Molecular investigation of electron transfer mechanisms involved in microbial selenate reduction

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Background

Microorganisms inhabiting selenium contaminated sediments are able to reduce dissolved selenate oxyanions to sparingly soluble elemental selenium. The reductive precipitation of selenium by Se-reducing bacteria has been proposed as a potential bioremediation strategy. However, in order to employ Se-reducing bacteria for practical bioremediation purposes, reliable models must be developed to predict microbial behavior, including when they are active, what mechanisms are involved, and under what conditions the mechanisms function. In this study, we demonstrate that anaerobic electron carriers play an essential role in governing the activity of a Se-reducing bacterium.

Methods

Transposon mutagenesis was used to generate mutant strains of Enterobacter cloacae SLD1a-1 that have lost the ability to reduce selenate. We characterized a mutant strain designated as 4E6 that was defective in selenate reduction activity. Genomic libraries of SLD1a-1 and 4E6 were constructed to clone the mutated operon that resulted in the loss of selenate reduction activity. Sequencing of the operon containing the transposon was obtained by restriction mapping and primer walking. Selenate reduction activity of wild-type and mutant strains were quantified using batch kinetic experiments. Finally, the ability of menaquinone analogues and precursor compounds to rescue the selenate reduction activity was tested.

Results and Discussion

Mutagenesis experiments showed that mutation of the menD gene in the menaquinone biosynthesis operon produces derivative strains that are deficient in selenate reduction activity. Complementation by the wild-type sequence and menaquinone analogues restored the ability of mutant strains to reduce selenate. Menaquinones are small lipid-soluble molecules that act as electron shuttles in the bacterial electron transport chain. The biosynthesis of menaquinone occurs under oxygen-limiting conditions, and is known to mediate anaerobic respiration of alternate electron acceptors. The results of this study indicate that anaerobic electron carriers are required for microbial selenate reduction.

Atmospheric noble gas signatures in deep Michigan Basin brines as indicators of a past thermal event

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Atmospheric noble gases in crustal fluids are introduced into the subsurface by recharge water in solubility equilibrium with the atmosphere (air saturated water - ASW). Because \(^{22}\text{Ne},^{36}\text{Ar},^{84}\text{Kr}\) and \(^{130}\text{Xe}\) are conservative in nature and are not produced in significant amounts by natural nuclear reactions in the crust, these isotopes in groundwater are only sensitive to subsurface physical processes. These include oil-gas-water phase interactions, as well as the occurrence of boiling and steam separation. Atmospheric noble gases can thus provide precious information with respect to the origin and evolution of subsurface fluids and thus, to the tectonic and thermal evolution of particular areas.

Here, we present \(^{22}\text{Ne},^{36}\text{Ar},^{84}\text{Kr}\) and \(^{130}\text{Xe}\) concentrations of 38 deep (down to ~3.6 km depth) brines from the Michigan Basin. These show a strong depletion pattern with respect to ASW. Depletion of lighter gases (\(^{22}\text{Ne},^{36}\text{Ar}\)) is stronger as compared to the heavier ones (\(^{84}\text{Kr},^{130}\text{Xe}\)). To understand the mechanisms responsible for this overall atmospheric noble gas depletion, conceptual phase interaction models were tested. While oil-water and gas-water interaction models could not, under reasonable assumptions, explain both the extent and the observed depletion pattern, the opposite is true with a model involving subsurface boiling and steam separation. Indeed, the latter not only explains the overall observed atmospheric noble gas depletion pattern, it also points strongly to the presence of a past thermal event. This finding is consistent with the presence of primordial solar-like He and Ne signatures in the basin previously identified in these same brines, and suggest a mantle origin for the occurrence of this thermal event. Such a boiling and steam separation model is also consistent with the presence of past elevated basin temperatures (e.g., >80-260°C) at shallow depths as suggested by numerous previous studies in the basin. We suggest that recent reactivation of the ancient mid-continent rift system underneath the Michigan Basin is likely responsible for the release of both heat and mantle noble gases into the basin via deep-seated faults and fracture zones. While heat has already escaped the system, such a thermal event can be still traced by the presence of the observed atmospheric noble gas depletion.
**Importance of carbonaceous materials on sorption of phenanthrene by sediments**

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Increasing studies indicate strong sorption of hydrophobic organic contaminants (HOCs) to carbonaceous materials such as black carbon (BC), coal, and kerogen in soils and sediments, which is possibly the reason for recent observations of elevated geosorbent-water distribution ratios, slow desorption, limited uptake, and restricted bioremediation. We evaluated the role of environmental BC and coal-like materials in the sorption of phenanthrene to polluted sediments from Hudson River and Baltimore Harbor, and tried to predict the fate and transport of PAHs and HOCs that are currently introduced to aquatic systems.

Organic petrographic analysis and wet chemical extraction method indicated that carbonaceous particles primarily composed of coal, coke, charcoal, soot, pitch, cenospheres, and wood. In the sediments, carbonaceous particles contributed 3-9% of the total mass and 60-90% of the PAHs.

Sorption isotherms of phenanthrene were determined for the original sediment (with organic matter, native sorbates, and BC), sediment from which >90% of the native sorbates were stripped (only OM and BC), and sediment combusted at 375 °C (only BC). It is shown that nonlinear sorption to carbonaceous materials can completely dominate total sorption of PAHs. The sorption isotherms of the original and stripped sediments were almost linear (Freundlich coefficient or $n > 0.9$), whereas the isotherm of the BC remaining after the sediment combustion was highly nonlinear ($n = 0.55$).

Phenanthrene sorption to BC in the combusted sediment was found to exceed the total PHE sorption in the original and stripped sediments. Competition between the added phenanthrene and the native PAHs and/or OM may explain this difference. This implies that it may not be possible to use a BC-water sorption coefficient measured in combusted sediment to estimate total sorption to the original sediment. Because sorption is a central process affecting contaminant behavior and ecotoxicity, understanding this process can strongly contribute to risk assessment and fate modeling.


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**Pelagosome climate record and the role of cyanobacterial biomineralization**

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Pelagosome is a dark, shiny, pisolithic mineral encrusting rocky coasts exposed to sea spray. X-ray diffraction and optical microscopy showed that pelagosome is aragonite with 2-3 micron thick alternating dark-light laminae. Assuming that the laminae represent yearly accretions, we produced time series through sections several hundred microns thick. Fourier transform power spectra show frequency peaks that match El Niño Southern Oscillation, North Atlantic Oscillation, and solar spot cycles. Power spectra are also consistent with instrumental climate data (yearly precipitation and mean annual temperature) continuously recorded at one of the sample sites since 1859. We conclude that pelagosome is a precise geochronometer for assessing neotectonic movements of rocky coasts, and a faithful recorder of Holocene climate cycles. A potential role for biology in the precipitation of pelagosome crusts is suggested by its growth on carbonate rocks with strong chemical corrosion textures. Molecular biological analyses of pelagosome crusts indicate that they are intimately associated with *Xenococcus*, a poorly known cyanobacterial genus previously found to colonize rocks in the littoral zone of California. A role for *Xenococcus* metabolism and/or cell surface chemistry in nucleating aragonite is suggested by previous studies of carbonate biomineralization, and is currently under investigation using microbial culturing, natural abundance stable isotope analyses, electron microprobe analysis, and synchrotron-enabled approaches including Scanning Transmission X-ray Microscopy (STXM).
Removal of radionuclides into biogenic metal phosphate matrices: A novel remediation strategy

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Bacteria can deposit crystalline metal phosphates via enzymatic hydrolysis of supplied phosphate esters. Uranium, plutonium, neptunium and americium can be immobilised in this way. Pu removal is expedited in the presence of a ‘priming’ deposit of another biogenic phosphate. This can comprise lanthanum phosphate (LaPO4) or hydrogen uranyl phosphate (HUP: HUO2PO4.4H2O) which facilitate Pu and Np removal. HUP is also an excellent ion exchange material for removal of 90Sr, 137Cs and 60Co and the former can also be co-crystallised enzymatically along with with HUP. For treatment of contaminated natural waters HUP is undesirable due to its chemical and radiotoxicity. Zirconium phosphates (ZrP) have been documented to have a similar ion exchange function. Application of the enzymatic manufacturing method synthesised a biogenic ZrP material that had a capacity similar to chemically produced α-Zr(HPO4)2 for Sr2+ and 7-fold greater for Co2+. The hydrolysable phosphate donor for ‘proof of principle’ was glycerol 2-phosphate but commercial use of this at large scale would be uneconomic. Phytic acid (inositol phosphate) is an attractive alternative since it is a plant storage material which is very widespread in soils and subsurface. Phytic acid contains 6 mol phosphate/mol, i.e. one phosphate group per carbon (as compared to 1:3 for glycerol 2-phosphate) and the waste carbon would pose less of an environmental burden. Bacterial phytases are widespread in nature. We will report on the potential for a ZrP-based remediation system made using bacterial phytase activity: a novel application for this enzyme.

Insights into the kinetics of acid corrosion reactions from direct analysis of surface morphology

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A quantitative understanding of corrosion reactions and their inhibition is critical in diverse problems involving the environmental impacts of waste disposal, catalysis, water treatment, and remediation of organic contaminants in groundwater. Conventionally, corrosion rate measurements have been accomplished by electrochemical techniques, e.g., double layer capacitance calculations from fitting of impedance spectra (Nyquist or Bode plots) to circuit models of the reactive interface (ac methods), calculation of corrosion current density from Tafel plots and linear polarization resistance (dc methods), as well as other (e.g. gravimetric change over time) methods. Integration of these methods permits straightforward comparisons of corrosion rate and evaluation of corrosion inhibitor efficiency [1]. However, in these various approaches the effects of surface heterogeneities that influence corrosion rate (i.e. surface defect density, impurities distributions, grain boundaries) are not directly analyzed and thus often incorporated as uncertainties within a given parameterization or the corrosion constant. In addition, calculation of corrosion rate from corrosion current may also involve problematic assumptions regarding sample surface area and the uniform distribution of corrosion rate. These assumptions may in turn result in underestimation of localized corrosion kinetics and their environmental significance.

In this unique study we combine information from electrochemical corrosion studies with direct measurement of acid corrosion rates using vertical scanning interferometry. This approach permits accurate resolution of surface kinetics and distribution of corrosion rates over significant areas of the metal surface. In addition, we adapt surface roughness parameters and convergence analysis [2] to characterize the intensity and distribution of corrosion reactions.

Mobility and fluid/melt partitioning of heavy metals in silicate liquids: Implications for magma degassing

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The volatilization of Cd, Re, Tl, Pb, Sb and Te from melts in the system CaO-MgO-Al₂O₃-SiO₂ has been investigated at 0.1 MPa and 1200-1350°C. Analysis of quenched glasses normal to the melt/gas interface produced concentration profiles for Cd, Re, Tl, Pb, Sb and Te to which a semi-infinite one-dimensional diffusion model could be applied to extract diffusion coefficients (D). At 1300°C, the fastest diffusing element was Cd having a logD_{Cd} = -6.5 ± 0.2. The slowest element was Re with logD_{Re} = -7.5 ± 0.3. Diffusivities of Sb, Te, Pb and Tl have intermediate values where logD_{Sb} = -7.1 ± 0.1, logD_{Te} = -7.2 ± 0.3, logD_{Pb} = -7.1 ± 0.2, logD_{Tl} = -7.0 ± 0.2 cm²/sec.

Fluid/melt partitioning was also measured in the system CaO-MgO-Al₂O₃-SiO₂-H₂O-Cl between 1200 and 1400°C at 1GPa. Mass balance calculations were used to calculate K_{d, fluid/melt}. In experiments where the fluid was only H₂O, K_{d, fluid/melt} for Re and Mo were 3.6 and 7.6 respectively. Addition of Cl greatly increased metal partitioning into the fluid where all Re and Mo partitioned into the fluid which, by using the detection limit in the glass as a lower limit, yields a minimum K_{d, fluid/melt} for Re and Mo that exceeds 400. Pb, Tl and W also partitioned into the fluid when Cl was present having K_{d, fluid/melt} of ~10, 8 and 4 respectively. Experiments have also been carried out to determine any dependence or K_{d, fluid/melt} on the fluid composition.

Differences in diffusivity of volatile heavy metal ions to a melt-gas interface lead to significant fractionation between these metals in magmas during degassing. Given the observed differences in Cd, Re and Sb diffusivities, our modelling predicts an increase in the normalized Cd/Re and Cd/Sb ratio in the gas phase with increasing bubble growth rate and during pre-eruptive degassing. Natural data from Kilauea support our model. Monitoring of the Cd/Re or Cd/Sb ratios in aerosols from degassing volcanoes may provide a tool for predicting volcanic eruption.

Scanning transmission x-ray microscopy (STXM) in biogeochemical environments

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In natural environments bacteria cell walls and extracellular structures transform the bacteria – solution interface into a highly heterogeneous environment that can promote mineral formation inside, outside or even some distance away from the cell surface. Understanding how microbes influence the nucleation of minerals and amorphous precipitates is important to understanding the cycling of trace elements in low-temperature environments. In addition, the nucleation of minerals at the cell surface can lead to entombment and eventual fossilization of the cell. Thus, understanding how microbes affect nucleation processes is also important in astrobiology.

In order to determine sites of nucleation associated with bacteria cells direct observations of the chemistry of the cell-mineral interface is required. Scanning transmission X-ray microscopy (STXM) combines the chemical contrast and chemical sensitivity of NEXAFS with a high spatial resolution X-ray microscopy to provide a way to investigate the chemistry of microbial cells to identify sites of mineral precipitation. In this study, STXM is used to investigate the role of biogenic structures in the nucleation of precipitates in biogeochemical systems.
Short length-scale compositional heterogeneity in basalts and their mantle sources

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Detailed studies of a number of volcanic systems in Iceland have found significant variation in the trace element and isotopic composition of basaltic whole-rock samples. Limited compositional heterogeneity is present in whole-rock samples from individual flows. However, neighbouring flows commonly have significantly different trace element and isotopic compositions. Flows with ages that differ by <10 kyr and whose eruptive vents are separated by less than 15 km show a range in trace element composition that is comparable to the total variability observed in samples from the Icelandic Rift Zones. Olivine-hosted melt inclusions from individual flows also show significant trace element and isotope heterogeneity. Inclusions from the Hvaleyabunga picrite of SW Iceland show a spread in $^{208}\text{Pb}/^{206}\text{Pb}$ that covers >50% of the total range observed in Atlantic MORB. This observation indicates that large amplitude compositional heterogeneity is present within the mantle source regions of an individual eruption. The coincident trace-element and isotope trends of melt inclusion and whole-rock data from the individual volcanic systems confirms a common origin of compositional heterogeneity for melt inclusions and whole-rock samples. The melt inclusion compositions can be reproduced by mixing between the two extreme inclusion compositions.

Fractional melting of compositionally heterogeneous mantle is predicted to generate a large range of melt compositions, filling a large volume in trace element and isotopic compositional space. However, the observed trends lie along mixing lines in such a space. At a fixed isotopic composition, the range in observed trace element ratios is limited. The melt inclusion compositions cannot, therefore, reflect the full range of melt composition generated in the melting region under Iceland. Their composition is dominated by mixing between two extreme melts. These observations may be accounted for by mixing during channelised flow of melt in the mantle. The depleted endmember melt is produced in the shallow parts of the melting region, while the enriched endmember is itself produced by mixing in channels of melts generated over a range of depths. The distribution of isotope compositions of MORBs is therefore controlled by melt mixing at the local scale and does not reflect the distribution of compositional heterogeneity in the upwelling mantle.

Origin and evolution of adakites and high Mg# andesites in the East Philippine Arc

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The Philippine Trench marks a nascent plate margin where subduction initiation is propagating from north to south. The East Philippine Arc, which is part of this margin, has generated adakitic and high Mg# andesitic rocks and provides a unique natural laboratory for determining the origin of these magma types.

In the immature southern arc, magmatism is dominated by a continuous spectrum of compositions from high-Mg andesite to adakitic dacite and rhyolite. Isotopic ratios and most incompatible trace element ratios of this suite are indistinguishable from contemporaneous calc-alkaline magmatism [1]. These similarities point to derivation from similar sources i.e. melting of metasomatised mantle wedge. Rare earth elements, notably Dy/Yb ratios, suggest that high Mg# andesitic and adakitic compositions developed through differentiation of hydrous basaltic magma at >30km depth, where garnet is stable. In the southern East Philippine Arc, where arc crust is thin, this represents sub-Moho depths.

Adakitic rocks also occur in the northern East Philippine Arc but are less common than those produced by low-pressure differentiation of hydrous basalt. This suggests that the magma plumbing systems beneath volcanoes in the more mature part of the arc resemble those found beneath most other subduction zone volcanoes.

The transition from adakitic and high Mg# andesitic magmatism to more typical arc magmatism is interpreted as a record of thinning of arc lithosphere as it is thermally eroded from below. Lithosphere is thicker beneath the younger, southern part of the arc causing basaltic magma to stall and fractionate garnet at high pressure. In the mature, northern section basaltic magma differentiates at shallower levels, at pressures where garnet is not stable. Local variations in lithosphere thickness suggest that thinning is rapid and may be piecemeal. Fluctuations in arc lithosphere thickness during the history of this margin appear to control spatial and temporal variations in magma compositions accumulating in the arc crust.

Significance of particle size distributions for size-dependent hematite nanomineral reactivity

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Nanomaterials exhibit size-dependent properties below threshold sizes. For minerals, these property changes lead to a size dependence of nanomineral geochemical reactivity. Natural and laboratory-synthesized minerals typically do not exhibit uniform size distributions. The significance of particle size distributions (PSDs) was explored for heterogeneous Mn(II) oxidation on hematite surfaces. Measured rates of surface-area-normalized heterogeneous manganese oxidation rates as a function of average particle diameter and pH (7.3-7.9) used in the analyses included those previously reported for hematite mineral suspensions with average diameters of 7 nm and 37 nm [1] and additional data for 8 nm average diameter suspensions. After accounting for pH variations with a 2nd order relationship, a power-law function was generated to fit the rate data as a function of mineral size. The continuous power law size-dependent reactivity function was then applied to each of the individual 7 nm, 8 nm, and 37 nm average diameter suspensions. For a binary mixture of the 7 nm and 37 nm samples, the calculated mass percentage of 7 nm sample at which it contributes more than half of the moles of Mn(II) reacted per time was 1.8% (using the full PSDs), 0.7% using mean diameters and reaction rates only, and 18% considering surface area only but not size-dependent reactivity. Thus, only a small mass fraction of <20 nm hematite is necessary to significantly influence the Mn oxidation rate due to size-dependent reactivity, far exceeding the influence of surface area alone.


Exploration of hydrocarbons in Mehsana, Cambay Basin, India Using geochemical techniques

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The hydrocarbons generated and trapped at depth in petroliferous basins seep in varying quantities to the surface through the processes of diffusion, effusion & buoyancy and are retained in the surface soils/sediments, producing the anomalous surface expressions. The soil gas survey for adsorbed light gaseous hydrocarbons gives direct and promising evidence of the seepage of subsurface hydrocarbons. It helps in demarcation of anomalous hydrocarbon zones and the compositional ratios of same predict the probable oil or gas potential of the region of interest [1].

Surface geochemical survey for the detection of adsorbed light gaseous hydrocarbons has been carried out recently in Mehsana region of Cambay Basin in north-western India. The stratigraphy of the basin extends from Paleocene to Recent with thick Cenozoic sediments of ~8-9 km overlying the Deccan basalts. The Eocene-Oligocene source rocks, reservoir facies, cap rocks and significant overburden maintained ideal relation for the generation and accumulation of large amount of hydrocarbons [2]. The soil samples have been analyzed for light gaseous hydrocarbons by Gas chromatograph equipped with flame ionization detector. The observed concentrations (in ppb) of some of the initial 37 samples vary from: CH4 = 2 - 276; C2H6 = 2 - 113; C3H8 = 1 - 59; i-C4H10 =1 - 6; and n-C4H10 = 1-12 respectively. The statistical treatment of the data obtained for these samples indicates excellent correlation (r>0.9) among the hydrocarbon variables (C1, C2, C3, & C4), suggesting that these are genetically related and are not altered during migration. As per Pixler plot (1969), all the samples are falling in Oil zone. The geochemical survey carried out in the region attempts to present the adsorbed soil gas results and discussion of other geochemical parameters.

Terceira lavas isotopic signatures and multi-scale mantle heterogeneity at the Azores Archipelago

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Terceira Island mafic lavas (< 30 ka), erupted from two main active volcanic systems, were analysed in this study: Fissural zone (F), interpreted as the sub aerial expression of the Terceira Rift, and Sta Bárbara central volcano (SB), which dominates the western topography of the island. These mafic lavas present a significant elemental range, with SB (Mg# <50) being generally more evolved than F (typically Mg# >50). However, if fractional crystallization explains the intra-system variability, it cannot be considered responsible for some chemical differences between those 2 volcanic systems. This is clearly demonstrated by distinct Ba/Th (200 vs. 80), Ce/Th (35 vs. 25) and 206Pb/204Pb ratios (19.93 – 19.99 vs. 19.34 –19.85), which clearly point to a heterogeneous mantle source. Terceira magmas formed from sources characterized by time-integrated depletion (εNd: 5.4 to 6.4; εHf: 7.7 to 10.7) significantly more marked than the observed for coeval lavas outcropping in the neighbouring islands of Pico and S. Miguel, the later also formed in relation with the Terceira Rift. In opposition Terceira is characterized by more radiogenic Pb isotopic ratios indicating a stronger HIMU presence at its source. From elemental reasoning, SB magmas were generated by lower % of partial melting being also characterized by higher 206Pb/204Pb ratios. This indicates that the HIMU domains of mantle source were preferentially sampled during the lower degree melting events. Considering the positioning of Terceira samples below the NHRL and the negative correlation between Nb/U and 206Pb/204Pb, the development of HIMU signatures is a relatively recent event. Our data strengthen the heterogeneous character of the sub-Azores mantle, which is evident even when mantle is sampled along the same structure (Terceira Rift) and, also, at the scale of an individual island.

Functional characterization of c-type cytochromes from Iron-respiring bacteria

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Cytochromes c have been shown to facilitate microbial Fe(III)-reduction in neutrophilic and acidophilic Fe(III)-respiring bacteria, and this study focuses on the functional characterization of several c-type cytochromes produced by the acidophile Acidiphilium cryptum and the neutrophile Geobacter sulfurreducens. UV-VIS spectrosocopy was used to determine heme coordination and redox spectra. Cyclic voltammetry was conducted to determine mid-point potentials and reactivity towards metals. Optical waveguide lightmode spectroscopy (OWLS) was used to examine adsorption kinetics of protein-surface interactions. Spectral analysis of periplasmic cytochromes ApcA and ApcB from A. cryptum indicate that both reduced cytochromes can be reoxidized by Fe(III) and Cr(VI) at pH 3.0 as well as pH 7.0. Mid-point potentials (pH 7.0) are 258mV for ApcB and 233mV for ApcA (vs. SHE). Protein sorption studies suggest that small periplasmic cytochromes such as G. sulfurreducens PpcA are compact, and adsorb and desorb more slowly to surfaces than outer membrane (OM) cytochromes (such as OmcB) that are less dense and contain much more solvent. Homology modelling of these proteins supports the conclusion that compared to dense and compact periplasmic proteins, OM cytochromes have discrete domains and a greater potential for conformational flexibility and interaction with mineral surfaces. Taken together, these data show that these proteins are specifically tailored for electron transfer in different cellular and extracellular locations, by virtue of their electrochemical and structural properties.
**Holocene mismatch of the East Asian and Indian summer monsoons**

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Oxygen isotope records from stalagmites in caves in southern China, interpreted as proxy rainfall records reflecting the intensity of the East Asian summer monsoon, indicate gradual monsoon weakening for the last ~9,000 years, as also documented for the Indian monsoon [1, 2]. Coupled with high-precision dating, the speleothem proxy records have been used to test monsoon links with orbital forcing, solar changes, iceberg discharges in the North Atlantic, ocean currents, and atmospheric methane [1]. However, these ‘benchmark’ cave records do not match other published, dated East Asian proxy rainfall records (based independently on loess/palaeosol magnetic properties [3], and cave oxygen isotope inter-comparisons[4]), which show variable East Asian monsoon intensity through the entire Holocene. Here is presented an explanation for the strong correlation of the cave records with the extra-regional Indian monsoon record yet their mismatch with other dated Chinese rainfall records. The implications of this for the Holocene evolution of the East Asian summer monsoon are also discussed.


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**The effect of tidal movements on Sulfur cycling in mangrove sediments using stable isotopes**

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The management and remediation of acid sulfate soils relies on an understanding of the processes that underlie their formation and biogeochemical behaviour. To help identify and understand these complex processes, stable isotopes of sulfur and oxygen can be used. Mangrove sediments represent currently forming acid sulfate soils, so understanding the processes operating as these sediments are laid down may provide some insight into the characteristics observed in much older materials. The aim of this study is to examine the influence of tidal movements on sulfur cycling in mangrove sediments using stable isotopes.

Mangrove sediment samples were collected from an estuary in Ballina, eastern Australia every 1.5 hours over a 12 hour period. Samples were collected to a depth of 40 cm and frozen with liquid nitrogen. Stable sulfur isotope ratios were determined on the sulfide and sulfate fraction of the sediment and accompanying pore waters.

The sulfur isotope signature of the sulfide fraction remained relatively consistent throughout the profiles and during tidal changes. The signature of the sulfate fraction however recorded a significant decrease from seawater sulfate values during low tide. When the sediments are exposed to air, sulfides which have a light isotope signature are oxidised to produce isotopically light sulfate. This light sulfate is retained in the sediment pore water during low tide until it is either washed from the profile or diluted by the isotopically heavier seawater sulfate during high tide.
High-resolution paleoclimate records from soils using SIMS approaches

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Soils are dynamic chemical systems that actively record climatic variations through the precipitation of secondary minerals in the soil, including opaline silica, carbonate and clays. The maximum age of a soil reflects the stabilization of an erosional surface, providing additional information about past climates and their effects. In situ dating of secondary minerals provides a means of determining the maximum age of a particular deposit (shoreline, terrace or alluvial fan) and can also provide long-term records that reflect local paleoclimate variations and provide genetic information pertaining to the formation of younger surfaces.

In situ dating approaches are necessary for developing long-term climate records from soils using pedogenic carbonate and silica because of the slow growth rates (ca. u/kyr), the possibility of episodic growth, and the complex mixtures of minerals and detrital contaminants that are often incorporated into pedogenic deposits. Using the ion microprobe (SHRIMP-RG) we have developed ²³⁰Th-U and U-Pb dating approaches that enable us to determine maximum soil ages and the age of different zones within the soil precipitate. Our approach uses opaline silica from soils because the extremely high U concentrations (ca. 100’s of ppm U) and apparent long-term stability of opal make it the most favorable target for ion microprobe analysis.

We have focused on three sites in western N. America that represent gradients in age, climate and geomorphic properties. Analyses of opal from different soil depths, modern soil waters, bulk soils and dust suggest that variations in initial (²³⁴U/²³⁸U) values and trace element concentrations in soil opal are driven by changes in the moisture flux through the soil. These variations are generally correlated with global and local climate records, with several differences in timing and magnitude of response between the sites that may reflect differential changes in atmospheric circulation in response to the advance and retreat of the ice sheet. Records also suggest that vegetation may play a role in stabilizing erosional surfaces. In comparison to regional speleothem records, soils show an enhanced sensitivity to climate shifts and, given their ubiquity, may provide a new means of studying terrestrial paleoclimate.

C-isotope variability in the Delhi Supergroup, NW India: Implications for Meso-Neoproterozoic transition

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The late Mesoproterozoic to early Neoproterozoic successions (1.3-0.85 Ga) from different parts of world have been studied for their isotope stratigraphy. In recent past new data set have been provided from successions worldwide and our understanding of Mesoproterozoic seawater evolution improves. The studies indicate that the late Mesoproterozoic to early Neoproterozoic successions (1.3-0.85Ga) exhibit moderately positive average δ¹³C values. The transition from a characteristically late Mesoproterozoic record of little δ¹³C change to the moderate variability noted in the early Neoproterozoic has not been reported frequently from any single succession.

Marine carbonate rocks from the Delhi Supergroup of Northwestern India show little deviation in whole rock δ¹³Ccarb values, which is generally around 0 ‰. This narrow range and almost constant δ¹³Ccarb values persist despite close sampling and through long sections. The data suggest that the global rate of organic carbon burial was probably constant during deposition of Delhi Supergroup. The nearly invariant C isotopic profile of the Delhi Supergroup is similar to C isotopic profiles of Mesoproterozoic carbonates older than ca. 1.3 Ga as reported from different parts of world. The carbonates occurring on the western margin of Delhi Supergroup however, have on average, moderately positive δ¹³C values (from 2 ‰ to + 4.96 ‰). These high δ¹³C carbonates may represent the Mesoproterozoic-Neoproterozoic transition (~ 1.25 to ~ 0.85 Ga), a period characterized by such high positive δ¹³C values globally.
Stabilization of iron oxide nanoparticles by the adsorption of sulfate, phosphate and arsenate

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Iron oxides are well known for their adsorption capacity of anions such as sulfate, phosphate, silicate, carbonate, and arsenate. It is easy to verify that ferrihydrite with adsorbed anions transforms to the more stable iron oxides (goethite, hematite) much more slowly than pure ferrihydrite. The difference in the transformation rate has been ascribed to the surface “poisoning”, where the anions located at the surface may hinder the dissolution-precipitation processes. In other words, the cause of the slower rates is considered to be purely kinetic. Here we show that the adsorption of the anions significantly stabilizes the hydrous ferric oxide (HFO) also in a thermodynamic sense.

We have synthesized a set of schwertmannite samples (a poorly crystalline iron hydroxysulfate) and a series of ferrihydrite samples with adsorbed arsenate and phosphate. The enthalpies of solution of these samples in 5 N HCl were then measured by acid-solution calorimetry. The dissolution enthalpies are markedly different for the pure ferrihydrite and for the HFO samples with adsorbed anions. The dissolution enthalpies ($\Delta H_{diss}$) of pure ferrihydrite vary between -510 and -570 J/g (depending on the crystallinity of ferrihydrite). On the other hand, the $\Delta H_{diss}$ for HFO with adsorbed arsenate, phosphate, or sulfate are significantly less exothermic, indicating stabilization of the iron oxide nanoparticles by the adsorption of the anions. The $\Delta H_{diss}$ values for the HFO with adsorbed anions vary between -370 and -270 J/g. Currently, we are calculating the formation enthalpies of the HFO with adsorbed anions in order to assess its stability with respect to the crystalline iron oxides and the crystalline iron oxysalts (sulfates, arsenates, phosphates).

Alternate method for Sulfate $\delta^{17}$O measurements

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Sulfate in the environment from natural or anthropogenic sources are often determined using isotopic analysis. Usually isotopic ratios of sulfur ($\delta^{34}$S) and oxygen ($\delta^{18}$O) of the sulfate samples are measured to obtain this information. Other isotopic ratios ($\delta^{33}$S, $\delta^{36}$S and $\delta^{17}$O) are generally not measured due to low abundances and are assumed to fractionate mass-dependently ($\delta^{33}$S = 0.515 * $\delta^{34}$S[1], $\delta^{36}$S = 1.91 * $\delta^{34}$S[1], $\delta^{17}$O = 0.5164 * $\delta^{18}$O[2]). Recent studies have found some sulfate samples do not conform to the mass-dependant rule for oxygen and, from these results, further details in the oxidation pathways of sulfate could be obtained.

Current published methods for $\delta^{17}$O measurements required thermal decomposition of sulfate samples to SO$_2$ and O$_2$ and analyzing both gases separately (SO$_2$ for $\delta^{34}$S and O$_2$ for $\delta^{18}$O and $\delta^{17}$O) using isotope ratio mass spectrometry (IRMS). An alternate method to obtain these values is proposed that concurrently uses SO$_2$ gas only. Assumptions made about sulfate samples are a) oxygen is uniformly distributed in the sample and b) sulfur fractionates mass-dependently. The method requires isotopic measurements of $^{64}$SO$_2$, $^{65}$SO$_2$ and $^{66}$SO$_2$ and application of mass fraction equations to determine the $\delta$ values for the sulfate sample which, in turn, provides a value for the oxygen anomaly ($\Delta \delta^{17}$O = $\delta^{17}$O$_{meas}$ - 0.52 $\delta^{18}$O).

