, there are considerable problems with experimental data in fluid-rich systems. Furthermore, experimental partitioning data for the more unusual HFSE such as W or Sb are scant and more quality experimental data are clearly needed. The mobility of the high field strength elements in metamorphic rocks depends critically on the solubility of rutile and other Ti-rich minerals in metamorphic fluids. I will also present some preliminary results on rutile solubility in high-temperature fluids, which indicate much higher solubility of rutile than previously anticipated.


Re-evaluating boron speciation in biogenic calcite and aragonite using 11B MAS NMR

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Understanding the partitioning of aqueous boron species into marine carbonates is critical for constraining the boron isotope system for use as a marine pH proxy. Previous studies have assumed that boron was incorporated into carbonate through the preferential uptake of tetrahedral borate B(OH)4−. In this study we revisit this assumption through a detailed solid state 11B magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopic study of boron speciation in biogenic and hydrothermal carbonates. Our new results contrast with those of the only previous NMR study of carbonates insofar as we observe both trigonal and tetrahedral coordinated boron in almost equal abundances in our biogenic calcite and aragonite samples.

In addition, we observe no strict dependency of boron coordination on carbonate crystal structure. These NMR observations coupled with our earlier re-evaluation of the magnitude of boron isotope fractionation between aqueous species suggest that controls on boron isotope composition in marine carbonates, and hence the pH proxy, are more complex than previously suggested.
**Constraints of carbon uptake by seafloor weathering of ocean plates**

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Seafloor weathering plays an important role in the long-term carbon cycle through the sequestration of seawater CO₂ during silicate weathering and carbonate precipitation. The uptake of carbon by seafloor weathering within lava sequences is investigated using drillcore from fourteen Ocean Drilling Program and Deep See Drilling Program sites, with crustal ages of ~6–170Ma. Carbon is stored as carbonate that forms by low temperature reaction between basalt and seawater, primarily within the upper most few hundred metres of the lavas. The CO₂ content of the drillcores identify two populations: Cenozoic sites (6.8 to 74 Ma) with low CO₂ contents (0.2–0.9wt%) and Mesozoic (110 to 170 Ma), sites with significantly higher CO₂ contents (2.0–4.1wt%). Carbon isotopes indicate inorganic precipitation. Temperatures of carbonate precipitation increase with crustal age (0 to 6 oC and 12 to 19oC), suggesting that higher bottom water temperatures may have facilitated carbon uptake. Strontium isotope ratios and trace element contents indicate that carbonate generally precipitates from seawater with a basaltic contribution. Calcite Mg/Ca and Sr/Ca ratios decrease with decreasing temperature due to the combine effects of basalt interaction and changes in bottom seawater chemistry with time. This study shows the influence of temperature and trace elements concentration of seawater on carbonate precipitate through geological time.

**Excess air as a proxy for hydrostatic pressure?**

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Dissolved conservative atmospheric gases in groundwater (e.g., noble gases) are usually found to exceed their respective atmospheric solubility equilibrium concentrations. This so-called ‘excess air’ in groundwater is most likely the result of the dissolution of entrapped air bubbles within the quasi-saturated zone. Excess air has been suggested as a tracer for past environmental conditions prevailing during groundwater recharge. The amount of excess air, which is often expressed as the relative supersaturation of Ne (ΔNe), has especially been used to constrain the pressure conditions at recharge. However, the formation of excess air and the physical processes involved have only sparsely been studied. Recent experimental and modeling results shed light on the formation of excess air and its evolution in space and time. The results show that the composition of the excess air component changes considerably during the progressive dissolution of entrapped air bubbles.

Simple lumped-parameter models have been developed to parameterize the excess air component using dissolved noble gas concentrations in groundwater samples, and to deduce the amount and fractionation of excess air, the amount of initially entrapped air, the temperature prevailing during recharge, and the pressure factor, giving the pressure in the gas phase relative to atmospheric pressure. Whereas some of these parameters (noble gas temperature, pressure factor) have proven to be quite robust and providing correct estimates over the entire process of gas bubble dissolution, our investigations imply that other parameters (amount and fractionation of excess air) only yield appropriate values during the very early stage of gas bubble dissolution.

Although ΔNe changes significantly during the course of bubble dissolution field data usually show a good correlation between ΔNe and the hydrostatic pressure estimated using the above mentioned lumped-parameter models. Therefore ΔNe seems to be a reliable proxy for hydrostatic pressure in such cases. However, if no additional data are available caution should be exercised when interpreting ΔNe in terms of hydrostatic pressure.
Interaction of dissolved and sedimentary sulfur species in a contaminated aquifer: Insights from stable isotope analysis

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Background and Objectives
Sulfur transformation reactions in a contaminated aquifer partly control the efficiency of biodegradation processes. Detailed investigation of the sulfur cycling may therefore provide essential information on the estimation of the overall natural attenuation potential at the contaminated site.

The investigated sulfate rich urban aquifer is contaminated with a variety of different BTEX species. To reveal the details of the sulfur cycling and to prove the occurrence of bacterial sulfate reduction (BSR), isotope investigations of different dissolved (sulfate and sulfide) and sedimentary sulfur species (monosulfide, disulfide, elemental sulfur) were conducted.

Results and Discussion
The enrichment of both heavy sulfur and heavy oxygen isotopes in dissolved sulfate and the simultaneous decrease of sulfate concentrations at several sampling locations provide clear evidence for the occurrence of BSR in the aquifer [1]. The isotope distribution pattern of sulfate suggests a straightforward bacterial reduction process. However, the isotopic composition of dissolved sulfide indicates the occurrence of secondary processes superimposing BSR.

Primary or secondary pyrite is the dominating sedimentary sulfur species in the aquifer matrix. The ubiquitous occurrence of sedimentary monosulfide is further evidence for a significant relevance of BSR. However, the presence of elemental sulfur and the isotope distribution pattern of sedimentary sulfur species point to a temporal variability of the hydrochemical conditions at the site with the occurrence of secondary sulfur transformations such as partly re-oxidation and disproportionation. Nevertheless, isotope and hydrochemical data indicate an overall high natural attenuation potential of the investigated aquifer.


Comparison of the pyrite oxidation rates by Acidithiobacillus ferrooxidans with a low initial cell population

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Methods
A batch experiment of pyrite oxidation by Acidithiobacillus ferrooxidans was performed with a initial cell population of less than 10^5 cells/ml at 30°C and the results of this batch experiment were compared with those of Yu et al. [1] whose initial cell numbers were approximately 2×10^6/ml. The batch solutions were regularly sampled and analyzed for Si, Al, Ca, Fe(total), Fe(II), K, Na, Cl, NO₃, PO₄, and SO₄ concentrations.

Discussion
The analytical results indicate that the transition from the lag phase to the exponential phase of the bacterial growth occurred after 400 hours elapsed from the beginning of the experiment, which is very close to what Yu et al. [1] showed. The oxidation rates calculated from the variation of SO₄ concentration were 9.9×10⁻³ mg pyrite/h and 3.2×10⁻² mg pyrite/h during the lag and exponential phase, respectively. These rates were about four and 13 times faster than the oxidation rate in a sterile control flask. The oxidation rates by the microbes starting with much higher initial cell number of Yu et al. [1] were very close to that of this study during the lag phase (9.6×10⁻³ mg pyrite/h), but approximately two times faster during the exponential phase (7.9×10⁻² mg pyrite/h). It shows that the oxidation rates are not simply proportional to the starting cell numbers.

Comparison of age pairs derived from cosmogenic $^{21}\text{Ne}$ and $^{10}\text{Be}$

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Currently, the precision of absolute production rates for the cosmogenically produced noble gases $^{3}\text{He}$ and $^{21}\text{Ne}$ is under debate. Elemental production rates from modelling [1] disagree with natural sample calibrations (see [2]). Furthermore, an altitudinal dependent scaling of stable and radioactive cosmogenic nuclides has been suggested, in particular for the pair $^{3}\text{He}$-$^{10}\text{Be}$ [3, 4] measured in various minerals (garnet, zircon, apatite, kyanite). In contrast, studies of $^{3}\text{He}$ and $^{21}\text{Ne}$ in artificial quartz targets suggest no altitudinal dependent attenuation length coefficients for stable nuclides [5]. A compilation of $^{21}\text{Ne}$-$^{10}\text{Be}$ exposure ages (in quartz, >120 pairs) covering altitudes from 0-5500m (latitudes of 20 - 90º) is presented. Excluded are pairs where either the $^{21}\text{Ne}$ concentration was biased by nucleogenic/ trapped components, exposure histories revealed a complex exposure (using the pairs technique), or samples where not taken for dating purposes. The remaining 65 $^{21}\text{Ne}$-$^{10}\text{Be}$ pairs yield a 1:1 (1.05±0.18) age correlation with altitude and suggest that (1) absolute production rates for both nuclides match very well (2) muogenic production for noble gases is not significant on the observed ages and respective erosion rates, (3) for some settings, $^{21}\text{Ne}$ concentrations are difficult too acquire (young ages in old rocks), and (4) no nuclide dependent scaling procedure is observed for the $^{21}\text{Ne}$-$^{10}\text{Be}$ pair - though such an effect was only observed for $^{3}\text{He}$-$^{10}\text{Be}$ pairs of latest Pleistocene ages at high elevations [3, 4].


Deriving and simulating the coupled biogeochemical and hydrologic processes governing Arsenic transport within evolving sedimentary basins of Southeast Asia

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Weathering of As-bearing rocks in the Himalayas has resulted in the transport of sediments down the major river systems such as the Brahmaputra, Ganges, Red, Irrawaddy, and Mekong. Groundwater in these river basins commonly has As concentrations exceeding the World Health Organization’s recommended drinking water limit (10 µg/L) by more than two orders of magnitude. Understanding the reason(s) for these elevated concentrations of As within the sediments of Southeast Asia has remained a challenge, owing to the difficulty of separating mechanisms responsible for As release (e.g. As and Fe reduction) and local to region hydrology. We deciphered, using a combination of field and laboratory measurements of biogeochemical and hydrologic factors, dominant mechanisms of As release and transport within surficial soils/sediments within an As-afflicted field area of the Mekong delta. Our results illustrate that clay (0-12m deep) underlying oxbow and wetland environments are subjected to continuously reducing conditions due to ample carbon input and saturated conditions. Ensuing reductive dissolution of As-bearing Fe (hydr)oxides releases As, which then migrates to the underlying sandy aquifer (>12 m deep). Reactive transport modeling using PHREEQC and MIN3P was constrained with chemical and hydrologic field measurements, and provides a calibrated illustration of As release and transport within our field site. Our resulting simulations indicate that As release occurs within the clays underlying organic-rich, permanently inundated locations providing sufficient As to the aqueous phase for widespread contamination of the aquifer, and that release occurs for several thousand years prior to depletion of As from the solid phase.
Anthropogenic radionuclides
distribution pattern in the Kara Sea:
Biogeochemistry facets

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We were aimed at study the following tightly related biogeochemistry facets and radionuclides behaviour in the Kara Sea [1]:

- Investigation of organic colloids of different molecular masses using ultrafiltration technique and water suspended material to justify the radionuclides Cs-137, Pu-239,240, Sr-90 behaviour in the river Yenisei and Kara Sea water area;
- Biogeochemistry of suspended organic matter and sediments, including organic carbon concentration and isotope composition along the quasimeridional section “river-sea” (69-78N) to compare the $^{13}$C$_{org}$ values and radiocaesium and radioplatinum activity in sediment;
- Distribution pattern of the $^{137}$Cs and $^{239,240}$Pu all over the surface sediment in the Kara Sea with relation to the redox condition and lithology of the sediment.