Measurements made to date have been completed with standards of known $\delta^{34}$S and $\delta^{18}$O to test the method. Preliminary results have found the ratio of $\delta^{17}$O/$\delta^{18}$O to vary between 0.6 and 0.4. Refinement of the method to reduce the ratio variation is currently in progress.

Origins of Cr-diopside in peridotite xenoliths

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The modal abundance of clinopyroxene (cpx) in mantle peridotite is a major factor in controlling the lithophile trace element budget of the lithospheric mantle. The abundance of cpx (along with garnet in some peridotites) strongly influences physical properties such as density. It is therefore critical to understand the origin and timing of cpx formation within mantle samples if we are to understand the potential temporal controls on the chemical and physical evolution of the continental lithosphere. We have investigated the possible origins of cpx in mantle xenoliths using detailed in situ Sr isotope and trace element analyses of individual cpx crystals (MicroMill and TIMS). We present results from Greenland, a craton with highly depleted lithosphere, where cpx is scarce, and Kimberley, Kaapvaal craton, where cpx is more abundant, along with other evidence of metasomatism. Greenland peridotites show remarkably homogenous Sr isotope values (0.703607 to 0.703672) with no isochronous relationship. Trace element concentrations show considerable variation but this does not correlate with the limited isotope variation or with textural characteristics. Cpx from Kimberley peridotites have much more radiogenic Sr isotopes (0.703607 to 0.703672) with no isochronous relationship. Trace element concentrations show considerable variation but this does not correlate with the limited isotope variation or with textural characteristics. Cpx from Kimberley peridotites have much more radiogenic Sr isotopes (0.70586 to 0.70412). This sample is also characterised by considerable variation in trace element abundances. Homogeneous isotopic compositions in some samples, coupled with varied trace element concentrations are inconsistent with long term enrichment or depletion implying that the majority of cpx is a recent metasomatic addition to the lithosphere. A global compilation of Sr isotope data for both on- and off-craton cpx mineral separates shows that the majority of cpx has a similar Sr isotope composition to OIB/MORB indicating that cpx is a metasomatic addition from a melt originating in the convecting mantle. In rarer cases where Sr isotope variation is marked, melt interacted with a more enriched component, possibly from an older event, in the lithosphere, or the cpx could have formed from a precursor mineral. However this is not representative of the majority of mantle cpx.

An important implication of these results is that the lithospheric mantle, contrary to common assumption, may not have been an incompatible element enriched reservoir throughout its history.

New views about the composition of Mercury’s core and its magnetic field origin

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According to previous models, the estimated oxygen fugacity, under which the core segregation of Mercury might take place, would be 3- 6 log units below the iron-wüstite buffer. Under such reducing conditions, the core of Mercury would contain several wt% of silicon, in addition to sulfur. The ternary Fe-S-Si has a vast immiscibility gap at low pressure, which might be closed after the core-mantle boundary of Mercury. This immiscibility gap raises the possibility that the mercurian core has a shell structure: (i) an outer layer of Fe-S-Si liquid, rich in S; (ii) a middle layer of Fe-Si-S liquid, rich in Si; and (iii) an inner core of solid Fe-Si metal; a fourth layer of homogeneous Fe-Si-Si liquid could also be possible, depending on the exact depth at which the immiscibility gap closes. The Fe-S-rich outer layer could contain significant amount of uranium, which is not possible with the two other important heat-producing elements thorium and potassium. Heat from the decay of uranium could thus contribute significantly to the genesis of Mercury’s magnetic field.
Contrasting magma sources in ultramafic-mafic intrusions of the Noril’sk area (Russia): Hf-isotope evidence from zircon

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World-class platinum-group-element (PGE)-Cu-Ni deposits closely linked to intracontinental paleorift-related ultramafic-mafic intrusions are located in the northwestern corner of the Siberian craton, Russia. Recent U-Pb SHRIMP studies [1, 2] identified distinct age groups of zircon from the main types of ultramafic-mafic intrusions of the Noril’sk area. Most of concordant U-Pb ages lie in the range 230-270 Ma. Minor zircon populations show older U-Pb ages, which cluster around 300 and 340 Ma.

In situ Hf-isotope data (~310 analyses) were collected on the dated spots within single zircon grains from the main lithological units of economic (Noril’sk-I, Talnakh and Kharaelakh) and non-economic (Nizhny Talnakh and Zelyonaya Griva) intrusions of the Noril’sk area. The analysis used a New Wave LUV213 laser-ablation microprobe attached to a Nu plasma MC-ICP-MS at GEMOC [3].

Zircons from economic intrusions with U-Pb ages between ca. 230-340 Ma yielded mean epsilon Hf(T) (parts in 10^4 difference between the zircon sample and the chondritic reservoir) values of + 9.4 (n=45) at Kharaelakh, + 11.3 (n=96) at Kharaelakh and + 12.2 (n=83) at Noril’sk-I, close to the mean value of the depleted mantle reservoir at that time. In contrast, zircons from non-economic intrusions with U-Pb ages between ca. 215-305 Ma yielded eps Hf(T) values +1.0 (n=80) at Nizhny Talnakh and +1.7 (n=11) at Zelyonaya Griva.

The Hf isotope data suggest that zircons from economic intrusions are characterized by the signature of a juvenile mantle-derived magma. The less radiogenic Hf isotope values of zircons from non-economic intrusions indicate mixing between mantle and crustal magma sources. Our new findings suggest the interaction of distinct magmas, indicating that ultramafic-mafic intrusions of the Noril’sk area have a more complex geological history than is commonly assumed.


State-of-the-art geodynamic modeling of subduction zones: From slab edges to flat and steep slabs

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In the recent years, significant progress has been made in computational geodynamics with the main purpose to bring observations from different fields into numerical simulations of subduction zones. Here we present up to date numerical models for three different subduction systems: Kamchatka, Chile and Mexico.

The first system is located adjacent to the Kamchatka-Aleutian junction where the Pacific slab edge is subducting beneath Kamchatka. We show that thermal state of the mantle wedge is the key factor governing the composition of arc magmas. Integrating results from petrology and numeric modeling we demonstrate that northward decrease of the mantle wedge temperature beneath volcanoes correlates well with decreasing slab dip, length of mantle columns and magma flux.

Recent studies suggest that variations in the slab geometries along the Chilean margin are related with strong variations in the upper plate structure. 2D time dependent geodynamic models show that the presence of a highly viscous thick continental lithosphere near the mantle wedge produces flat slabs. Then, the long-term exposure of the base continental lithosphere to the fluid fluxes from the slab will drop the viscosity and the two plates start decoupling, the subduction regime switching back to steep slab. Our results show that the whole cycle, from step to flat and back to steep slab takes 8-10 Ma in good agreement with estimations from chemistry of magmatic rocks in Northern Chile.

The last study area is the Mexican subduction system, with a focus on its central part where the subducting Cocos slab is in flat regime for the last ~20 Ma. Our numerical simulations show that time-space variations in the mantle wedge viscosity and shape change the slab shape through time. The transformation of the low viscosity wedge into just a low viscosity channel located between the subducting and the overriding plates produces perfectly flat slabs. The geodynamic models explain reasonable the two opponent characteristics: flat slab and the lack of upper plate deformation.
Near-solidus solubility of alkali feldspar-mica-quartz in H$_2$O at 1 GPa: Implications for crustal fluids

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At temperatures just below the quartz-saturated wet solidi of albite (Ab) and K-feldspar (Ksp) in the middle and lower crust, quartz (Qz) solubility in H$_2$O is high [1] and there is strong complexing between aqueous Al and Si [2,3] and possibly alkalis. These observations suggest that near-solidus fluids may be quite concentrated solutions which are capable of substantial mass transfer. We carried out experiments on the solubility of Ab+Qz (580-630°C) and Ksp+Qz (700°C) in H$_2$O at 1 GPa. Experiments were conducted in a piston-cylinder apparatus using 2.5-cm NaCl-graphite furnaces and a double-capsule method [4]. In both systems, mica (paragonite, Pg, or muscovite, Mu) was present in all run products, indicating that Ab+Qz and Ksp+Qz dissolve incongruently in Pg, or muscovite, Mu) was present in all run products, indicating that Ab+Qz and Ksp+Qz dissolve incongruently in H$_2$O. The bulk solubility of Ab+Pg+Qz doubles from 4 to 8 wt% as the solidus (640°C) is approached, with corresponding increases in Si, Al, and Na molalities. Over the same range, molar Na/Al and Na/Si respectively decrease (2.1 to 1.5) and increase (0.15 to 0.18), indicating that fluids are Na- and Si-rich peralkaline solutions far from Ab stoichiometry. The bulk solubility of Ksp+Mu+Qz at 700°C is even greater (25 wt%), and molar K/Al=15 at K/Si=0.33. Measured Ab+Pg+Qz solubility at 580°C is in fair agreement with predictions from extrapolated thermodynamic data [5], but becomes much greater than predicted as T increases to the solidus. Ksp+Mu+Qz solubility at 700°C is also much greater than predicted. The observations point to strong, pre-melting increases in the extent of polymerization of aqueous species in the narrow 50°C interval immediately below the solidi in these model granitic systems. Polymeric aqueous species involving Na and/or K, along with Al and Si, predominate in model near-solidus and melt-saturated fluids, and provide a simple mechanism for metasomatic mass transfer in deep magmatic systems and Barrovian metamorphism [6].


Relationships between µm-scale melt inclusions and oscillatory trace element zoning in olivine

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Oscillatory zoning of trace elements P, Cr and Al in otherwise unzoned magmatic olivines may preserve information on early crystallisation histories [1, 2], because the higher diffusivities of Mg, Fe, Mn, Ca and Ni inhibit preservation of such clues in the major and minor elements. Concentrations of P in trace-element-rich bands exceed expected equilibrium values, and similar enrichment bands are observed in olivines grown experimentally at constant cooling rate [2]; thus, it seems likely that this phenomenon in natural olivine reflects local kinetic processes during crystal growth rather than oscillations in magma temperature or bulk composition.

Olivines from a subaerial Hawaiian basalt contain P-rich bands, some of which contain 1-5µm melt inclusions. The geometry of these inclusion-bearing bands suggest that they represent “stratigraphic markers” formed during crystal growth, outlining euhedral crystal shapes visible in 3-d. The melt inclusions appear to have nucleated on 1-2 µm Cr-spinels and all share the same orientation regardless of the P-zonation planes (bands) in which they occur. We hope to determine whether disequilibrium growth effects or transcrystalline melt transport (driven by thermal [3] or chemical gradients) control this peculiar melt inclusion distribution, and to what extent melt inclusions and trace element zoning are causally linked.

We used a nanoSIMS 50L ion microprobe to examine the relationship between µm-scale trace element zonation of olivine surrounding linear arrays of melt inclusions within P-rich bands. Initial imaging at 200nm resolution indicates that such bands are 3µm wide. As with meso-scale X-ray mapping [1], Cr and Al are positively correlated with P variations, although they exhibit broader (0.7-1.5µm compared with 0.3-0.8µm for P) compositional gradients at the edges of each band, consistent with diffusive broadening of an initially sharp gradient over a timescale of weeks to months.

2.67 Ga high-Mg andesites from the Musoma-Mara greenstone belt, northern Tanzania

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Neoarchaean (2.67 Ga) High-Mg andesites occur in the Musoma-Mara greenstone belt, northern Tanzania. They are associated with dacites and Na-granitoids both of which are adakitic in composition. The high-Mg andesites are characterized by higher contents of MgO (2.42 – 9.47 wt %), Cr (41-797 ppm) and Ni (11-254 ppm) than those of normal island arc andesites. Their La/Yb ratios are 9.87 – 22.5 whereas their Sr/Y ratios are 20 – 131. These characteristics are similar to those shown by Cenozoic Setouchi High Magnesian Andesites (HMA). These rocks are characterized by $^{143}$Nd/$^{144}$Nd ratios that range from 0.511062 ± 7 to 0.511308 ± 12 with corresponding $\varepsilon_{Nd}(t)$ of +0.44 and +1.81.

The high contents of Mg, Cr and Ni argue in favour of equilibration of their parental magma with mantle peridotite whereas their relatively low La/Yb ratios argue against the involvement of garnet and amphibole as residual phases during partial melting. Thus, the high-Mg andesites are interpreted to have formed by partial melting of the mantle peridotite that has been fluxed by slab-derived fluids. Overall, the geochemical features of high-Mg andesites, their close association with adakitic rocks in the MMGB together with the short time interval taken for their emplacement are interpreted in terms of a ridge-subduction model. It is considered that such a model was important for generation of late Archaean continental crust.

Extraterrestrial $^3$He and constraints on eolian fluxes and provenance in sediments from the Shatsky Rise

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Extraterrestrial $^3$He in deep-sea sediments has been used successfully as a constant-flux proxy [1]. Such proxies permit accurate assessments of changing mass accumulation rates through time. Although the flux of extraterrestrial $^3$He is slightly more variable across the long timescales of the late Cretaceous and Tertiary, on shorter timescales, such as the Quaternary and the Paleocene, this flux appears to be relatively invariant [1, 2]. Across a 1-Myr interval in Shatsky Rise sediments of late Paleocene age, several eccentricity cycles have been identified. At this time, the Shatsky Rise was located in the central tropical Pacific far from any continent, and virtually all of the sedimentary $^3$He (>99%) is of extraterrestrial origin. Assuming a constant flux of extraterrestrial $^3$He, we calculate bulk sediment accumulation rates that range from about ~0.5 to 2 g cm$^{-2}$ kyr$^{-1}$, similar to those found in the central equatorial Pacific today. By using $^4$He concentrations as a proxy for the eolian component [3], we determine that there are approximately 2- to 3-fold changes in the flux of dust. Further work will elucidate the extent to which changing patterns of dust accumulation are related to variations in orbital insolation. Additionally, we shed light on the provenance of the eolian fraction by examining the $^3$He/$^4$He isotope systematics. Changes in sedimentary provenance can be caused by changes in response to climatic shifts in the a) aridity of competing dust sources or b) prevailing patterns of atmospheric circulation and, therefore, location of the intertropical convergence zone.

Precise calibration of Oxygen isotope paleotemperature equations for several taxa of benthic foraminifera

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Benthic foraminiferal δ18O has been used for several decades to reconstruct bottom water δ18O (global ice volume and salinity) and temperature. Yet there remains no strong consensus regarding which benthic paleotemperature equation(s) are most accurate, with widely applied equations varying in slope by as much as 20%. This uncertainty arises, at least in part, from a general lack of high-precision calibration studies.

We use a suite of 30 high-quality multicore tops collected in the Florida Straits in 2002 to calibrate benthic foraminiferal δ18O versus bottom water temperature. Modern water temperatures are unusually well constrained by matching bottom water salinities (measured on waters collected using a Niskin bottle mounted to the multicorer) to nearby CTD casts. Seawater δ18O was also measured using the Niskin waters, allowing us to precisely regress foraminiferal δ18O (in the form δ18O - δ18O of seawater) against temperature. We present calibrations for the benthic taxa Cibicidoides, Planulina, Uvigerina, and Hoeglundina, and compare them to published data. In agreement with previous studies, we find that Cibicidoides and Planulina fall closest to inorganic precipitation data that are believed to approximate “equilibrium.” The infaunal Uvigerina exhibits higher δ18O values, and the aragonitic Hoeglundina is higher still. Since our sites span a pH range of 0.24 units, we also attempt to evaluate the hypothesis that benthic foraminiferal δ18O varies with pH, by comparing our regression slopes to those derived from theory and from the planktic foraminifer Orbulina.

Br/Cl partitioning in chloride minerals in the Burns Formation on Mars

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Introduction and Objectives

Within Gusev Crater and Meridiani Planum on Mars, the Mars exploration rovers have found Br concentrations in soils and rocks in the hundreds of ppm range. Relative to Earth seawater, these are “high” Br concentrations. Because of low Br concentrations on Earth, Br largely precipitates from seawater as a minor constituent in halite crystals rather than as a separate phase mineral. This is also likely to be the case for Mars. But given that the surface chemistries on Mars are significantly different than on Earth, minerals other than halite could serve as sinks for Br. The specific objectives of this presentation are to (1) incorporate Br solution phase chemistries into the FREZCHEM model, (2) integrate the Siemann-Schramm (2000) Br/Cl mineral model into FREZCHEM, and (3) apply this mineral model to Br/Cl partitioning in Burns formation rocks as an indicator of past environments in the Meridiani Planum region of Mars.

Discussion of Results

The main conclusions of this work are: (1) a molar-based model for Br substitution into halite and bischofite provided a better fit to experimental data than the standard mass-based model; (2) all of the soluble salts (Na, Mg, Ca, Cl, Br, and SO4) in the Burns formation, except for Ca, were significantly related to profile depth (Fig. 1); (3) the likely precipitation of Ca as gypsum on Mars precludes Ca precipitating as a CaCl2 salt; (4) bischofite was a much more important sink for Br than halite; (5) the source of the Burns formation salts most likely came from windblown playa materials, where Br and Cl were fractionated in the playas; and (6) the high concentrations of Br in the surface layers of the Burns formation suggest that there was little water leaching in the late stages of profile development.

Figure 1: The concentration of individual ions (mol/kg) and cations and anions (equivalents/kg) in the Burns formation.
Microporous and micropermeable subgrain microtextures in K-feldspar

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K-feldspar has potential to yield a wealth of information on the temperature-time evolution of the rocks in which it is found, as long as we can understand Ar diffusion behaviour with respect to the retentiveness of microtextures. Patch perthite microtextures are characterised by mosaics of slightly misaligned submicron- to micron-sized incoherent subgrains with abundant dislocations along their boundaries and are also typically associated with micropores. Studies suggest subgrain microtextures are not retentive of radiogenic \(^{40}\)Ar even at low-temperatures.

Authigenic K-feldspars show microtextural similarities to patch perthites; that is subgrains separated by dislocation rich boundary networks that potentially act as fast diffusion pathways for radiogenic argon. We analyzed authigenic K-feldspar using Ar-Ar geochronology as a direct analogue for the patch perthite microtexture. Samples were naturally exposed to temperatures in excess of the predicted Ar closure temperature, but unexpectedly still yield Ar-Ar ages representative of precipitation and not cooling.

We propose a theoretical microtextural model that highlights fundamental differences between the microtextures of deuterically formed patch perthites and authigenic K-feldspars, explaining the apparent robustness of authigenic K-feldspar with respect to Ar-retention. The model suggests that whereas short-circuit Ar-diffusion is the dominant process observed within patch perthite, lattice volume diffusion governs Ar-diffusion from authigenic K-feldspar.

Re-Os geochronology of the Várzea do Macaco chromite deposit and Ni-prospect, Jacurici Complex, Brazil

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The Jacurici Complex, located in the NE of the São Francisco Craton, is constituted by several N-S mafic-ultramafic bodies - possible fragments of a single larger sill. The complex evolved from a very primitive parental magma, later disrupted and metamorphosed under amphibolite-facies conditions during regional tectonism [1]. The Complex hosts the largest Brazilian chromite deposit and one recently discovered Ni-Cu sulfide prospect (Várzea do Macaco body).

Six samples of chromite separates (five from chromitites and one from a disseminated interval) and four pyrrhotite separates (two from a magmatic ore and two from a metassomatized interval) from the Várzea do Macaco body were selected and performed at the Department of Terrestrial Magnetism/Carnegie Institution of Washington.

All chromites from chromitites show sub- to near-chondritic initial Os isotopic composition (\(\gamma\)Os(2085Ma) = -4), but the disseminated chromite show significantly higher initial Os composition than typical of the mantle (\(\gamma\)Os(2085Ma) = +18). The same relationship was observed when comparing typical magmatic sulfide (\(\gamma\)Os(2085Ma) = -2 to +2) and sulfide associated to metasomatized intervals (\(\gamma\)Os(2085Ma) = +11 to +15).

A Re-Os isochron using all data was not possible. One the other hand, considering the higher \(\gamma\)Os samples as a group, the three samples yield an isochron age of 2084±0.9Ma (2\(\sigma\), MSWD=0.43). The data from the sub to near-chondritic \(\gamma\)Os samples show some scatter (chromites have very low \(^{187}\)Re/\(^{188}\)Os ratios), but suggest an older age.

Similar ages were already previously reported as the age of magmatic crystallization (2085±5Ma SHRIMP U/Pb in zircons) and as the age of the intrusive and undeformed Itiúba Syenite (2084±16 Ma SHRIMP U/Pb in zircons) [2].

The results obtained suggest that the complex is possibly older than considered before and the Ni-sulfide mineralization was partially remobilized during an event at 2084Ma. Metamorphism or the Itiúba intrusion are both significant thermal events that could remobilize the sulfides and also reset the Re-Os isotopic system in some chromites.

This study is supported by Rede GeoChronos.

As part of the CRONUS-Earth $^{36}$Cl project, geological calibrations of in situ production rates of cosmogenic nuclides, including $^{36}$Cl, are being conducted as part of a larger project to improve the accuracy of techniques employing cosmogenic nuclides. $^{36}$Cl production rates have been particularly difficult to calculate, partially due to the fact that there are three main production pathways for chlorine-36: spallation of potassium, spallation of calcium, and thermal neutron absorption. We are currently focusing on the potassium production pathway. Calibration rates published by different authors range from 137-228 atoms/ gram K/ year. Using data generated through the CRONUS-Earth project from Scotland, Antarctica, and Utah, independent calibration rates for potassium have been calculated. These production rates are all reasonably consistent. This is a step towards finally resolving the discrepancy between different $^{36}$Cl production rates, although more comprehensive examination of all production pathways will be required to provide secure production parameters.
Molecular-scale biogeochemical mechanisms affecting the mobility of Hanford Site contaminants


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At the United States Department of Energy’s (U.S. DOE’s) Hanford Site, uranium (U) and technetium (\(^{99}\)Tc) are major risk driving contaminants due to their high solubility in oxidized circumneutral site groundwaters. Migration of these contaminants is predicted through aquifer regions and ultimately to a final discharge into the Columbia River. Consequently, understanding the factors limiting the mobility of these contaminants in the subsurface represents an important step towards reducing the risk of Hanford contaminant migration into the Columbia River. Under anoxic conditions, dissimilatory metal reducing bacteria (DMRB) have potential to limit mobility of these radionuclides in the environment by the enzymatic bioreduction of U(VI) or Tc(VII) to insoluble oxides, U(IV)O\(_2\)(s) or Tc(IV)O\(_2\)(s).

Due to our recent discovery of \textit{Shewanella} sp. in sediments from the Hanford Reach of the Columbia River, we have investigated the role of putative redox-active proteins from \textit{Shewanella oneidensis} MR-1 for their role in the transfer of electrons to U(VI) and Tc(VII). Kinetic studies with wild type and mutant resting cells revealed that \(c\)-type cytochromes were essential for the reduction of U(VI) and formation of extracellular UO\(_2\) nanoparticles independent of the electron donor source. Extracellular nanoparticulate UO\(_2\) accumulated in association with a complex exopolymeric substance (EPS) that contained outer membrane \(c\)-type cytochromes (OMCs). One EPS-associated OMC was shown to be capable of directly transferring electrons to U(VI) \textit{in vitro}. In contrast, the mechanism of Tc(VII) reduction was found to be dependent on the source of reducing equivalents. The NiFe hydrogenase was involved in the H\(_2\)-driven reduction of Tc(VII) presumably through a direct coupling of H\(_2\) oxidation and Tc(VII) reduction. In the presence of lactate, Tc(VII) reduction was slower than H\(_2\)-driven reduction and catalyzed directly by OMCs, suggesting that electron donor availability may influence strategies designed to enhance biogenic Tc(VII) reduction. These studies represent important steps towards determining the principal mechanisms that govern the biomineralization and reactivity of these redox reactive contaminants.

Tracking precipitation seasonality and vegetation features in Asian Oligo-Miocene mammal tooth remains

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The carbon isotope difference between C3 and C4 vegetation can be exploited to determine ecological and climatic changes in the past. C3 and C4 plants have \(\delta^{13}\)C values averaging approximately -27 and -12‰, respectively. The ratio of C3 to C4 plants in the ecosystem is recorded in the diet of herbivores and eventually in the tooth enamel. Mammalian tooth enamel is enriched by about 14‰ compared to the vegetation. The oxygen isotope ratio in the tooth reflects that of the body water, which is in turn in equilibrium with that of the drinking water. Exploring patterns of C and O uptake in the elemental composition of incrementally grown biological structures such as the retzius striae of the teeth deposited with seasonal or more frequent periodicity give opportunities to improve the climatic and environmental reconstructions. Here we explored spatial variations of stable isotopes within tooth enamel of several asian mammal species (Pakhtistan) to reconstruct the Asian Oligo-Miocene seasonal changes in (monsoon) precipitation and diet. Carbon isotopes indicate a mosaic of savanna and forest ecosystems and high-resolution measurements of oxygen isotopes in tooth enamel show that the Asian monsoon system existed ~14Myr ago.
Detailed “supervolcanic” ash record in dry Lake Tecopa, California: $\delta^{34}$S, $\delta^{18}$O and $\Delta^{17}$O of soluble volcanic sulfate

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When emitted into the atmosphere, volcanic SO$_2$ is oxidized into sulfate (SO$_4^{2-}$) aerosols that are capable of changing the chemical and physical properties of the troposphere and stratosphere. Large quantities of SO$_2$ are released during super-eruptions and have an unquantified impact on the Earth’s climate. The significant $\Delta^{17}$O excess in volcanicogenic sulfate requires that volcanic SO$_2$ was oxidized by ozone-derived compounds such as OH radicals [1-3] and this signature is preserved in the geologic record despite potential dilution by sediment-derived sulfate without $\Delta^{17}$O-anomaly.

We present new analyses of oxygen ($\delta^{18}$O, $\delta^{17}$O) and sulfur ($\delta^{34}$S) isotopes in soluble sulfate leached from meters-tick three volcanic ash layers deposited in dry Lake Tecopa in California. We sampled and analyzed 45 volcanic samples from the 0.64Ma Lava Creek Tuff and 2.04Ma Huckleberry Ridge Tuff eruptions of Yellowstone (1000km$^2$ and 2500km$^2$), the 0.76Ma Bishop Tuff eruption from Long Valley caldera (750km$^2$), and 23 enclosing sediments.

The whole data set shows a significant range in $\delta^{34}$S (12-20‰), $\delta^{17}$O (0-12‰) and $\Delta^{17}$O (0-2.26‰) but the maximum $\Delta^{17}$O of up to 2.3‰ are found only in the sulfates from the three volcanic ash layers. Sediment leached sulfate does not possess $\Delta^{17}$O >0.5‰ and the existence of $\Delta^{17}$O >0.5‰ in sulfate can be interpreted as coming from the ash. Based on the isotopic ratios we provide proportion of sediment-derived sulfate in ash, and ash-derived sulfate in sediment. Our previous analyses of $^{32}$S and $^{33}$S in five sulfate leachates from Lake Tecopa ash beds did not yield mass independent S behavior [3].

The ash layers sampled here are not interpreted as only resulting from stratospheric deposit. Instead, we infer that sulfuric acid rains that follows large eruption events are able to transfer the ozone-derived $\Delta^{17}$O signature into the ash layer blankets covering the surface soon after the eruption, via percolation and then precipitation of gypsum having a $^{17}$O excess. We speculate on the potential impact of large amounts of SO$_2$ on the depletion of the ozone layer.


Sanukitoids: Transition from felsic melt- to fluid-dominated mantle metasomatism in subduction zones

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Sanukitoids and Closepet type granites occur in most Archaean terrains where they mostly emplace near the Archaean Proterozoic boundary. They display geochemical characteristics intermediate between Archaean TTG (low Yb and high (La/Na) and modern calc-alkaline magmas (high K/Na). Their petrographic and geochemical characteristics suggest that they derived from melting of a mantle peridotite, previously metasomatised by felsic melts of TTG composition.

Experimental studies of the melting of peridotite—TTG mixtures reveals that, over a very large range of P-T conditions and TTG/peridotite ratios, the melts formed cluster around an intermediate, magnesian composition similar to the sanukitoid primitive magmas, (nearly) insensitive to the nature of the residual phases or the degree of melting. The differences between sanukitoids and Closepet-type plutons can be ascribed to different degrees of melting of the source.

A subduction environment seems the most realistic setting to allow melting of the hydrous basaltic source of TTG under a peridotite slice such that TTG—mantle interactions would be possible. We propose that the limited temporal occurrence of sanukitoids can be explained as follows:

In the Archaean, important heat production allowed the relatively shallow melting of the subducted slabs. As the Earth cooled down, melting became possible only at greater depth, and in lower proportions, resulting in increasing TTG-mantle interactions. At the end of the Archaean, the TTG generation had so much declined that the TTG melts were completely consumed during interactions with the mantle, whose subsequent melting yielded sanukitoids (and Closepet-type) magmas. Eventually, after the end of the Archaean slab melting became impossible or very rare, and the dominant process was slab dehydration ultimately leading to the formation of BADR series.
4000 years of climate change in Northern Spain from speleothem records

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Coetaneous stalagmites from three different caves in N. Spain (Ojo Guareña, Atapuerca and Cobre) have been investigated in order to reconstruct the regional paleoenvironmental conditions related to the North Atlantic climatic variability through the last four millennia. This reconstruction, based on a multi-proxy approach which includes oxygen and carbon isotope profiles and microfacies analysis, has been calibrated by means of present-day hydrogeochemical monitoring programs of the environment of the caves as well as historical archives in the area.

The investigated caves, located inland Spain, show significantly different local climatic conditions, ranging from the high-mountain climate of the Cantabrian Ranges (Cobre Cave) to the drier and warmer climate of the Meseta (Atapuerca), and are thought to be strongly sensitive to medium to long-term NAO oscillations.

Comparative analysis of the reconstructed series demonstrates an overall correspondence which allows establishing the regional pluvio-thermal changes at decadal to millennial scales for the 4000 years, but also notable differences that are attributed to local or karst-related factors. Spectral analysis of stable isotope values yields significant periodicities that could correspond to known solar cycles, supporting the idea that long-term NAO changes strongly respond to solar forcing.

Also, comparison of geochemistry of recent and ancient speleothems reveals quite unique, extreme climate conditions for the last years, related to 20th Century global warming. Comparable conditions to those of today were reached only during few, relatively short intervals, throughout the last four millennia in N Spain.

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Surface charge and zeta-potential of metabolically active and dead cyanobacteria

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Zeta potential and acid base titrations of living, inactivated, and dead Planktothrix sp. and Synechococcus sp. cyanobacteria were performed to determine the degree to which cell surface electric potential and proton/hydroxyl adsorption are controlled by metabolism or cell membrane structure. Surface OH-excess from potentiometric data shows differences in surface charge between active and dead cyanobacteria for the pH range of 3 to 10. An average zero salt effect pH of 5.8 ± 0.1 and 6.3 ± 0.1 was obtained for active Planktothrix sp. and Synechococcus sp. respectively. Zeta potentials of active Planktothrix sp. and Synechococcus sp. were positive at alkaline conditions, with a maximum of +13.7 ± 1.5 mV at a pH of 9.0 ± 0.1 for both species. This positive potential diminished in the presence of 1 mM HCO₃⁻. The zeta potential of Planktothrix sp. and Synechococcus sp. cells was negative at alkaline pH following their exposure to NaN₃, a metabolic inhibitor. Their average potential was -18.4 ± 1.8 mV at a pH of 9.14 ± 0.02 following a 3 hours exposure to NaN₃. The zeta potential of dead cyanobacteria was negative for Planktothrix sp., in the pH range of 2.5 to 10.5, at -30 to -20 mV. Dead Synechococcus sp. recorded negative potentials to a minimum of -30 mV at pH 8, positive potentials were recovered to a maximum of +10 mV at pH 9.1. Zeta potentials for dead, but non-acidified Synechococcus sp. remained negative at -30 mV from an initial pH of 5.6 to 10.5, reflecting differences in cell wall structure between these species. Taken together, these results indicate that Planktothrix sp. and Synechococcus sp. may metabolically control their surface charge to electrostatically attract bicarbonate anions at alkaline pH, required for photosynthesis.
Antimony(V) sorption and mobility in calcareous soils

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Sorption and mobility of Sb(V) onto natural calcareous soils have been studied in batch and column experiments. Batch experiments were carried out with 0.5 g of soil in contact with different Sb(V) solutions at a constant ionic strength (0.01M NaClO₄) and temperature (25.0±0.1°C). Results show that the sorption kinetics was similar compared to Sb(V) sorption onto other soils or onto goethite. Kinetic data were modeled considering a pseudo-second order reaction, with kinetic constants varying from 0.0338 to 0.061 kg·mol⁻¹·d⁻¹ and sorption maximum capacities between 1.67·10⁻³ and 2.28·10⁻³ mol·kg⁻¹, depending on the soil sample.

Column experiments were performed in order to determine the mobility of Sb(V) in the soils. Sorption and desorption experiments were carried out and Kᵣ values were obtained by using the CXTFIT code. The values obtained (0.97-1.55 dm³/kg) are in agreement with the ones given by the EPA for the Sb sorption onto different soils (0.41-2.7 dm³/kg). Antimony K-edge X-Ray absorption spectra of the sorbed soil samples were collected at the Rossendorf Beamline at the European Synchrotron Radiation Facility (ESRF), in order to determine the surface species involved in the sorption process.

On the origin of the EM-1 component in Santiago Island (Cape Verde)

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The outcropping magmatic rocks on Santiago Island have been forming for at least 10 Ma as a result of the plume activity responsible for the generation of the Cape Verde archipelago. The primitive studied lavas (<6 Ma) are highly SiO₂-undersaturated and exhibit significant REE fractionation and enrichment in incompatible elements. Previous elemental studies indicate a variable and heterogeneous residual paragenesis (garnet, amphibole and/or phlogopite) and a carbonatic lithospheric metasomatic event, responsible for the generation of the hydrous mineralogy.

The observed [1] isotopic (Sr, Nd and Hf) variation implies a complex mantle source with a significant contribution of HIMU and an enriched mantle component. In detail the Santiago lavas display a trend in 143Nd/144Nd-87Sr/86Sr space that deviates from the hypothetical mixing line between HIMU and EM1 end-member, considering Pitcairn, Tristan da Cunha, and Gough as their proxies. The deviation towards lower 143Nd/144Nd strongly suggests that pelagic sediments do not played a significant role on the origin of the EM 1 component. This is endorsed by the lack, at Santiago lavas, of negative Nb and/or Ce anomalies. Low 146Nd/144Nd for a given 87Sr/86Sr displayed by Santiago lavas is compatible with the influence of lower crustal garnet-bearing mafic granulites, which being interpreted as melting residues, would evolve towards high 176Hf/177Hf, given the high compatibility of Lu in garnet [2]. This would explain the fact that some of the studied samples plot above the Nd-Hf mantle array. However, such granulites are characterized by extreme depletion in incompatible elements leading us to favour the contribution of lamproitic subcontinental lithospheric derived melts in order to explain the EM1 component in Santiago Island.

This is a contribution of the FEDER/FCT project PLINT (POCTI/CTA/45802/2002) and a PhD scholarship from FCT (SFRH/BD/17453/2004).

**Biological and geochemical impacts on the solubility of Mercury in sediments**

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Three stratigraphically adjacent soils were sampled from a site in the south of England known to suffer from historic mercury contamination. Anoxic microcosms were set up containing differing quantities of organic carbon to promote microbial activity and half the samples were then treated with mercury (II). Biological, chemical and geochemical indicators were then monitored for 4-6 months to determine (1) the impact of mercury on a range of terminal electron accepting processes, and (2) the fate of the metal as the microcosms aged. It was found that the three soils behaved in distinctly differing manners, most notably in their ability to sorb mercury at the start of the experiment.

At the end of the experiment the sediment was extracted using 5 progressively more aggressive reagents, starting with de-ionised water and finishing with aqua regia and the solutions analysed for Hg by IPC-AES. Again the three soils responded very differently, with a significant proportion of the mercury unaccounted for, and presumed lost through processes other than sorption, such as biomethylation or bioreduction and subsequent volatilisation.

Samples were also analysed at the beginning and end of the experiments by classical microbiological and DNA-based techniques, to characterise both the active biomass and the changes in microbial community structure during incubation. These results were then linked to the geochemical indicators to give a greater understanding of the biogeochemical controls on Hg solubility in sediments. The results from this study will be used to quantify the need for action against mercury contamination on site and to investigate the best remediation or bioremediation strategy.

**Identification of palaeo-drought episodes in eastern Australia: High resolution dust flux records as an indicator of teleconnections and associated drought in the Australian region**

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Australia loses more sediment with wind than with water. Severity of dust emissions are strongly related to rainfall and therefore make excellent proxies for drought. Periods of prolonged drought are a feature of much of the Australian landscape [1] and these have significant economic, social and environmental implications. Contemporary drought episodes can occur over multi-year to multi-decadal time scales and have been linked to telecommunications such as El Niño Southern Oscillation (ENSO) that operates on a 3 to 7 year cycle and/or the Pacific Decadal Oscillation (PDO) that changes phase every ~20-50 years [2]. The operation of these cycles may in turn be superimposed on millennial scale variability in climate.

In this study we construct dust deposition chronologies from alpine peat deposits both within New Zealand and Australia to serve as a proxy for climate variability and drought in eastern Australia. This is possible because the provenance of dust was able to be established by matching the chemical fingerprints of dust samples with those from potential source sediments using trace elements [3] The results show variability in dust deposition through time, indicating that the climate of eastern Australia has experienced marked changes in aridity over the last 7000 years. In general, conditions became more arid and variable during the last 3000 years, especially between 3000 and 1000 years B.P. There is also evidence of cyclic wet-dry phases occurring at a frequency of 30-60 years for at least the last 3000 years. This pattern, which is possibly attributable to the PDO, has significant implications for water resource management in eastern Australia, particularly as the effects of these natural drought episodes may be amplified by the predicted impacts of climate change due to global warming.

Application of a microscopic chemical imaging system to characterize ambient particulate matter

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Many urban and industrial areas suffer from high levels of ambient PM$_{10}$ and PM$_{2.5}$. In order to evaluate the health impacts of the particulate matter and develop effective pollutant abatement strategies, one needs to know the source contributions to the observed concentrations. The most common approach involves the collection of ambient air samples on filters followed by laboratory analysis (IC, AA, XRF, automated colorimetry, thermal/optical reflectance for OC/EC, and GC/MS for PAHs) and application of receptor modeling methods such as the chemical mass balance receptor model (CMB). This process is expensive and time consuming. One possible method for physically characterizing and apportioning the sources of ambient PM is the application of microscopic chemical imaging (MCI) to identify and apportion the sources of ambient particulates.

The MCI method involves measuring individual particle fluorescence coupled with morphological data to develop unique source profiles that form the basis of a source identification library. Ambient filter samples can then be analyzed using the MCI method and source attribution based on individual particle analysis followed by identification using the source library. Using this approach, the apportionment of ambient PM to specific sources can be performed in near real time. In this paper we describe the MCI technique and present the results of efforts to apply the technique for aerosol characterization and source apportionment.

Calculation of cosmogenic nuclide production rates in the Earth atmosphere and in terrestrial surface

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Introduction

Considerable progress has been achieved in calculations of GCR particles production and transport in the atmosphere and in the Earth surface by Monte Carlo approaches [1-3]. Results of such simulations are presented here.

Calculational Methods

Production rates were calculated using depth dependent proton and neutron differential spectra within the atmosphere [2] calculated by the GEANT and MCNP codes. Cross sections used were the same as used in recent calculations for stony meteorites [3]. Production rates were calculated for present geomagnetic field intensity and solar GCR modulation parameter of 550 MeV that was proposed as long-term averages of solar GCR modulation [3].

Results

Calculated globally averaged production rates are compared with values obtained by different calculations in Table 1. Significant differences in obtained results are obvious from the table. One reason of the differences can be attributed to the cross sections, mainly for neutron induced reactions. This underscores the importance of their further investigations.

<table>
<thead>
<tr>
<th>GCR modulation parameter</th>
<th>Globally averaged production rate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{10}$Be</td>
<td>$^{7}$Be</td>
</tr>
<tr>
<td>$\Phi = 630$ MeV</td>
<td>0.045</td>
<td>0.081  [4]</td>
</tr>
<tr>
<td>$\Phi = 550$ MeV</td>
<td>0.0201</td>
<td>0.0129 [1]</td>
</tr>
<tr>
<td>$\Phi = 550$ MeV</td>
<td>0.0184</td>
<td>0.0354 [2]</td>
</tr>
<tr>
<td>$\Phi = 550$ MeV</td>
<td>0.0209</td>
<td>0.0402 this</td>
</tr>
</tbody>
</table>

Table 1: Calculated globally averaged production rates [atoms cm$^{-2}$ s$^{-1}$] of atmospheric $^{10}$Be and $^{7}$Be.

The influence of the cation vacancies on the minerals formation processes

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There were studied the pyrrhotine samples by using X-ray after being synthesized and kept in the atmosphere at a temperature of 20°C for 29 years (Table 1).

<table>
<thead>
<tr>
<th>The composition</th>
<th>Vacancies in the cell 1C</th>
<th>Goethite</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₈₋ₓSₓ</td>
<td>In X-ray grams As calculated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₈₋ₓSₓ</td>
<td>26</td>
<td>0.8</td>
<td>0.55</td>
</tr>
<tr>
<td>Fe₈₋ₓSₓ</td>
<td>27</td>
<td>1.25</td>
<td>1.13</td>
</tr>
<tr>
<td>Fe₈₋ₓSₓ</td>
<td>28</td>
<td>1.88</td>
<td>1.68</td>
</tr>
<tr>
<td>Fe₈₋ₓSₓ</td>
<td>29</td>
<td>1.91</td>
<td>2.26</td>
</tr>
<tr>
<td>Fe₈₋ₓSₓ</td>
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<td>3.15</td>
<td>2.84</td>
</tr>
<tr>
<td>Fe₈₋ₓSₓ</td>
<td>31</td>
<td>3.38</td>
<td>3.40</td>
</tr>
<tr>
<td>Fe₈₋ₓSₓ</td>
<td>32</td>
<td>4.93</td>
<td>4.00</td>
</tr>
</tbody>
</table>

Table 1: The parameters of some studied samples.

In the vacuum the pyrrhotines containing an excess of sulphur, turned into a stable state. As a result, there was formed the pyrrhotine having the composition Fe₇S₈ and the pyrite. But in the atmosphere there was formed Fe₇S₈ and goethite.

As it is seen from the table, the raised content of sulphur relative to the stable Fe₇S₈, leads to the increase in the cation vacancies concentration. Part of the ferric ions close to these vacancies, will be in non-equilibrium state. The substitution of the surface vacancies by the water molecules, leads to the goethite formation. The calculated contents of the goethite in terms of ferric ions in non-equilibrium positions as well as experimentally observed goethite content on the X-ray photograph are in good correspondence.

Thus, the non-equilibrium ferric ions and the adsorbed water form the goethite whose percentage corresponds to the vacancies contents.

Nanosized aluminosilicates (allopehane): Formation mechanisms and sorption capacities

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Introduction

Imogolite and allophan are two naturally occurring nanostructured aluminosilicates. There is a growing interest for these materials since they are likely to play a significant role in the carbon storage in soils as well as in the mobility of trace metals in the environment. Imogolite and allophane, because of their nanostructured nature, are also excellent candidates for industrial applications (adsorbents for e.g. remediation processes, catalysis…) since they can be easily obtained by coprecipitation of aqueous aluminum and silicon. The structure of the tubular imogolite is known whereas allophane is less well characterized. However, nucleation and growth mechanisms of these phases are only partially elucidated at best. In the present work, we focused on allophane because of its higher sorption capacities as well as the higher yield of the synthesis compared to imogolite.

Results

We examined a series of systems at various hydrolysis ratios R (=[OH]/[Al]) and thus pH values, before and after the heating step in the synthesis protocol. The recovered solids were analyzed by a combination of techniques: X-ray diffraction, electron microscopy, FT InfraRed spectroscopy and solid-state NMR, viz. "standard" one dimensional MAS experiments for Al-27 and Si-29, as well as two dimensional MQMAS Al-27 spectra. With increasing R, the expected Q⁰-3Al signature became predominant within the end-product. In the allophane precursors (i.e. before heating) Al is present only as octahedral species (MQMAS NMR shows unreacted monomers and edge sharing Al octahedra). Upon heating, a sizable amount of tetrahedral Al is formed along with low quantities of Al in a presumably highly distorted octahedral or even Al(V) coordination. Consequences in terms of metal sorption (Ni, Cu...) have been investigated.
Multiple sulfur isotopes in pyrite and barite-rich sediments from the Barberton Greenstone Belt: Evidence for microbial sulfur cycling?

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The appearance as early as 3.4 Ga of microbial SO2-reduction [1, 2] and S2 reduction or disproportionation [3] has been suggested by stable S isotope variations in sulfide minerals from Archaean greenstone belts. Here we attempt to identify traces of these metabolisms in previously unstudied exceptionally fresh drill core material from the Lower Mapepe formation (3.26 to 3.23 Ga), Barberton Greenstone Belt, South Africa. The core was drilled into the main workings in the Baryte Valley Syncline on farm Heemsteede 378 JU. Samples are taken from a 100 m section of shales, cherts, tuffs and conglomerate that cuts four barite horizons of syn-sedimentary origin [4]. Rare earth element and Y data in cherts and dolomitic units support a pervasive marine influence. Trace elements in pyrite indicate a low temperature sedimentary origin (Co/Ni= 0.1-1, Se/S <5 x 103).

We report individual mineral multiple S isotope data (33S, 34S, determined by SIMS) for: (1) interstitial grains and inclusions of pyrite from massive barite beds, (2) syn-sedimentary microcrystalline pyrite layers in chert and reworked barite sand deposits, and (3) isolated euhedral pyrites in massive chert and barite rich units. ∆34S in bedded barite and barite sands varies between +4 and +6‰, whilst pyrites show a greater range from +5 to -8 ‰. Pyrite ∆33S (-1 to +4 ‰) is extremely heterogeneous on a scale of micrometers, but individual laminations and petrographic associations of pyrite define much more limited values of ∆33S (within 0.5 ‰) over a range of ∆34S. Our results are consistent with models for combined microbial S0 disproportionation and S2 reduction [3], although microbial versus inorganic fractionation remains difficult to resolve.


Microbiological characteristics of circulation mud fluids during the first operation of riser drilling by the deep-sea drilling vessel “Chikyu”

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Quality assurance and control is significant for the scientific drilling in order to accurately characterize physical, geochemical, and biological properties in the cored deep subseafloor materials. To explore deep subseafloor life and its biosphere, identification and control of microbial contamination in drilling cores is critical for highly sensitive molecular analyses as well as cultivations, especially for the evaluation of low biomass and/or extremely harsh deep environments.

We studied some microbiological characteristics of circulation mud fluids before and after the first riser drilling operation by the newly constructed deep-sea drilling research vessel “Chikyu”. During the “Chikyu” shakedown expedition CK06-06 in 2006, we used the riser system for drilling 547 to 647 meter below the seafloor into the sediments offshore the Shimokita Peninsula of Japan. Cultivation experiments showed that no microbial growth was observed in the pre-circulation mud fluid, while 4 x 107 colonies per 1 ml were observed in the post-circulation mud fluid; all cultured bacterial isolates were found to be Halomonas. Using culture-independent molecular analysis, 16S rRNA gene sequences of Xanthomonas, which is used for industrial production of the mud fluid viscosifier ‘xanthan gum’, were predominantly detected in the pre-circulation mud fluid, while Halomonas sequences consistently dominated the clone library constructed from the post-circulation mud fluid. Archaeal 16S rRNA genes were amplified only from the post-circulation mud fluid; these archaeal clone sequences were affiliated to the Marine Crenarchaeota Group I (MGI), Marine Euryarchaeota Group II (MGI), Miscellaneous Crenarchaeotic Group (MCG), South African Gold Mine Euryarchaeotic Group (SAGMEG), Soil Group, and Methanococcus aeolicus. These results suggest that Halomonas contaminated and grew in the tank of circulation mud fluids, and other indigenous deep subseafloor microbial components, especially deep subsurface archaea, were also mixed into the post-circulation mud fluid.
Low level Selenium analysis for water monitoring purposes: A simple approach

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Selenium (Se) has been recognized as a significant pollutant of fresh water systems, and it is hazardous to aquatic life and human health [1]. Se contaminated groundwaters affect millions of people in China, Colombia and the US [2], yet analytical methods for monitoring low-level Se in natural waters are usually complex, technologically demanding and expensive, specifically for monitoring purposes in 3rd world countries. In this work, a simple and inexpensive spectrophotometric Se determination procedure in aqueous media is presented. The developed mechanism and protocol (schematic below) follows a 2-step reaction that is based on the azo coupling of amines to form a red azo compound.

![Schematic diagram of Se determination procedure]

The maximum absorbance of the azo dye is at 545nm, it has a maximum absorbivity of 2.85×10^4 L mol^-1 cm^-1 and follows the Beer’s law between 0.01 to 2.50mg/L. Quality parameter checks showed that total Se is determined with a sensitivity of 0.0124mg/l, an accuracy of +/- 1% and a precision with standard deviations of 2.5% at the low end of the concentration range. Various tests showed that sample preparation must convert all Se species to Se(IV) and interfering ions (e.g., Fe, Cu) must be removed or masked. This method can be easily adapted for aqueous Se analyses in natural waters following standard sample handling protocols [3]. Thus, accurate, rapid, simple and cheap low-level Se determination can be achieved and this will aid establish if Se levels in drinking waters are within the WHO drinking water quality guidelines [1].


Study of the C-rich phases of two cometary particles with electron microscopy and nanoSIMS

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We investigated the presence and nature of carbon in two Wild 2 particles called Ada (~12 µm) and Febo (~8 µm). Ada is composed of nodules of fayalite each surrounded by rims of crystalline SiO₂ (tridymite). Febo is composed of a large pyrrhotite grain, two silicates (enstatite and fayalite) and fine-grained material. Microtomed sections of each particle were first analyzed by TEM coupled with EELS to locate and characterize C-rich phases and to determine the particles mineralogy. Then the sections were analyzed with a NanoSIMS 50L for their C, N, O and H isotopic compositions. TEM analyses revealed the presence of amorphous carbon in small (<200 nm) regions in both particles. NanoSIMS isotopic images show that the C-rich spots observed with EELS are ¹⁵N-enriched. In Febo we found five spots showing an enrichment in ¹⁵N (δ¹⁵N from 420 to 639 ±20 to 70 ‰, 1σ) that were clearly associated with the C-rich regions. The carbonaceous material has approximately solar C and D/H isotopic compositions, and the bulk O isotopic composition was found to be δ¹⁸O=−18 ± 13 ‰ and δ¹⁷O=−37 ± 12 ‰ (1σ). In Ada we found a C-rich phase with enrichments in the isotope ¹⁵N (δ¹⁵N =550 ± 70 ‰, 1σ) and the isotope D (δD=610 ± 254 ‰ 1σ). The C isotopic composition at this phase is normal (−4±19 ‰). ¹⁵N enrichments overlaid to the organic material prove that the latter is indigenous to Wild 2, not contamination, and implies formation in cold (~10 K) environments. The O isotopes show homogeneous distributions (fayalite: δ¹⁸O=−3.1±13.9 ‰; δ¹⁷O=−3.1±6.7 ‰ and crystalline SiO₂: δ¹⁸O=-9.0±12.1 ‰; δ¹⁷O=−10.4±5.6 ‰).
Raman spectroscopic feature of the noble gas carrier Q in meteorites

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The phase Q contains most of the heavy noble gases in primitive meteorites although it is only 0.02-0.04% of the meteorites (Lewis et al. 1975). Q is most likely carbonaceous matter although the precise feature of Q is still unknown. Here we report Raman spectroscopic results of Q-rich fractions from the Allende meteorite, which were prepared with two different methods.

We made the Raman spectroscopic measurement of the chemical residue and the oxidized residue of Allende that were newly prepared. We also made measurement of several fractions of the “floating fraction” C1-8 that were obtained by colloidal and density separation in Amari et al. (2003). Matsuda et al. (1999) firstly found that the black material that floated on the water surface during the freeze-thaw method was similar to the chemical residue in noble gas features. Amari et al. (2003) further applied the colloidal and density separation to the “floating fraction” C1-8 and found that half of Q in this fraction was concentrated in the fraction C1-8D with the density of $1.65 \pm 0.04$ g/cm$^3$. We made measurement of Raman spectroscopy of C1-8D and also other different density fractions; C1-8J ($1.1 - 1.6$ g/cm$^3$), C1-8G ($1.97 \pm 0.06$ g/cm$^3$) and C1-8K ($2.2 - 2.3$ g/cm$^3$).

Raman spectra were obtained in Tokyo Medical and Dental University using 532nm YAG laser (5-6mW at the sample surface). We performed measurements of five to eight spots in each sample. The typical Raman spectrum of graphitic carbon (G band of about 1580 cm$^{-1}$ and D band of about 1350 cm$^{-1}$) was obtained in our all samples, which is common in the carbon material in carbonaceous meteorites.

We compared these Raman spectroscopic features of the acid residue (containing Q), oxidized residue (not containing Q) and the density separated floating fractions (being enriched and depleted in Q) of the Allende meteorite. As a result, we have concluded that Q is the graphitic carbon with the crystal size of about 50-60 Å from the Raman features.

Impact of human population on heavy metal concentration of stream sediments in the Trinity River, Texas, USA

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Introduction

The river sediment is basically composed of clastic materials derived from the surface of the Earth. Purpose of our study is to clarify the quantitative estimation of ratio of influence given to river sediment of nature and human activity by using of heavy metals [1, 2]. Trinity River is one of the biggest rivers which flows through Dallas and Fort Worth two big cities of USA and are highly populated. Trinity River drains into the Gulf of Mexico.

Results and discussion

Sediment samples collected from various points along the upper and lower streams were subjected to content analysis and elution analysis (using liqurate (flow) out test) on the heavy metals like Cd, CN, Pb, Cr, As, Hg, Ni, Zn and Cu from the river sediment for the purpose of environment assessment. A total of 22 sample points were identified from upper stream to lower stream and samples were collected such that almost the whole stream length of Trinity River is covered. Results show that heavy metal content through out the river stream is below the recommended limits posing no immediate environmental threat. However, the experimental results show clear impact of human population in bigger cities on heavy metal concentrations in the river sediments as compared to smaller cities with low human population. It could be seen from the analysis that all the heavy metals show relatively high content and high elution value in Dallas and Fort Worth. As we move away from the big cities, the value of content and elution of sediment decreased by natural dilution effect by the river.

Behaviour of noble gases during dehydration processes in the subducting oceanic crust

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Since the early years of terrestrial noble gas geochemistry, the origin of an isotopically atmosphere-like noble gas component found in many mantle-derived samples has been a matter of debate. Recent recognition that there might be a significant input of atmospheric noble gases by subduction of hydrated oceanic crust and its sediment cover is largely based on circumstantial evidences suggested from isotope analysis on natural mantle-derived samples (e.g. [1-4]). However, there are many unresolved issues about the feasibility of air recycling — for example, the presence of a carrier in subducting materials that can relay air-like noble gas into the deeper mantle regions. In order to clarify the possibility of noble gas recycling, we carried out high-pressure dehydration experiments on materials analogous to the subducting crust. Unlike the case of trace element study, choice of starting material is more critical for noble gases due to the possible diffusive input of atmospheric noble gases in a pressure chamber under high pressures and temperatures. To circumvent this problem, we have selected starting materials enriched in radiogenic noble gas isotopes (such as 4He, 21Ne, 40Ar and 129, 131-136Xe) as isotope markers. Then dehydration experiments under upper mantle P/T conditions were carried out by using muti-anvil high-pressure apparatus. Comparision of concentrations of radiogenic noble gas isotopes before and after the dehydration experiments suggests that virtually 100% of helium is removed from the slab upon dehydration, whereas up to 4% of argon can survive amphibolite dehydration process. This is consistent with the previously found signatures in natural mantle samples with suspected recycled atmospheric noble gases.


Zn isotopes as tracers of atmospheric emissions from a Pb-Zn smelter

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As atmospheric deposition is a major mechanism for metal input to soils and terrestrial organisms, metallurgical activities are among the major sources of airborne Zn, which needs to be better isotopically characterized.

The present work closely examines the Zn isotope fractionation during pyrometallurgical processes, compared to dry fallouts within a 5-km zone around a Pb-Zn refinery (in France).

Zn isotopic ratios are measured on a Nu Plasma MC-ICP-MS, after a Zn purification performed by a novel chromatographic method on micro-columns.

From the enriched ores (mean δ66Zn:0.11‰), dusts produced by the successive Zn extraction steps show strong variations in δ66Zn values and reveal pronounced Zn isotope fractionation (δ66Zn:-0.66‰) in the Pb blast furnace, where the highest temperature of the process is reached (up to 1700K). Assuming a Rayleigh fractionation in the volatized zinc, the Zn isotope fractionation factor α(ore/vapour) is 1.00083.

Considering the balanced Zn outputs of the main plant chimney stacks and the isotopic/elemental compositions of Zn emissions, a theoretical average δ66Zn of the total Zn smelter atmospheric emissions gives -0.13‰. Dry fallouts located from 1720 to 4560m from the smelter show such negative δ66Zn values (-0.52 to -0.02‰). In contrast, proximal dry fallouts reflect a main contribution of resuspension of slag heaps and local emissions of sintering units.
Differences in FTIR spectra measured in olivines derived from depleted and metasomatised sections of the Earth’s mantle

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The defect structure of olivine depends on the conditions of its crystallization/equilibration [1]. The concentration of various hydrogenated point defects in the olivine structure can be measured using FTIR spectroscopy. The position and intensity of OH IR absorption peaks reflect differences in pressure and silica activity (aSiO₂).

We measured FTIR spectra of olivines from different types of mantle xenoliths: depleted diamondferous harzburgites from the Finsch kimberlite, olivine xenocrysts from metasomatized cpx-rich mantle under the Superior Craton carried to the surface within Victor kimberlite, and an equigranular amphibole-bearing xenolith (DW211) from Dreiser Weiher (Eifel) [2].

Olivines from depleted harzburgites show different FTIR spectra compared to olivines from xenolith which likely interacted with low aSiO₂ melts (carbonatitic, alkaline-rich calcic melts). While olivines from both groups of samples showed IR OH absorption bands in the wavenumber range between 3440 and 3650 cm⁻¹, peaks at 3356 and 3328 cm⁻¹ were observed only in olivines from non-metasomatised peridotites. Such peaks were also commonly observed in olivines experimentally equilibrated with orthopyroxene at hydrous conditions [1]. In spite of a change in crystallization/equilibration conditions [1], the observed absence of lower frequency IR OH absorption bands could be due to a deficit of the octahedral defects in the olivine defect structure, which is likely to occur at low aSiO₂ conditions [1]. In spite of a lower frequency, IR OH absorption bands could be due to a deficit of the octahedral defects in the olivine defect structure, which is likely to occur at low aSiO₂ conditions [1]. In spite of a lower frequency, IR OH absorption bands could be due to a deficit of the octahedral defects in the olivine defect structure, which is likely to occur at low aSiO₂ conditions [1].

The results of this study suggest that FTIR spectroscopy of mantle olivine can be used as a complimentary tool to detect cryptic low aSiO₂ metasomatic events.


Impact of organic co-contaminant complexation on Th sorption to sand

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Understanding radionuclide speciation is fundamental to predicting the behaviour of radioactive contaminants in the environment. Specifically, the distribution of radionuclides between solid and solution phases will be determined by a combination of physico-chemical parameters, particularly pH and ligand availability, that control speciation. Anthropogenic chelating agents such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid are common complexing agents that are present as co-contaminant species in low and intermediate level nuclear wastes. They form stable complexes with tri- and tetra-valent cations, and it is known that complexation will increase radionuclide solubility and hence mobility; they are therefore of particular interest when assessing environmental risk from radioactive contaminants. This presentation will detail our work investigating aqueous radionuclide-ligand speciation, and the effect of speciation on radionuclide sorption using thorium as model tetravalent actinide.

Electrospray ionisation mass spectrometry (ESI-MS) was used to provide direct observation of aqueous Th complexation with EDTA and NTA, and the impact of these species on Th sorption was assessed in a series of batch experiments using a relevant environmental sand matrix and 1:1 molar ratios of Th:ligand. Thorium and Th-complexes showed slow sorption kinetics, and reached equilibrium partitioning by 7 d. At pH 4, [ThEDTA] and [ThNTA]⁺ species dominate in aqueous solution, and the sorption behaviour of these species was concentration dependent. At 5 µM concentration, the ligands enhanced the interaction of Th with the solid phase, but at 400 µM concentration, the ligands increased its solubility. At pH 8, the dominant EDTA species included [ThEDTA(OH)]⁻, and the only NTA species detected was [Th(NTA)₂]²⁻. These species were significantly more soluble than Th at both 5 and 400 µM concentrations, which is consistent with their anionic forms. Determination of the dissolved organic carbon quantified ligand interactions with the solid phase, thus the overall sorption mechanisms will be described and presented within a geochemical model.
REE-chloride complexing in hydrothermal fluids with new data on Lanthanum chloroaqua complexes

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Direct investigations of the speciation and complex formation of rare earth elements (REEs) in chloride-bearing aqueous fluids at high temperatures (T) and pressures (P) are needed for a greater understanding of the transport and deposition of rare earths in hydrothermal systems. We present new data on La3+-chloride complexing in low-pH aqueous solutions up to 500 °C and 230 MPa. Synchrotron x-ray absorption spectroscopy (XAS) measurements were made on a 0.02 m La/0.12 m HCl aqueous solution on the PNC-ID 20 beam line at the Advanced Photon Source, Argonne National Laboratory in the 25 - 500 °C T-range and up to 230 MPa. Analysis of the XAS shows that the La3+ aqua ion is the predominant species in the aqueous solution at 25 °C. From 150 to 500 °C, stepwise inner sphere chloroaqua complexes of the type La(H2O)n–3Cl(n+1)/2 are formed in the aqueous solution. The average total ligand number (δ) of the lanthanum chloroaqua complex species decreases from roughly 10 to 7 whereas the average number of Cl– ligands (n) increases steadily from 1.5 to 3.1 with increasing temperature over this temperature range. These results indicate that the degree of chloride complexation for La is slightly greater than for Nd and significantly greater than for Gd and Yb, in acidic aqueous solutions under similar P-T conditions. The greater stability of light REE (LREE) chloride complexes in high-temperature acidic aqueous solutions suggests that LREE may be transported more effectively than heavy REE (HREE) under similar conditions in chloride-rich hydrothermal fluids. Because simple ionic interactions alone are insufficient to account for the greater stability of LREE over HREE in acidic chloride-bearing hydrothermal fluids, additional REE-ligand interactions or steric effects may have to be invoked. The results from our XAS studies of REE (including La) in aqueous solutions up to 500 °C show negligible pressure dependence for pressures up to about 0.5 GPa.

Comparison of isotopic trends revealing the fate of injected CO2 in two geological storage projects in mature oilfields in Canada

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Monitoring and verification of CO2 storage is an essential component of geological storage projects. We present evidence from two enhanced oil recovery projects in Canada that geochemical and isotopic techniques can be successfully used to trace the fate of injected CO2. Geochemical and isotopic data for fluids and gases obtained from multiple wells at the International Energy Agency Greenhouse Gas Weyburn CO2 Monitoring and Storage Project (Saskatchewan, Canada) and from the Penn West Pembina Cardium CO2-Enhanced Oil Recovery Monitoring Pilot (Alberta, Canada) were collected before and throughout the CO2 injection phase. Carbon isotope ratios of injected CO2 in the Weyburn project were significantly lower than those of background CO2 in the reservoir. In contrast, δ13C values of injected CO2 at Penn West’s Pembina Cardium CO2-Enhanced Oil Recovery Monitoring Pilot were markedly higher than those of background CO2. After commencement of CO2 injection, the concentrations and δ13C values of CO2 and HCO3⁻ in fluids and gases repeatedly obtained from monitoring wells were determined. Increasing CO2 and HCO3⁻ concentrations in fluids in concert with δ13C values trending towards those of the injected CO2 revealed effective solubility and ionic trapping of injected CO2 at several monitoring wells at both study sites [e.g. 1]. In addition, changes in the δ18O values of reservoir fluids provided independent evidence for dissolution of injected CO2 in the produced waters. We conclude that geochemical and isotopic monitoring techniques, in concert with other monitoring approaches, can play an essential role in verification of CO2 storage, provided that the isotopic composition of the injected CO2 is distinct.