Direct positive correlation was established in sediments between concentration organic carbon, $\delta^{13}$C$_{org}$ and $^{137}$Cs activity. The correlation of caesium with $\delta^{13}$C$_{org}$ values in sediment might be explained by the presence of common carrier – clayey minerals - for terrestrial organic matter and $^{137}$Cs. $^{137}$Cs was present in the water suspension and did not associated with organic colloids. Most of $^{239,240}$Pu is associated with organic colloids of high molecular mass (>$2000$Da), whereas about $80\%$ of $^{90}$Sr was present in the fraction of lower molecular mass (<$800$Da) [2].


Olivine-Ti-clinohumite veins and their relation to partial dehydration of high pressure serpentinites

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A major question concerning the dehydration of subducted ultramafic (UM) rocks is the extent to which they are open to externally sourced fluids during their metamorphic history. In the present study we explore peak-metamorphic veining during the evolution of high pressure (HP) serpentinites of the Erro-Tobbio Unit (ET), Ligurian Alps, Italy. The ET Unit represents ultramafic mantle (UM) that was hydrated on the Tethys ocean floor. The UM rocks were then subducted to depths of 65-80 km at around 550-600°C and developed olivine (Ol) + Ti-clinohumite (Ti-Cl) + antigorite (Atg) + clinopyroxene (Cpx) + magnetite (Mag) peak mineral assemblage. The same minerals dominate adjacent HP veins, but their proportions are different. Olivine has abundant Mag and fluid inclusions (FI) in wall rocks as well as in the veins, and is often accompanied by FI-rich Ti-Cl. The ET HP serpentinites went through partial dehydration to form Ol + Atg from brucite (Brc) + low-T serpentine polymorph (Srp) [1]. Fluid in the ET rocks was partly channelized and migrated as attested by the veins. Vein bulk rock trace element concentrations show enrichment in Ti, Ba, Nb, Li, HREE and Cu relative to the wall rocks, accompanied by depletion in Cr. Based on trace element distribution in Srp of recent ocean-floor serpentinites decomposition of Brc + Srp produces relatively dilute fluids. This requires high net fluid flux to produce HFSE-rich veins. However, disequilibrium in and around fluid conduits may enhance reactions and trace element uptake from the fluid. High concentration of certain trace elements in vein Cpx (e.g. Sr 191-202 µg/g) and Ol (e.g. Li 9.8-35.5 µg/g) are therefore not necessarily indicative of significant addition of these elements from an external source. Our study emphasizes the importance of mineral stability and trace element chemistry in influencing bulk rock geochemical evolution.

A snowpit record of atmospheric Fe deposition in West Antarctica at the WAIS Divide site

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The West Antarctic Ice Sheet Divide Deep Ice Core (WDC) is being drilled in a high-accumulation area (79.468° S, 112.086° W) that should yield a 100,000-year record with annual resolution to 40,000 years. In late 2005 a 3 m snow pit was dug at the site of the present borehole, resulting in 63 samples at 5 cm resolution. We here present the results of ICP-MS analysis of these snow pit samples, including the four different Fe fractions (particulate Fe, dissolved Fe, biologically available Fe and total Fe), which represent the first Fe data recovered from the WDC site. Based on annual variability of S concentrations, the samples cover nearly 6 years of accumulation (total water equivalent accumulation of ~125 cm for 1999-2005), consistent with the average water equivalent accumulation at the site of ~24 cm/a. Average Fe concentrations in the total fraction of 1.836 µg/L and in the biologically available fraction of 0.586 µg/L give a geometric mean solubility of 35%, comparable to the 32% geometric mean solubility seen at other Antarctic sites. Based on results from the remaining two Fe extractions at WDC and a comprehensive comparison with all available snow/ice Fe data in Antarctica, we will discuss possible reasons for observed Fe spatial and chemical variability.

The crystal structure of a new Ca-Na-Mn3+-arsenate from a small metamorphic Mn deposit in Italy

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In Northern Italy several metamorphic Mn deposits show assemblages of rare and unusual Mn arsenates, vanadates and silicates. In the Montaldo mine, Borgata Oberti, Cuneo Province, Piedmont, from which the rare Ca-Na-Mg-arsenate garnet berzelite was recently described [1], a new Ca-Na-Mn3+-arsenate was found and its crystal structure was determined. Acid-treating of calcite in the quartz matrix of a single specimen had revealed a blackish (very dark red translucent) blocky grain, ~0.15 mm in size and accompanied by hematite, hollandite/cryptomelane, a greyish diopside-augitic clinopyroxene and a Mn-bearing reddish mica.

The crystal structure of the new mineral was solved from single-crystal X-ray diffraction data (RT, Mo Kα); R(F) = 1.95%. The phase is orthorhombic, with space group Pbcm and a = 8.885(2), b = 7.535(2), c = 11.707(2) Å, V = 783.8(3) Å³, Z = 4. The asymmetric unit contains two Ca/Na, one Mn, two As and seven O sites; one of the latter appears to be partially protonated. The mineral has a framework structure based on a dimer composed of two trans edge-sharing, Jahn-Teller distorted Mn3+O6 octahedra (Mn-O range: 1.8082(7) - 2.1741(11) Å) that are corner-linked to AsO4 tetrahedra and adjacent dimers. One AsO4 tetrahedron shares all its corners with dimers, while the other exhibits a ‘free’ corner, the O atom on which is undersaturated (1.64 v.u.) and loosely bonded (distinctly elongated displacement ellipsoid). Two [7]-coordinated Ca/Na sites occupy voids in the framework. The following chemical formula has been derived on the basis of occupancy refinements, bond-valence calculations and crystal-chemical considerations: (Ca0.84,Na0.16)(Ca0.46,Na0.54)-Mn2O(O,OH)(AsO4)2. The (O,OH) site, bonded to two Mn atoms, has a bond-valence sum of 1.52 v.u.; the Ca-rich and –poor sites have sums of 1.85 and 1.69 v.u., respectively. Since a quantitative chemical analysis has not been done yet, the chemical formula is somewhat preliminary.

It is hoped that the ongoing study of the mineralisation of the Montaldo mine will provide more material enabling a complete characterisation of the new species.

Marco Ciriotti is thanked for submitting the specimen for analysis.

Partitioning of P, V, Mo, and Ni during precipitation of ferric oxyhydroxides and implications for Archean ocean nutrient availability during BIF deposition

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During the Archean and Paleoproterozoic, large amounts of iron precipitated from seawater to yield Banded Iron Formations (BIF). It has been argued that during this time, the presence of abundant and highly reactive iron oxyhydroxides may have limited critical nutrients as a consequence of various adsorption and co-precipitation processes. These arguments have previously centred on the role of phosphorus, which is currently a major nutrient controlling the degree of ocean productivity. In this study, we add to the debate regarding nutrient availability in the ancient oceans at the time of BIF deposition by evaluating the degree to which ferric oxyhydroxides may sequester aqueous Mo, Ni, and V; these transition metals act as enzymatic co-factors that are critical, and at times limiting, for specific biological functions in modern microbes. Furthermore, it is generally assumed that dissolved silica was more abundant at the time of BIF deposition. As dissolved silica may influence elemental partitioning through a combination of competitive surface adsorption and co-precipitation processes, we also consider its role in the sequestration of these nutrients into iron oxyhydroxides. Finally, we evaluate our experimental data in light of the concentrations in which these elements are found in BIF, and estimate their degree of availability in ocean water at the time of BIF deposition.

The geochemical behaviour of Sb, Mo and W in subduction zones

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Due to their high charge-size ratio, Sb, Mo and W are part of the high field strength element (HFSE) group which is traditionally regarded as behaving immobile in subduction fluids. We present new high-precision W, Nb, Ta, Zr, Hf concentration data of lavas from various arc settings obtained by isotope dilution and MC-ICP-MS. Antimony and Mo were analysed in combination with other incompatible trace elements by conventional quadrupole ICP-MS measurements. Glasses from the UPL suite from Troodos, Cyprus permit to evaluate the mobilization of HFSE by fluids derived from subducting sediments (Cameron et al. 1985). The HFSE budget in these magmas is compared to that in Solomon arc lavas that have only been overprinted by fluids and melts derived from subducted oceanic crust (Schuth et al. 2004; König et al. 2007). Measured Ta/W in both suites are lower (<2.9) than values for MORB (ca. 5), indicating that W is more mobile in subduction components than Nb and Ta. Correlations between Ce/Pb, Sb/Ce and W/Th support an effective mobilization of Sb and W by slab-derived fluids and clearly resolve a more pronounced W and Sb enrichment in slab fluids originating from subducted sediments, reflecting the higher initial abundances of both elements in sediments. Tungsten and Mo abundances correlate well in the Solomon arc suite where negligible amounts of pelagic sediments were subducted, whereas both abundances are decoupled in the Cyprus suite with subducted pelagic sediments present in their sources. This difference possibly reflects variable redox conditions during dehydration processes in subducting oceanic plates.
Polycrystalline diamond inclusions in Jack Hills zircon: Carbonado?

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Mineral inclusions in detrital zircons from the Jack Hills of Western Australia contain the only direct evidence about the earliest crust on Earth. Diamond inclusions were first reported in Jack Hills zircon by [1]. We have found that some zircons contain dark colored, rod shaped inclusions (~5 µm in diameter and several tens of µm long). We have investigated these inclusions using optical microscopy, scanning electron microscopy (SEM) / focused ion beam (FIB) system, and transmission electron microscopy. The rodlike inclusions are composed of polycrystalline diamonds (~1 µm dia.) in random crystallographic orientation, a C-rich foliated mineral (probably graphite), an Al-oxide mineral (possibly corundum), a La/Ce- mineral (probably phosphate), and voids among the microcrystals. The texture and mineral assemblage are most like carbonado [2] vs. framesite or other forms of polycrystalline diamond. Carbonado is widely thought to form by meteorite impact on terrestrial continental crust [2].