Reactive transport analysis of mineralogical controls affecting metal release from polymetallic carbonate waste rock

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Mineral weathering and metal leaching from mine waste is of worldwide environmental concern. Specific challenges exist under neutral drainage conditions in waste rock with a high carbonate mineral content. Such rock types are present at the Antamina mine site in Peru. Mining of the polymetallic skarn deposit produces waste rock containing multiple sulfide minerals that potentially liberate metals including Cu, Mo, Pb, and Zn. Prediction of the release of these metals from mine waste is difficult and depends on a number of hydrogeological and geochemical processes and parameters. In this study, we use reactive transport modelling to conceptually investigate the effect of thermodynamic and kinetic parameters on metal concentrations in drainage water with a specific focus on Mo. Parameters considered in the analysis include the mineralogical composition of the waste rock, which shows great variability at the site, and the rate of oxidation of the various sulphide minerals in relation to each other. In addition, the formation of secondary minerals including oxides, carbonates and hydroxides is considered. However, it is also possible that metal release is affected by the formation of molybdates, which further limits predictability of metal release. The effect of thermodynamic constants and rates for secondary mineral formation are also evaluated. Model results are compared with experimental data from field cells and laboratory experiments.

The rate of AMD and environmental affects of heavy metals (Cu, Pb, Zn, As, Hg, Cd and Fe) at Taknar Polymetal Mine, Bardaskan, Iran

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The Taknar polymetal (Cu, Zn, Au, Pb) massive sulfide deposit was formed within the Taknar formation (Ordovician). The Taknar zone is a wedge shape block situated between two faults, Darouneh to the south and Rivash to the north. Paeozoic, Mesozoic and Tertiary intrusive rocks are exposed within the Taknar zone. The Taknar Mine area is divided into four Taks: I, II, III and IV. Waste dumps from Tak's tunnels, which have been left unmanaged at the main river limits, created many problems related to the chemicals in stream water, stream sediments, layers of surface soil and ground water. These problems are responsible for increasing the rate of AMD and the transportation of waste dumps material by surface water and wind. Therefore the total waste dumps not only have increased the heavy metal concentrations in downstream sediments, but also a large volume of sediments have precipitated far from spoil heaps.

Based on EEC and EPA standards, the total concentration of trace elements (Pb, Zn, Cd, As, Hg) in the main river bed sediments close to minning activities is much higher than standard. Minning activities have been causing considerable amounts of minning wastes, especially at the vicinity of Taks I, II, III tunnels. The source of water contamination seems to be the northern tunnel of Tak III. This tunnel is also responsible for AMD generation as well as high pollution of the main river sediments. The structure of tunnel, high oxidation of sulfide minerals and its close distance to the river are the main reasons for the pollution. Water samples from this tunnel and some other localities confirm the high content of copper, hydrochemical parameters SO⁴ and TDS. This water indicated a high acidity and high salty condition.

Water contamination has also influenced the groundwater and Qanats of downstream villages in this area. Acceptable standard limits in drinking water (WHO, EPA and Iran National Standard) for heavy metals have also been used in order to compare the samples results. Having these type of pollution a special pollution source management must be arranged for the future.
Trace element characteristics of hydrothermal titanite from iron-oxide-Cu-Au (IOCG) mineralization

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Hydrothermal titanite is a common accessory mineral in the alkali-chloride alteration assemblages accompanying iron oxide-Cu-Au (IOCG) mineralization. Sensitive High Resolution Ion Microprobe-Reverse Geometry (SHRIMP-RG) trace element analyses of titanite from a suite of worldwide IOCG deposits of diverse age and host rock composition have several distinctive features that differentiate these metasomatic titanites from those of associated igneous or metamorphic origins. The most notable difference is in the relative distribution of the rare earth elements (REE). Regardless of host rock composition, the IOCG metasomatic titanite is notable enriched in the light REE, peaking at La (sometimes Ce), with values up to 20,000 times chondrite in some cases. Magmatic titanite from typical metaluminous granitoid compositions is also light REE-enriched, but peaks at Pr or Nd (somewhat less commonly at Ce and rarely at Sm), having values as high as about 12,000 times chondrite. A distinct but less widespread REE pattern observed in some IOCG titanite grains is represented by a marked middle REE enrichment peaking at Sm, Gd or possibly Eu, to about 8,000 times chondrite. This latter REE pattern is attributed to a later hydrothermal or metamorphic growth when the light REE are no longer available. In titanite from both magmatic and metasomatic systems, Eu anomalies (Eu/Eu*) may be positive or negative, although within a given sample set, particularly among analyses with overall higher REE concentrations, negative Eu anomalies tend to dominate. In addition to differences in REE abundances and patterns, other trace elements may also be distinctive in metasomatic IOCG titanite, and may indeed provide complementary petrogenetic information. Whereas the generally similar REE patterns appear to be largely a function of fluid chemistry, greater variability in trace transition metals such as Sc, V and Cr demonstrates a more significant dependence on the composition of the rock column through which the mineralizing fluids passed.

Sediment pore fluid geochemistry from Krishna-Godavari basin (Bay of Bengal): Possible influence of methane hydrate occurrences


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Seismic data show regional presence of gas hydrate manifested in the form of Bottom Simulating Reflector (BSR) in the K-G Basin [1]. Drilling and logging activities on-board JOIDES Resolution in the Indian margin under the aegis of Indian National Gas Hydrate Program confirmed the existence of massive gas hydrate deposits in the K-G Basin [2]. K-G basin is a peri-cratonic rift basin located in the middle of the eastern continental margin of India. The study areas lie within the continental slope region. Recently large number of long cores (25-50 m) were collected on board Marian Dufresne (MD-161: May, 2007) using a Giant Calypso piston corer over a water depth range of 650-1600 m from K-G Basin Core locations were selected based on sub-bottom profiler (SBP) data. Cores have been collected under various geological environment viz., mud diapirs, mass flows, and hemipelagic sediments. Sulfate and C1-C3 hydrocarbon, chloride concentrations, total carbonate alkalinity, and carbon stable isotope ratios of CH4 and CO2 have been measured in several cores. The depth of sulfate-methane interface (SMI) from the sediment surface varies from 5 to19m. Three sulfate concentration profiles have been recorded, viz., concave up with with high gradient, sigmoidal and kink types. δ13C of CH4 (as low as -110‰) and C1/C2+C3 ratios (as high as 4193) below the SMI are typical for biogenic hydrocarbon gases. The SMI is a zone of intense methane oxidation mediated by anaerobic methane oxidizing archaea. In one of the cores we have recorded thick beds of authigenic carbonates with δ13C values ranging from -41 to -52‰ VPDB possibly suggesting a paleo methane venting location. Instability of hydrate layers and fluctuation in vertical methane flux has happened in KG basin through geologic past. Multidisciplinary investigation is carried out to understand the geological conditions favourable for hydrate formation.

Redox interactions of Technetium with Fe(II) mineral phases

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Iron minerals influence the redox behaviour and mobility of metals in the environment, including the radioactive element technetium. Here, we have investigated several environmentally relevant reduced iron minerals with the potential to control the biogeochemistry of technetium in environmental media. Technetium is highly mobile in its oxidized form pertechnetate (Tc(VII)O42−), however, when it is reduced to Tc(IV) it immobilizes via precipitation or sorption. Pertechnetate was added to samples of both biogenic and abiotically synthesized Fe(II) mineral phases (magnetite, vivianite, siderite, and an amorphous Fe(II) phase). The pertechnetate was reduced and immobilized on all of the Fe(II) mineral phases (magnetite, vivianite, siderite, and an amorphous Fe(II) phase). The reduced iron mineral phases were exposed to oxidizing media.

This study highlights the utility of studying specific Tc-mineral interactions, to better understand the biogeochemistry of Tc behavior in complex environmental media.

Phosphorus zonation as a record of olivine crystallization history

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Rapid diffusion of divalent cations through olivine at magmatic temperatures can result in relaxation of their zoning profiles and a loss of information regarding early crystallization history. Recent studies [1-3] show that zoning of P (and often associated Al and Cr) is ubiquitous in igneous olivines from a range of rock types, even in crystals homogenized with respect to divalent cations. We present results of 1-atm controlled cooling rate experiments (5-15°C/hr; QFM) that crystallized olivine from a natural Hawaiian basalt to which olivine was added (liquidus = 1287°C) and a P-free but otherwise compositionally identical synthetic analog. Experiments were either initially superheated to 1300°C for 3 h (leading to destruction of olivine nuclei) or held at subliquidus conditions for 3 h (1280°C; resulting in ~5% olivine nuclei), followed by linear cooling, and then quenching at 1150°C.

Our experiments replicate zoning features (i.e., sector and oscillatory zoning) seen in natural olivines. Individual olivines from each experiment lie on generally well defined trends in Al-Cr-P space that depend on the details of the experiment; however different sectors within a single crystal define distinct parallel trends. Al and Cr are positively correlated and are generally positively correlated with P in P-bearing runs suggesting connections between their modes of incorporation into olivine. Although Al and Cr zoning are spatially correlated with P zoning in some natural olivines and in olivines from the P-bearing experiments, the presence of P is not a prerequisite for zoning of Al and Cr as such zoning also occurs in olivines from the P-free runs. There are differences in some of the details of the P-Al-Cr systematics between olivines grown in initially superheated experiments and those from subliquidus experiments and natural samples. These differences plus the lack of a strong correlation of the results with cooling rate suggest that (1) crystal growth rate is the dominant factor in the development of zonation of these elements in igneous olivine, and (2) that P-Cr-Al zoning probably largely reflects local processes occurring at the crystal-melt interface. Our results also demonstrate that observed oscillatory zoning in magmatic olivines can form in magmas undergoing relatively simple cooling histories and that variable olivine growth rates can occur for such magmas.

Constraints on hydrogen generation during serpentinization of ultramafic rocks

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In recent years, serpentinized ultramafic rocks and minerals have received considerable attention as a source of H₂ for hydrogen-based microbial communities and as a potential environment for the abiotic synthesis of methane and other hydrocarbons within the Earth’s crust. Both of these processes rely on the development of strongly reducing conditions and the generation of H₂ during serpentinization, which principally results from reaction of water with ferrous iron-rich minerals. We will present numerical geochemical models combined with a review of laboratory experimental studies to evaluate constraints on H₂ production during serpentinization. The results suggest that thermodynamic constraints on mineral stability and the distribution of Fe among mineral alteration products as a function of temperature are predominant factors controlling the extent of H₂ production. At high temperatures (>~315ºC), rates of serpentinization reactions are fast, but H₂ concentrations may be limited by the attainment of stable thermodynamic equilibrium between olivine and the aqueous fluid. Conversely, at temperatures below ~150ºC, H₂ generation is severely limited both by slow reaction kinetics and partitioning of Fe(II) into brucite. Peak temperatures for H₂ production occur at 200-315ºC, indicating that the most strongly reducing conditions will be attained during alteration within this temperature range. Fluids interacting with peridotite in this temperature range are likely to be the most productive sources of H₂ for biology, and should also produce the most favorable environments for abiotic organic synthesis. The results also suggest that thermodynamic constraints on Fe distribution among mineral alteration products have significant implications for the timing of magnetization of the ocean crust, and for the occurrence of native metal alloys and other trace minerals during serpentinization.

New high-resolution records of dustiness over recent centuries from Greenland and Antarctic ice cores

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Archived in glaciers and ice sheets are long term records of dustiness. Dust impacts Earth’s radiative forcing directly by modifying the radiation budget and affecting cloud nucleation and optical properties, and indirectly through ocean fertilization which alters carbon sequestration. Because of their short atmospheric lifetimes, dust aerosol concentrations are highly variable in both time and space. The mineralogy and elemental characteristics of dust aerosols may indicate provenance and so past climate and atmospheric circulation and transport.

We present continuous ice core records of continental dust deposition during recent centuries at a number of ice core sites in Greenland and Antarctica. These new records were developed using a novel ice core analytical system which allows for simultaneous measurements of more than 30 elements and chemical species. We explore the similarities and differences between the records and use model simulations to evaluate relationships between dustiness and recent climate change and land use in possible source areas.
Catastrophic ice sheet collapse and future sea levels: Lessons from the last interglacial

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There is now growing evidence that the land-based icesheets of the West Antarctic and Greenland underwent catastrophic collapse during previous warm interglacial periods, inducing rapid rises in sea levels. Compared to the full range of glacial to interglacial transitions of typically 100 m to 130 m, the likely future increase in sea level is relatively small, of the order of ~3 m to 6 m. However with many coastal cities being subject to inundation with even modest sea level rises, constraining the critical thresholds for greenhouse-driven collapse of the terrestrial based icesheets is of paramount importance.

In order to provide new constraints on this problem we have undertaken a study of the southern-most known occurrence of Last Interglacial coral reefs that occur along the southern coastlines of Australia. These reefs flourished during the warmest period of the Last Interglacial with temperatures similar to those predicted for 2100 from Greenhouse warming. A new locality has been discovered at a latitude of 34° S, in a small embayment (Foul Bay) that is ~15 km north of Cape Leeuwin in Leeuwin-Naturaliste block of southwest Western Australia. The reef consists mainly of Goniastrea sp. together with lenses containing abundant gastropods (Turbo sp.) and opercula, and rare bivalves. The main reef occurs at a height of 3-4 m above present-day sea level with a smaller subsidiary reef at ~0 to 1 m. Very precise U-Th MC-ICPMS dating of multiple sub-samples of in situ coral indicates a narrow range of ages from ~128 ka to 125 ka. This shows that during the first part of the Last Interglacial, both warmer conditions and higher sea levels prevailed, approximately coincident with the maximum in Northern Hemisphere summer insolation. This points to the Greenland icesheet being a significant contributor to the higher sea levels during the Last Interglacial whereas today the maximum summer insolation is in the Southern Hemisphere. Thus with further greenhouse warming effecting global temperatures the West Antarctic icesheet is argued to be most susceptible to catastrophic collapse although an important role for the Greenland icesheet cannot be discounted. Regardless, there is an imperative to reduce greenhouse emissions to minimise the magnitude of future increases in sea levels.

14C variability in two late Holocene stalagmites and the implications for climate forcing mechanisms

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Putative links between late Holocene climate variability and solar output remain controversial and are difficult to demonstrate unequivocally. Here we show that temporal changes in initial 14C activity in calcite deposited in two late-Holocene stalagmites (from Attaehöhle, Sauerland, Germany and Grotte de Clamouse, S.E. France) vary synchronously with changes in atmospheric 14C production during the critical time interval between 2.7 and 2.2 kyr. B.P. Atmospheric 14C production changes were computed using the atmospheric (tree-ring) 14C dataset and a multi-box carbon-cycle model. The new ‘wiggle-matched’ 14C data for these late-Holocene stalagmites provide independent support for their U-series chronology, and eliminate the need for chronological ‘tuning’ as in published δ18O-atmospheric 14C comparisons. In stalagmite CL26 from Grotte de Clamouse, the carbon isotope systematics (δ13C and 14C) undergo a significant perturbation at 2.4 ka. Prior to 2.4 ka the initial 14C in the stalagmite tracks that of the atmosphere, implying open-system behaviour, but after 2.4 ka the initial 14C activity correlates strongly with δ13C, apparently reflecting a more closed-system behaviour. Monte Carlo simulations that involve the generation of synthetic δ18O time-series datasets were used to evaluate the statistical robustness of correlations between atmospheric δ13C production and stalagmite δ18O. The study highlights the utility of time-series 14C measurements in stalagmites as a means to interpret correctly their oxygen and carbon isotope variability.
Mantle convection and K/U

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Models for the deep Earth must be challenged. Where are we with respect to understanding the composition of the Deep Earth? Researchers continue to challenge the dominant paradigm of a compositionally homogenous pyrolitic model at the gross scale. A major focus now is on the nature of the core-mantle boundary and what might potentially exist in this remote location.

The distribution of heat producing elements in the Earth drives convection and plate tectonics. Recent results from geoneutrino studies are coincident with pyrolitic-type models for the Th and U content of the Earth. Geoneutrino detectors continue to come on line and count events, thus their data are increasing in quality and uncertainties continue to reduced with time (at present 2 detectors are accumulating data). Geochemical models posit that ~40% of the heat producing elements are in the continental crust, with the remainder distribute throughout the mantle. Our recent data on K/U for oceanic basalts revises considerably the mantle value from 13,000 to 18,000. Although models of core formation allow for the incorporation of heat producing elements, the core contribution of radiogenic heating is considered to be negligible. The Mantle Urey (Ur) ratio (radiogenic heat contribution to the total mantle heat flux) is estimated to be ~0.3 from chemical and isotopic data. Such a low mantle Urey ratio is at odds with the paradigm of parameterized convection models (i.e., Ur = 0.7) for the Earth. Thus, recent results challenge the dominant geophysical models of mantle convection and call for a significant contribution heat from secular cooling of the mantle.

In situ geochemical and Sm-Nd isotopic fingerprinting of high-T hydrothermal alteration

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A combination of EPMA imaging and analysis, LA-ICPMS trace-element quantification, and LA-MC-ICPMS Sm-Nd systematics has been applied to two alteration styles (calic-sodic vs. potassic) characteristic of Fe-oxide-Cu-Au (IOCG) mineralization from the Southern Curnamona Province (SCP), Australia. The LREE-enriched nature of these systems gives rise to accessory minerals (e.g. monazite, allanite, apatite, titanite) that can be exploited using these in situ analysis techniques to define the temperature, timing, and crustal affinity for episodes of superimposed alteration over the course of collisional orogenesis.

Calic-sodic alteration is characterized by epidote-albite-magnetite-quartz hosting abundant chalcopyrite. This assemblage is superimposed on an older allanite-quartz assemblage. Whereas allanite contains elevated Be, P, Zn, As, Ba, LREE and traces of Au (10 ppb), altered allanite domains and neighbouring epidote are enriched in Cu, Sn, and Sr. In situ Sm-Nd systematics reveal that allanite has a Nd-isotope affinity to ~1620 Ma A- and I-type granites documented elsewhere in the SCP, whereas fluids responsible for ~1575 Ma epidote-bearing alteration were sourced from the underlying metasedimentary sequence.

Potassic alteration is characterized by K-feldspar, biotite, muscovite, and quartz with minor chalcopyrite and pyrrhotite. Accessory minerals include monazite, xenotime, apatite and rare titanite. Monazite typically forms as aggregates intergrown with either apatite or xenotime. The latter yield monazite-xenotime solubility temperatures between 550 to 600°C indicating alteration under amphibolite-facies conditions. In situ Sm-Nd systematics for monazite clusters within biotite yield precise initial-Nd that are indistinguishable from ~1575 Ma calcic-sodic alteration.

Construction of these in situ datasets reveals a long-lived interplay between magmatic, magmatic-hydrothermal, and hydrothermal fluids over the course of collisional orogenesis. This approach also provides a means to understand variations in metal associations and redox conditions in IOCG deposits as a function of temperatures, ages, and Nd-isotope signatures extracted directly from hydrothermal accessory minerals.
Testing the response of $^{230}\text{Th}$ and extraterrestrial $^3\text{He}$ to sediment redistribution at the Blake Ridge, western North Atlantic

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The constant flux proxies $^{230}\text{Th}$ and extraterrestrial $^3\text{He}$ ($^3\text{He}_{\text{ET}}$) have the potential to provide unique insights in paleoceanographic studies by allowing estimates of vertical rain rates and rates of lateral sediment redistribution. Fractionation associated with redistribution may separate $^{230}\text{Th}$ from $^3\text{He}_{\text{ET}}$, however, biasing accumulation rate data; it has been suggested that $^{230}\text{Th}$ may be enriched in clay-sized particles [1], while $^3\text{He}_{\text{ET}}$ is thought to reside primarily in larger grains [2]. In this study, we evaluate the fractionation between $^{230}\text{Th}$ and $^3\text{He}_{\text{ET}}$ in Holocene and last glacial samples from two cores from the Blake Ridge, a drift deposit in the western North Atlantic. At the end of the last glacial period, both cores received large amounts of advected sediment, enriching the cores in fine material. We find no evidence for fractionation between $^{230}\text{Th}$ and $^3\text{He}_{\text{ET}}$ related to sediment focusing. We also find that despite large temporal and spatial differences in sediment redistribution, normalization to $^{230}\text{Th}$ and $^3\text{He}$ produces mass accumulation rates that are generally internally consistent. High terrigenous contributions to glacial samples require a correction for terrigenous $^3\text{He}$ for some samples. We discuss new data constraining the terrigenous endmember as well as $^{230}\text{Th}$ and $^3\text{He}_{\text{ET}}$ distributions in different grain size fractions.


Double dating of zircon via SHRIMP U/Pb and (U-Th)/He methods

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Combined zircon (U-Th)/He and U/Pb dating methods have previously been applied to provenance and sediment recycling studies [eg. 1, 2] where the U/Pb analysis was preformed by LA-ICPMS. In this work we have combined SHRIMP U/Pb analysis with traditional (U-Th)/He methods to obtain double dates on zircon from a kimberlite pipe.

Zircon grains were abraded to remove the outer 20µm and eliminate the need for an alpha-ejection correction. Ablated grains were mounted in epoxy and lightly polished to expose a flat surface, then analysed by SHRIMP. Grains were then extracted from the epoxy and analysed by standard (U-Th)/He methods. A test using in-house zircon standards was made to determine whether the ion microprobe sputtering process affected He diffusion from the sample. Virtually identical ages (ex-SHRIMP (U-Th)/He age = 10.8 ± 0.3 Ma vs Standard (U-Th)/He age = 10.3 ± 0.2 Ma) and Th/U ratios were obtained to within error.

We applied the double dating technique to a zircon mineral separate obtained from a bulk sample from the Sacramore pipe located in the Merlin kimberlite field in the Northern Territory of Australia. The zircon U/Pb ages for the Merlin kimberlite (n=14) clustered around the mean of 1694 (±156) Ma while the zircon (U-Th)/He thermochronometry (n=33) yielded a mean age of 376 (±62) Ma, within error of previously determined emplacement ages for the Merlin pipe (380 Ma[3]).

The double dating method indicates that all of the zircon grains in the Merlin kimberlite were xenocrysts that originated from lower- to mid-crustal regions (>6 km).

Effect of host mineral species on the fidelity of fluid inclusion compositions

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Prior to trapping in a host, a hydrothermal fluid's composition is controlled by simultaneous equilibria with several species of minerals. Once trapped within a specific host mineral, the isolated inclusion fluid can reequilibrate only with that species during uplift and cooling of the rock. Its room temperature composition is therefore affected by the solubility behavior of that host species during cooling.

An equilibrium modeling approach is used to predict the effects of different host mineral species on post-trapping chemical changes in fluid inclusions during uplift and cooling of hydrothermal ores. A fluid with a composition typical of Upper Mississippi Valley-type Pb-Zn ores is first equilibrated with a mineral assemblage containing quartz, barite, calcite, galena and sphalerite at 100°C. The fluid is then isolated and cooled to 25°C in a stepwise manner in equilibrium with only calcite, quartz or sphalerite, respectively. Predicted changes in chemical and isotopic composition of the trapped fluids are derived.

The masses of crystals that precipitate or dissolve in the inclusions during cooling cannot be resolved optically, but have dramatic effects on fluid metal and isotopic compositions. Fluid in calcite hosts dissolves calcite and precipitate quartz, whereas fluids in quartz and sphalerite hosts become undersaturated in calcite and precipitate quartz and barite. Small amounts of metal sulfide minerals are also precipitated. Metal concentrations in calcite-hosted fluid decrease by 10⁴, while those in quartz- or sphalerite-hosted fluids decrease by 10². In calcite, δ¹³C of the fluid decreases by 2 permil and that of CO₂ gas by 7 permil. These effects, caused by calcite dissolution and a slight pH shift, make inclusions in calcite the least representative of the original fluid's composition. These predicted differences in post-trapping behavior among host minerals should be considered when sampling and micro-analyzing fluid inclusions to interpret the nature of hydrothermal fluids.

Investigating the dynamic consequences of compositional density heterogeneity in Earth’s lower mantle

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Seismic observations hint at compositional heterogeneity in the lower mantle, particularly in regions associated with the two large, low-velocity provinces beneath Africa and the Pacific, observed in shear-wave tomography. Several dynamic hypotheses have been developed in recent years to explain the possible cause of the low-velocity provinces, each of which has significant consequences for the nature of smaller-scale processes, Earth’s heat budget, and the temperature and chemical structure of the mantle. These hypotheses typically involve the presence of lower mantle material that is intrinsically more-density dense than surrounding mantle. Large volumes of dense material may form large, long-lived, thermochemical piles or oscillating superplumes, whereas smaller volumes and/or a lower intrinsic density of this material may result in compositionally heterogeneous clusters of smaller plumes. Here, we investigate the utility of combining geodynamic predictions with seismic observations of shear-wave tomography, CMB topography, and location of the Ultra Low Velocity Zone (ULVZ) to test these different hypotheses in an attempt to constrain the nature of large scale mantle convection. We find that each hypothesis is expected to provide unique predictions that can be tested against observations. We also find that the source compositional heterogeneity (e.g., core-mantle reaction products, iron entrainment, segregation of basaltic crust, or primordial material) plays a significant role in the dynamic characteristics of these different scenarios.
Inclusions of immiscible sulfide melts in olivine phenocrysts from mantle-derived magmas

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Sulfide inclusions, droplets of immiscible sulfide melt trapped during crystal growth have been observed in olivine phenocrysts in lavas from a variety of tectonic settings including MORB, OIB, BABB, Island Arc and Continental Flood Basalts. These inclusions may present the only direct evidence for sulfur saturation and the composition of an immiscible sulfide liquid early in the fractionation history of a mantle-derived magma.

Figure 1: Naturally cooled (A) and reheated (B) sulfide inclusions in olivine (Fo90-96). Both inclusions are 40 µm diameter.

Sulfide inclusions are rare (in 0.1-3.5% of phenocrysts), range in size from <10-100 µm and are generally coarsely recrystallised, to a three phase assemblage, during cooling (Fig. 1A), as described by Danyushovsky et al. [1]. Suitable inclusions were therefore reheated, in a custom-built low-inertia high-temperature heating stage, to 1100-1250°C and quenched to produce a ‘homogeneous’ 2- or 3-phase sulfide assemblage (Fig. 1B).

Compositions of the reheated sulfide inclusions were determined by EMPA and LA-ICPMS in order to evaluate the range of their variations within, and between, samples and to address the question of whether immiscible sulfide liquid compositions vary systematically between magmas from different tectonic settings.

We will present major and trace element composition of the sulphide inclusions and their host phenocrysts from 15 samples.


Geochemistry of the Martian crust and constraints on the mantle

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Chemical compositions of Mars surface rocks and soils from orbital spectroscopy have been modified by weathering processes or represent incomplete analyses. The most complete chemical characterizations of Mars rocks and the regolith derived from them are based on in situ APXS analyses by rovers and on laboratory analyses of Martian meteorites. The cosmic-ray Mars launch ages of meteorites cluster into petrologically consistent groups, suggesting at least seven sites have been sampled – far more than by landed missions. A comparison of the compositions of Gusev RAT-ground rocks analyzed by MER and Mars meteorites indicates all are basaltic (as do orbital GRS measurements) with variable abundances of alkalis. None of these rocks are calc-alkaline, as inferred from some orbital remote sensing data, casting doubt on that interpretation. Depletion in Al, a defining geochemical characteristic of Mars meteorites and Mars Pathfinder rocks, is not observed in Gusev rocks and soils. Ca-Mg and Ni-Mg systematics, used to classify the meteorites, are distinct in Gusev rocks. However, Fe-rich compositions appear to be a general characteristic of all Mars rocks. Highly fractionated rocks, inferred from some orbital spectra, are not observed among surface materials and must be uncommon.

Not surprisingly, the mantle source regions for Martian igneous rocks are revealed to be diverse in the kinds of basaltic melts generated, as well as in their radiogenic isotope and incompatible trace element compositions and oxidation states. Primary liquid compositions represented in these suites are consistent with derivation from a mantle composition with high Fe/Mg and volatile element abundances, possibly including H₂O although that remains controversial.
Global patterns of dust deposition deduced from dissolved Al in the surface ocean

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High resolution dissolved aluminium data (Al) from surface waters obtained during the CLIVAR repeat hydrography program is being used to create a global map of dust deposition to the surface of the oceans. The results so far show generally good agreement with the existing GESAMP predictions of oceanic deposition that were based on land based aerosol sampling. In some regions though we see evidence of surface water dust input that is not represented in current atmospheric deposition models, notably the southern Indian and Pacific oceans, downwind of Australia. Additionally, in the NW Pacific the models appear to be overestimating dust deposition. High resolution depth profiles along the CLIVAR cruise tracks show preferential imprinting of the sub-tropical mode waters formed in the western parts of the Pacific and Atlantic Ocean. These sub-surface signals result from the subduction of surface water labeled with Al by dust deposition in the mode water formation regions. Thus the Al signal may be a potential paleo proxy of the mode water formation process. The GEOTRACES sampling program which will incorporate multiple trace element and isotope sampling across geochemical gradients, will help identify new geochemical tracers of processes such as atmospheric deposition. These new tracers will constrain our understanding of both contemporary geochemical processes in the ocean as well as forming the basis of new paleo proxies of physical and biological processes.

Composition of low-degree hydrous melts of fertile spinel- or garnet-bearing lherzolite

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We have experimentally determined the composition of low degree hydrous mantle melts in equilibrium with spinel and garnet-lherzolite mineralogy around 1050-1100 °C at 1.0 and 2.0 GPa. The maximum amount of water that can be stored in upper mantle lherzolite is about 0.5 wt% [1]. This water is mostly stored in amphibole and will be released by amphibole breakdown (between 1050 and 1100 °C in fertile mantle compositions; [2]) inducing partial melting of the mantle. Amphibole breakdown thus marks the lowest possible temperature where melting occurs in the absence of a free fluid phase.

Experimental melts produced by amphibole breakdown are in equilibrium with olivine, orthopyroxene, clinopyroxene, and either spinel (1.0 GPa) or garnet (2.0 GPa). Comparison with subsolidus experiments allows calculating amphibole breakdown reactions:

\[ 1 \text{amp} + 0.2 \text{opx} = 0.2 \text{ol} + 0.4 \text{cpx} + 0.01 \text{sp} + 0.4 \text{melt} \]
\[ \text{amp} + \text{opx} = \text{ol} + \text{cpx} + \text{gt} + \text{melt} \text{ (preliminary)} \]

in the spinel and garnet stability fields, respectively.

Melt compositions are very similar to the compositions of low-degree melts of dry lherzolites (e.g. [3]). However, similar melt compositions (in terms of Si, Al, Mg contents) are obtained at much higher degrees of melting, resulting in lower incompatible element (e.g. Na and K) concentrations, and thus less pronounced silica-undersaturation.

Although silica-rich, experimentally produced melts are compositionally far from typical high-Mg andesites, being much less magnesian at a given silica content, and too rich in alkalis. This strongly suggest that high-Mg andesites cannot be produced by fluid-absent melting of fertile (or even worse, metasomatized) mantle. Instead, generation of mantle derived high-Mg andesites requires high-water content (water-saturation = flux melting process), and high degrees of melting of a depleted mantle source (harzburgite).