Figure 1: SEM image of a FIB-milled surface showing a polycrystalline diamond inclusion in zircon. Note that plucking and contamination above diamond complicates analysis from the polished surface.

Development of a $^{58}$Fe-$^{57}$Fe double spike for Fe isotopic analysis using a Nu Plasma 1700 MC-ICP-MS

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Fe isotope analysis by high-resolution MC-ICP-MS shows great promise for high precision measurements in natural materials. Specifically, the Nu Plasma 1700 is capable of high mass resolution, allowing complete separation of the Fe mass peaks from polyatomic (Ar-N-O) interferences, further augmented by the use of a desolvating nebulizer (DSN-100) to reduce liquid (O-N) introduction. In order to increase reproducibility, we developed a double spike technique to correct for mass-dependent fractionation resulting from chemical separation and/or instrumental artifacts.

The double spike composition was chosen based on an error analysis, which evaluated the potential precision using both iterative and non-iterative data reduction routines [1, 2], as well as different potential double-spike compositions. Using a full range of $^{52}$Fe-$^{58}$Fe or $^{54}$Fe-$^{58}$Fe double spike compositions, varying from pure double spike to pure standard, and randomly perturbed one thousand times up to the internal precision, the iterative data reduction with a $^{57}$Fe-$^{58}$Fe double spike (0.1 mol fraction $^{58}$Fe) is predicted to provide the best internal precision. Thus, we prepared such a $^{57}$Fe-$^{58}$Fe double spike from high-purity enriched Fe isotopes, and then calibrated against a gravimetric standard.

Initial double spike analyses of several rock standards show an external precision of ~0.05‰ (2σ). Our analysis protocol currently consists of ~50 cycles at 15-20V signal intensities ($^{56}$Fe), simultaneously collecting masses 52, 54, 56, 57, 58, 60. Polyatomic interferences are avoided at a resolution of ~2500, and we monitor $^{52}$Cr and $^{60}$Ni to correct for interferences by $^{54}$Cr and $^{58}$Ni. Sample introduction in weak HNO$_3$ has a lower background and better washout in the DSN-100 than HCl. In addition, we found higher frequency of peak centering increased internal precision.


Figure 1: SEM image of a FIB-milled surface showing a polycrystalline diamond inclusion in zircon. Note that plucking and contamination above diamond complicates analysis from the polished surface.
Phosphorus inactivation by Aluminum in lakes and sediments

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Non-calcareous, phosphorus (P)-rich lake sediments typically release P associated with iron hydroxide (Fe(OH)3) during the development of hypolimnetic anoxia. Naturally or artificially elevated concentration of aluminum hydroxide (Al(OH)3) in such sediments can prevent the P release [1, 2], provided the Al(OH)3 to Fe(OH)3 ratio is >3 [3], because Al(OH)3 provides an additional redox-insensitive sorption capacity to sediments. The high Al(OH)3:Fe(OH)3 ratios are typical for sediments of (i) atmospherically acidified lakes with elevated terrestrial export of ionic Al (Al i), (ii) lakes treated with Al salt, and (iii) alpine lakes with high erosion of aluminosilicate soil [3]. High Al(OH)3 concentrations may occur in sediments of circum-neutral forest lakes, with little Al i input, but receiving organically-bound Al (Al o) [4].

Palaeolimnological data on a ~14,000-yr sediment from Plešné Lake (Czech Republic) suggest that photochemical liberation of Al o [5] has been a significant natural source of Al i for the lake, and Al(OH)3 for its sediments throughout the Holocene [4]. The Late Glacial sediment had most P associated with Fe(OH)3, calcite, or apatite, and would have released P during anoxia. The Holocene sediment had negligible P release during anoxia, because P was immobilized by Al(OH)3. The P-sorption characteristics of sediment changed due to soil formation in the de-glaciated watershed. Soil organic acids bound and carried Al o to the lake, where it was liberated by solar radiation. Similar sediment composition of lakes in Maine (USA) [2] suggests that this P-immobilizing process is general.


Mineralogy of natural diamond-forming fluids

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Fluids parent to diamonds are elusive and can be directly studied only when trapped in rare diamond inclusions. We present data on the geochemistry and mineralogy of fluids hosted by 20 fibrous diamonds from Kongo. The fluids are in sub-micron inclusions that range in composition from silicic to carbonatitic. X-ray diffractometry is proven to be the most effective tool for an integral mineralogical analysis of the entire volume of included diamonds. Using XRD patterns, compositional trends, FTIR and Raman techniques, we significantly expanded the list of minerals that may precipitate from diamond-forming fluids. Most common phases in the fluid are found to be phlogopite, complex Na-Ca-Mg-Fe carbonates, apatite, KCl brine and gaseous CO2. Other minerals occurring in lower abundances include hydrated micas and other sheet silicates, carbonate hydrates, Ca-Al-Fe oxide carbonate hydrate, Na chlorate hydrate, and several hydrous aluminosilicates. The majority of the diamonds contains CH2 groups bonded to sp3-hybridized carbon. We suggest the hydrocarbons are associated with carbonate minerals in inclusions as 1) Diamonds with high CH2 peaks are lower in SiO2, K2O, have higher contents of CaO, MgO and FeO, and higher intensities of IR carbonate peaks; 2) CH2 peaks are often reported in IR patterns of gem-quality inorganic carbonates. A wide range of hydrous and carbonate minerals found in the fluid is preserved due to high activity of H2O and CO2 locked by the host diamond.
**$^{40}$Ar-$^{39}$Ar dating of a melt inclusion from Dhofar 323 (H5): An early impact event**

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Certain unshocked H-chondrites record chronological information of the period shortly after parent body formation [1], e.g. Dhofar 323 [2]. In this weakly shocked (S1) H5 chondrite [3], we found an achondritic inclusion: medium-grained (40-100 µm) crystalline rock composed of equilibrated olivine, pyroxene, and feldspathic glass, with silicate chemistry similar to that of the host chondrite but strongly depleted in metal and troilite. Hence, this inclusion most probably represents recrystallized impact melt produced on the H-chondrite parent body. Within an ongoing initiative to elucidate chondrite thermal histories [1,2,4,5], we performed high resolution $^{40}$Ar-$^{39}$Ar dating. The inclusion age is 4508±9 Ma. It is indistinguishable from the host material [2] and the age of unshocked H5 chondrites reset by thermal metamorphism [e.g. 1,6], and corresponds to about 20-30 Ma after CAIs if corrected for K decay constant bias [7-10]. The presence of this melt inclusion in unshocked chondritic material suggests an early impact event, accompanied by melt penetration into the H5 layer of an onion-shell structured parent body that was slowly cooling after metamorphism. In most cases the impact ages of H-chondrites are <1.3 Ga [e.g. 6]. The oldest impact-induced H chondrite silicate melt was found in Ourique with an $^{40}$Ar-$^{39}$Ar age of 4.45±0.02 Ga [11]. The Dhofar 323 inclusion appears the most ancient achondritic material currently found in H-chondrites.


**Chemical and isotopic characterisation of highly saline sedimentary pore water**

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Pore water chemistry and isotopic composition were investigated using common indirect methods (leaching and isotope diffusive-exchange technique) on drillcore samples from the DGR boreholes drilled by Ontario Power Generation (OPG) at Bruce, southern Ontario, into Palaeozoic rock of the Michigan Basin. Previously, these methods were successfully applied to characterise pore waters of the Opalinus Clay drillcore samples from Mont Terri, Switzerland, which showed a maximum Cl content of approx. 14 g/kgH 2O. In contrast to the Opalinus Clay, however, the Michigan Basin samples are characterised by highly saline pore water, which induces several methodological difficulties.

The conversion of aqueous leaching data to mass of pore water requires the knowledge of rock’s porosity and thus its water content, grain and bulk densities. The measurements of densities and water content are, however, affected by the mass and volume of evaporated pore-water salts and the dry weight of the rock sample requires a correction related to the pore water salinity. Applying the common salinity-correction method in combination with the general trend in the depth profile given by the water activity data of the rock samples allows an evaluation of the chloride content and main salt components (NaCl vs. CaCl 2) of the pore water over a range of salinities from seawater to halite saturation.

The high salinity also affects the indirect methods for the pore-water stable isotope determination. In the isotope diffusive-exchange technique, where the isotope exchange between a test water and pore water of rock samples occurs via the vapour phase, there exists a risk of liquid-vapour isotope fractionation of oxygen and hydrogen between the test water and the highly saline pore water. Differences in the water activity will result in saturation/desaturation processes and possible precipitation of (hygroscopic) salts in the rock sample over the course of the experiment. We propose to minimise this fractionation by fitting the water activities of the test-water solution to that in the investigated rock sample by adding NaCl or CaCl 2 to the test water. Similar perturbations of the in situ isotope signature during the experiment and measurements will also have to be expected for other pore-water stable isotope techniques.
Using composition to assess pairing relationships among lunaites

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More than 120 named lunar meteorite stones have been recognized since 1982. Three quarters of them have been announced in the last 5 years as collectors scour the world’s deserts for new meteorites. A first-order question with each new find is “Is this stone paired with another?,” i.e., is it another piece of an already known meteorite that fragmented during or after it encountered Earth’s atmosphere. For lunar (and Martian) meteorites, a second first-order question is “Is this stone launch paired with another?,” i.e., did a single impact on the Moon launch multiple stones that made the Moon-Earth trip. Launch-paired meteoroids can land on different continents.

For lunar meteorites, bulk-composition data are powerful for establishing or rejecting potential pairings because compositions of lunar meteorites are far more variable than are those of meteorites from any other parent body. For example, among lunar meteorites Sc concentrations range from 4 ppm (feldspathic) to 94 ppm (basaltic) and incompatible elements vary over factors of several hundred (e.g., 0.2–75 ppm Sm).

We divide samples of 0.1–0.3 g into (typically) 4–10 subsamples which we subject to instrumental neutron activation analysis for trace elements. Most lunar meteorites are breccias, and subsample data often reflect variation in plagioclase to pyroxene + olivine. Useful elements are Fe, Na, Sc, Cr, Sm, Eu, and Th. Stones with overlapping compositional ranges are candidates for further tests based on petrography and cosmic-ray exposure data. For example, Dho 1436 (Oman), Northeast Africa 001 (Sudan), and Yamato 791197 (Antarctica) are potential launch pairs on the basis of composition (figure).

Laser ablation MC ICP-MS U-Pb zircon dating using multiple channeltron ion counting detection

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Since the introduction of laser ablation (LA) ICP-MS, the goal of the Earth science community has been to achieve figures of merit (e.g. spatial resolution, precision) comparable to those of already established in situ isotopic techniques, such as secondary ion mass spectrometry or TIMS combined with micro-sampling. Precision and accuracy of laser ablation ICP-MS U-Pb dating of accessory minerals is largely limited by uncontrolled elemental fractionation of Pb and U during laser ablation and also by variable mass discrimination of the ICP-MS instruments. The use of short laser wavelength, homogeneous laser beam, ablation in He, improved sampling strategies, and recently also the implementation of short-pulsed (fs) lasers have all contributed to reduction of laser-induced Pb/U fractionation. The effect of Pb/U fractionation on the precision of U-Pb age data can be further reduced by using shorter analysis/ablation time. Combination of short ablation with ability to detect small isotopic signals should also result in significant improvements of spatial resolution of the analysis.

We report results of U-Pb dating of different zircon reference samples by laser ablation (213nm Nd:YAG) multiple ion counting ICP-MS (Thermo Finnigan Neptune). The array of eight channeltrons allows for simultaneous detection of $^{202,204}\text{Hg}$, $^{203,205}\text{Tl}$, $^{204,206,207,208}\text{Pb}$ ion signals and one of the $^{235,237}\text{U}$ isotopes. Detection of all isotopes required for U-Pb dating and monitoring the instrument mass bias in electron multipliers, rather than in a mixed faraday - multiplier detector array, eliminates potential difficulties with detector cross-calibration due variable response of faradays and electron multipliers and slow decay of faraday resistors. This method is limited by maximum ion beam intensity that can be reliably detected by the channeltrons (ca. 200 Keps) and by reproducibility of channeltron cross-calibration (ca. 0.5-1 %). Precision of measured Pb/U ratios in zircon after 20 seconds of ablation is better that 5 permil (2 sigma), resulting in routinely achieved precision of U-Pb ages obtained by external calibration of ~1 percent or better. In addition, the short ablation required to achieve such precision results in spatial resolution that is superior to comparable U-Pb zircon analyses by single collector ICP-MS.
Goldschmidt Conference Abstracts 2008

Finite speed of mantle homogenization and Hf-W assessments of the Earth's core age

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Assessments of the core formation time based on Hf-W isotopic system vary from 45±5 Ma [1] to about 30 Ma [2] since CAI creation depending of the assumptions of initial $^{182}$Hf/$^{180}$Hf and some features of the core segregation styles. Another important connivance for such calculations is that all the mass of the proto-earth material had been separating to silicate and metal phases homogeneously, or produced W isotopic heterogeneity of mantle rocks was erased very fast, for first millions of years. If it was not the case, above assessments of core formation time are highly underestimated.

Observed long-term Pb-Sr-Nd-Os mantle isotopic heterogeneity, having mean age about 1.8 Ga, imply impossibility of fast isotopic homogenization of mantle as a whole, even at much higher temperature and partially melted state.

In contrast to short-living isotopic systems using of U-Pb system does not yield a significant shift in mean core formation age calculation. Effective time of the core formation is about 120 Ma that is based on lead model age of MORB.

Numerical modelling was used to test various scenarios of one- and two-stage prolonged core formation without fast mantle isotopic homogenization. In two-stage models the first stage could be related with primary metal segregation and the second one – with Fe$^{3+}$ disproportionation on silicate Fe$^{3+}$ and metallic Fe$^0$ [1, 3].

Both $^{142}$Nd anomalies in ancient rocks of West Greenland [4] and Pb-Pb isotopic system in rocks and feldspars of West Greenland [5] evidence that the first “basaltic” crust was formed no later than 4.3 Ga ago. At this stage water was only on the surface of the Earth. The process of gradual oxidation initially highly reduced mantle became a driving force for the ascent of the first plums formed at the core-mantle boundary. Later melting of hydrated basaltic crust under the influence of ascending plums produced first tonalitic crust after 4.0 Ga.


Adsorbophysical fields and atmosphere composition

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New Method of Atmosphere Composition Formation

Our new method of the atmosphere composition formation presents a model of natural processes taking place during photoradiation of the gas-mineral system. Adsorbophysical fields of gas-mineral system [1] and correlation between molecular processes in gas phase and atomic processes in a mineral adsorption phase and electronic processes in the mineral itself were studied. For example, during irradiation of oxygen-fine-dispersion mineral systems many ionic forms can be formed. These ionic forms define all consequent natural processes (see Fig. 1).

![Figure 1: Ionic forms in radiated oxygen-mineral system](image)

Discussion of Results

It was experimentally shown that surface reconstruction by photostimulated defect formation is characteristic of oxide containing fine-dispersion mineral systems. During reconstruction, gas phase oxygen can compete with moving oxygen ions of oxygen containing fine-dispersion mineral system lattice if it captures energetically beneficial position. Thus, minerals could be generators of oxygen and other molecules from atmosphere. We revealed mechanism of transformation of lattice oxygen into free form atmosphere oxygen through adsorbed forms. Contrary reaction is also possible.

Use and abuse of Sm-Nd whole-rock isochron data for komatiites

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The Volotsk komatiite-basalts suites have been regarded as the oldest volcanic rocks of the Baltic Shield, with Sm-Nd ages of 3391 ± 76 Ma [1]. We proposed that the age of the Volotsk suites is much younger and obtained a new Sm-Nd age of 2701 ± 84 Ma for different samples [2]. This is unexpectedly young, considering the ages of komatiites in the region (2.95 – 2.90 Ga).

A recent Nd study of the Volotsk suites [3] showed that LREE-depleted samples plot around a regression line that yields an age of 2850 ± 84 Ma. An internal regression line, obtained by using Sm-Nd mineral (Pl, Hbl) and whole rock data, corresponds to an age of 2653 ± 29 Ma. Thus, the former 3.4 Ga age has no geological significance, but is rather a mixing line [3].

Thus, there are three Sm-Nd regression lines reported for the komatiites of the Volotsk suite (~ 3.4, 2.85 and ~ 2.7 Ga) (Fig. 1).

We have dated zircons from a gabbro dyke that cuts the Volotsk suite, by the U-Pb method (TIMS). This yielded an U-Pb age of 2840 ± 3 Ma.

Figure 1: Sm-Nd diagram for whole-rock samples of Volotsk suites.

Following [3], we argue that the age of the Volotsk suites is 2.85 Ga, and that the 2.7 Ga Sm-Nd regression line demonstrates open-system behaviour in some samples, due to later tectono-thermal events.


Mineral surface reactions and the role of solvent structure dynamics and ion hydration in solution

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We use reactions of barium sulfate in the presence of simple ionic salts as a model system to illustrate how solution composition can affect thermodynamic and kinetic properties of mineral growth and dissolution. We show that rates of reactions, mode of growth and morphological features change under conditions of constant thermodynamic driving force (supersaturation) and constant ionic strength (IS) depending on the salt used to modify the IS. Salt-specific effects on dissolution and precipitation processes show systematic behavior that correlates with the effects of respective electrolytes on water structure dynamics and on lattice ion hydration in solution.

Furthermore our results indicate that morphology modification by additives does not necessarily imply specific additive-surface interactions as the same changes in the shape of nuclei as observed in the presence of different background electrolytes can be obtained just by varying water temperature, which has a similar effect on water structure dynamics as the addition of the respective salt. Nanoscale morphological features such as shape of islands, which are also reflected in the bulk crystal appearance, rather express the solvation properties of the solvent and its affinity with the solute.

We propose a theoretical explanation of the role of solvent properties and solute hydration on crystal behavior. Simple 1:1 electrolytes used to modify the solvation environment can give insight into the principles which can be subsequently extended to more complex systems. We show how understanding the interdependence of ion properties, solution structure and crystal growth/dissolution behavior can help us to explain such phenomena as impurity incorporation and crystal growth in the presence of organic additives.
Synthesis and mineralogical characterization of members of the voltaite group

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We performed detailed studies of the mineralogical properties of the voltaite group, which, despite its large number of different members, still lacks a comprehensive characterization. The samples precipitated from an acidic solution that contained the corresponding metal sulfates. The proportions of these salts were chosen either according to the respective chemical formula or in compliance with the methods of Mereiter [1] or Gößner [2]. The crystallization process took place at a temperature of 353 K and lasted between two and three days.

The thus obtained euhedral voltaite crystals were analyzed using an electron microprobe, yielding an excellent agreement with the theoretical formula K$_2$Me(+II)$_5$Fe(+III)$_3$Al(SO$_4$)$_{12}$·18H$_2$O, where Me(+II) = Fe(+II), Mg, or Zn. The phase identification and subsequent Rietveld refinement was performed by means of powder XRD and the crystallographic software package GSAS. The refinement showed a systematic decrease of the lattice parameter in the solid solution from the Fe(+II)- to the Mg-endmember. This result is consistent with the smaller effective ionic radius of Mg compared to that of Fe(+II). When viewed in plane-polarized light, the Mg and Zn endmembers of the voltaite group were colorless, whereas all other solid solutions of the Fe(+II)-Mg-Zn system exhibited a typical green color. Under crossed polarizers, the crystals, which were up to 0.5 cm across, showed an anomalous anisotropy towards the edges. These optical anomalies increased with the increasing substitution of Fe(+II) by Mg or Zn, and suggest at least small deviations from the nominal cubic symmetry of voltaite. Further characterization of the synthesized voltaite-group members by means of IR and Raman spectroscopy, single-crystal XRD, and DTG are planned for the near future.


Interaction between Paramecium bursaria and Europium(III)

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Introduction

It is known that activity of microorganism has a great impact on the geological migration of the radionuclides leached from radioactive waste forms. Retardation by adsorption on the cells is the most desirable function of bacteria. It is also known that protozoa, who prey bacteria, are found in deep ground water. To elucidate the role of protozoa in the migration of radionuclides, the behavior of Paramecium bursaria in media containing Eu(III) with or without addition of bacteria as a food source was investigated. Eu(III) was used as simulant of trivalent actinides.

Results

When cells of P. bursaria, which were cultured, harvested, and washed beforehand, were contacted with a salt solution containing Eu(III) for 24 h, a fraction of the cells died at 0.05 mM or higher concentrations of Eu(III) (Table 1). This result indicates that Eu(III) is toxic to P. bursaria.

<table>
<thead>
<tr>
<th>Eu(III) concentration</th>
<th>Fraction of the cells survived</th>
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<tbody>
<tr>
<td>0</td>
<td>1.00</td>
</tr>
<tr>
<td>0.01 mM</td>
<td>1.00</td>
</tr>
<tr>
<td>0.05 mM</td>
<td>0.90 ± 0.05</td>
</tr>
<tr>
<td>0.1 mM</td>
<td>0.27 ± 0.06</td>
</tr>
<tr>
<td>0.5 mM</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 1: Survival fractions of P. bursaria in Eu(III) solutions. The solutions contained 2360mg/L of NaCl, 267mg/L of Ca(NO₃)₂, 26.7mg/L of MgSO₄, 0.9mg/L of Fe₂(SO₄)₃, and 99.2mg/L of C₆H₇Na₂O₆P. The pH was adjusted to 7.0. The Eu(III) added was Eu(CH₃CO₂)₃.