Mesozoic intra-continental progressive evolution in middle-upper Yangtze region of China: Evidence from thermochronology and balanced cross-section

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The geometrical evolution of the 400 km wide middle-upper Yangtze thrust belt from western Hunan-Hubei to eastern Sichuan has been established over a time interval of 118 Ma. Based on FT and balanced cross-section analytic results (Tables 1 & 2), we have suggested that the Mesozoic

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\rho_s) (10^5/cm)</th>
<th>(\rho_i) (10^5/cm)</th>
<th>T(Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>6.25(2197)</td>
<td>19.31(917)</td>
<td>198.4±10.4</td>
</tr>
<tr>
<td>1-2</td>
<td>25.54(894)</td>
<td>13.77(482)</td>
<td>154.1±10.2</td>
</tr>
<tr>
<td>1-3</td>
<td>228.0(35)</td>
<td>24.0(30)</td>
<td>93.4±23.5</td>
</tr>
<tr>
<td>1-4</td>
<td>1.881(523)</td>
<td>4.525(1258)</td>
<td>88.2±8.6</td>
</tr>
<tr>
<td>1-5</td>
<td>3.297(511)</td>
<td>8.006(1241)</td>
<td>84.9±5.1</td>
</tr>
<tr>
<td>1-6</td>
<td>9.762(812)</td>
<td>21.194(1763)</td>
<td>80.3±4.7</td>
</tr>
</tbody>
</table>

Table 1: Fission track analytic results of apatite

Table 2: Analytic results of balanced cross-section

The concentrations of REE in agricultural soils and its use for tracing the geographic origin of vegetable oils

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Tracing the geographic of food has become an increasing economic factor. In this respect, stable light isotope ratios have been used to identify the geographic origin of food products. There have attempts with radiogenic isotopes (e.g. Pb, Sr, Nd etc.) and trace element distribution patterns as potential indicators.

In this work we used REE distributions of edible oils, in particular of pumpkin seed oil, a local specialty protected by the EU. From several geographic regions samples were taken from the topsoil, the pumpkin meat, the seeds and the oil extracted from the seeds (Soxhlet) and oil produced from these seeds in a local pumpkin oil mill. The sample locals are from Lower Austria and Styria, Serbia, Hungary, Russia and also from China.

The important outcome of this study is that the distribution patterns of the oils follow that of the continental crust. The chondrite normalized REE patterns of soils do show regional differences. But the most interesting observations is that the regional variation of the REE distributions of the extracted oils is much larger than the those of the soils. In addition we find Ce and Gd anomalies, but the latter only related to the Styrian region. Since REE are non essential elements for plants, our original hypothesis, that the REE distribution patterns reflect that of soils substrate has be falsified. Nevertheless, the patterns do show regional differences, which could be used for tracing the geographic origin but no reason can be given for this observation.

In search of the deglacial carbonate preservation maximum: Why is it missing?

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One hypothesis for lower atmospheric CO₂ levels during glacial periods invokes increased ocean stratification with a corresponding shift of dissolved inorganic carbon and nutrients from intermediate depths to deep waters. Under this scenario, both increased efficiency of the ocean’s biological pump and carbonate compensation contributed significantly to CO₂ drawdown. If the rapid deglacial rise in atmospheric CO₂ (~17 – 14 ka) were caused by a breakdown of this stratification and increased ventilation of deep water masses, then one consequence would be increased CaCO₃ preservation in deep sea sediments.

We present down core records of carbonate preservation for the last 21,000 years from 16 cores in the tropical and subtropical Pacific and Atlantic Oceans. Our preservation records are based on a multi proxy approach involving a new calcite dissolution proxy (the Globorotalia menardii Fragmentation Index), size normalized foraminifer shell weights and 230Th-normalized carbonate accumulation rates. We find that in most of our cores the expected deglacial carbonate preservation maximum is missing. The reasons for this vary with location: (1) in the eastern equatorial Pacific down core variations in the ratio of organic carbon to calcite flux strongly obliterates the deglacial preservation maximum because the deglacial was a time of high productivity in this region, (2) in the western equatorial Pacific most cores have very low sedimentation rates and the deglacial preservation maximum is likely obscured due to bioturbation, and (3) in the equatorial Atlantic the dominance of bottom waters by Antarctic Bottom Water (which is corrosive to calcite) lead to a deglacial dissolution maximum in our cores.

Coastal ocean Iron time series

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Iron (Fe) is an essential micronutrient in the ocean. The depletion of Fe has been linked to limitations in biological production [1] which has implications to the global carbon cycle. Major sources of Fe are atmospheric deposition [2] and the flux of Fe from sediments [3]. In order to understand the temporal changes in Fe within the coastal environment we participated in a coastal ocean time series, at the UCLA Santa Monica Bay Observatory site, where we measured dissolved Fe concentrations.

We observed seasonal changes in both the Fe concentration and pattern of the Fe depth profile. In addition, there were several types of high Fe peaks which were consistently observed in the time series. All of these peaks followed temperature changes in depth. One of these types of peaks was located just below the thermocline, and correlated with lithogenic silicates. We hypothesize that this high Fe peak originates from the continental slope, and is derived from sedimentary Fe.

Fe concentrations were also observed at depth, just above the sediment/water interface. This elevated Fe concentration followed an exponential trend, decreasing in concentration with increased height above the ocean floor. In addition, the rate of change in Fe concentration with height has a seasonal signal. Summer bottom water Fe concentrations have a greater rate of decrease with increasing altitude as compared to both winter and spring bottom water concentrations. We hypothesize that this trend is the result of Fe adsorption onto biologically derived particles, such as biogenic silicates, which were observed to be higher after the spring blooms and summer. Future work will include modelling the flux of Fe from the sediment over time.

Impact of sulfide separation on Ag and Mo budgets in arc magmas

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To understand the impact of sulfide separation on the metal budgets of Ag and Mo in arc magmas, experiments have been performed on the partitioning of these metals among pyrrhotite, a rhyolitic melt, and an immiscible Fe-S-O liquid. Previous experimental work on the partitioning of pyrrhotite and chalcopyrite with respect to Cu and Au in magmatic settings relevant to intrusion-related hydrothermal ore deposits, show a strong potential for the depletion of these metals by the segregation of the sulfide phases from silicate melts [1, 2, 3]. This sequestration of metals in sulfides may play a role in determining the relative abundances of these metals in associated deposits, or possibly even preclude ore formation. Evacuated sealed silica tube experiments were performed at 1042°C, log $f_{O_2}$ between FMQ and NNO, and log $f_{S_2} = -1$ bar. Partition coefficients for Ag and Mo between pyrrhotite and silicate melt (Ag 58±8 [1σSDOM]; Mo 35±3), and between Fe-S-O liquid and silicate melt (Ag 120±20; Mo 90±10) have been determined. Uncertainties represent one standard deviation of the mean. Based on these values, limits may be placed on the proportion of the initial metal budget that may be removed by the segregation of these sulfides. During Rayleigh fractionation (F=0.1) where sulfides compose 0.1wt% of the assemblage, pyrrhotite would sequester Ag (13%) and Mo (8%) less effectively than the Fe-S-O melt (24% and 19% respectively). Although these reductions might lead to variations in the tenor of associated ore they appear to be unlikely to significantly inhibit ore formation on their own. However if the magma metal budget is augmented through interactions with other magmas or by the assimilation of reduced sulfide-bearing sediments, the effects would be enhanced. Under the same conditions with 0.3wt % sulfides, Fe could remove 33% of the Ag and 21% of the Mo, whereas Fe-S-O melts could remove 51% of the Ag and 46% of the Mo. This suggests that exogenous additions of sulfur to arc magmas can affect their ore metal budgets.


Figure 1: GC/MS chromatogram (total ion count) of hydrocarbon inclusions in quartz from Berbes. Sq: squalene.

These results suggest that the hydrocarbons included in quartz source well preserved biomarkers which be of great interest for early Earth biosphere and planetary studies.

The genesis of these hydrocarbons is probably related with (a) dolomitization of the host rocks, or (b) hydrothermal degradation of underlying shale. Speculative, these processes would lead to the formation of nearby gas and oil fields.
Quartz crystal connections between magmatic, plutonic, and hydrothermal environments

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We use geochemical and textural records preserved in quartz crystals to investigate different generations and styles of high temperature quartz growth in felsic intrusions and related ore bearing veins from the porphyry-Cu-Mo deposit at Butte, Montana. Relationships between magmatic and hydrothermal realms are complex and often overlooked but are essential to understanding the evolution of porphyry deposits. Our goal is to understand better how different generations of quartz are related texturally, geochemically, thermally, and temporally. We use SEM cathodoluminescence (CL) imaging, trace element concentrations, TitaniQ geothermometry, and Ti diffusion calculations to arrive at this goal.

CL textures of some quartz in the Butte host granite reflect a quartz eye form resembling that of porphyry dikes suggesting that the pluton was once a porphyritic magma. We present geochemical modelling to further test this hypothesis.

Porphyry dikes and mineralizing fluids were derived simultaneously from a parent pluton cupola. We have found vein cross-cutting relationships in CL showing significant quartz temperature fluctuations, supporting the hypothesis that dike and mineralization events are episodic in nature.

TitaniQ temperatures we have calculated for different quartz generations overlap considerably (host granite quartz ~770º to 790º C, porphyry quartz ~630º to 780º C, deep hydrothermal quartz ~480º to 740º C). However TitaniQ temperatures of quartz veins (600º to 740º C) that apparently grew by pressure-drop are up to 75º C hotter than temperatures indicated by alteration minerals. We hypothesize that this is due to non-equilibrium incorporation of excess Ti into quartz, suggesting that the TitaniQ geothermometer may need to be used with caution for some hydrothermal quartz. Alternatively, the alteration temperature estimates may reflect retrograde resetting.

Analyses of trace Ti, Al, K, and Fe show that Ti positively correlates with CL intensity. Assuming Ti is the primary CL activator, we have made preliminary Ti diffusion calculations based on CL images which should allow us to estimate temporal relationships between the magmatic, plutonic, and hydrothermal aspects of the system.

Geochemical evidence for a transient change in mantle melting from the deglaciation of Iceland

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At the end of the last glacial period ~10,000 BP a large pulse of volcanism took place in Iceland with eruption rates up to 100 times higher than in glacial or modern times [1]. Geophysical models (e.g. [2]) suggest that the rapid melting of a large ice sheet caused a transient increase in decompression mantle melting. Geochemical data (e.g. [1, 3], this study) support this interpretation. However, while previous studies have sampled only surface flows, this study provides a temporal perspective on a vertical sequence of lavas. Geochemical data was collected for lavas from Stóravíti volcano, which is the largest postglacial lava flow in the Theistareykir region of the Northeastern Volcanic Zone. Using technical climbing techniques, a vertical sequence of lavas was sampled from Lilavíti pit crater, which is located ~700m from the volcano summit. Major element, trace element, and isotopic (Sr, Nd, Hf, and Pb) data were obtained for five samples spaced around the crater rim and for thirteen samples at various depths (~2m to ~36m) along the crater wall. Like other postglacial lava flows in Iceland, the Lilavíti samples have lower Sm/Yb, lower La/Sm, and higher Mg#s than glacial and modern lava flows. Isotopically, the Lilavíti samples are more depleted than glacial and modern lava flows. However, compared with postglacial lava flows sampled on the flanks of Stóravíti, the Lilavíti lavas are more homogeneous and fall on the enriched, fractionated end of the postglacial data set and thus trend toward glacial and modern lava compositions. Therefore, the Lilavíti lavas are believed to represent the final stage of the Stóravíti postglacial eruption as melting rates in the region returned to steady state.

Geochemistry of volcanic and plutonic rocks from the southern Musoma-Mara greenstone belt: Implication for the evolution of the Tanzania craton

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The Neoarchean Tanzania craton contains patches of greenstone belts set in granitoid masses that occupy a large percent of the craton. Because of limited geological, geochronological and geochemical information, very little is known about this craton and its constituent terrains. We report new U-Pb chronological, Nd-Hf isotopic and major and trace element data for volcanic and granitoid rocks from the southern Musoma-Mara greenstone belts of the Northeast Tanzania craton. The volcanic rocks are mainly basaltic with minor felsic volcanic rocks. The intrusive rocks are mostly calc-alkaline with minor depletions of Nb and Ti relative to N-MORB. Geochemically, the basalts are tholeiitic and MORB-like but with minor depletions of Nb and Ti relative to N-MORB. The felsic volcanic and granitoid rocks are calc-alkaline with normal arc to adakitic signature. The basalts yielded a Sm - Nd isochron age of 2842 ± 65 Ma (εNd = +2.1, MSWD = 1.6) and εHf = +1.7 - +3.2. One granitoid yielded U-Pb zircon age of 2689 ± 12 Ma which is similar to those reported for the oldest rocks in the North Musoma-Mara greenstone belt [1], and is interpreted to represent the age of granitoids and felsic metavolcanic rocks. The felsic volcanic rocks have εNd = +0.1 - +1.6 that are within error of those for granitoids and meta-basalts. Collectively, these data show that the basaltic rocks may not be related to the felsic volcanic and intrusive rocks by fractionation but were likely formed from equally depleted sources, possibly in arc-back arc environment. The spatial association of MORB-like tholeiites and arc-like volcanic and granitoid rocks is not uncommon in the Tanzania craton [2], as well as other late-Archean cratons worldwide [3, 4], and may imply that the tectono-magmatic processes that produced this association were widespread during this period.


Galactic chemical evolution and the short-lived radioactivities

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Nucleosynthesis in stars over roughly seven to eight billion years of Galactic history created the Solar System’s supply of isotopes of carbon and heavier elements. Over those seven to eight billion years, the isotopic composition of the interstellar medium became increasingly enriched in heavy elements as nucleosynthesis in one generation of stars built upon the composition of the previous generation. This build up is known as Galactic chemical evolution (GCE). In general, to study Galactic chemical evolution, one constructs models based on a rate for infall of metal-poor gas to build up the Galaxy, an appropriate star formation rate, and stellar nucleosynthetic yields. One then follows the time evolution of the mass fractions of the isotopes in the interstellar medium (ISM) (e.g. [1]).

The abundance of the short-lived radioactivities in the early Solar System may be analyzed in the context of Galactic chemical evolution models. In a chemical evolution model with infall, one may compute the average ISM ratio of the abundance of a radioactive species to its stable reference isotope [2]. One may then apply more sophisticated models that divide the ISM into multiple phases (e.g. [3, 4]). When one compares the abundance ratios of short-lived species to their stable reference isotopes in the molecular cloud phase (the phase in which the Sun is thought to have formed) of the multi-phase models to the values inferred for the early Solar System, one finds that 53Mn, 146Sm, and 182Hf are in line with expectations from ongoing nucleosynthesis; 107Pd, 125I, and 244Pu are low and apparently require a decay interval; and 26Al, 40Ca, and 60Fe are high and probably require injection from a nearby supernova [4].

To facilitate study of this issue, we have developed an online tool for analyzing the abundances of radioactive species in the phases of the ISM. It is the Three Phase ISM Tool available at http://www.webnucleo.org/. We are also developing full multi-dimensional GCE codes that we will make freely available at the above web site.

Erosion rates on different timescales in river catchments of low mountain ranges

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In order to unravel the Late Quaternary landscape evolution in a mountain range typical for central Europe, we determined erosion rates on timescales of 10^1 to 10^4 years. Four different catchments in Germany, ranging from 8 to 379 km² were investigated. Two of them, the Aabach and Möhne catchments are located in the Rhenish Massif and drain Paleozoic sediments. The other two, the Gutach and Acher catchments in the Black Forest are situated in Late Paleozoic granites. Long-term erosion rates derived from the concentration of cosmogenic \(^{10}\)Be in stream sediments are consistent in the Rhenish Massif (47 to 65 mm/ka) but more variable in the Black Forest (26 to 109 mm/ka). These erosion rates integrate over the past 6 to 23 ka and are similar to local rates of river incision and rock uplift during the Quaternary as well as to local average denudation rates since the Mesozoic derived from thermal modelling of fission track data.

The determination of short-term erosion rates, quantified from the suspended and dissolved river loads, requires corrections to obtain realistic geogenic values. The dissolved loads were corrected for atmospheric and anthropogenic inputs using major dissolved ions, precipitation data, and carbon isotopic compositions of dissolved inorganic carbon. The suspended loads were measured especially during high-discharge events and were calculated by using calibration curves relating discharge to the amount of suspended load. These erosion rates integrate over the last 5 to 80 years and vary between 9 and 25 mm/ka. They are only about one third of the erosion rates derived from \(^{10}\)Be. These erosion rates are complemented by erosion rates derived from the volume of sediment trapped in three reservoirs over periods of 13 to 28 years (2 to 10 mm/ka).

Fate of chlorinated compounds in a sedimentary fracture rock aquifer in South Central Wisconsin

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The study site, located in south central Wisconsin, is a deep fracture rock aquifer contaminated by various chlorinated compounds. Spills of PCE, TCE, 111TCA, BTEX and ketones occurred in the 1950s and 1960s and DNAPL can still be found in the source zone. Based on hydrogeological and geophysical data, the deep (more than 600 feet) fracture rock system is divided into 7 hydrogeological layers. Collected Contamination has mainly been found in Layer 5 at a depth of 160-170ft and the length of the plume, defined by an extensive monitoring network (more than 200 monitoring wells including monitoring ports in multilevel wells) is now more than 8000 feet long. Historical and current data show that extensive dechlorination has been occurring at the site and the composition of chlorinated compounds in the groundwater has been evolved to mainly cis-12DCE and 11DCA which are degradation products of TCE and 111TCA respectively. Geochemistry data (Fe, Mn, and SO\(_4\)) together with field parameter data (DO) and dissolved gases data (methane) show very different redox conditions in different areas of the aquifer, ranging from aerobic to methanogenic which is consistent with the degradation patterns observed in these areas. Complex transport and degradation patterns were revealed at this site and degradation pathways were proposed based on VOCs concentration data. Carbon and chlorine isotope data of these chlorinated compounds (mainly chlorinated ethenes) provide additional information for evaluation of the degradation patterns in different part of the aquifer. These data show different isotopic patterns for biodegradation of cis-12DCE which could be linked to two different spills. These data also showed that 11DCA, a by-product of biodegradation of 111TCA, is also attenuated by biodegradation. The biodegradation patterns inferred from the isotope data agreed with the variable redox conditions observed in the aquifer.
**In situ** Raman spectroscopic investigation of the structure and speciation of aqueous zinc bromide solutions to 500°C and 0.9 GPa

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A Raman spectral study was carried out on three aqueous solutions of varying concentration and bromide/zinc ratio. Spectra were collected at 11 different temperature-pressure conditions ranging from ambient to 500 °C and up to 0.9 GPa. Raman band assignments for aqueous zinc bromide complex species reported in previous studies were used to determine the relative concentrations of ZnBr$^{2-}$, ZnBr$^-$, ZnBr$_2^-$, and ZnBr$^+$ species at various temperatures and pressures. Our results are in close agreement with X-ray absorption spectroscopic (XAS) data [1], and confirm that the tetrabromo zinc complex, ZnBr$^{2-}$, is the predominant species up to 500 °C in solutions having high zinc concentrations (1 m) and high bromide/zinc molar ratios ([Br]/[Zn] = 8). This result is consistent with the observed predominance of the ZnCl$^{2-}$ complex in chloride-rich fluid inclusion brines at high temperatures [2]. In agreement with previous Raman spectroscopic experiments [3], our measurements also indicate that species with a lower number of halide ligands and charge are favored with increasing temperature in dilute solutions, and solutions with low bromine/zinc ratios ([Br]/[Zn] < 2.5). The Raman technique provides an independent experimental means of evaluating the quality of XAS data obtained from high temperature disordered systems, and the combination of these two techniques provides complementary data on speciation and the structure of zinc (II) bromide complexes.


**H2O and Cl in basalts from Lau back-arc basin**

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The subduction influence (fluid mobile elements) in basalts along the back arc Eastern Lau Spreading Center (ELSC) increases in several sharp gradients as the distance to the Tofua volcanic arc diminishes from 100 km in the north (19°S) to 40 km in the south (23°S). The six tectonic segments of ELSC display mixing relationships in trace element and isotopic ratios in which one end member is a subduction component that is distinctive for each segment. Basalts from the three well-sampled northern segments (ELSC-1, -2, and -3, from 19.2-20.7°S) are best for the study of volatiles because most did not lose H2O by degassing, and because they display a wide range of H2O/Cl element values on a local scale: from MORB-like to much higher values.

ELSC-1 has distinct trends of H2O vs. Cl and of H2O vs. Ba or Cl vs. Ba compared to ELSC-2. It is likely that higher Cl/H2O and Cl/Ba along ELSC-1 are not caused by crustal assimilation but are primary mantle characteristics because 1) there is no correlation of Cl/Ba or Cl/H2O with MgO; 2) no axial magma chamber has been detected seismically; 3) there is a good correlation of Cl with H2O that extends to adjacent seamounts. However, a few samples have much higher Cl/H2O, suggesting assimilation occurs sporadically here.

The correspondence of tectonic segmentation with volatile ratios is consistent with volatiles being supplied to each segment by separate hydrous diapirs that get their distinctive H2O/Cl from the part of the slab from which they are initiated. Trends for each segment are generated by mixing between diapiric melts and melts from depleted, upwelling MORB-like mantle. Alternatively, geochemical segmentation might reflect focused magma supply to each segment from a distinctive heterogeneous source with redistribution of magmas along axis at crustal levels. The coherence of H2O/Cl with segmentation despite rapid along-axis mantle flow beneath ELSC [1] suggests volatiles are transferred quickly from slab to surface. Large along-axis differences in H2O output of the arc/back-arc suggests that H2O is not removed with equal efficiency along-axis and that some H2O may be retained in the wedge or in the slab.

Mineral and chemical composition of aeolian material from the Tatra Mts. (S Poland)

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Studies of aeolian dust are important in interpretation of airborne dust source, transport, concentration, formation of aerosols, climatic effects of aerosols, and their contribution in soil formation.

Aeolian material deposited with snowfall during the night 23/24 March 2007 was collected on 25th March 2007 at the Hala Gąsienicowa meadow (1510 m a.s.l.) in the Tatra Mts. (S. Poland). Dust is composed mainly of quartz with subordinate amount of feldspars (both plagioclases and K-feldspar), micas, I/S minerals and traces of kaolinite. Grain size varies from below 1 µm to 25 µm. Aggregates composed of mica and quartz grains, often containing organic matter and iron oxides, are common. Determination of the source area of the dust is impossible based on mineral and chemical composition.

Pollen of trees and shrubs (Alnus, Pinus, Betula, Corylus, Carpinus, Acer, Ulmus, Picea, Fagus, Salix) and herbs (Compositae, Cyperaceae, Chenopodiaceae, Caryophyllaceae) determined in the dust represent local vegetation from the Carpathian Mts.

Several dust falls were noted in S Poland in XIX and XX centuries. Source area was localized usually in the area between Black Sea, Sea of Azov and Caspian Sea. Dust material deposited in 2007, derived from local source area in Carpathians, is very similar in mineral composition and grain size to the material from other dustfalls noted in S Poland. Lack of calcite in the local material is the only one significant difference.

Evaluating the structure of poorly-crystalline iron oxyhydroxides

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Poorly crystalline iron phases commonly form in contaminated aqueous geochemical systems such as acid mine drainage environments. In particular, the ferric iron oxyhydroxide known as ferrihydrite is an important component in both the soils and waters of these systems due to its tendency to scavenge potential environmental contaminants. With individual particle sizes typically less than 10 nm, ferrihydrite exhibits a large amount of reactive surface area and is known to associate with metal and metalloids via processes of coprecipitation and adsorption. The reactivity of this phase is therefore important in controlling the fate and transport of contaminants in the environment. The increased reactivity of ferrhydrate and other nanosized phases is inextricably related to atomic structure. Conventional methods of structure determination are generally inadequate for quantitatively evaluating the 3-dimensional arrangement of atoms in nanosized solids. However, the recent application of high energy X-ray total scattering for pair distribution function analysis has led to considerable advancements in our understanding of the structures of both synthetic and natural samples of ferrihydrite. In the case of naturally occurring samples, this phase often precipitates under complex conditions and in aqueous systems containing a variety of species including organics, metals, and metalloids. The effects of these species on the resulting poorly crystalline precipitates are only partly understood. New results on samples collected from acid mine drainage sites build on recent work conducted on fully synthetic ferrihydrite and provide new insight into the structure of this important phase.
Structural characteristics of synthetic amorphous calcium carbonate

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Amorphous calcium carbonate (ACC) is an important precursor phase involved in biomineralization by a wide variety of invertebrate organisms and is of technological interest in the development of functional materials. An understanding of the transformation of ACC to crystalline forms and the selection of final product polymorph has been hindered by the difficulty in assessing structure of the amorphous phase. This is mainly due to its metastability and limitations of conventional structure determination methods. We present new findings from the application of two techniques, synchrotron X-ray based pair distribution function (PDF) analysis and nuclear magnetic resonance spectroscopy, to synthetic, hydrated analogs of ACC and provide new insight to short and intermediate range structure. PDF results for ACC formed in vitro using two common preparation methods show that structural coherence extends over less than ca. 15 Å, confirming that the synthetic ACC is truly amorphous. Results also demonstrate that the short- and intermediate-range structure shows no distinct match to any crystalline structure in the calcium carbonate system. NMR results show that most of the hydrogen in ACC is present as structural H2O, about one-half of which undergoes restricted motion on the millisecond timescale near room temperature. NMR results also demonstrate that most of the carbonate in ACC is monodentate, making it distinctly different from monohydrocalcite. These results complement X-ray absorption spectroscopy studies and provide a baseline for future experiments evaluating biogenic ACC and samples containing additives that may play a role in stabilization of ACC, crystallization kinetics, and final polymorph selection.

Speciation of REE(III) in chloride-, fluoride-, and sulphate-bearing solutions: Solubility and spectroscopic studies

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Experimental studies of REE speciation at elevated temperatures have been largely restricted to a few REE in chloride-bearing solutions, and consequently our understanding of the behaviour of other REE in hydrothermal fluids comes primarily from theoretical predictions [1, 2]. In order to evaluate the stability of REE complexes with atomic number and to verify theoretical estimates, we have therefore conducted a systematic experimental investigation of REE speciation in chloride-, fluoride-, and sulphate-bearing solutions.

Experiments were performed at temperatures up to 250 °C and pressures up to 100 bar, and initially consisted of spectroscopic studies of REE speciation in homogenous chloride- and sulfate-bearing solutions containing one of the REE (e.g. Nd(III), Sm(III), and Er(III)) and one of the ligands. Later experiments involved determination of the solubility and speciation of Nd(III) fluoride in F-bearing aqueous solutions. Finally, we evaluated the solubility of REE fluorides in multi-component systems involving all REE (except Pm) and one to two ligands (F−, or F−+Cl−, or F−+HSO4−). The resulting data were used to derive formation constants of the corresponding aqueous complexes.

The experimental data obtained in this study show that the theoretical predictions of Wood [1] and Haas et al. [2] overestimate the stability of fluoride complexes of REE at elevated temperatures, and that this overestimation increases with increasing temperature. Formation constants obtained for chloride species are in fair agreement with the predictions of Haas et al. [2] for HREE, but show higher stabilities for LREE at elevated temperatures. The first formation constants for sulphate complexes are in reasonably good agreement with those predicted by both Haas et al. [2] and Wood [1], but the data indicate that REE(SO4)2− is progressively more stable than predicted as temperatures above 150 °C.

The new data of “Catalogue of the Earth’s impact structures”
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The Description of the Catalogue
The original table of the catalogue includes 822 records, each being characterized by 41 attributes. On the website (omzg.sscc.ru/impact/index1.html) there are only seven of them, however the descriptive part of some records is added with a card of the detailed description with decoding of the coded data. This card information contains mineral-petrographic, impact-metamorphic and geophysical attributes. As compared to [1] the given catalogue is supplemented with 94 new records (among them 5 are proven: Couture, Crawford, Karankas, Ust-Kara, etc.) and a lot of attendant information, especially, bibliographic references and their abstracts, that has increased the site volume into 300 times. The data sources are both the recent publications, and written private messages of researchers.

The New Data
Among the recently added structures are: Bolzano (Fig. 1a), Groppovisdomo, Montecchio Maggiore Italy craters, five Madagascar structures (Fig. 1b), all of them were found out and in part explored by Matteo Chinellato and F.Pezzotta (Venezia, Italy). One of the recently entered into the DB structures is Meggyespuszta (Fig. 1c), discovered by Kakas Kristof (Eotvos Lorand Geophysical Institute of Hungary). It is necessary to note the personal results of Karl Sasse (Bremen) concerning Bogemskaia structure; and James Corbett. (Ireland) regarding Corbett crater.

The data bank consists of 196 proven, 215 probable, 359 possible and 52 discredited cosmogenic structures and is open for extension with new information.

Figure 1: New impact craters.


Iron isotope fractionation during Fe(II) sorption to mineral surfaces
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Stable Fe isotopes provide a potential new tool to trace biogeochemical Fe cycling. Many studies revealed kinetic and equilibrium Fe isotope effects in field and laboratory systems. However, the mechanisms controlling the Fe isotope distribution in natural systems are only partially understood. Sorption of Fe(II) to mineral surfaces has been shown to result in Fe isotope fractionation, but the significance and the magnitude of this process are subject to debate. Previous studies used Fe(III) (hydr)oxides as sorbents for Fe(II), where interfacial electron transfer and atom exchange may have obscured the fractionation during sorption. To separate the different contributions to Fe isotope fractionation during Fe(II) sorption, we performed batch and column experiments in which Fe(II) was sorbed to different (hydr)oxide surfaces (goethite, quartz, aluminium oxide).

All experiments were conducted at pH 7.2 ± 0.1 under strictly anoxic conditions in a glovebox. Batch experiments with different Fe(II)/sorbent ratios were performed to study equilibrium Fe isotope fractionation between solution and sorbed species. Column experiments were used to study kinetic and equilibrium Fe isotope effects during sorption and desorption of Fe(II) on different mineral surfaces. Iron isotope ratios were measured by high-resolution MC-ICP-MS (Nu 1700, Nu instruments). Experimental data were described with adsorption isotherms and isotope fractionation models.

The batch experiments revealed significant equilibrium isotope fractionation during Fe(II) sorption to goethite and quartz, but not to aluminium oxide. Heavy Fe isotopes were preferentially sorbed, resulting in isotopically lighter solutions. In the goethite system, the sorption-induced isotope effect was superimposed by surface atom exchange, leading to a δ56Fe shift in solution towards the isotopic composition of the goethite. A mass balance of the column experiment with goethite-coated quartz suggests that almost the complete goethite surface exchanged isotopically. By comparison of column systems with and without Fe surfaces, we are able to disentangle Fe isotope effects caused by Fe(II) sorption alone (quartz) and by a combination of Fe(II) sorption and atom exchange with surficial Fe (goethite-coated quartz). Our results imply that sorption processes may exert a significant influence on Fe isotope signatures in natural systems.
Physicochemical controls on Uranium(VI) migration at the intermediate scale

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Prediction of uranium migration within the context of long-term stewardship of contaminated sites requires models that can incorporate temporal and spatial heterogeneities at the field scale. However, most transport studies are completed at the bench scale, and often simplify either the physical or chemical heterogeneity in order to determine fundamental migration behavior. Thus there is an informational gap in how fundamental behaviors are exhibited at the field scale. In this presentation we report on experiments at the intermediate scale (~2m); the express goal of these experiments is to elucidate methodologies to 'up-scale' reactive transport models from the bench to the field.

An intermediate scale tank (2.44m x 0.61m x 7.6 cm) has been constructed; a macroscopically heterogeneous packing has been completed using the <0.250mm and 0.250-2mm size fractions of uranium contaminated sediment from the Naturita Uranium Mill Tailings Remedial Action (UMTRA) site. The size fractions were generally packed in layers, with an added 'block' of <0.250mm fraction present at the upgradient end to further perturb the flow field. Kinetic hindrances to uranium desorption were examined through the use of stop flow events. Once the tank exhibited tailing behavior, the composition of the influent was altered (CO₂ concentration increased from atmospheric to 2%) to determine the effects of temporal chemical gradients.

Effluent uranium concentrations started at 12.3 µM, and declined to between 2-3 µM within 30 days (0.5 pore volumes). This corresponds to a uranium flux out of the tank of 0.0756 µmol U/(kg sediment * L water) after four days of flow, and 0.0299 µmol U/(kg sediment * L water) after 35 days of flow. Uranium distribution within the tank was found to vary with pH, alkalinity, dissolved calcium, rate of U release from the different particle size categories, and the nature of the heterogeneity distribution.

Rhenium isotopes in natural systems

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We investigate variations of ¹⁸⁷Re/¹⁸⁵Re in various natural systems. Samples are analyzed by MC-ICP-MS; instrumental mass fractionation is corrected for using a combination of standard-bracketing and external W-correction according to an exponential law. External standard reproducibility is 0.04‰ (2SD). Data are reported as δ¹⁸⁷Re, relative to NIST SRM 989 [1].