After P. bursaria cells were cultured with the B. subtilis cells on which Eu(III) was adsorbed in advance, a fraction of the Eu(III) was found in liquid phase as organic colloid and another fraction was detected in extracellular polymeric substances formed by the growth of the P. bursaria cells. This result indicates that the activity of Paramecium sp. may change chemical and physical states of radionuclides.
Intratest oxygen isotope variability in planktonic foraminifera: New insights from in situ measurements by ion microprobe

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Intratest oxygen isotope variations in the planktonic foraminifera Neogloboquadrina pachyderma sinistral (left coiling) from North Atlantic core top and multi-net samples were assessed by ion microprobe analysis using a primary beam size of approximately 2x3 µm. In the core top sample comprising both ontogenetic and gametogenic calcite, δ18O varies from 0.32‰ to 3.45‰ [PDB] (2 SD = 0.76), exceeding the range of equilibrium δ18O [1] in the specimens' habitat by a factor of three. The isotopic difference between the ontogenetic and gametogenic calcite averages to 1.7‰. None of the two phases of foraminiferal calcite precipitates in equilibrium with ambient seawater. The ontogenetic calcite exhibits a negative fractionation of 0.5 to 1‰ relative to the lowest equilibrium δ18O values during peak summer temperatures in the euphotic zone. In contrast, a positive fractionation of about 0.5‰e was observed in the gametogenic calcite crust with respect to the heaviest equilibrium δ18O values at water depth below 200 m. Hence two counterbalancing vital effects are effective within a single foraminiferal test, indicating that 'whole test' values of this species are highly sensitive to the degree of gametogenic encrustation. The preferential incorporation of 16O into ontogenetic calcite was verified by ion microprobe analysis of four nonencrusted net samples reflecting three different depth intervals. Intra-ontogenetic δ18O ranges from 0.41 to 2.74‰ (2 SD = 0.55) and exhibits a negative fractionation similar to that observed in core top samples. Stable isotope microanalysis in single foraminiferal tests is a promising approach for paleoceanographic reconstructions and contributes to our understanding of the organisms’ life cycle and its vital effects.


The general criterions of difference of the convergent rocks

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In geological understanding convergence is a formation of products of similar type from various sources and various ways. A subject of our studying - mountain rocks-hydrolysates, i.e. products of natural hydrolysis, them metamorphosed analogues - metahydrolysates. Some of these rocks have dual convergence the nature: they can be formed both in eluvial, and in endogenic hydrothermal-metasomatic processes. There are some diagnostic attributes of genesis metahydrolysates [2]. Formation attribute: the finding metahydrolysates in structure of lepigenic sedimentary formations is their important certificate hypergenic (instead of hydrothermal-metasomatic) the primary nature. This attribute testifies in favour of the eluvial-crust of the nature of ours rocks. Substratum-formation attribute: gravitation metasomatic hydrolysates (type of secondary quartzites and argillizites) to volcanicogenous strata. In our case we observe gravitation of such rocks, as diasporites, to sour vulcanites. Zonal-morphological criterion: presence of symmetric ash value - the good attribute of the hydrothermal nature hydrolysates - is not characteristic for eluvial-soil columns. In the sections studied by us about any ash value to speak very difficulty. Mineralogical attributes. At the exogenous (low-temperature) metasomatosis there are many metastable phases while for high-temperature endogenic metasomatite fast course of process is characteristic, therefore metastable phases are short-lived. Besides for exogenous process are rather characteristic pseudomorphs whereas for endogenic they are uncharacteristic as the period pseudomorphism very much short. Such picture is observed in ours metamorphic slates for rare earth phosphates, arsenates, etc. Most likely, these minerals were formed in a Cambrian crust of weathering. At the same time in diasporites there are the minerals absolutely unusual for crust of weathering: for example, euclase, ardennite, chernovite and gasparite. Geochemical attributes: to number of attributes hydrothermal-metasomatic hydrolysates it is possible to carry their sour composition. Metasomatic hydrolysates it is possible to consider as other characteristic attribute deep division of aluminium and iron with formation of spatially isolated mineral congestions. Such division is precisely shown in our rocks. Thus, the studied metahydrolysates, from our point of view, are products metasomatism [1].

Redox-dependent phosphorus burial and regeneration in Cretaceous black shales and Mediterranean sapropel S5

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Phosphorus (P) is a key nutrient and its availability can limit marine primary productivity. The efficiency of marine P burial is strongly dependent on the oxygenation state of bottom waters. The feedbacks between P availability, primary productivity, oxygen depletion and P regeneration from marine sediments may have played a crucial role in initiating and/or sustaining periods of high marine primary productivity and organic carbon burial in Earth's history.

Two type examples of organic-rich (organic carbon (OC) > 1%) sediments from such periods are the black shales deposited during oceanic anoxic event 2 (OAE 2, 93.5 Ma), and the Eastern Mediterranean sapropel S5 (~125 ka). In both sediments, enhanced OC/total P ratios indicate enhanced release of P from organic matter with negligible 'sink-switching' to authigenic P-containing minerals. Clear differences in P cycling are observed for the two sediment types, however, attributable to varying degrees of oxygen depletion in the water column. Phosphorus burial nearly shut down in OAE 2 black shales under severe euxinia (ODP Leg 207, site 1260) while it increased during formation of sapropel S5. This increase is likely the result of enhanced preservation of fish debris.

Our results show that local conditions such as the degree of (bottom water) oxygen depletion affect not only the efficiency of P burial, but also the relative importance of the various P phases. In particular, biogenic Ca-P (fish debris) can become a major burial sink for P under anoxia.

Iron oxide photodissolution in the presence of siderophores

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Iron is an essential nutrient for almost all known organisms and its low bioavailability limits primary productivity in large scale ecosystems. High affinity iron acquisition mechanisms involving the synthesis and exudation of iron specific ligands (siderophores) are widespread among procaryotic microorganisms. Marine phytoplankton that is responsible for much of the marine primary productivity does not exude siderophores and is not efficiently taking up iron-siderophore complexes. However, previous work has shown that sunlight also promotes iron oxide dissolution by a photoreductive dissolution mechanism. This process generates siderophore photoproducts and transient reduced iron species, potentially increasing iron bioavailability to phytoplankton in the photic zone. In this presentation we will discuss mechanistic aspects of this ecologically important process in terms of the siderophore speciation at the mineral surface as measured by IR-spectroscopy and of its reactivity as inferred by measurements of the reaction rates.

Release of Fe(II) from lepidocrocite irradiated with simulated sunlight but in the absence of organic ligands was observed in control experiments. We conclude that intrinsic photochemical processes at the mineral surface lead to reductive dissolution of the mineral. A further increase of dissolution rates of irradiated suspensions was observed in the presence of DFOB, a trihydroxamate siderophore that forms non-photoreactive complexes in solution. Similar effects were observed in the presence of aerobactin, a siderophore possessing an alpha hydroxy carboxylate functional group. Comparison with citrate suggest that ligand to metal charge transfer is not a dominant photodissolution process in the presence of aerobactin. Alternative mechanisms by which siderophores promote lepidocrocite photodissolution are discussed.
**Emplacement of regional high-silica deposits on Mars**

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Surface materials in the mid-to-high latitudes of Mars are higher in silica content compared to other areas of Mars [1, 2]. Silica enhancement is expected for the alteration of mafic Martian crust [3]. The presence of high-silica surfaces in both the northern and southern hemispheres of Mars suggests a genetic link to the recent Martian climate and distribution of near-surface water ice [4]. Silica was likely enriched in these regions by interaction with the cryosphere in recent Martian history. High-silica mineraloids may have been formed in aqueous solutions generated by periodic snowmelt or pedogenic processes in icy soils, forming thin coatings on rocks and particles, consistent with remote sensing observations [4, 5]. While such a model may explain the presence of high-silica materials in both hemispheres, important differences between north and south must be explained. High-silica materials are more concentrated in the northern plains than the southern hemisphere [1]. Also, Fe, K, and Th are enriched in the northern lowlands, while K/Th is higher in silica content compared to other areas of Mars [1, 2].

These hemispheric differences may result largely from the physical redistribution of materials, with mechanical weathering ultimately affecting chemical and mineralogical observations. The high-silica northern hemisphere is dominantly in the Vastitas Borealis Formation (VBF), the reworked sedimentary residue of Martian outflows [6]. The chemistry of the northern plains may reflect the nature of VBF sediment source material and its subsequent alteration and weak diagenesis. Silica enrichment in the northern plains may derive from deposition of high-silica phases from flood waters in addition to later cryospheric weathering. The boulders observed in HiRISE images of the VBF may be, in part, sedimentary rocks cemented by flood-produced silica.


**Distribution of $^{230}$Th, $^{10}$Be and $^{231}$Pa in sediment particle classes**

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The $^{230}$Th$_{\alpha}$-normalization method is a widely used tool for the calculation of vertical fluxes to marine sediments, correcting for the influence of lateral sediment transport. However, the strong particle surface reactivity of thorium may lead to a grain size specific distribution of $^{230}$Th. Lateral transport during particle settling might have a sorting effect on particles, thus affecting the sedimentary $^{230}$Th signal as well. In this study, the specific distribution pattern of $^{230}$Th within different particle classes is investigated in carbonate-rich sediments and opal-rich sediments from the Atlantic Ocean. Sediments were split into distinct particle classes by wet-sieving and settling. The results show a clear preference of $^{230}$Th for the smallest particle sizes. Both in carbonate-rich and opal-rich sediment, most of the $^{230}$Th is bound within the particle size class <20µm accounting for 60-77% and 90% of the total $^{230}$Th inventory, respectively, whereas this size fraction was only 45% and 72% of sediment mass, respectively. In the opal-rich material, $^{230}$Th does not show any preference for opal or non-opaline material.

We also compare similar neighbouring deep-sea sediment cores (PS1768-8 and PS1769-1). While the difference in sedimentation rates is a factor of 2-3, the grain-size distribution in the two cores, as well as the $^{230}$Th-distribution between the grain sizes, does not differ significantly. These results indicate that syndepositional sediment redistribution at the sea floor may be a process that does not necessarily have a major impact on the grain size distribution.

In addition, results from $^{10}$Be and $^{231}$Pa measurements of the same size-fractionated sediment samples will be presented. In contrast to the $^{230}$Th, it is expected to find these isotopes preferentially adsorbed on biogenic substances (opal, carbonate). The isotope ratios $^{10}$Be/$^{230}$Th and $^{231}$Pa/$^{230}$Th are used as palaeoproductivity and palaeocirculation proxies. If $^{230}$Th, $^{10}$Be and $^{231}$Pa are bound to different particle types, lateral transport involving particle sorting might affect the isotope ratios.
Rb-Sr dating of mylonites along major intra-cratonic and craton margin shear systems of the Precambrian Dharwar Craton, Southern India and tectonic implications

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Large-scale brittle-ductile shear zone systems, at both intra-cratonic and craton-margin settings, comprise a prominent deformation fabric of the Precambrian Dharwar Craton. Mylonites from a number of shear systems were dated by the Rb-Sr whole rock-biotite isochron method in an attempt to constrain chronology of latest deformation along the shear zones and improve our understanding of the temporal evolution of the craton in terms of deformation, magmatism and uplift events since the Archaean.