Total range of natural isotopic variation is approximately 2‰. Isotopic variation is observed in every substrate type observed to date, including sulphide minerals, meteorites, organic-rich sediments, liquid samples, and industrial Re. In sulphides, we see values of 0.75‰ and 0.12‰ for Archaean and Proterozoic MoS₂ while a modern ReS₂ has a value of -0.22‰. Among meteorites, Allende has a δ¹⁸⁷Re of -0.50‰ while that of Canyon Diablo Troilite is -0.21‰. Organic-rich sediments show a range of about 0.7‰. Dissolved samples analyzed thus far include seawater (-1.25‰) and acid pit mine water (-0.13‰). Industrially available Re exhibits a total isotopic range of -0.3‰.

Data will be presented on Re isotope variations in the modern marine environment (seawater, reducing marine sediments, oxide crusts) for comparison with the better established Mo, and U isotopic systems [2, 3]. Solid and dissolved phase samples will be used to describe the effects of weathering on the Re system. Case studies will include a naturally weathering black shale profile, as well as an anthropogenically influenced mine site.

Highly-evolved silicic magmas: Volcanic vs. plutonic conundrums

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Evaluating the origins of highly-evolved silicic magmas and relations between granites and rhyolites is guided by 2 considerations: (1) Very low Sr and Ba of high-Si rhyolites (HSRs) and evolved granitoids require extensive fractional crystallization; (2) SiO$_2$ > 77 wt% in HSRs implies shallow crustal fractionation; highly evolved granites have a wider range of SiO$_2$, reflecting equilibration at a range of P. Thus evolved shallow granites may be trapped equivalents of HSRs, but disparity in volume and possibly geochemistry may suggest otherwise. Glazner et al. (2008 Geology) note that REE patterns in Sierran aplites (“U”: MREE depletion, sphene effect) are distinct from those of HSRs in large ignimbrites (“seagull”: straight, large Eu anomaly), and infer that large plutons and HSRs are probably not related.

The voluminous Miocene magmatic suite of the Colorado River region includes highly-evolved granites and rhyolites (small-volume to giant Peach Springs Tuff). Increasing depletion in Sr and Ba correlate generally with depletion of MREE (transition from seagull to U patterns), providing evidence for a common fractionation pathway involving sphene (more evident in volcanic glasses than whole-rock volcanics – cf. Bachmann et al. 2005 CMP: Fish Canyon Tuff).

Compositional variability in evolved silicic magmas reflects environments of crystal growth (especially accessories) but does not distinguish between shallow granites and HSRs. Greater volumes of the largest HSR ignimbrites than of evolved granites in plutons may reflect the importance of the effectiveness of melt extraction and its influence on chamber stability (cf. Bachmann & Bergantz 2008 Elements)

The 2.74–2.66 Ga Kenogamissi complex (Abitibi): Evolving sources of plutons mirroring geodynamics

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The Late-Archaean Kenogamissi complex, in the SW Abitibi Subprovince (Canada) is a large plutonic complex emplaced between 2740 and 2660 Ma, synchronous with the formation of the surrounding greenstone belts. P-T conditions for orthogneiss in the complex are in the amphibolite-facies (P = 7-8 kbar), well above the pressures recorded by the surrounding greenstones. Thus the Kenogamissi Complex includes the mid-crustal component of the Abitibi Along with geochronological, geochemical and structural data, the evolution of the Abitibi is now believed to include plume-related volcanism with discrete episodes of subduction-related magmatism, leading to magmatic accretion of a plateau or LIP before ~2690 Ma, followed by collision and folding.

The pre-2700 Ga plutonic rocks comprise three groups of tonalites: a 2740 Ma tonalite-diorite association (Rice Lake batholith, Chester complex); a younger composite gneiss unit, with enclaves of 2735 Ma tonalites and diorites in a 2720 Ma tonalitic to trondhjemitic matrix (Gogama orthogneiss); and 2710 Ma leucotonalite plutons (Regan tonalite). The post-2700 Ga association include several 2700-2695 Ma biotite granodiorite plutons (McOwen, Roblin) and a 2682 Ma hornblende granodiorite (Neville pluton). A 2660 Ma pink granite (Somme pluton) represents the latest Archaean plutonic event.

O-isotope, major and trace element geochemistry reveal the petrogenetic evolution of the different groups. The diorite-tonalite units can be derived by partial melting of mafic rocks at the base of a thick plateau-like crust, whereas the leucotonalites and trondhjemites require melting of a mafic source at greater depth (ca. 20 kbar). This is consistent with the accretion of a thick oceanic plateau or LIP, re-melting of its base, and limited subduction-related (slab melt) inputs. The granodiorites require a crustal source, and reflect syn-collisional melting of the previously accreted crust. Sanukitoids at 2685 Ma require both crustal and mantle-derived components, reflecting partial melting of a mantle metasomatized during the previous subduction events. The latest granites, at 2660 Ma, are purely crustal melts that reflect the thermal relaxation of the Abitibi orogenic crust.
Zircon recycling in felsic magmas

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The ubiquity of zircon and its utility for radiometric dating make it a primary tool for obtaining age information from metaluminous to weakly peraluminous felsic igneous rocks, which comprise most of Earth’s felsic plutonism and nearly all compositionally equivalent continental volcanism. At anatectic conditions for felsic metaluminous magmas (e.g. biotite and amphibole dehydration), the magmas are likely undersaturated (or perhaps barely saturated) in zircon when they leave their sources. Thus the 10^3 to several 10^5 yr age spread often observed in geochronological studies of metaluminous volcanic and plutonic systems is commonly attributed to mixing of magmatic zircons that grew at different times within a focused zone of intrusion. The ability to now link zircon ages (single crystal TIMS or in situ methods), with geochemical variations (e.g. REE patterns), textures (CL imaging), temperature variations (Ti-in-zircon), and isotopic variations (δ18O, 176Hf/177Hf) in zircons within one magmatic system, promises a much more detailed picture of zircon recycling. Using some of these different data sets, our studies so far show that within a single sample, zircons have either strongly contrasting thermal histories and distinct chemical and isotopic signatures, or in marked contrast show remarkably limited variation even when ages vary by several 10^3 yr. Where zircons from plutonic and volcanic rocks from the same magmatic system can be compared, plutonic zircons show greater temperature and chemical variation than their volcanic counterparts; textural and chemical evidence for resorption and thermal rejuvenation is observed in both. Our ongoing studies within different magmatic systems are aimed at integrating these complementary data sets to discern if recycling involves: (a) rapid unification of isolated intrusions of varying age in large but ephemeral, melt-rich magma reservoirs; or (b) protracted growth in large but persistent, perhaps mushy, eutectic magma chambers; or (c) assimilation of intrusive precursors (plexus of dikes, pods, and sills) as magmas traverse upward.

Chemical modification of oceanic lithosphere by hotspot magmatism: Seismic evidence from subduction of the Ninetyeast Ridge along the Sumatra-Andaman arc

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Tomographic images of the upper mantle, which represent perturbations in P-wave, shear wavespeed, and bulk-sound speed, illustrate the Indo-Australian plate subducting beneath the Eurasian plate along the Sumatra-Andaman arc. The detailed images of the subducting slab are well constrained by the large number of intermediate depth earthquakes and moderate seismic station coverage along the entire Indonesian-Sumatra-Andaman arc. The coherent, steeply dipping slab is defined by Benioff zone seismicity and high seismic velocity perturbations, beneath the entire arc, but at approximately 9.5-12.5°N and at a depth of 60-160 km, the slab is characterized by low P-wave perturbations, yet with only a small decrease in the S-wave speed, and a modest decrease in bulk sound speed. At this position along the arc the inactive Ninetyeast Ridge, suggested to be a plume-fed spreading ridge, is being subducted beneath the arc. The negative P-wave and bulk sound speed anomalies in the slab, along with only a small decrease in S-wave speed perturbations cannot be explained by thermal variations alone, therefore it suggests this is a result of change in composition. We find that the seismic anomalies in this region of the subducting Indo-Australian plate are best fit by orthopyroxene-rich zones within the peridotitic lithospheric mantle. We speculate that these pyroxene-rich lithologies formed by the interaction of upwelling magmas beneath the Ninetyeast Ridge with pre-existing oceanic lithospheric mantle before subduction occurred. Our observations represent one of the first seismic evidences for extensive chemical modification of lithospheric mantle.
Cr(III) oxidation by soluble Mn(III) chelates: A potential biogeochemical pathway for the enhanced mobilization of Cr from spinels

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Soils derived from ultramafic (UM) rocks are enriched in Cr(III), mainly due to the presence of chromite (FeCr2O4) and other Cr(III)-bearing spinels. Weathering of UM rocks in the Coast Range and Sierra Nevada mountains of California has impacted the geochemistry of alluvial soils in the Sacramento Valley, which are enriched in Cr (30-1420 µg g⁻¹) relative to the U.S. geometric mean (37 µg g⁻¹). Although much of the Cr in these soils appears to be bound in refractory spinels, some mobilization of Cr is apparent in the coincidence of enriched soils with elevated Cr(VI) in ground water (up to 50 µg L⁻¹). It was recently reported that dissolution of chromite can be driven by the oxidation of the released aqueous Cr(III) on soil Mn oxides [1]. We are studying the oxidative dissolution of chromite by soluble Mn(III) as a an additional Cr mobilization pathway. Free aqueous Mn(III) is a strong oxidant but rapidly disproportionates to Mn(II) and Mn(IV). Various chelates such as oxalate and pyrophosphate can stabilize Mn(III) in solution. Mn(III)-oxalate is produced by extracellular enzymes of white-rot fungi and acts as a diffusible oxidant in lignin degradation. Pyrophosphate (PP) is a hydrolysis product of ATP and is also a component of some fertilizers. Its reaction with soil Mn oxides can result in soluble Mn(III)-PP. We measured the reduction potential of a 1 mM solution of Mn(III)-PP as a function of pH. The E° decreased from ~1.1 V (versus SHE) at a pH of 2 to ~0.6 V at a pH of 7. Consistent with these measurements, Mn(III)-PP oxidized a greater percentage of aqueous CrCl3 at lower pHs. After 2 weeks reaction time, 94, 63, 28, 3, and ~1% of Cr(III) was oxidized to Cr(VI) at pH of 3, 4, 5, 6 and 7, respectively. Forty-five times as much Cr(VI) was produced from chromite grains (63-150 µm diameter) incubated for 8 days in a Mn(III)-PP solution at a pH of 3 than incubated with solid manganese oxides at the same pH. As expected, the chromite and Mn(III)-PP incubation produced 10-fold less Cr(VI) at pH 5 than at pH 3. Our initial studies of Mn(III)-oxalate suggest its ability to oxidize aqueous CrCl3, but only in a narrow, circumneutral pH range.


Comparing the compositional patterns of volcanic and plutonic rocks using the NAVDAT database

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Igneous rock compositions generally fall along a line between basalt/gabbro and rhyolite/granite. Differences between volcanic and plutonic rocks across that range are poorly defined. A key question is whether plutons are largely cumulative residues of volcanic rocks, or are instead samples of magma that froze in the crust before eruption. Large geochemical datasets can be used to explore connections between volcanic and plutonic magma systems.

We used geochemical data for Cenozoic volcanic and plutonic rocks (~2000 ea., between 40 and 80 wt.% SiO2) from the NAVDAT database (www.navdat.org) to identify major and minor chemical trends, chemical divergence between volcanic and plutonic rocks, and age-dependent variation in the systems. Equal numbers of analyses of volcanic and plutonic rocks were randomly selected from compositional bins (40-50, 50-60 wt.% SiO2, etc.) to avoid bias between the rock types (e.g., volcanic rock data are dominated by basalts).

Preliminary observations include: 1) trends in compositional space are essentially identical for volcanic and plutonic rocks, 2) outliers for selected elements (e.g., CaO, Y, Ba, Nb) tend to lie on opposite sides of the main trends for volcanic and plutonic rocks, and 3) the average age of analyzed volcanic rocks is much younger (mean ~16 Ma) than the average age of analyzed plutonic rocks (mean ~37 Ma).

Plutonic rock analyses are limited for young ages from 0-20 Ma, but are relatively consistent from 20-65 Ma. In contrast, the majority of volcanic rocks are less than 30 m.y old, with an asymptotic decline in the number of analyses from 30-65 Ma.

Overall, the analysis shows no evidence for a complementary relationship between typical volcanic and plutonic rocks, with plutons representing unerupted residue from differentiating magma systems. Rather, plutonic compositions are dominantly equivalent to those of volcanic rocks. However, minor differences in trace-element trends may relate to important, yet to be understood processes that lead to eruption. The similarity of volcanic and plutonic rocks combined with the observation that volcanic rocks become scarce as one goes back in time, indicates that plutonic rocks are as useful as volcanic rocks for understanding the chemical evolution of continents.
Te, Sb and W mineralization at the Black Pine mine, Montana

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The Black Pine mine is located 14.5 km NW of Philipsburg, Granite Co., Montana, USA (46°26′52″N, 113°21′56″W), and has been sparcitically mined since the 1880s for Au, Ag and W. The ore zone is also enriched in Te, Sb, As and P, resulting in a large suite of secondary minerals - approximately 50 species have been reported to date. The Black Pine mine is also the type locality for one new mineral, phillipsburgite. Our current investigation is centered on the mineralogy of the secondary Te minerals and the crystal chemistry of Sb and W substitution in arsenates.

So far several tellurates have been identified including dugganite and a new mineral, the P-analogue of dugganite [Pb2Zn4Te6O16(PO4)(OH)3]. This new mineral occurs in various shades of purple, as barrel-shaped or flattened crystals up to about 0.5 mm across. The barrel-shaped crystals can be colour zoned, with purple, greyish purple and colourless most prominent. Single crystal studies show this new mineral to be P321 with a = 8.392(5) and c = 5.204(3) Å. Its crystal structure comprises of heteropolyhedral sheets of edge-sharing TeO6 octahedra and PbO6 disphenoids oriented parallel to (001). The sheets are cross-linked by PO4 and ZnO6 tetrahedra, which share corners to form an interlinked, two- and three-connected two-dimensional net parallel to (001). This new mineral appears to be different from the previously described tellurate koksite, Pb2Zn4Te6O16(PO4)2, described as orthorhombic Cmcm, C2221, Cm2m or Cmm2. Several other tellurates are under investigation and may also prove to be new.

The extent of Sb and W substitution in oxysalt minerals is not well understood. At the Black Pine Mine, Sb occurs in large quantities in several Pb arsenates, namely carminite and sagnetite-beudantite, whilst W is elevated in sagnetite-beudantite specimens. A systematic crystallographic study is underway to track the amount of Sb and W substitution in the crystal structures of these minerals. EMPA data show that there is potential for at least a partial substitution between carminite and a theoretical new end-member, with a composition of PbSb2(AsO4)2(OH)2.

Effects of pH on the release of Cr(VI) from sparingly soluble Cr(OH)3(s) by MnO2(s) under circumneutral conditions

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Contamination of soil and groundwater by hexavalent chromium, Cr(VI), is a worldwide concern mainly due to the wide range of industrial applications of chromium. The deleterious effects of Cr are attributed to Cr(VI) because of its toxicity and carcinogenicity. Since Cr(VI) exists as oxyanion in aquatic systems, it is highly mobile in the subsurface. Moreover, chromate, the dominant species of Cr(VI), has weak tendency to adsorb to oxides and clay minerals under neutral to alkaline conditions. Reportedly, Cr(VI)-contaminated soil and groundwater have been successfully remediated by reducing it to less toxic Cr(III) using various reductants, Previous studies have shown that the reduction product, Cr(III), can easily be reoxidized to Cr(VI) by manganese oxide minerals under acidic conditions but may be stable under circumneutral conditions because it readily precipitates on the surface of manganese solid phases as Cr(OH)3(s), which is suggested to hinder the heterogeneous oxidation. Our results, however, show that substantial amounts of Cr(VI) are released from Cr(OH)3(s) in the presence of MnO2(s) at pH > 6.

We examined the reactions occurring in the mixed suspensions of Cr(OH)3(s) and MnO2(s) at pH 6, 7, and 8. The suspensions were prepared with 1 g/L each of Cr(OH)3(s) and/or MnO2(s) in 0.01 M NaNO3. The values of pH were maintained using 10 mM HEPES or TRIS buffers. Dissolved Cr or Mn was not detected even at pH 6 when either solid phase presents alone. In the mixed suspensions, however, dissolved Cr(VI) concentrations increased with time at pH 7 and 8 and the rate of Cr(VI) release was higher at pH 8 by a factor of 1.7 than at pH 7. Dissolved Cr(VI) concentration reached up to 17.7 µM in 550 h at pH 8, whereas it was only 0.55 µM at pH 6 in the corresponding reaction period. By contrast, dissolved Mn concentrations increased substantially (up to 71.4 µM) at pH 6 but was not detected at higher pH’s during the reaction periods. The opposite pH dependence of the Cr(III) oxidation by MnO2(s) was predicted because the corresponding redox reactions consume protons. The apparent pH dependence is attributable to the different sorption behaviors of the reaction products, Cr(VI) and Mn(II).
Do we really know Apex Chert? Newly identified micro- and dubio-fossils

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The 3465 Ma old Apex Chert is probably the most studied Precambrian rock to date, since carbonaceous filaments, interpreted as cyanobacteria, were found more than two decades ago [1]. The occurrence of microfossils has been recently contested on the basis of the mineralogy of the sample and the carbon isotopes of the filaments, which suggests an inorganic, hydrothermal origin for the carbon [2]. Apex Chert has been studied with the most advanced techniques in microscopy and geochemistry, yet there are not evidences of other bacteriomorph structures than the carbonaceous filaments above mentioned.

We analyzed a slightly polished section of Apex chert using a HITACHI S-4300SE/N with field effect scanning at variable pressure at GEOTOP. The sample was collected at the « Schopf Locality » at Chinnaman Creek, Pilbara Craton, Western Australia. SEM-EDX analyses allowed identifying euhedral and anhedral barite; native metals containing Zn, Cu and As; rare euhedral Ca-aluminosilicates; jarosite-alunite. The observed mineral assemblage is consistent with an hydrothermal origin of the chert [2]. We observed isolated sinuous flatted silica filaments and clusters of silica needles (0.1 µm wide; 2 µm long). Silica needles have rounded extremities, smoothed surfaces and several among them show an open tube in the centre. These morphologies are similar to those observed during encrustation of unsheathed microbes by amorphous silica. More interesting, we found ramified, sinuous, tubular structures in cavities previously occupied by sulfates (likely jarosite-alunite). These morphologies look similar to cyanobacterial mats observed in Paleozoic jaspilites. We cannot yet decipher if these silica structures are syngenetic to Apex Chert or of secondary origin. However, these results clearly show that Apex Chert has not yet completely revealed its content and new investigations are neded to resolve its origin.


The origin, nature and consequences of the Circum-Superior 1880 Ma Large Igneous Province

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In the last two decades, the advancement in high-precision U-Pb geochronology has led to the recognition of a new Proterozoic (1.88 Ga) large igneous province (LIP) circumscribing a significant portion of the margins of the Superior craton in Canada. This province consists of mafic-ultramafic lavas, sills and dykes, as well as minor felsic, carbonatitic and lamprophyric volcanics and intrusives. Previous petrogenetic models have not considered the various segments as part of the same LIP and instead have invoked several geodynamic origins such as mid-ocean ridge spreading, back-arc rifting and foredeep basin flexure. This project will utilise new geochemical, isotopic and geochronological data to assess the petrogenesis of the ‘Circum-Superior LIP’ and represents the first attempt to explain its petrogenesis as a mantle-plume-related single entity.

A plume origin is considered a possibility given the presence of a giant radiating dyke swarm with a focal point in the Molson-Thompson promontory of the Superior craton. These dykes extend into the interior of the craton and along with several carbonatite complexes mark the presence of ~1880 Ma magmatism in the craton centre as well as on its margins. Geochemical analyses thus far are in support of a plume origin. Many of the magmatic rocks possess rare earth and trace element patterns similar to Phanerozoic oceanic plateaux such as the Ontong Java and have Nb/Y-Zr/Y consistent with plume-derived magmas. A heterogeneous source region is suggested by the presence of basaltic lavas on the Flaherty Islands with enriched trace element signatures and positive Nb-Ta anomalies.

The Circum-Superior LIP is also of interest as it offers the opportunity to look into the links between LIPs and Ni-Cu-PGE sulphide deposits and is coeval with a major environmental disturbance and several other LIPs or remnants of LIPs in Archaean cratons worldwide.
Nanogeoscience: There’s plenty of room at the ground

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Nanogeoscience is emerging as a new discipline bringing together two very distinct scales of length: the micro (atomic at nanoscale) and the macro World. In our group at Kyoto University, we have focused on the possible applications of Nanogeoscience on the Mining and Oil & Gas industry by studying the fundamental interactions of water-oil-rocks interfaces under controlled and realistic conditions. By using First Principles calculations where the systems are treating all materials. This is also valuable information to EOR combined with CO₂ geological sequestration to estimate and tuning cementitious materials to prevent CO₂ leakage.

Structure and coordination of aluminum in aqueous solution and on mineral surfaces

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The chemical reactivity of soil surfaces can be significantly altered by the adsorption of metals and the formation of clay coatings. The unique chemistry of the Al³⁺ ion plays a central role in clay nucleation and growth as it sorbs to soil surfaces. However, mechanism governing these processes remains largely unknown. Elucidating these mechanisms requires a detailed understanding of the structure and coordination of Al, both in solution and at the mineral-water interface.

The geometric and electronic structures of aqueous Al complexes were studied using Al K-edge X-ray absorption spectroscopy and Density Functional Theory (DFT). Al solution spectra confirmed the expected presence of octahedral Al(H₂O)₆³⁺ at low pH and tetrahedral Al(OH)₄ at high pH. Spectral comparisons also revealed subtle electronic structure differences among various 6-coordinate complexes. The spectra of Al-organic structures, dominated by a single Al 3p – O 2p orbital contribution, appeared narrower than the Al(H₂O)₆³⁺ spectrum, which included Al 3p – O 2s and split O 2p contributions. Mixed aquo-organic complexes exhibited features intermediate between full-aquo and full-organic ligation, illustrating the utility of this technique in assessing aqueous Al complexation.

Aqueous Al results were then applied to the study of Al adsorption on Fe-oxide (goethite, ferrihydrite) and Si-oxide (silicic acid, quartz) substrates under different physicochemical conditions. The coordination geometry of sorbed Al was found to be highly sensitive to pH (4.0 – 9.0), aqueous Al concentration (100 – 1000 µm), and reaction time (minutes to months). At low pH, Al sorbed to silica exhibited tetrahedral coordination. As pH and Al loadings were increased, Al on crystalline silica converted to octahedral coordination, while Al on amorphous silica remained tetrahedral. In contrast, Al coordination on Fe-oxides was primarily octahedral for all pH values and Al concentrations examined. We are also using scanning transmission X-ray microscopy (STXM) and micro-diffraction (µ-XRD) to understand the distribution and mineralogy of Al phases on reacted substrates. Details of these results and their implications will be discussed.
Crustal growth along a 1.1 Ga non-collisional cratonic margin: U-Pb and Lu-Hf evidence from the Peruvian Eastern Cordillera

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The results of a coupled laser ablation (MC) ICPMS U-Pb and Lu-Hf isotopic survey of zircons from the Eastern Cordilleran intrusives of Peru reveal 1.15 Ga of magmatic activity along the western Amazonian margin largely dominated by mid-Phanerozoic (i.e. Gondwanide) plutonism related to the assembly and break up of Pangea. Hitherto unknown occurrences of the late Mesoproterozoic and Neoproterozoic granitoids from the south central cordilleran segment define magmatic events at 691 ± 13 Ma, 751 ± 8 Ma, 985 ± 14 Ma and 1071 to 1123 ± 23 Ma, broadly coeval with the Braziliano and Sunsás-Grenville orogenies. The Hf isotope systematics of magmatic zircons from the Eastern Cordillera batholiths are invariably characterised by a range in the initial 176Hf/177Hf compositions for a given intrusive event suggesting mixing of material derived from the Paleoproterozoic crustal substrate and variable Neoproterozoic to recent juvenile sources. The periods of well documented compressive tectonics correspond to negative mean εHf values of -6.73, -2.43, -1.57 for the Ordovician Puna-Famatinian, Carboniferous-Permian and late Triassic respectively, suggesting the minimum crustal contribution between 74% and 44% by mass. The average initial Hf systematics from granitoids associated with intervals of regional extension such as the middle Neoproterozoic, Permian-Triassic and Cenozoic Andean back arc plutonism are consistently shifted toward the positive values (mean εHf = -0.7 to + 8.0) indicating systematically larger inputs of juvenile magma (22% to 49% by mass). In the absence of the collisional tectonics, the time integrated Hf record from the proto-Andean margin of western Amazonia suggests crustal recycling as the dominant process during episodes of arc magmatism and implies that most of continental growth took place vertically via crustal underplating of isotopically juvenile, mantle derived magma during intervals of crustal attenuation.

Bentonite colloid generation from a deep geological repository in granite: An in situ study

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The role of bentonite colloids on radionuclide transport in crystalline rocks still presents large uncertainties. The present study includes first in situ analyses on bentonite colloid generation carried out at the Grimsel Test Site (Switzerland), where the FEBEX experiment, reproducing at a real scale a high-level waste repository in granite, was installed 10 years ago.

To analyze the formation of bentonite colloids, in realistic conditions, two hydro-geochemical boreholes (FUN1 and FUN2) were drilled quasi-parallel to the tunnel and at a distance of approximately 30 and 60 cm from the bentonite surface. Other 19 boreholes in radial position in respect to the tunnel already existed. Water sampling was performed both in the new and old boreholes.

The water in the FEBEX tunnel is slightly alkaline (pH 7-8) and with low (~100-200 µS/cm) electrical conductivity. In these conditions, bentonite colloids are expected to be stable. Several techniques were used for detection and characterisation of colloids in these waters (PCS, LIBD, SEM, FESEM, EDX). ICP-MS analyses of the water before and after ultra-centrifuging were carried out to know which trace elements are present in colloidal form.

Clay colloids were detected in some interval of the FUN 1 borehole and compared to those obtained in the laboratory studies of bentonite colloid generation. The similarity in both microstructure and composition was shown.

The quantification of bentonite colloids is still a difficult issue even so it’s clear that at approximately 30 cm from the bentonite, the quantity of bentonite colloids cannot be higher than 1 ppm. Higher colloid concentration was measured by PCS, showing that artifacts, possibly introduced during the excavation of the new boreholes, exist. The analysis of these artifacts for a better quantification of the “source term” it’s a very important issue at moment.

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Novel approaches to investigate microbe-mineral interactions under flow conditions

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The interaction of microbes and biofilms with geological components has mostly been investigated in closed-system experiments. However, they do not allow the input of new nutrients and reactants, and export of geochemical products and microbial waste products. This severely limits the ability to link laboratory based geomicrobiological experiments with field scale processes in the natural environment [1].

The use of novel mineral-containing open-faced flat-bed flow reactors, which allow microbe-mineral interactions to be observed in real-time and at the individual cell resolution, provides a powerful tool to explore the hydrodynamic controls on geomicrobiological processes. This invited presentation will discuss the utility of such reactors for investigating the attachment and respiration of Shewanella oneidensis on hematite during dissimilatory iron reduction under natural-flow conditions.


Microbially enhanced carbonate mineralization and the geologic containment of CO₂

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Geologic sequestration of CO₂ involves injection into deep underground formations including oil beds, un-minable coal seams, and saline aquifers with temperature and pressure conditions such that CO₂ will likely be in the supercritical state. Supercritical CO₂ injection into the receiving formation will result in elevated pressure in the region surrounding the point of injection, and may result in an upward hydrodynamic pressure gradient and associated “leakage” of supercritical to gaseous CO₂. Therefore mechanisms to reduce leakage and to mineralize CO₂ in a solid form are extremely advantageous for the long-term geologic containment of CO₂.

This paper will focus on microbially-based strategies for controlling leakage and sequestering supercritical CO₂ during geologic injection. We will examine the concept of using engineered microbial barriers [1, 2] which are capable of precipitating calcium carbonate [3, 4] under high-pressure subsurface conditions. These “biomineralization barriers” may provide a method for plugging preferential flow pathways in the vicinity of CO₂ injection, thereby reducing the potential for unwanted upward migration of CO₂ as well as mineralizing injected CO₂. A summary of experiments investigating biofilm and associated calcium carbonate formation in porous media using a unique high pressure (8.9 MPa), moderate temperature (≥ 32 °C) flow reactor will be presented, and the potential for biomineralization enhanced CO₂ sequestration discussed.

Role of fluids in melt generation in the Cascade arc: Constraints from U-Series data from Central Oregon

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We report new U-Th-Ra-Sr-Nd isotope data for late Holocene lavas from the Three Sisters region of the Oregon Cascades to investigate the processes responsible for melt generation. Our samples span the compositional range from basalt to rhyolite. The Sr and Nd data define fairly restricted ranges of ~ 0.7032-0.7036 and +4 to +5.6 εNd units. Evidence for the involvement of fluids in the petrogenesis of Cascade arc lavas is ambiguous, with previous 230Th/238U data suggestive of dry melting [1-3], contrary to inferred high water contents of primitive lavas [4]. All our samples show 230Th over 238U enrichment, with three basaltic andesite samples showing marked 230Th enrichment ([230Th/238U] = 1.21 – 1.42), more than previously reported for other Cascade volcanoes [1, 2, 3]. The corresponding K-values for these samples are 2.75 – 3.25. In contrast, the remainder of the less evolved samples, with [230Th/238U] ~ 1, have K-values closer to the MORB value of ~ 2.5. The two rhyolitic samples have [230Th/238U] ~ 1, but higher K-values of ~ 2.9. Ra-Th disequilibrium measured in a sub-set of samples provides further constraints on fluid sources and melting processes. Most samples are close to secular equilibrium or show modest 226Ra enrichment, with [226Ra/238Th] ~ 1.2. These values are in the range reported for other Cascade lavas [1, 2]. The most enriched sample is a rhyolite, with [226Ra/238Th] of 1.6.

The 230Th/238U data are consistent with decomposition melting and variable addition of a high K component, likely mafic lower crust. The high-K values for the rhyolites were most likely generated by assimilation of this component, consistent with them having the highest 87Sr/86Sr and lowest 143Nd/144Nd ratios. Lack of U enrichment may be due to reducing conditions in the mantle wedge, but the lack of Ra enrichment argues against it, consistent with limited oxidation state data [6]. The high (226Ra/230Th) value measured in the rhyolite is likely related to fluid-based addition of Ra from the slab but crystal fractionation and mixing processes.


Trace element geochemistry of nyerereite and gregoryite phenocrysts from Oldoinyo Lengai natrocarbonatite lava

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Natrocarbonatite lavas erupted by the active volcano Oldoinyo Lengai (Tanzania) are characterized by high modal abundances of phenocrystal nyerereite [(Na,K)3Ca(CO3)2] and gregoryite [(Na,Ca,K)3(CO3)2] set in very fine-grained matrix consisting of halite, sylvite, fluorite, K-neighborite, Sr-REE-bearingapatite, Ba-nyerereite, a gregoryite-like phase and a Ba-Sr-Na-Ce carbonate related to khannesite. Although bulk rock geochemical studies have established that natrocarbonatites are highly enriched in light REE there is a paucity of data on the trace element contents of the constituent minerals. We have in this study determined by high resolution laser ablation ICP-MS the abundances of Li, P, V, Mn, Rb, Sr, Y, Cs, Ba, and REE within and between nyerereite and gregoryite phenocrysts.

Our data show that nyerereite is enriched in Rb (118-256 ppm), Sr (12800-33624 ppm), Y (1.3-7.3 ppm), Cs (1.8-5.9 ppm), Ba (4261-17228 ppm), and REE but poorer in Li (22-52 ppm), P (823-1906 ppm), and V (6.3-37 ppm) relative to gregoryite (Rb = 58-98; Sr = 5071-7009; Y = 0.3- 09; Cs = 1.1 - 4.8; Ba = 1793-3231; Li 151-391; P = 6790-15861; V=38-97 ppm). Nyerereite is highly enriched in REE (La = 262-1010 ppm) relative to gregoryite (La = 64-177 ppm). Chondrite normalized REE distribution patterns for both minerals are parallel and linear with no Eu anomalies, and show extreme enrichment in light REE (La/Sm-CN = 74-89) relative to bulk rock compositions (La/Sm-CN = ~43). Individual coexisting nyerereite and gregoryite phenocrysts are zoned with respect to all trace elements determined. Significant differences in the abundances of trace elements between coexisting crystals suggest that the phenocryst assemblage is derived by mixing of different batches of natrocarbonatite magma.
XAFS study on the behaviors of Antimony and Arsenic in soil-water system under various redox conditions

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Antimony (Sb) is a toxic element and belongs to group 15 of the periodic table, under arsenic (As). The geochemical behavior of Sb in environment is still largely unknown. Since the behavior of Sb in the environment depends on its oxidation state, Sb analysis in environmental samples requires quantitative measurement of Sb(III) and Sb(V). The aim of this study is the speciation of Sb and As in both solid and water phases to understand the reaction of Sb in soil-water environment and to compare the Sb behavior with As examined in mine tailing (Ichinokawa mine, Ehime, Japan) in a natural system and in a soil-water system synthesized in laboratory [1]. The oxidation states and host phases of Sb and As in soil samples of mine tailing (Ichinokawa mine, Ehime, Japan) and in laboratory systems were determined by X-ray absorption fine structure (XAFS) spectroscopy. HPLC-ICP-MS was used for speciation of Sb and As in soil water.

In the natural soil-water system, Sb was present exclusively as the oxidized form, Sb(V), over a wide redox range (from Eh = 360 to -140 mV, pH 8), while As was present as a mixture of As(III) and As(V). This finding was confirmed in the laboratory experiments. EXAFS analyses of Sb and As suggest that the host phases of Sb and As in soil were Fe(III) hydroxides under all redox conditions in this study. Under reducing condition, Sb abundance in soil water decreased in both the natural laboratory systems opposite to the findings of As. Microscopic observation of Ichinokawa soil grains using µ-XAFS shows that significant Sb(III) was locally observed at the rim of the Fe hydroxides particles, while Sb(III) was not observed at the core of the particle. It is reported that the solubility of Sb(III) is much lower than that of Sb(V). Therefore, the findings obtained by the microscopic analysis suggest that Sb reduced to Sb(III) was precipitated on the mineral surface due to its low solubility and that the precipitates containing Sb(III) like Sb_2O_3 may cause the fixation of Sb to the solid phase under reducing condition.


Distribution of Rare Earth Elements in riceplant (Oryza stiva var. japonica)

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The concentrations of 15 rare earth elements (REEs: Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) in riceplant (Oryza stiva var. japonica) were determined. Pot experiments were performed by planting three seedlings in each pot (30 cm of diameter and 30 cm of height) containing soil from the farm in Kyusyu University. The pots were kept outside and water was supplied if necessary. Three pots were prepared to harvest at three different stages of the plants' growth; one month after planting the seedlings, and one week and one month after the appearance of ears. Riceplant shoots were cut off with a plastic knife near the soil surface and washed. The roots were separated from soil by washing carefully with de-ionized water. The plant materials were dried at 80 °C for 48 hours and the dried plant tissue was weighed and finely ground with agate mortar and pestle before REEs determination.

The concentrations of REEs in riceplant shoots and roots were determined by ICP-MS(Agilent 7500). Sample solutions for ICP-MS measurement were prepared by a series of pretreatment consisted of 3 main stages: dissolution of samples, removal of Fe and Al, and REEs concentration with calcium oxalate. In this method, the recovery of REEs was confirmed to be more than 90%.

The observed concentration of REEs in riceplant mostly ranged from 0.05 to 10 ppm. There was not observed clear difference among the samples harvested at different stage of growth. All samples showed similar REE pattern, i.e., light REEs enriched REE patterns. However, concentrations determined in roots were almost 10 times higher than those in shoots. These results suggest that REEs have strong tendency to be retained in/on roots of riceplant.
**Subduction influence of Philippine Sea plate on the mantle beneath Kyushu, SW Japan: An examination of boron contents in basaltic rocks**

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Volcanism in Kyushu is associated with subduction of Philippine Sea Plate (PSP). Kyusyu-Palau Ridge subducts nearly at right angles to central Kyushu, marking the boundary between young (26-15 Ma) PSP in the north and old (60-40 Ma) PSP in the south.

We analyzed boron (B) contents in volcanic rocks from Kyushu to investigate the influence of these contrasting oceanic plates on the mantle composition. Since B is distinctly concentrated into slab-derived fluids among the earth’s materials, we can estimate the subduction contribution to the subarc mantle composition based on the B data in volcanic products.

The across-arc variation of B/Nb is not observed in the northern Kyushu basalts (NKB), whereas it is observed as a smooth depletion curve in southern Kyushu basalts (SKB). In Kyushu volcanic front, lavas from Aso and Kirishima volcanoes which are located in the central Kyushu show the highest value of B/Nb (3.0-3.7). The B/Nb ratios of the SKB (1.2-2.0) are higher than those of the NKB (0.2-0.9).

These observations indicate the young and old segments of PSP subduct beneath northern and southern Kyushu, respectively. In northern Kyushu, the dehydration of the young slab is probably completed before it reaches the volcanic front because of the high geotherm. In contrast, the dehydration of the old slab probably occurred continuously from volcanic front to backarc in southern Kyushu.

The highest value of B/Nb observed in Aso and Kirishima basalts implies the subduction of seamount chain which is the extension of Kyushu-Palau Ridge.

**REE-distribution between Cpx and Grt in Siberian garnet peridotites: In situ measurements vs. lattice strain model calculations**

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We present new REE-distribution coefficients between clinopyroxene (cpx) and garnet (grt) of garnet peridotites from Vitim (Siberia) measured with the high spatial resolution of electron microprobe and SIMS (secondary ion mass spectrometry). By using the *in situ* technique it is possible to detect major and trace element variations within the mineral grains and to avoid inclusions or cracks.

The literature shows that calculated Kds from natural samples (whole-grain separates) and those from experimental run products can differ remarkably. To address these discrepancies and to find out which factor controls the distribution of elements in a sample we measured grt and cpx of grt-peridotites from the well studied Vitim volcanic field in Siberia. These samples do not show any evidence of metasomatism or other secondary processes and formed over a restricted P-T range (1050-1200°C, 2.1-2.5 GPa). For the calculation of the REE-distribution coefficients we used only core compositions from samples with unzoned minerals.

Our newly calculated REE-distribution coefficients are consistent with the experimental data of Burgess & Harte (2004) at temperatures between 900° and 1000°C. Blundy & Wood (e.g. 1994) developed a lattice strain model to predict partitioning of trace elements between cpx and melt. This model was extended for grt compositions by Van Westrenen et al. (e.g. 2001). Because there is no coexisting melt in these samples, we use a measured distribution coefficient (here Sm) to predict the others (Lee et al., 2007). Using Sm gives the best fit between measured and predicted Kds (average deviation for La 11%, Eu 18%, Yb 63%) because there are no interference corrections and concentrations are sufficiently high in both minerals. Using the HREE cannot be recommended, because of interference corrections, the extremely low HREE concentrations in cpx and the resulting large errors on these measurements.
Seasonal controls of methane gas solubility and transport on anaerobic oxidation of methane in shallow water marine sediments

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Sediments with free methane gas are a common occurrence in shallow water marine environments which receive high organic matter flux to the sediment surface. Methanogenesis of buried organic matter occurs below the zone of sulfate reduction and results in the formation of dissolved methane. Subsequently, free methane gas forms when dissolved methane exceeds the solubility concentration. Upward migration of dissolved and gaseous methane sustains the microbially-mediated anaerobic oxidation of methane (AOM) coupled to sulfate reduction in the sulfate-methane transition zone (SMTZ). Since pressure and temperature govern methane solubility, temporal variations in these parameters affect the location and volume of gaseous methane, and thus, biogeochemical reaction rates. In this study, a reactive-transport model is applied to investigate the transient (diurnal and seasonal) dynamics of methane cycling in a marine sediment environment triggered by the individual and combined effects of temperature and pressure fluctuations. The model, which explicitly accounts for the total sediment volume occupied by gas, is calibrated with data from Eckernförde Bay, Germany, where intense AOM occurs above the gas-containing sediment. Results reveal that seasonal temperature fluctuations control the depth of gas formation and dissolution, and that typical diurnal-scale pressure variations due to tides and atmospheric conditions lead only to centimeter-scale vertical shifts in the depth of the gas horizon. Our transient simulations ultimately suggest that methane is efficiently oxidized within the sulfate-methane subsurface barrier, and can only escape to the water column when large and abrupt decreases in sea level reduce rapidly the gas solubility, allowing increased transport rates of gaseous methane through the sediment.

Hydrogeochemical controls on Arsenic enrichment in waters and sediments of the Humboldt River, North-central Nevada

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The Humboldt River (HR) with an area of approximately 43,700 km² is the only source of water for municipal uses, irrigation and mining activities in northern Nevada. The river drains through several geothermal hot springs, and hydrothermal alteration zones and epithermal deposits, including silver, copper, and arsenic-rich gold. As a result, the waters and sediments from the HR system are highly enriched in many elements besides arsenic (As). The concentrations of As in the waters range from 11.9 ppb to 65.8 µg/L (average 31.0 µg/L), whereas the concentrations in stream sediments range from 0.6 to 1785 mg/kg. The water in the HR system is alkaline (pH ranges from 8.4 to 9.3), oxic (average 12 mg/L of dissolved O₂, and +139.9 mV of ORP), and saline with an average of 1035 µS/cm of specific electrical conductivity and highly enriched in B (average 717.2 µg/L), Li (average 141.4 µg/L), and S (average 6500µg/L).

Correlation between As and S in the waters indicates that oxidation of As-rich sulphides may play a role in As enrichment. Lack of correlation between As and dissolved iron in the waters may indicate removal of iron into solid phases. High concentrations of As are commonly associated with high concentrations of B and Li in this system indicating geothermal source of these elements. Ongoing sequential extraction analyses and factor analyses of the stream sediments will shed significant insights on the source, partitioning and release mechanism of dissolved As in the area.
An investigation of the origin and groundwater discharge to Bazangan Lake, Eastern Kopet-Dagh Basin, Iran, using geochemistry and stable isotopes approaches

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The origin of Bazangan Lake, the largest lake is located 120 km northeast of Mashhad city-Iran, and the groundwater/surface water interaction in this lake is investigated using geochemistry and stable isotopes. Bazangan Lake is surrounded by red siliciclastic sediments of Pestehleigh formation (Paleogene) and the carbonate cliffs of Kalat formation (Maastrichtian). Lake water mainly supplied from the Mozdouran and the Kalat karstic formations. The groundwater of these formations discharges to the lake water through several springs and underground seepage face. The fairly enriched 13C value of dissolved inorganic carbon in lake water (average of -4.5 ‰) confirms the contribution of calcite dissolution from these karstic formations. The high electrical conductivity (15500 µmhos/cm) of the lake water is attributed to the dissolution of underlying gypsum layers and to the high evaporation rate at this area (average of 2700 mm/year). This can be confirmed by high concentration of SO4 (4600 mg/l) and the enriched isotopic values of 18O and 2H (average of 1.7 ‰ and -6.2 ‰, respectively) for the lake water. DOC of lake water (8.5 mg/l, 27.7 ‰) is higher than that of recharge spring water (0.6 mg/l, 26.2 ‰), which is due to the presence of phytoplankton groups within the lake water.

Hydrogeochemical prospecting studies for identifying PGE mineralization in Sittampundi Anorthosite Complex, Southern India

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Hydrogeochemical exploration is an important tool for prospecting mineral deposits. The underlying principle is defined by the contact between groundwater and the mineralized zone, and leaching of trace/heavy metals under favourable pH-Eh conditions. PGE solubility in water is dependent on acidic conditions and oxygen fugacities [1]. Recent studies have shown that platinum group elements (PGE) anomalies occur when groundwater comes in contact with primary mineral deposits and the concentration depends upon the distance from the source.

Hydrogeochemical exploration studies were carried out near the Sittampundi Anorthosite Complex in southern India. The major rock types exposed in this area include chromitite, chromite-bearing pyroxenite, meta-pyroxenite, hornblende-anorthosite gneiss, and biotite gneiss ± garnet of Bhavani Group with intrusives of quartz and pegmatite veins. PGE bearing chromitite occurs as detached linear bodies manifesting pinching swelling characteristics, lenses, pods and boudins within the hornblende-anorthosite gneiss. Earlier studies on the chromitite, chromiferous pyroxenite and contact zone anorthosites indicated total PGE values ranging from 200 ng/g to 6.9 µg/g [2].

Water samples collected from representative bore wells and dug wells covering an area of about 200 Km² with a sample interval of about 1 Km. The pH, Eh, Ec and salinity were measured in the field. The samples collected were pre-concentrated by two different procedures involving cation-exchange and activated charcoal methods followed by ICP-MS, XRF analysis. Chromitite samples were also collected and examined for their petrological and PGE geochemical characteristics. In all the analyzed samples, Pt is higher than Pd. Pd/Ir ratio show large variation in these rocks. The data on PGE in groundwater as well as its relation with the occurrences of PGE bearing chromitite body are dealt in detail in this paper.

The first hydrogen economy: A sulfur isotopic record of S\(^0\) metabolisms for early life

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Many hyperthermophilic, deep-branching organisms in the domains Bacteria (Thermotogales, Proteobacteria) and in various Archaea (sub-Domain Crenarcheota and Pyrococcus, Thermoplasmata in sub-Domain Euryarcheota) reduce S\(^0\) to H\(_2\)S in elemental sulfur reduction (ESR) with either H\(_2\) (derived for example from serpentinization reactions in the hydration of ultramafic rocks) or hydrogenated organic compounds, as an electron donor. Perhaps this pathway emerged from the first proto-metabolic metal-S cycles? Now it involves a short electron transport chain controlled by S reductase, polysulfide reductase and hydrogenase. Anaerobic respiration with S\(^0\) is performed by both deep-branching bacterial and archaeal lineages that eat hydrogen to reduce sulfur, so ESR could be an inherited trait from an early high-temperature biosphere. These organisms can readily obtain their sulfur from rapid cooling of fumarole gases and then catalyze the reaction:

\[ 4S^0 + 4H_2O \rightarrow 3H_2S + SO_4^{2-} + 2H^+ \]

With Fe hydroxides present and abundant in the early oceans, the reaction:

\[ H_2S + 4H^+ + 2Fe(OH)_2 \rightarrow 2Fe^{2+} + S^0 + 6H_2O \]

can proceed. This chemistry potentially feeds back into anaerobic photoautotrophic Fe(II) cycling. Transition metal-sulphur chemistry figures prominently in the biochemistry of many deeply-branching microbes beyond Fe-S. Many metals such as Zn, Mo, Co and Ni are abundant in mafic and ultramafic rocks and readily react with S. Yet, most of the various catalytic roles of metal-S clusters other than Fe await experimental verification from analysis of controlled (culture) experiments. Such experiments represent an important new avenue for research into the question of a biological origin for the most ancient multiple (\(^3\)S, \(^32\)S, \(^34\)S and \(^36\)S) S-isotope fractionations found in the geologic record (up to ca. 3.85 Ga) and the nature of the biomes that constituted this first “hydrogen economy” on Earth.

Geochemistry and isotope tracing of the subduction related volcanism in the Timok magmatik complex, East Serbia

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The Timok volcanic complex (TMC) is part of the mineralized ABTS (Apuseni-Banat-Timok-Srednogorie) belt in SE Europe. During the upper Cretaceous this belt was formed in an arc setting due to the northward subduction of the Vardar Ocean under the European platform. In the TMC the calc-alkaline volcanism can be approximately divided into three stages; (1) the initial stage in the eastern part mainly composed of subaerial adesitic volcanism; (2) middle subaqueous basaltic to andesitic volcanism in the central and western part; (3) last stage intrusive granites in the western part. The magmatic products are represented in extrusive as well as intrusive facies, whereas only the initial stage shows porphyry Cu mineralization.

Literature data show that the magmatic activity and related ore formation in the initial stage occurred during 92-60 Ma (Late Cretaceous-Paleocene). Nevertheless these K/Ar ages are not very precise. First high-precision U/Pb single zircon analyses indicate an age of 86.2-84.6 Ma for the initial volcanism in the eastern part of the TMC. \(\varepsilon_{Hf}\) data for zircons are ranging between \(+8\) and \(+13\) showing a mantle derived origin. The second phase volcanism (82.7-82 Ma) together with the last intrusive phase (70.5 Ma) show lower \(\varepsilon_{Hf}\) zircon data (+4 to +8) indicating a rising influence of crustal material. \(^{87}\)Sr/\(^{86}\)Sr isotope data also indicate this increasing crustal influence. \(^{87}\)Sr/\(^{86}\)Sr values are changing from 0.7039 in the initial stage to 0.7055 in the last stage intrusive volcanism.

Fluid-mobile elements such as Cs, Rb, U and K show enrichment due to their transport from the slab into the source region. The High Field Strength Elements (HFSE) like Nb, Ta and Hf in contrast are depleted. The relatively flat middle (MREE) to heavy (HREE) rare earth element patterns probably reflect pyroxene and plagioclase fractionation. Most of the samples show an additional slight negative Eu anomaly confirming the plagioclase fractionation. High Sr/Y (>20) show an adakite-like signature that may be the product of melting of eclogitic portions of the subducted slab. However this scenario may be unlikely because of the subduction of Jurassic “cool” oceanic crust in the late Cretaceous.
Sapphirine granulites of the Gruf Complex (Central Alps, N-Italy):
In situ monazite dating by SHRIMP and confocal synchrotron µ-XRF

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The age of granulites in the Gruf Complex has been a matter of debate, because of conflicting evidence from U-Pb dating of zircon mineral separates [1] and field evidence. We used a novel in situ confocal synchrotron technique for chemical U-Th-Pb dating of monazite to resolve this.

The use of chemical dating has been restricted by high detection limits (EMPA ca. 100 ppm) and low spatial resolution (µ-XRF ca. 150 µm). A confocal experimental set-up at the µ-spot beamline at BESSY II has been used here (excitation volume of ca. 20 µm), to allow in situ analysis in polished thin sections, in contrast to mini-XRF (e.g. [2, 3]). Three isotopically dated and chemically characterized monazite standards used to calibrate Ranchins formula parameters [4] yielded ages within < 4% of the isotopic results. The Pb detection limit is ca. 7 ppm for 1000 sec counting times. The obtained chemical dates range from 32-86 Ma, the youngest of which agree within error with in situ analyses on the same grains by SHRIMP, which did not detect any older relics. The older chemical dates are thus artefacts produced by excess common Pb, dominant in such young grains at this low level of detection. 32 Ma can now be reliably interpreted as the age of the HT event in the Gruf Complex (coeval with the Bergell intrusion, because the monazites are inclusions in HT-minerals (orthopyroxene, sapphirine).


Localisation of groundwater sources by combining δ18O, δD and Rare Earths studies

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Stable isotopes (δ18O and δD) are commonly used to characterize the source of groundwater. Different from stable isotopes the distribution rare earth element (REE) in groundwater reflects the leachable components of sediments and rocks of the catchment area. This is because after a long time of W/R interaction REE adsorbed onto pore surfaces are in equilibrium with the percolating groundwater. This is also the case if the lithology changes. Thus, groundwater sampled from wells and springs still show the REY distribution pattern established in the catchment area. Only if the groundwater leaches soluble, REY-bearing salts from deeper aquifer rocks, different from the catchment, the REY pattern is varied. In Israel, groundwater from sandstones, Cretaceous and Eocene limestones, and basalts show distinctly different REY patterns. Applying the REY signature as a grouping criterion of groundwaters, δ18O vs. δD plots yield a new dimension in interpreting isotope data. Examples will be shown from studies in Israel. For instance, the combination of isotope and REE data prove that the water extracted from the cover basalt of the southern Golan originates from the limestones of the Hermon Massif far north, thus proving long-distant movement of groundwater in this area. Groundwater from the cover basalt in the Bet Shean area originates from Eocene limestones further to the west. In the Arava Valley the groundwater extracted from the Graben fill of the adjacent mountains either originates from the Kurnub sandstone or the Judea limestones. These two water types occur side by side without significant mixing.

Sulfide oxidation and acid neutralization reactions in a high-sulfide tailings impoundment

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When sulfide minerals contained in mine tailings are exposed to atmospheric oxygen and water, they oxidize releasing acid, dissolved metals and sulfate to the adjacent pore water. Within tailings impoundments, the principal geochemical processes affecting the transport of dissolved metals and sulfate are sulfide oxidation and acid neutralization reactions. During sulfide oxidation, a series of mineral dissolution-precipitation reactions control pH and metal mobility. Typically, the series consists of calcite (pH 6.5-7.5), siderite (pH 4.8-6.3), Al hydroxides (pH 4.0-4.3), Fe(III) hydroxides (2.5-3.5), and aluminosilicates (pH <2). The former Sherritt Gordon Mine, located in Northern Manitoba, Canada, contains a tailings impoundment consisting of 60 wt% sulfide minerals that have undergone over 70 years of weathering. Oxidation reactions in the tailings have resulted in extensive depletion of sulfide minerals in the upper 50 cm tailings. Porewater pH in the tailings increases with depth in 3 distinct steps separated by plateaus occurring at a pH of 1.4, 4.3 and 5.6, corresponding to the dissolution of aluminosilicates, Al hydroxides and carbonates, respectively. The extremely low pH of the pore water (pH 0.67–2) in the upper 90 cm of the tailings has depleted nearly all biotite, chlorite, and smectite. There is also evidence that the more stable aluminosilicates have been susceptible to replacement, thereby contributing to acid neutralization. Grains of albite, cordierite and amphibole exhibit rims and veinlets of secondary silica that have partly replaced the minerals. The depletion of aluminosilicate minerals in the upper meter of the tailings, and the presence of residual sulfide minerals observed at a depth of 50 cm suggest that the zone of low-pH pore water will likely expand as sulfide oxidation and acid generation continue.

Simultaneous back-arc spreading and arc magmatism since upper Triassic in Iranian continental block

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The subduction of the northern Tethyan Ocean beneath the active continental margin (the Sanandaj-Sirjan zone) of Iranian block is documented by arc magmatism and back-arc spreading from upper Triassic to Cretaceous in the Sanandaj-Sirjan zone and from Eocene to Plio-Quaternary in the Urumieh-Dokhtar magmatic zone. By virtue of K-Ar and stratigraphic ages, back-arc spreading was firstly started from upper Triassic (Sikhoran ophiolite) to upper Jurassic-lower Cretaceous (Kahnuj and Baft ophiolites), continued to middle Cretaceous (Nain and Shahr-e-Babak ophiolites), to upper Jurassic-lower Cretaceous (Kahnuj and Baft ophiolites), to middle Cretaceous (Nain and Shahr-e-Babak ophiolites), to upper Jurassic-lower Cretaceous (Kahnuj and Baft ophiolites), to middle Cretaceous (Nain and Shahr-e-Babak ophiolites). These phases of back-arc opening were due to the oblique subduction of the Tethyan Ocean beneath the Central Iranian blocks. Moreover, during the Mesozoic time, the Sanandaj-Sirjan zone behaves as the active continental margin over the Tethyan subduction, as witness by the presence of calc-alkaline magmatism. Since Eocene to Plio-Quaternary, the magmatic arc migrated to the north, crosscutting the Central Iranian block as the Urumieh-Dokhtar magmatic belt. Change of magmatism from calc-alkaline to shoshonitic and adakitic from Eocene to Plio-Quaternary can be interpreted by change in the dip of the subducted slab or change in the velocity and/or obliquity.
**Central Iranian volcanic belt: Implication of the transtensional basin system**

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Urumieh-Dokhtar magmatic zone has been considered as a place for the main magmatic activities in the Central Iranian continent in the Cenozoic age. Explosive activities in Paleogene and early Neogene were commonly from fissure eruptions and feeder dikes had a dominant role for creation of thick sequences of magmatic and pyroclastic rocks. In the late Neogene, central vent eruptions caused for creation of strato-volcanoes in the study area and variant of volcanic domes in continental environment. The Neogene volcanic activities are divided into two phases: Ngv1 and Ngv2. At the first stage (Ngv1), volcanic rocks contain basalt to andesite-basalt as lava or pyroclastic materials. The explosive event was followed by the volcanic to subvolcanic associations of Ngv2 with products of mainly andesitic to rhyolitic composition. The volcanic domes of Ngv2 and their diverse modes of emplacement are especially characteristic of this phase as Kuh-e-Aleh.

Geochemical and Isotope geochemistry data confirm the presence of transtensional regions along the Urumieh-Dokhtar magmatic zone, opened during Paleogene and early Neogene due to the collision of the Arabia platform and Central Iranian continent.

**Coral Li/Ca in micro-structural domains as a temperature proxy**

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Coral skeletons are valuable geochemical archives of environmental change, although coral physiology has to varying degrees imprinted a ‘vital effect’ complicating paleoclimate reconstructions. In order to decipher environmental from physiological effects we have utilised high sensitivity laser ablation ICPMS to examine Li/Ca variations in the aragonite theca of living specimens of shallow (C. caespitosa) and deep-water (L. pertusa) corals at different temperature-depth regimes, together with samples cultured in temperature-controlled tanks. The Li/Ca variations at micron-resolution are large and correlated with centres of calcification versus fibrous aragonite. The Li/Ca composition of the fibrous aragonite however appears to be primarily controlled by water temperature with the distribution coefficients ($D_{Li/Ca}$) of $L. pertusa$ rapidly decreasing with increasing water temperature indicating a stronger sensitivity for Li/Ca at lower temperatures, whereas the $D_{Li/Ca}$ for $C. caespitosa$ follows an exponential regression. The application of coral Li/Ca paleothermometry on specifically identified micro-structural domains thus offers a unique opportunity to reconstruct changes in water temperatures at different depths in the water column.
Growth of a Se⁰/calcite composite using hydrothermal carbonation of Ca(OH)₂ coupled to a complex selenocystine fragmentation

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In this study, the hydrothermal method was carried out in order to produce an elemental selenium (Se⁰)/calcite composite. Under O₂-poor conditions (i.e. with a purge step using Argon), the composite was mainly characterized by spherical selenium nanoparticles (<500nm) deposited on the calcite matrix. The carbonate matrix was constituted by nano- and micro-rhombohedral crystals (<2µm) and micrometric agglomerates and/or aggregates (<5µm). For this case, the spherical Se nanoparticles give a stable red coloration to the composite. In contrast, under O₂-rich conditions (i.e. without a purge step), the composite was characterized by hexagonal selenium microparticles (<25µm) dispersed in the calcite matrix. For this case, a gray coloration of composite was observed [1].

In conclusion, the complex selenocystine fragmentation mechanism leaded the precipitation/growth of elemental selenium with different morphologies and particles sizes. Furthermore, it was noticed that the selenocystine fragmentation also participates to the precipitation/growth of calcite particles with star-like morphologies. Finally, the results presented here demonstrate that Se⁰/calcite composite, with spherical or hexagonal morphologies for elemental selenium can be produced, this composite could possibly has a high potential for medical (ex. dietary supplement) or industrial (ex. pigments) applications. In addition, this study may have implications in the field of biomineralization.


Fractionation of ²³⁸U/²³⁵U in modern and ancient anoxic marine environments: A paleoredox tracer?

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Uranium is a redox sensitive trace element that is strongly enriched in anoxic sediments. It has been shown that burial of U from seawater into such sediments is coupled with U-isotope fractionation [1]. While seawater has a constant δ²³⁸U = -0.41‰ (relative to SRM 950a), modern sapropels (e.g. Black sea) display heavier U isotope composition ranging from ≈ -0.2‰ to + 0.44‰ [1]. Black shales are also isotopically heavier than the crust (δ²³⁸U ≈ -0.3‰), the major source of U to the oceans. There is a crude positive correlation of U-isotope compositions with U concentrations and TOC for euxinic sediments. In contrast, oxic sediments display U-isotope compositions, which are slightly lighter than that of seawater. The U-isotope fractionation between oxic and anoxic environments is similar to that observed for Mo [2, 3], although contrary in directions and extents. Thus, a shift in the abundance of oxic versus anoxic sinks through geological timescales should affect the oceanic mass balance of U-isotopes, similarly as previously observed for Mo [4].

We are focusing our investigations on ancient black shales from periods, which are believed to represent anoxic events of global extent, such as the mid-Cretaceous OAE-2 [5] and the Toarcian OAE [6]. We will present a comparison of U- and Mo-isotope systematics and abundances of redox sensitive trace metals. Preliminary U-isotope data of black shales from OAE-2 and the Torcian OAE also display heavier U-isotope compositions (≈ -0.3‰ to ± 0‰) than that of modern seawater. However, they may be shifted by 0.1-0.3‰ towards lighter compositions compared to modern black shales. OAE-2 samples from Leg 207, core 1261 (an open ocean setting), which provides a continuous record through the entire OAE, are also isotopically lighter than black shales from the time before the onset of the OAE. These findings may indicate a larger extent of anoxic environments during both OAEs compared to modern times.

Humidity cell analysis of waste-rock from the Diavik Diamond Mine, NWT, Canada

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Acid rock drainage can significantly effect the environment surrounding mine sites. The potential for acid rock drainage can be predicted with the use of kinetic tests such as humidity cells that represent ideal experimental conditions. Humidity cell analysis was conducted on twelve samples of sulfur-bearing waste rock from the Diavik Diamond Mine, based on the flood leach method of the ASTM Standard D 5744 [1]. Samples were characterized and subjected to controlled dissolution testing for 455 days to 665 days (65 – 95 weeks). Four samples of each type of waste-rock was placed into humidity cells. Waste-rock on-site is segregated into three classifications based on low to high sulfur content; Type I is a clean granitic material with a sulfur content less than 0.04 wt.%, Type II has a sulfur content between 0.04 and 0.08 wt.%, while Type III is a biotite shist with a sulfur-content greater than 0.8 wt%. Weekly leachates from the humidity cell were collected and analyzed immediately for pH, Eh, conductivity and alkalinity. Samples were filtered, and the leachate analyzed to determine the concentrations of anions, nutrients and cations.

Effluent pH varies depending on the waste-rock type. The most significant decline in pH occurs in two samples of type III had a pH that dropped to 3.9 – 4.0 from 6.4 in 57 – 63 weeks. At the same time some concentrations have increased, such as; Al, Cu, Fe, Ni, Zn and SO4. The remaining two samples of Type III show a significantly different pH trend, a range of pH of 6.8 – 8.3 over the duration of the test. The range of pH for types I and II is less dramatic with a gradual decline of 1 – 1.5 pH units. Analysis of the leachate chemistry from the humidity cells tests are used to determine the rates of sulfide oxidation, which will be compared to rates measured on the large-scale waste rock piles.


Origin and geochemical evolution of mafic magmas from the Cascade arc, Mount Baker, Washington: Probes into mantle processes

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Mt. Baker is an active stratovolcano in the Garibaldi Belt of the Cascade arc in northern Washington. The composition of this volcanic field is largely andesitic, with basalt comprising only ~1% of the total eruptive components. Heretofore, knowledge of the geochemistry of the mafic flows on Mt. Baker has been restricted to major elements of a very limited number of samples. Whole rock chemistry reveals the diversity between these mafic lavas, which must be derived from distinct sources.

Five mafic lava flows have been sampled and analyzed for major, trace and REE chemistry: the basalts of Park Butte (49.3-50.3 wt.% SiO2, 7.9-8.4 wt.% MgO), Lake Shannon (50.7-52.6 wt.% SiO2, 5.3-6.4 wt.% MgO), and Sulphur Creek (51.2-54.6 wt.% SiO2, 5.0-5.5 wt.% MgO), and the basaltic andesites of Tarn Plateau (51.8-53.9 wt.% SiO2, 7.0-7.9 wt.% MgO), and Cathedral Crag (52.1-52.9 wt.% SiO2, 3.8-8.3 wt.% MgO). The Tarn Plateau basaltic andesite and Park Butte basalt flows are the most primitive, with Mg# (100[Mg/(Mg + Fe³⁺)]) ranging from 60 to 67, Ni content from 59 to 67 ppm, and Cr content from 176 to 267 ppm. Mg# is not correlated with SiO2 content, as the Tarn Plateau basaltic andesite has the highest Mg# of all the lavas. The Park Butte flow is classified as low-K tholeiitic basalt (compositionally similar to LKOT found elsewhere in the Cascade arc), while the remainder of the flows are classified as medium-K calc-alkaline basalts and basaltic andesites.