Multiple samples of mylonites from the intra-cratonic shear zones bounding the Bababudan, Chitradurga and Ramagiri greenstone belts indicate a spread of ages between 2515 Ma and 2220 Ma. The results bear evidence for recurrent Palaeoproterozoic reactivation of the boundary zones that separate large tracts of greenstone belts and granite-gneiss domains. While the older ages could relate to a terminal stage of Late Archaean thermo-tectonic events involving east-west shortening and thrusting in the Dharwar Craton, the younger ages may correspond to thermal and tectonic events such as the emplacement of mafic dyke swarms and development of large intra-cratonic sedimentary basins like the Cuddapah basin.

Unlike the intra-cratonic shear zones, an overwhelming number of Rb-Sr biotite ages of mylonites and gneisses in the vicinity of the Palghat-Cauvery shear zone system and the Eastern boundary thrust zone of the Cuddapah basin, which mark the southern and eastern margins of the Dharwar Craton, cluster around 486 Ma. These shear zones straddle the boundaries between the Archaean Dharwar Craton and the high-grade mobile belts which are generally believed to have accreted during the Proterozoic, but the chronology of their accretion has been ambiguous. The present age data constrain the latter events at late Neoproterozoic/early Palaeozoic. The results are consistent with age data on analogous tectonic settings elsewhere in the Gondwana supercontinent.

Mass dependent isotope fractionation of Hg during biotic degradation of methyl-Hg & reduction of Hg(II)

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The extent of fractionation of mercury (Hg) stable isotopes during 1) degradation of monomethyl-Hg (MMHg) via the mercury resistance (mer) pathway in Escherichia coli JM109/pPB117 and 2) Hg(II) reduction by three Hg(II) reducing strains, including a Hg(II) sensitive anaerobic strain, was investigated. It was found that MMHg and Hg(II) that remained in the reactors with microbes became progressively heavier (increasing δ²⁰⁴Hg) with time and underwent mass dependent Rayleigh fractionation with fractionation factors (δ²⁰⁴/²⁰⁵Hg)reactant-product of 1.0004 and 1.0016 ± 0.0005, respectively. We did not observe mass independent fractionation (MIF) and based on the nature of microbe-Hg interactions suggest that the nuclear spin dependent MIF is unlikely to occur during biological processes. Because of the important implications of the absence of MIF during biological processes on Hg isotope systematics, we will discuss experimental strategies that could be used to confirm this suggestion.

The mer mediated MMHg degradation is a multi-step process that involves two enzymes, organomercurial lyase (MerB) and mercuric reductase (MerA). The mer mediated Hg(II) reduction is also a multi-step process involving a dedicated Hg(II) transport system and MerA. We provide a multi-step framework for understanding the extent of fractionation seen in our MMHg degradation and Hg(II) reduction experiments and suggest which steps in the process could cause the observed extent of fractionation based on the biochemistry and kinetics of the various steps involved in the two mer mediated pathways. A clear effect of Hg(II) bioavailability on the extent of fractionation of Hg both during reduction of Hg(II) and degradation of MMHg via the mer pathway was observed and is also discussed. Knowledge of fractionation during individual steps, i.e., enzyme transformations, transport, adsorption, and diffusion, will further constrain the extent of Hg fractionation expected during various biotic processes. The framework provided in this study can guide future experiments on isotope fractionation during other transformations in the Hg biogeochemical cycle, including fractionation during Hg(II) methylation, and ultimately in the more rigorous development of Hg isotope systematics.
Evolution of planet-satellite system due to accumulation of dispersed material from protoplanet cloud

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Recently a hypothesis of the planet-satellite systems formation based on the concept of the rotational collapse of a gas-dust cloud with further growth of the planet embryos by accumulation of the dispersed material was suggested [1-3]. This hypothesis satisfies the geochemical constraints on the Earth and Moon composition, which can not be explained by the Giant Impact hypothesis.

In the presented lecture we investigate the third stage of the planet-satellite system formation, according to the mentioned hypothesis. A combined computational-analytical model of the system evolution is developed. First, the ratio of particles, captured by each body in a planet-satellite system is obtained from the computer simulation. This ratio is obtained as a function of the planet-satellite mass ratio. Then this function is used in the analytical model of the growth of the bodies due to the dispersed material accumulation.

The analysis of the presented model shows, that the greater body (the planet) grows much faster then the smaller one (the satellite). Both bodies are considered to be initially formed in the process of the rotational collapse of the gas-dust cloud. Therefore the high-temperature embryos of the planet and its satellite were equally depleted in iron and volatile elements. Later on, both the planet and its satellite acquired the colder material from the residual part of the cloud. However, the satellite accumulated little, maintaining the iron deficiency, whereas, the planet embryo collected the major fraction of the surrounding material, whereby the composition of the planet became closer to the composition of the cloud as a whole. These results are in a good correspondence with the current composition of the Earth-Moon system, were the Moon has considerably less volatile elements and iron then the Earth.


Quantum mechanical calculation of hydrogen isotope exchange thermodynamics and kinetics on organic compounds

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This study has used quantum mechanical methods to calculate the equilibrium isotopic fractionation factors, activation energies and rate constants for H-D exchange on various sites in alkanes. Both isolated alkane molecules and alkane + water exchange have been modeled. Results will be presented for the test system 2-methyl butane to predict the fractionation thermodynamics and kinetics at primary, secondary and tertiary C-H sites. Results on the biomarkers pristane and phytane will also be presented.

The advent of molecular-specific deuterium analyses has provided a powerful and precise means for evaluating organic hydrogen isotopic signatures and the fractionations associated with biological, environmental and geochemical processes. This advance has generated a surge of interest to establish molecular-specific $\delta$D values as indicators of paleoclimate. However, studies based on organic-rich sedimentary rocks have demonstrated that the $\delta$D signature of branched compounds shifts to more enriched values with increased thermal exposure. The equilibrium fractionation factors and kinetics of H/D exchange are not known for these reactions, so estimating these values will provide constraints on possible modifications of original $\delta$D values.

Test calculations for H-abstraction on methane suggest that the thermodynamics of these reactions can be computed to within an accuracy of a few kJ/mol. The activation energy barriers to these reactions have not been measured, so comparison to experimental values for alkanes is not possible at this time, but the thermodynamic accuracy indicates that the energy barriers should be reasonably accurate to estimate H-D exchange rate constants as a function of temperature. Equilibrium isotopic fractionations are calculated more accurately based on the theoretical frequency shifts of C-H bonds with D-substitution.

The results from this computational study can be employed to help interpret molecular H-isotopic data from preserved organic matter. Applications to paleoenvironmental studies will be discussed.
Carbon and hydrogen isotope effects in contaminant volatilization and phase partitioning – Implications for contaminant attenuation studies

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The standard practice in contaminant attenuation studies utilizing CSIA (compound-specific isotope analysis) is to attribute the observed isotope effects to degradative processes. Published data on isotope effects upon phase partitioning, volatilization etc. have suggested that these processes result with minor isotope fractionation and therefore they should not interfere with the isotopic signatures of degradation. Experimental results will be shown to demonstrate that pathways involving vapor phase transfer (experimental models were set for simulation of phase partitioning, passive volatilization and dynamic vapor extraction) are likely to result with measurable changes of isotope ratios in contaminants such as MTBE and benzene remaining in the aqueous or NAPL matrix. For processes involving unidirectional mass flux (e.g., vapor phase extraction), isotope fractionation can be described in terms of Rayleigh model, with cumulative isotope effects that increase with progressive mass removal. The enrichment factors of the studied non-degradative processes are lower than those resulting from most biotic or abiotic degradation processes. On the other hand, enrichment factors characteristic of a number of degrading organisms (e.g., some of the published carbon isotope enrichment factors of aerobic MTBE degraders) are low and similar in magnitude to those resulting from volatilization. The practical significance of the non-degradative interferences varies depending on the site context. The key elements are the type of contaminant and the degradation process (defining the magnitude of isotope fractionation attributable to \textit{in situ} degradation) and the relative significance of mass attenuation by degradative vs. non-degradative pathways. Evaluation of \textit{in situ} biodegradation for weakly fractionating compounds, in particular those with few sampling points and those utilizing only one isotope species (as opposed to 2-D CSIA) should take into account the potential for isotope effects caused by non-degradative attenuation. Adjustments to “traditional” protocols of CSIA data evaluation will be proposed to account for the isotope effects resulting from non-degradative processes.

Climate variability in the Mojave Desert over the past 43 ka

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Noble gas concentrations and oxygen isotopes in groundwaters from the western Mojave Desert, California contain a ~43 ka paleoclimate record denoting that mean annual temperatures in the late Pleistocene, during the period from ~43 ka BP to 12 ka BP, were 4.2 ± 0.8 °C cooler than from ~10 ka to the present day. Groundwaters recharged during the period from 43 ka to 12 ka BP also contain higher concentrations of excess-air (entrained air bubbles), enrichments in $^{18}$O. Interpreted ages from the dissolved inorganic $^{14}$C in the groundwaters were used to constrain the records.

Higher concentrations of excess-Ne (a proxy for ‘excess-air’) prior to 12 ka BP suggest more vigorous aquifer recharge, while enriched $^{18}$O/$^{16}$O ratios may indicate greater rainfall or more intense precipitation events during this period. Combined, these parameters provide evidence that the Mojave climate during the late Pleistocene was more humid than present-day arid conditions.

Taken together, the noble gas, oxygen isotope, and excess-air based paleoclimate archives proffer evidence that the Mojave desert of southern California was both cooler and wetter prior to the Last Glacial Maximum. More humid conditions may have resulted from an enhanced hydrological cycle throughout the southwestern United States, which is consistent with chemical, biological and geological evidence of extensive late Pleistocene pluvial lakes and lacustrine phase during this period.
Correspondences of helium isotope compositions between gabbros or abyssal peridotites with basalts: A view for heterogeneity inferred from the volcanics in uppermost mantle

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The heterogeneity of helium isotope compositions in uppermost mantle has been predicted from the extrusive volcanic facies, e.g. glassy chilled margin of basalts, or phenocrysts of the phylic basalts, in oceanic environment.

Correspondences of helium isotope compositions between gabbros or clinopyroxene separates from abyssal peridotites and near-site basalts has been reported [1, 2]. Even in the unusual area where basalts show low 3He/4He down to 6.3 Ra [3], clinopyroxene separates and a pyroxenite chunk also showed similar 3He/4He of 6.2 or 6.3 Ra [4].

Here we report two supporting observations. A laser probe helium isotope measurement applied to a single olivine grain of 8.0mg in weight. It was separated from a highly olivine-phryic alkaline basalt dredged at 10°53.5'E in the Joseph Mayes segment of Southwest Indian Ridge. It also showed phyric alkaline basalt dredged at 10°53.5'E in the Joseph Mayes segment of Southwest Indian Ridge. It also showed ~6Ra of 3He/4He under 10% contribution of blank correction. Thus, such low 3He/4He has been confirmed as a certain isotope signature reflecting mantle heterogeneity; it comes from the mantle source via magma chamber throughout the basaltic lava erupting in the area.

As another example, two aliquots of gabbro section of drill cores have also been selected. The drill core obtained in IODP Exp.304/305 on Atlantis Massif. The conventional step-heating method were applied them. They showed 8.2 and 8.8Ra of 3He/4He, respectively, which is well within the range of 3He/4He variation of the ridge-axis samples.

Experimental research of casing cement alteration by interaction with supercritical CO₂ for geological sequestration

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In CO₂ geological sequestration, the most important thing is to prevent leakage of CO₂ from the reservoir. The alteration of the casing cement by exposed supercritical CO₂ may cause the leakage of CO₂. The purpose of this study is to know the influence of alteration degree by supercritical CO₂ between the casing cement–sandstone interface.

Experimental specimens are composed of Berea sandstone and oil well cement. The sandstone is prepared in the form of cylinder (25 mm in diameter and 90 mm in length) with a drilled hole (7 mm in diameter) at the center. Then oil well cement is solidified in the hole. The experimental specimens and solution are set in reaction cambers. Two kinds of solutions are prepared (distilled water and 3% NaCl solution). Then the chambers are backfilled with CO₂. The temperature and pressure in the cambers are kept at 60°C and 10MPa, respectively, during experiments (3 or 9 weeks). In these conditions, CO₂ exists as supercritical fluid. After the experiments, the specimens are examined by microscopic observation and analyzed by SEM-EDS and XRD.

In all experimental specimens, mineral precipitation was observed in the pores of sandstone at 0.6-0.8mm far from the interface of the cement. The precipitation was identified as aragonite and calcite.

This short period experiment result implies that carbonate mineralization in the pore of sandstone near cement might disturb flowing of CO₂ and water in the reservoirs and that the cement degradation may be constrained. There is an possibility that the carbonate minerals precipitated in the pore could be dissolved due to continuous interaction with acide brine and that the long period experiments must be done.

Residual strain and domain orientation in quartz

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Quartz commonly exhibits undulatory extinction when examined with a polarizing microscope with crossed polarizers. This effect is known to be caused by fragmentation of the single crystal into domains separated by dislocation walls and showing some degree of rotational disorder around the c-axis. This domain structure is attributed to deformation in a non-hydrostatic stress field. In this case, quartz crystals showing these optical effects might exhibit some residual strain, up to the maximum elastic limit.

We performed Laue X-ray microdiffraction on several quartz samples using the micro-diffraction beamline 12.3.2 of the Advanced Light Source at the Lawrence Berkeley Laboratory [1]. The experiments were done with a 1 x 1 µm white (5 keV < λ < 22 keV) X-ray beam with spatial resolution between 5 and 25 µm. We document significant residual strain in quartz crystals in stishovite-bearing rocks from the Vredefort meteor impact crater in South Africa and granite adjacent to the Santa Rosa mylonite zone in Southern California.

The residual strain, expressed as equivalent strain ε' = \sqrt{ε_{11}^2 + ε_{22}^2 + ε_{33}^2}, reaches mean values around 5 x 10⁻³ with a distribution maximum around 1.5 x 10⁻³ in the Venedefort sample. This is an order of magnitude higher than the strain measured in a hydrothermally grown synthetic single crystal. Furthermore, the amount of equivalent strain measured seems to anticorrelate with the fragmentation of the individual crystals. The fragmentation, as evidenced by the number of sub-peaks a given Laue spot envelope is comprised of, is observed on a sub-micron level in the shocked quartzite. The quartz grain from the unshocked Santa Rosa granite sample shows single crystal fragments of several 10’s of microns in size.

The orientational variation between domains within an undulatory grain shows an amplitude of about 3 degrees.

REE distribution in the Mesoproterozoic uranium-bearing sandstones from the Karku deposit (NW Russia)

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The main subject of the study is relationship between U and REE content in the sandstones drilled from the Karku unconformity-type deposit. Three groups of sandstones are identified according to alteration grade and uranium content: 1) low-grade (with 0-5 ppm of U content), moderately-grade (5-100 ppm) and high-grade (above 100 ppm).

Total REE content shows significant variation (from 10 ppm to 430ppm) both within the individual wells and between them. All the analyzed samples display LREE enrichment relative to HREE with flat to slightly depleted HREE patterns and variable Eu-anomalies. Eu-enrichment is typical for low- and moderately-grade altered sandstones and Eu-depletion in high-grade altered sandstones. The average REE content and calculated ratios are given in table.

<table>
<thead>
<tr>
<th>Low-grade</th>
<th>Moderately-grade</th>
<th>High-grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>∑REE</td>
<td>110</td>
<td>154</td>
</tr>
<tr>
<td>La/Lu</td>
<td>131</td>
<td>133</td>
</tr>
<tr>
<td>La/Sm</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Eu/Eu*</td>
<td>0.93</td>
<td>1.14</td>
</tr>
</tbody>
</table>

U show positive correlation with LREE (0.80), but not with HREE.

Sandstones are divided into groups in accordance with predominant secondary mineral content: hematite-chlorite bearing, carbonate-bearing or clay-bearing show averaging in the REE content and calculated ratios. However, only clay-matrix sandstones display LREE enrichment comparable with that in highly altered sandstones.

26Al-26Mg systematics and petrological study of chondrules in CR chondrites

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Chondrule formation ages have been obtained from primitive chondrites (type 3.0-3.1) using 26Al-26Mg systematics (a half life 0.73 Ma), ranging 1-3 Ma for L, LL and CO [1-3], and 2-4 Ma for CR chondrites [4] after CAI formation with the initial 26Al/27Al of 5×10^-5. Detailed petrological study, however, reported that even type 3.0 chondrites show lower grade metamorphism [5]. In order to evaluate if the 26Al-26Mg systematics were disturbed after the formation of chondrules, we examine isotopic and petrological study of plagioclase of chondrules from CO3.05 [6] and CR2 chondrites.

Manganesium isotopic compositions of plagioclase were measured in three type I chondrules from CR2 chondrites, Yamato-793495 and Yamato-790112 using the Cameca ims-1270 SIMS. One of three type I chondrules show 26Mg-excess corresponding to the initial 26Al/27Al ratio of (5.2±2.1)×10^-6. For the other chondrules, we obtained the upper limit of the initial 26Al/27Al of < 7.8×10^-6 and < 1.3×10^-6. The relative age of the chondrules would be 2.4(-0.4/+0.6) Ma, > 2.0 Ma, and > 3.3 Ma, respectively, with the initial 26Al/27Al of CAI, 5×10^-5. These results are consistent with those obtained from other CR chondrites, which indicate slightly later chondrule formation relative to ordinary and CO [4]. We examined elemental distributions in plagioclase by line-analyses with EPMA, and found that some plagioclase grains in the CR chondrules show chemical zoning in terms of MgO. The zoning patterns of MgO and its high abundance (0.8-1.0 wt%) in plagioclase would be due to crystallization at high temperature. Therefore, we concluded that lower initial 26Al/27Al ratios in these chondrules are primary.

Glacial-interglacial cycles of the atmospheric $pCO_2$: Effects of physical change in the ocean

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It is well known that, at the Last Glacial Maximum (LGM), the atmospheric $CO_2$ pressure, $pCO_2$ hereafter, was 80-100 ppm lower than the pre-anthropogenic value. We have performed some numerical experiments by using an ocean general circulation model (OGCM) coupled with biogeochemical processes to evaluate quantitatively the effects of changes in various conditions upon an oceanic carbon cycle and $pCO_2$.

We have investigated the effect of various changes in physical conditions of ocean (the circulation field, temperature, salinity, and the sea-ice extent) on $pCO_2$ by numerical experiments. We consider several model-ocean physical-fields which are based on reproduction by an atmosphere-ocean coupled general circulation model (MIROC3.2). We found that, if a LGM physical ocean field reproduced by MIROC3.2 was assumed, $pCO_2$ was lowered by ~30 ppm compared to the interglacial value. Most of the 30 ppm reduction can be explained by higher solubility of $CO_2$ into the ocean due to the glacial lower sea-surface temperature. In particular, the reduction in sea-surface temperature in the North Atlantic had a greatest effect. On the other hand, the effect of change in the circulation was small. This would be because the variation in physical $CO_2$ transport to the deep ocean and biological counterpart induced by the circulation change would offset each other. We also found that the effect of sea-ice expansion in the Southern Ocean was trivial resulting in only a several ppm reduction in $pCO_2$ (also see [1]). Furthermore, if we assumed other model ocean physical fields, the effect of the solubility change was still dominant.


Geochemistry and geochronology of Gaima Basaltic Lava Plateau, Northeast China

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We report comprehensive data set of major and trace element compositions, Sr, Nd and Pb isotopic compositions, and K-Ar ages of the Gaima basaltic lava plateau in Changbaishan area, northeast China. The lava plateau has been formed as intraplate volcanism on the Sino-Korean Paraplatform since Cenozoic time, and Tianchi Volcano is now active on the plateau.

Rock samples used in this study were collected mainly from the northern and the western part of the lava plateau. All samples are basaltic in composition, but the K2O contents are various, ranging from 0.5 to 2.5 wt%. The trace element concentration pattern of the lavas is characterized by positive spikes of Ba and Pb. The isotopic compositions are relatively homogeneous, falling within the ranges of $87Sr/86Sr = 0.7048-0.7055$, $143Nd/144Nd = 0.5125-0.5126$ and $206Pb/204Pb = 17.4-17.8$, and are similar to those reported by Basu et al. [1].

The K-Ar ages of the studied samples (n=13) range from 0.5 to 4.2 Ma, except for one sample (20.7 Ma). The result of the age dating indicates that some activities of the northern and western Gaima plateau were contemporaneous with the formation of the Tianchi basalt shield (<2.8 Ma; [2]).

No significant spatial variation of the geochemical features is found. On the other hand, weak temporal variations are observed, and it seems that Sr and Pb isotopic ratios tend to become more various from ~4 Ma to ~0.5 Ma. The variations might have resulted from gradual changes of mantle processes due to the transition of tectonic environment from extensional to compressional at ~3 Ma [3].

Geochemical implications of basaltic products from Develidag volcanic complex, Central Anatolia, Turkey

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Extensive magmatic activity was developed at Develidag volcanic complex which is situated at the southeastern part of Kayseri in central Anatolia. Volcanic complex is dominated mostly by Basalts, Basalticandesites, and associated with minor amount of Andesites. During the volcanic episodes, develidag has undergone different types of development processes.

Basaltic products of volcanic complex are represented by low LIL (Rb, K, Ba, Th) and high HFS (Nb,Zr,Hf,Y) element contents whereas andesites generally have high both LIL and HFS values except Nb and Zr. Variable amount of Pb (3.11-12.09) and U (0.36-2.64) is also observed associated with relatively high Ba content within the rocks suites. Although low Nb/La (0.6-0.7) and relatively high Ba/Nb ratios indicate the crustal involvement for the basalts, high Zr/Ba (0.5), Zr/Hf (42-47) relatively high Nb/U (27-32), Th/U (3.13-4.69) ratios imply the contributions from the asthenospheric source component. Furthermore, such a high values of Zr/Hf is the indicative of primitive mantle source. (>36, [1]) Primitive mantle normalised spidergrams exhibit that develidag basalts have similar trace element signature that those of the Columbia River Tholeiites(CRT), Steens Mountain Flood Basalts (USA), Rio Grande Rift Axis products and Lassen region calc-alkaline basalts for Cascades range. Andesites have similar trace element patterns that those of Central and Eastern Anatolian calc-alkaline products and Central American (El Salvador) basalts.

Zr/Hf, Zr/Ba, Nb/Th, Sr/Sc Th/U ratios indicate N-Type MORB mantle source for the generation of basaltic products. Basalts and basalticandesites seem to be derived from a spinel peridotite source via partial melting whereas andesites reflect subduction signature, Nb/La, Ba/Nb incompatible element ratios express more or less crustal involvement. Although the melting model that indicates generation from a spinel peridotite source (% 3-4 melting), is not the unique process responsible for the magma extraction, the ongoing effects of AFC process seem to be responsible for the relatively evolved product as well as the melting issue, in such a complex tectonic setting. Typical tholeitic calc-alkaline associations are also observed among the volcanic products as a consequences of either melting process and crustal involvement or changing of the rate of melting degree. Furthermore, the lack of alkali products that is conventionally observed at final stage of many central Anatolian volcanic centers, seems to be attributed to either the lack of extensional development or deficient extensional rate before the late miocene.


Experimental research of plagioclase-gas-water interaction at hydrothermal conditions caused by CO2 sequestration

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Underground disposal of CO2 have been proceeded in the world, where a part of the CO2 can be dissolved into brine and react with surrounding rocks to form carbonate minerals. The rates of this gas-water-rock(mineral) interaction are mainly controlled by temperature and the pH and salt concentrations of the brine. In this paper, plagioclase such as anorthite was reacted with CO2 saturated water at hydrothermal temperature to examine the reaction rates of carbonate mineralization and to apply for CO2 sequestration into relatively high temperature fields in Japan.

Outline of Experiments

The experiments have been performed with crushed anorthite (7g; grain size is 05 to 2mm) and Kyoto tap water (70ml). They were enclosed with CO2 (10MPa) or N2 gas after evacuating in a teflon reaction container and heated up to 150 in an electric furnace with rotation (1 rpm). After 1 to 15days, the solutions were analyzed for their chemical compositions and mineral surfaces were observed by SEM-EDS.

Results

The concentration of Ca in the solutions reacted with CO2 quickly increases within 1 day and is ~50mg/L higher than those without CO2 (with N2 gas). The saturation index shows that the solutions with CO2 are saturated with respect to carbonate such as calcite and aragonite during the reaction. In these samples, calcite was observed on the anorthite surfaces by SEM-EDS and other mineral such as kaolinite were not identified. These results indicate that Ca can be released from rocks (silicates) easily and might be removed as CaCO3 during CO2 sequestration into relatively high temperature (geothermal) fields. Also, Ca-rich plagioclase (anorthite) is a good potential of CO2 fixation as carbonate.
PGE and Os and Nd isotopes from the Oman Ophiolite: Implications for MANTLE Heterogeneities

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This study investigates mantle heterogeneities introduced by melt percolation and refertilisation processes via silicate and sulphide melts. Os isotope ratios of peridotites from the Oman ophiolite cover a wide range from highly unradiogenic to radiogenic values. The most unradiogenic harzburgites \(\frac{^{187}Os}{^{188}Os}(t = 90\text{Ma}) = 0.1149\) and \(0.1169\) yield Re depletion ages of \(~2\text{Ga}\). They represent the most depleted members of oceanic lithosphere (e.g. \(Yb_N\) (cpx) \(~1.1\); \(Ti_N\) (cpx) \(~0.3\)), (Pd/Ir)\(_N\) ratios of \(< 1\). Rare sulphides (Pn and minor Cp) with grain sizes ranging from 10-60 \(\Phi_m\) are associated with opx or olivines. The remaining residual harzburgites \(\frac{^{187}Os}{^{188}Os}(t = 90\text{Ma}) \sim 0.124\) have broadly chondritic relative PGE abundances with the exception of high Pd/Ir\(_N\) and positive Pd anomalies. These samples have sulphides which occur typically as interstitial, subhedral or anhedral grains with curvilinear boundaries. The grains sizes frequently range up to 400 \(\Phi_m\) and the sulphides are closely associated with spinel and/or cpx. A second type of samples belongs to a non-residual group comprising cpx- and plag enriched peridotites, dunites and pyroxenitic dikes. These samples are characterized by melt-type low PGE abundances with the exception of high Pd/Ir\(_N\) and positive Pd anomalies. These samples have sulphides which occur typically as interstitial, subhedral or anhedral grains with curvilinear boundaries.

Geochemical processes including sorption and incorporation of heavy metals and arsenic by scoria and steel slag

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Kinetic and equilibrium sorption experiments on scoria from volcanic cones of Jeju Island and steel slag (basic oxygen furnace slag: BOFS) from the Pohang Iron & Steel Works, Korea, were performed to investigate the geochemical processes affecting the removal of heavy metals (Pb(II), Cu(II), Zn(II), Cd(II)) and arsenic (As(III)) from aqueous solutions. The scoria is vesicular and consists of forsterite, pyroxene, labradorite, hematite and traces of clay minerals. The BOFS is massive and comprises free lime, calcium silicates, calcium iron aluminum oxide, and magnetite.

Batch-type kinetic sorption tests showed that removal efficiencies of heavy metals (except Pb(II)) and arsenic were generally slightly higher for BOFS than scoria. However, hydration of the slag material resulted in a relatively high pH (>11) in solutions. The observed changes of ionic concentrations during sorption suggested that geochemical removal of heavy metals was mainly caused by cation exchange for scoria and the precipitation as metal hydroxides for BOFS. In contrast, arsenic removal appeared to result from the physical adsorption onto hematite (for scoria) and calcium-arsenite precipitation (for BOFS). The results from sorption kinetic experiments fitted better to a pseudo-second-order sorption model than to a first-order model (i.e., Lagergren equation). The equilibrium sorption tests showed that at alkaline pH conditions the removal of heavy metals by scoria was enhanced by precipitation as hydroxides due to an increase in pH. In a multi-component solution containing heavy metals and arsenic, the arsenic removal efficiency increased with increasing pH, which can be attributed to the coprecipitation of As with metal hydroxides. The equilibrium sorption of heavy metals onto scoria was consistent with the Langmuir isotherm, while that of arsenic followed the Freundlich isotherm.
Mineralogical controls of acid generation and metal leaching at contrasting sedimentary exhalative sulphide deposits in the Yukon Territory, Canada

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The Anvil District and the Howard’s Pass area of respectively central and southeastern Yukon Territory, Canada, are renowned for their stratiform Zn-Pb deposits. Both camps are located within the Selwyn Basin and the prevalent Zn-Pb deposits are all interpreted to be sedimentary exhalative (SEDEX) in origin. The Anvil deposits are pyrite-rich and have undergone significant regional and contact metamorphism. Recrystallization during metamorphism has resulted in an increase in average grain size and the conversion of the associated carbonates into calc-silicates and some of the pyrite into pyrrhotite. These have in turn effected a reduction in acid buffering capacity and a partial enhancement of sulphide reactivity in the host rocks, which are not fully compensated for by a decrease in specific surface area derived from the coarser grain size. Consequently, acid mine drainage and metal leaching have plagued the mining development both during active mine operation and site decommissioning. In contrast, the Howard’s Pass deposits contain less pyrite (25%) and exhibit well-preserved sedimentary structures. The abundance of carbonates within and surrounding the sulphide deposits provides most of the country rocks with an inherent acid neutralization potential. Limited metal leaching (mainly zinc and cadmium) in the mineralized zones occurs as a result of galvanic interaction among the prevalent sulphide minerals. Natural acid rock drainage has been observed only in overlying black shale units with little carbonates. Given the differences in detailed mineralogy and sulphide oxidation mechanisms, it would appear that the Howard’s Pass deposits could be exploited with less significant environmental impacts than the Anvil deposits if proper planning and precautionary measures are taken.

Variations in $^{238}U/^{235}U$ ratios in natural uranium ore minerals from sedimentary basins

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Current investigations indicate that uranium isotopes fractionate as a result of nuclear volume effects predicted by Bigeleisen in his initial calculations of natural isotopic variations in minerals [1]. More recently, it has been suggested that $^{238}U/^{235}U$ ratios will vary as function of uranium oxidation state and will be the highest in reduced species [2].

Uraninite from sedimentary basins is susceptible to recrystallization, reprecipitation and alteration to a variety of secondary uranium minerals that are often produced by interaction with oxidizing fluids. This interaction should therefore be reflected in the observed $^{238}U/^{235}U$ ratios.

The $^{238}U/^{235}U$ ratios of uranium minerals from sandstone-hosted and calcrete-type uranium showings and deposits worldwide have been measured by multi-collector ICP-MS (Neptune) and reported relative to uraninite from the McArthur River unconformity-related deposit in Saskatchewan, Canada. The total variation of the $\delta^{238}U$ values during measurement of the in-house standard is ±0.15 per mil, whereas the total variation of $\delta^{238}U$ values for uranium minerals is 1 per mil. As predicted, uraninites with the lowest apparent ages, and have suffered repeated recrystallization [3], have the highest $\delta^{238}U$ values as a result of $^{235}U$ loss during interaction with oxidizing fluids. Additionally, more oxidized secondary minerals have lower $\delta^{238}U$ values. In conjunction with Pb isotopes and uraninite geochemistry, uranium fractionation could potentially be used in the study of uranium deposits and as an exploration tool.