The REE patterns differ from flow to flow, with varying slopes. Park Butte (LKOT) has the flattest REE pattern and the lowest abundances of REE of all the lavas, with (La/Sm)N at ~1.7 and (LREE)N values from 25-35. Tarn Plateau has a relatively steep REE pattern, with (La/Sm)N at ~2.2 and (LREE)N values from 40-55. However, the most differentiated lava (Cathedral Crag) has the steepest REE pattern, with (La/Sm)N at ~2.3 and (LREE)N values from 45-70. Ba, Sr and Th cannot be correlated between the most primitive flows (Tarn Plateau and Park Butte), demonstrating that these lavas are not genetically related. We describe multiple mantle sources that generate mafic magmas of such varied compositions.
Ancient analogs for ultramafic-hosted vents: Water-rock-derived energy for deep subsurface chemosynthesis

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Microbial utilization of energy sources derived from ultramafic rock is not restricted to the marine environment. Recent studies demonstrate that deep fracture fluids in Precambrian Shield rocks in Canada, South Africa and Finland contain large quantities of hydrocarbon gases as well as up to 10mM dissolved H₂. Active H₂ consuming microbial communities are under investigation to identify agents of nutrient cycling and the manner in which these organisms interact with their local geological and hydrogeological environments. Understanding microbial characteristics that permit growth in these environments will help quantify subsurface contributions to nutrient cycling on Earth and also highlight suitable extreme environments for detecting subsurface biospheres in other regions of the solar system.

We collected samples from near 4,000 foot depth at the Birchtree Mine in Thompson, Manitoba. High water salinities resulting from extended periods of water-rock interaction reflect the isolation of these fracture systems from surface inputs. We deployed biofilm units, consisting of glass wool enclosed within a Teflon housing, into boreholes. Phospholipid fatty acids (PLFA) were harvested from the units after their retrieval and PLFA diversity indicated growth of a viable microbial community. Stable isotope (δ¹³C) composition of the PLFAs ranged from -28 ‰ to -24 ‰, minimally offset from the acetate composition (-26.7 ‰). We are assessing the role of acetogenesis in carbon cycling between the dissolved inorganic carbon (δ¹³C of -15.0 ‰), lipid, and acetate carbon pools present within these isolated fracture systems.

A role for proteins in extracellular metal-sulfide and Selenium biomineralization?

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Our recent data point to a role for microbially derived proteins in extracellular zinc-sulfide (ZnS) and elemental selenium (Se⁰) biomineralization by a natural community of Desulfobacteraceae sp. and pure cultures of Geobacter sulfurreducens, respectively. In the former case (Fig. 1), these proteins are associated with a biofilm growing under microaerophilic conditions, and may serve in a metal-binding capacity. In the latter case (Fig. 2), preliminary data suggest a role for sulfur redox proteins in mitigating the precipitation of Se⁰. We will discuss possible roles for proteins and other organic macromolecules in mitigating the form and fate of aqueous and nanoparticulate metals in natural waters and sediments.

Figure 1: Natural aggregate of biogenic ZnS nanoparticles formed by biofilm sulfate-reducing bacteria (SRB). (A) SDS-PAGE gel image of proteins extracted from biofilm. (B) Gel image of proteins (box) extracted from ZnS.

Figure 2: G. sulfurreducens cells and biogenic Se⁰ nanospheres. (A) SDS-PAGE gel image of proteins extracted from cells. (B) Gel image of proteins (box) extracted from Se⁰.
Are noble gases subducted in the deep mantle?

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Staudacher and Allegre [1] proposed that noble gases are not subducted in the mantle. However, new Ar and Xe results challenge this concept of “noble gas subduction barrier”. The $^{38}\text{Ar}/^{36}\text{Ar}$ ratio is atmospheric in mantle-derived rocks (MORB & OIB), whereas a solar-like value is expected based on Ne. Furthermore, $^{124-128}\text{Xe}/^{130}\text{Xe}$ in CO$_2$ well gases appear to be different from air, showing a mixture air-solar [2]. These two observations may suggest a recycling of air-like noble gases in MORB and OIB sources. We developed a model of degassing-subduction for noble gases in order to constrain the subduction fluxes and to discuss the consequences of such a subduction. Our model assumes that mantle was initially solar, Atmosphere was different from mantle due to gas loss or late veneer and subduction started 4.4Ga ago. Both radiogenic and primordial isotopic ratios are used to constrain the subduction fluxes. In order to obtain atmospheric $^{38}\text{Ar}/^{36}\text{Ar}$ and $^{124-128}\text{Xe}/^{130}\text{Xe}$ and present-day MORB radiogenic isotopic ratios, 3 observations have to be made. A. The mantle was fully degassed at the end of accretion (>99.999%). B. The subduction of xenon is massive (>80%). C. The radiogenic isotopic ratios were much higher in the Archean mantle, which is not observed in the few available archean samples. Finally, this noble gas subduction has to occur in all mantle, including the OIB reservoir. Therefore, it appears difficult to consider that the mantle had initial solar isotopic compositions. Another explanation has to be found for the air-like compositions of heavy noble gases in the mantle, for example the SW irradiation of the parent bodies and solar nebula processes.


Ionization and speciation of water in silicate melts

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Water in silicate melts is commonly assumed to take the form of molecular water (H$_2$O$_m$) and hydroxyl groups (OH), the latter bounded to network formers (T) as T-OH groups. Although free hydroxyls (OH$^-$) were only recently ascertained in depolymerized melts [1], the amphoteric behavior of water, was already suggested long ago [2] and preliminarily modelled considering redox data [3]. However, autoprotolysis of water has not been assessed in silicate melts hitherto, because of the rather complex nature of such a solvent. Here, a simple theoretical frame is developed based on the extended two-sublattice hypothesis of Temkin. The theory accounts for acid-base properties of the melt phase, and reconciles differing notations. An independent proof of our appraisal is given by an algorithmic approach to chemical equilibria between O and H in polymeric silicate melts. The assessment of the ionization constant of water in melts can explain the conditions at which precipitation of hydrous minerals can occur. Because of the amphoteric behavior, melt polymerization can be affected less than that normally perceived and assumed, depending on bulk composition. This has implications for the redox behavior, which is strictly connected to melt acid-base properties, hence polymerization. These connections must be accounted for when modelling magmatic equilibria.

Seafloor hydrothermal fluid evolution: A fluid inclusion study

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Fluid inclusions offer the only available samples of uncontaminated sub-seafloor fluids. To date, microthermometry of such fluid inclusions trapped in rocks of the ocean crust has revealed that there exist fluids of a wide range of salinities in fluids trapped in both modern and ancient hydrothermal systems. Here we report direct analyses of the chemistry of individual inclusions using LAICPMS. This method allows assessment of multiple generations of fluids within the same sample, giving information on the full range of fluids, rather than simply bulk compositional data.

Samples from different levels in the hydrothermal systems in both the Troodos ophiolite, Cyprus and ODP/IODP Hole 1256D are being studied. By studying ophiolitic and in situ ocean crust in tandem it is hoped a greater understanding of fluid evolution will be reached as well as establishing any further oceanic-ophiolitic similarities or differences.

Microthermometry from Troodos samples has revealed a combination of fluids of black smoker vent salinity (~1.5-7 NaCl wt% eq) and hyper-saline fluids (~25-45 NaCl wt% eq) in the system. Given the relatively good constraints on temperature and pressure in these systems it is evident that these fluids are not a single phase separated pair, if assuming a purely seawater fluid source.

Heating and freezing of fluid inclusions from the sheeted dikes and upper plutonics in Hole 1256D indicates trapping temperatures ranging from 250 to 470°C. Many of these fluid inclusions fall within the temperature-salinity range observed in black smoker vent fluids, however many are more saline and trapped at higher temperatures. The samples from the granoblastic dikes at the base of the sheeted dike complex and some plutonic samples also host hyper-saline (>40 NaCl wt% eq), high temperature (>450°C) fluid inclusions.

Subsequent laser ablation of fluid inclusions from both sites has provided a much more detailed insight into the nature of the fluids, indicating that the fluids take up metals very efficiently and it is apparent that Mg loss from the seawater is slow, with it still being present in reasonable quantities at the base of the system.

Geochemical modeling, based on the fluid chemistries of these systems is in progress and will be presented at the meeting.

Igneous, alteration and exhumation processes recorded in abyssal peridotites from an oceanic core complex of the Central Indian Ridge

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Oceanic core complex (or megamullion) has been interpreted to be the exhumed footwalls of long-lived detachment faults at slow spreading ridges [1, 2]. Data on oceanic core complex has never been reported from the Central Indian Ridge (CIR). We conducted Japanese submersible SHINKAI 6500 dives on an oceanic core complex in the CIR at 25°S (termed 25°S OCC hereafter). It is interesting to note that an unique hydrothermal field (Kairei hydrothermal field) which is characterized by relatively high H\(_2\) content in hydrothermal fluid and unique ecosystems is located at the east of the 25°S OCC [3].

Two less-deformed serpentinized peridotites were recovered from the ridge-facing slope whereas three highly deformed talc-chlorite-serpentine schist were from the top surface of the OCC. The massive peridotites are clinopyroxene-bearing harzburgite. One less-deformed peridotite was cut by leucocratic veins and was geochemically modified by a melt for the formation of the leucocratic veins. The Cr\# (=Cr/(Cr+Al) atomic ratio) of spinel not modified by the melt is overlapped with higher range of that in the other abyssal peridotites collected from the CIR [4], indicating moderate degree of partial melting. The schist also contains ilmenite-bearing altered gabbroic fragments, indicating that the deformation and alteration of both gabbros and peridotites were localized along the detachment fault during the formation of the OCC.

*In situ* microanalysis of trace elements of the primary igneous minerals and their secondary minerals revealed that selective elements, such as Rb, Sr, Ba, Pb and U, are enriched in the secondary minerals. In particularly, Uranium content is steeply increased at the outermost margin of orthopyroxene pseudomorph, indicating that the uptake of U was occured in the later alteration processes at lower temperature conditions.

**Improved and automated cell count system for rapid enumeration of microbial cells in deep subseafloor sediments**

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Direct count (DC) and quantification of prokaryotic population in sediments have provided fundamental information for understanding the life and biosphere in deep marine subsurface. We tried to improve the conventional method by decreasing the non-specific fluorescent backgrounds and to develop an automated system for acquiring fluorescence image and number of DNA-stained cells.

SYBR Green I is known to specifically bind to the double strand DNA; however, we still observed some autofluorescent objects in the superheated (450°C, 3 hours) control sediments. Newly developed acid-wash treatments successfully removed these background objects. However, we found that the centrifugation of sediment slurry caused serious loss of cell number in a control experiment using *E. coli* cells.

To gain the cell recovery rate during the centrifugation steps, we used blocking reagents or EDTA in the slurry suspension.

To obtain statistically meaningful fluorescent images, we constructed a computer-assisted automated cell counting system. Using XY-stage and Z-mortar equipped with an epifluorescent microscopy, which is controlled by image-scanning software, the system can automatically scan 1 mm x 0.5 mm filter area within 15 min. Using the newly developed method and system, we compared the cell populations in core sediments by SYBR Green I- and acridine orange-stain, resulted in the statistically meaningful, consistent number of the deep subseafloor microbial population.

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**The structurally controlled Zn-Pb-Ag Blende deposit, Yukon, Canada: Geochemical constraints on sulphide mineralization**

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The Blende Zn-Pb-Ag deposit is located approximately 75 km northeast of Keno Hill, Yukon, within the southern Wernecke Mountains. Epigenetic mineralization is hosted by dolomitic silstone of the Paleoproterozoic Gillespie Lake Group, the uppermost unit of the Wernecke Supergroup. Sulphides are found as cements in breccias developed in an axial planar cleavage within the hinge zone of a kilometre scale anticline.

The sulphide paragenesis consists of three stages of growth. The earliest is pyrite veining with minor sphalerite which have δ\(^{34}\)S values of +9.4 to +58.1‰. This is crosscut by main stage mineralization consisting of sphalerite and galena with δ\(^{34}\)S data that ranges from +15.6 to +34.9‰ and a Pb-Pb age of 1.50 to 1.44 Ga, with some pyrite and minor tetrahedrite and chalcopyrite. Coarser euhedral sphalerite and galena make up the late stage of sulphide growth and have isotopic values of +16.3 to +32.8‰ and a Pb-Pb similar to that of the main stage galenas.

The gangue minerals consist of fine to coarse grained dolomite and quartz, and are present in five paragenetic stages. These include the host rock with δ\(^{13}\)C of 0.0 to +1.0‰ and δ\(^{18}\)O of +19.6 to +21.7‰. There are two vein sets that predate sulphide mineralization and these have δ\(^{13}\)C values of 0.0 to +0.5‰ and δ\(^{18}\)O values of +19.6 to +21.7‰. The main stage veining that accompanies the main stage sulphides has a range in δ\(^{13}\)C and δ\(^{18}\)O from 0.0 to +0.3‰ and +18.0 to +20.8‰, respectively. Finally, euhedral dolomite that occurs with the late stage sulphide has carbon isotopic data that ranges from -0.5 to +0.2‰ and δ\(^{18}\)O from +18.1 to +19.0‰.

Evidence suggests a Mesoproterozoic age of mineralization that postdates a Paleoproterozoic deformation event, involves circulation of seawater transporting metals and sulphur, and derived components for the gangue mineralogy from the host dolomitic silstone.
Isotopic evidence of microbial methane in ultrabasic reducing waters at a continental site of active serpentinization in N. California

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Gases exsolving from ultrabasic reducing groundwater at a site of shallow, low temperature, active serpentinization in Northern California were studied to determine if the gases were microbial, thermogenic, and/or abiogenic in origin as has been recently suggested for sites on the seafloor. A clear geochemical distinction was evident between springs at higher and lower elevations. The upper springs were characterized by high levels of N₂ (up to 66%), H₂ (up to 23%) and CH₄ (up to 17%), with trace amounts of C₂H₆ and C₂H₂ gases. The lower springs were dominated with H₂ (up to 50%) and N₂ (up to 54%), and lesser amounts of hydrocarbon gases. Carbon and hydrogen isotopic values of CH₄ (-68.4 to -57.5 ‰ and -368 to -302‰ respectively) along with gas compositions (CH₄/C₂H₆ up to 66%) indicated that in all springs the primary source of CH₄ was microbial methanogenesis via acetate fermentation pathway. In the lower springs there is evidence of a secondary differentiation between the upper and lower springs demonstrates that within the extreme conditions of the ultrabasic nutrient poor groundwater there is heterogeneity with respect to microbial activity, but all sites provided the first clear evidence of microbial methanogenesis within groundwaters associated with terrestrial serpentinization.
Weathering and transport of Cr and Ni in northern California soils

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Geologic, geomorphic, hydrologic and anthropogenic controls on soil geochemistry were investigated across a 22,000 km² area including the Sierra Nevada, the Sacramento Valley, and the northern Coast Range. The results indicate that soil geochemistry in the Sacramento Valley is primarily controlled by the transport and weathering of parent material from the Coast Range and Sierra Nevada. Ultramafic (UM) rocks crop out extensively in both ranges and these rocks and associated soils have high concentrations of Cr and Ni. Soils derived from these UM rocks contained 1700 to 10,000 ppm Cr and 1300 to 3900 ppm Ni. Valley soils west of the Sacramento River contained 80 to 1420 ppm Cr and 65 to 224 ppm Ni, reflecting significant contributions from UM sources in the Coast Range. Valley soils on the east side of the Sacramento River contained 30 to 370 ppm Cr and 16 to 110 ppm Ni, which reflects a dilution of UM material by granitic weathering products from the Sierra Nevada.

Petrographic, XRD and SEM studies show that Cr occurs in UM rocks and soils as Cr(III) hosted by the refractory minerals chromite and other mixed composition spinels containing Al, Mg, Fe, and Cr. Evidence of spinel dissolution is seen in SEM analysis of soils. We defined a Cr reactivity index as the ratio of the Cr concentration determined by a 4-acid digestion (HNO₃, HCl, HF, HClO₄), which does not completely dissolve chromite, to that determined by lithium metaborate fusion (LiBO₂), which gives total Cr content. A higher reactivity index in valley soils suggests Cr is in a more labile form in the valley soils relative to UM sources. Additionally, clays (<2 μm fraction) in valley soils were enriched in Cr and Ni relative to the bulk soil (<2 mm), whereas clays in UM soils were lower in Cr and Ni relative to bulk soils. Regional groundwater data shows elevated Cr(VI) content west of the Sacramento Valley (up to 50 μg L⁻¹), suggesting that a redox mechanism occurs in the release of Cr from solid phases. Our results show that regional-scale transport and weathering of UM constituents has resulted in enrichment of Cr and Ni in Sacramento Valley soils and a change in the residence of these elements.

Calcite nucleation and epitaxial growth from high ionic strength NaCl solutions

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The concentration of NaCl was varied from 0.5 to 5 molal in solutions containing low Ca²⁺ concentrations (~10⁻² m) and the supersaturation with respect to calcite was adjusted by varying carbonate alkalinity and pCO₂. Iceland spar calcite was used as the host substrate for epitaxial overgrowth experiments.

Calcite did not nucleate directly from solution, but instead formed on the surface of homogeneously precipitated vaterite crystals. No aragonite was observed. Subsequently vaterite recrystallization initially produced euhedral, well-formed calcite rhombs up to tens of microns in size. Further reaction of this calcite in supersaturated solutions produced surface roughening, macro steps and an increase in kink distribution, suggesting a different growth mechanism.

Epitaxial calcite growth on Iceland spar calcite produced a variety of different surface structures that changed with time and degree of supersaturation. The most common overgrowth was submicron crystals that formed incomplete layers in a manner characteristic of surface instability. Overgrowth layers were often observed to inherit macroscopic surface patterns of the underlying host calcite substrate. Longer reaction times (months) produced extensive recrystallization and heterogeneous evolution of large surface features.
Geochemical prospecting studies in Sinai, Egypt

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The present geochemical work was carried out at two areas in southern Sinai, namely Wadi Nissriyn and Khashm El-Fakh.

Stream sediments, soil and bed-rock samples were collected and chemically analyzed by emission spectrograph for eighteen selected elements. The chemical results were treated with simple and multivariate statistical methods, where copper is shown to be the most abundant element at Nissriyn area, while Zn, Pb, Ag and Bi are associated elements. At Khashm El-Fakh, anomalous values of iron were found beside copper and zinc.

R-mode factor analyses show two factors one is Cu-Zn-Mo-Pb which was termed a copper mineralization factor, while the second factor which is Fe-Be-Yb was considered as a bed rock factor.

Phosphorus burial in Baltic Sea sediments with contrasting redox conditions

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Increased human input of phosphorus (P) to the Baltic Sea from agricultural practices and sewage has led to enhanced primary production and the increased occurrence of hypoxic bottom waters (O₂ < 2 mg/l) throughout the various submarine basins. As yet, the role of the sediments as a temporary and permanent sink for P is not well-quantified. Here we present detailed porewater and sediment data for three sites with contrasting bottom water oxygen regimes. These range from temporarily hypoxic (Arkona basin), predominantly hypoxic (Bornholm basin) to almost exclusively anoxic (Gotland deep). At Arkona, a large pool of Fe-oxide bound P was observed in the surface sediment. Porewater Fe²⁺ and PO₄ profiles indicate mobilization of the Fe-bound P pool near the sediment surface when bottom waters become hypoxic. This confirms earlier suggestions based on water column data that sediments in the Baltic can act as a major internal source of PO₄ [1]. Phosphorus speciation data for the Bornholm basin and Gotland deep suggest that these accumulation basins may be an important burial sink for reactive P. At the Gotland deep site, reactive P burial appears to be inversely correlated to terrigenous input and authigenic Ca-P, organic P and Fe-bound P act as the major sinks of P.

40Ar/39Ar geochronology and Pb isotopic evidence for the role of ridge subduction in generating orogenic gold mineralization in the Otago Schist Belt, New Zealand

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Orogenic gold mineralization in the Otago Schist Belt (OSB) of South Island, New Zealand, occurs as syn- to late tectonic veins and disseminations in brittle-ductile shear zones (e.g., Hyde-Macraes, Rise&Shine), as well as in late and post-tectonic fissure veins. Gold is hosted within lower to upper greenschist facies metaglastic rocks of the Otago Schist that comprise part of a long-lived (Triassic to mid-Cretaceous) accretionary complex that developed along the active margin of Gondwana. Orogenic gold mineralization in the OSB is thought to have formed from fluids produced during prograde dehydration reactions within the Otago Schist at depth that also liberated and mobilized S and metals (including Au). 40Ar/39Ar dating of muscovite within veins at the Macraes Mine (Hyde-Macraes shear zone) and the Glenorchy District yield ages in the range of 135-141 Ma, and are interpreted to represent the age of veining. Previous 40Ar/39Ar dating of muscovite from the Rise&Shine shear zone and several late gold-bearing fissure veins elsewhere in the OSB suggest ages for that mineralization of ~101-106 Ma. Pb isotopic analyses of 48 sulphide separates from all of the various styles of gold mineralization within the OSB define two distinct clusters: a less radiogenic cluster of analyses that includes samples from Macraes and Glenorchy, and a more radiogenic cluster that includes samples from the Rise&Shine shear zone and other veins that have yielded younger 40Ar/39Ar ages. Together the age and Pb isotopic data suggests that gold mineralization in the OSB formed during two discrete and relatively short-lived pulses, at ~135-141 Ma and ~101-106 Ma. The highly episodic nature of the gold mineralization argues that hydrothermal activity that produced orogenic gold mineralization in the OSB was not simply part of a steady-state process related to the normal development of an accretionary complex, but rather was related to specific tectonic events that affected the wedge. Age and geochemical studies of the associated arc complex suggest that a ridge subduction event occurred under the OSB at ~135-140 Ma, and reconstructions of probable plate motions in the region appear to require a younger ridge subduction event at ~100 Ma. We suggest that gold mineralization in the OSB was related to two discrete ridge subduction events, analogous to gold mineralization in the Chugach accretionary complex in southern Alaska.

Zircon U-Pb age discordance and trace element alteration due to deep, post-impact flow: Implications for planetary chronology

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The discovery of a new process whereby U-Pb isotopic ages in normally robust, crystalline zircon are made discordant, and primary trace element compositions are altered, has broad implications for geo- and cosmochronology. Here we present the first definitive evidence for partial to complete U-Pb age discordance due to a sub-solidus, ductile deformation event that, in our case, was triggered by large meteorite impact. The zircons occur in mylonitic mafic xenolith samples of the Archean lower crust exhumed by the 0.15 Ga Lace kimberlite, 60 km from the center of the 2.02 Ga, 300 km-diameter Vredefort impact structure. We have combined in situ and single-zircon U-Pb isotope analysis (SHRIMP, ID-TIMS) with microstructural analysis by micro-XRD, EBSD and colour SEM-CL to directly date the deformation fabric at 2023±15 million years, indicating deep level flow in the aftermath of crater excavation and rebound. LREE enrichment proportional to degree of discordance in a ‘shear zone’ within a single zircon suggests Pb-loss was fluid-assisted along fast-diffusion pathways on sub-grain boundaries. Our discovery demonstrates the importance of microstructural analysis when interpreting isotopic and trace element mineral compositions as primary, and proves a new technique for strain chronometry of planetary materials.
Investigating applicability of Kirpich method for estimating time of concentration of flood

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Time parameters are used mostly in hydrologic and hydraulic models. The most often used time parameter in hydrology is time of concentration.

Time of Concentration is the time required for a particle of water to travel from the hydrologically most distant point in the watershed to outlet or design point. Time of Concentration is used for designing spillway, estimating flood volume, preparing flood hydrograph and many other hydrologic analyses.

Many methods (empirical equations) are available for estimating time of concentration. Among the empirical time of concentration methods, the kirpich method has found widespread use, especially in the rational method applications.

The aim of this research is investigating applicability of kirpich method for estimating time of concentration in the studied basin. To achieve the said aim, a field method based on measurement of travel time by salt solution is used, then the difference between values obtained by using kirpich method and the field method is determined.

Results of this research show that kirpich method is best suited for watersheds with slopes ranging from 3 to 7 percent, but the method is not applicable for watershed with slopes outside this range.

Metal-mineral-microbe interactions in experimental microcosms using New Zealand thermophiles

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Experimental microcosms using inoculants from New Zealand hot spring areas have been used to grow microorganisms that produce biogenic elemental sulfur. Several metals have been added to these microcosms to test the hypothesis that biogenic sulfur has properties that differ from its abiogenic equivalent.

The apparatus consists of a bioreactor capable of temperature and pH control and a peristaltic pump providing concentrated Na2S solution feed. Minimal media is used in all experiments. Several control experiments were made using sterilized media only, media with sulfide feed, and bacteria-only using Anoxybacillus flavithermus. The sulfide-oxidizing cultures are initially grown in minimal media in serum bottles. These concentrated cultures are added to the bioreactor that is initially at pH 4. Once sufficient bacterial growth has occurred, excess H2S is purged using N2. The suite of metals is added to give a concentration of 2 – 4 ppm. The bioreactor is sampled as the pH is shifted from 4 to 8 and then back down to 3 in single pH unit intervals. Samples of unfiltered, filtered and digested (dilute aqua regia at 95°C overnight) media were collected.

The system is complex and includes: inorganic mineral reactions; bacterial interactions with dissolved metals and particulates; interactions with biogenic sulfur; and the effects of settling in the bioreactor. Initial interpretations are based on chemical analysis and SEM EDS study. Divalent cations including Cd, Co, Mn, Ni, Zn and Sr show adsorptive behaviour (or possibly reversible hydroxide precipitation and dissolution). Other elements such as Al, Fe, Ga, and In precipitate as metal hydroxides with filtered samples containing no measurable metal at pH values above about 5 but reappearing in filtered samples when pH was decreased. Metals including Ag, Au, Bi, Cr, Cu, Hg, Sb and Pb show variable behaviour with some evidence of segregation in mineral precipitates and some evidence of adsorption.

16S rDNA gene analysis indicated that the bioreactor community consisted of three phylogenetic groupings related to Acidicaldus, a sulfur-oxidising heterotroph; Acidobacterium, a chemo-organotroph and Thiomonas, a sulfur-oxidizing facultative chemolithoautotroph.
Is there an Archaean TTG series?
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The Archaean continental crust is dominated by grey orthogneisses, typically described as being of TTG (Tonalite—Trondhjemitel Granodiorite) composition. TTG are juvenile, sodic (Na,O>K,O) granitoids with high La/Yb and Sr/Y ratios, reflecting melting of a garnet-present mafic source. However, the Archaean plutonic complexes are not exclusively made of TTG; they typically feature a large range of rock compositions, all with low Y (<30 ppm) and Yb (<3 ppm) contents and correlatively high Sr/Y or La/Yb ratios, ranging from “true” TTG to granodiorites or monzogranites, with K,O/Na,O ratios up to 2 or 3; the potassic components can occur either as well-defined, individual plutons (“late potassic granites”) or as component of the “grey gneiss” complexes. TTG appear as the sodic end-member of a wider family of Archaean granitoids (Tonalite—trondhjemit—granodiorite—monzogranite, or TTGM).

This compositional spread reflects the melting of a range of sources, from mafic to felsic, yielding melts ranging from sodic to mildly potassic.

Furthermore, the TTG s.s. can be further subdivided in a high-silica, high Sr/Y (and La/Yb), high Na subsseries (trondhjemites and leuco-matic granitoids, or TT), and a low-silica, lower Sr/Y and La/Yb, lower Na subsseries (tonalites, occasionally diorites or granodiorites, TD). The TT subsseries reflects low melt fractions and deep (20 kbar) melting of a mafic source; the TD series corresponds to shallower melting (12 kbar) and higher melt fractions.

The TTGM series that form the Archaean Grey Gneisses define a range of composition between at least three end-members: (1) tonalites, granodiorites and monzogranites corresponding to intracrustal melting of felsic lithologies (older grey gneisses); (2) trondhjemites and leuco-trondhjemites, formed by deep and cool melting of a mafic source; (3) tonalites and diorites, formed by shallow and hot melting of a mafic source. Between these three end-members, there is a complete range of composition with intermediate rock types corresponding to diverse sources or depth of melting.

The term of “TTG” therefore corresponds to the grouping of two of the three main end-members of a range of compositions; extracting TTG from the wider “TTGM” group creates an artificial boundary between petrogenetically related rock types. TTG (or, worse, TTGM) are not one single, uniform rock type, but to a collection of plutonic rocks whose individual origins must be discussed before any geodynamic inference can be made.

Synthesis of mineral semiconductor thin films: Toward mineral-based photosynthesis
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The use of semiconductors as photocatalysts for carbon reduction has been the subject of research interest over the last few decades in the disparate but fundamentally related areas of solar energy conversion and research on the origins of life and of photosynthesis. Here, we combine the photocatalytic properties of hematite (toward water oxidation) with those of tausonite, whose conduction band is sufficiently energetic to reduce bicarbonate to formate.

We have used two different synthetic pathways for SrTiO, Dip-coated films of SrTiO made by a polymeric precursor method [1] show photocurrent activity. We have also made hematite films (originally made by chemical vapor deposition) dip-coated with SrTiO, particles that also show photocurrent activity. One purpose of coating hematite with SrTiO is to put the SrTiO in the role of hole scavenger [2]; the valence band of SrTiO is at slightly higher energy than the valence band of hematite, so that holes generated in the hematite can be quickly filled by electrons from the SrTiO valence band and thus removed from the high recombination rates encountered in hematite. This is anticipated to increase the overall efficiency of water oxidation over that exhibited by hematite alone.

Previous studies have documented the ability of SrTiO (tausonite) to photoelectrochemically reduce carbon. However, measured quantum efficiencies for carbon reduction by SrTiO are very low, and have been mainly attributed to back-reaction of the reduced compounds with photogenerated valence band holes on the semiconductor surface. This research aims to test the hypothesis that SrTiO semiconducting thin films may more efficiently photoreduce carbon via a photoelectrochemical tandem cell with hematite (Fe2O3), in which the Fe2O3 photoanode can oxidize water to O2 and the photocathode (SrTiO) can reduce CO2 to formate. The tandem cell will physically separate the sites of carbon reduction and water oxidation, as well as isolate the conduction band of the photocathode through dye-sensitization, thereby eliminating the problems of back-reactions on SrTiO.

Dating the first stage of planet formation via Mn-Cr chronometry

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Stage-I is the least understood among the three stages of planet formation because there are very few observational constraints and the physics of grain growth in the solar nebula from micron-sized particles to kilometer-sized bodies is not well understood. Here we use 53Mn-53Cr isotopic records discerned from primitive meteorites to constrain the timescale of stage-I of planet formation [1]. Carbonaceous chondrites are cosmic sediments made of refractory materials such as Ca-Al-rich inclusions (CAIs), and chondrules (molten silicate droplets) that are “cemented” together by fine grained dust materials rich in organics and presolar grains. The preservation of organic matter and pristine presolar grains in the matrix testifies that the parent bodies of the carbonaceous chondrites were never heated to high temperatures. Therefore their size were on the order of a few kilometers to <20 km at most to effectively dissipate heat. Thus the parent bodies of carbonaceous chondrites can be regarded as products of stage-I of the planet formation. We demonstrate that all carbonaceous chondrites exhibit 53Cr* anomalies that are correlated with 55Mn/52Cr ratio. By comparing the resulting initial 53Mn/55Mn ratio of (8.5±1.2)×10^-6 with the 53Mn/52Cr ratio of angrite LEW86010 and its absolute Pb-Pb date, an absolute age of 4568.0±0.91/1.17 Ma for the carbonaceous chondrite is derived. This age is very similar to Pb-Pb ages obtained on CAI fragments (4567.2 ± 0.6 Ma) from the CV3 chondrite Efremovka [2]. The age deduced from the initial 53Mn/55Mn ratio for the bulk carbonaceous chondrites is the same as that for the CAIs, therefore the formation of the first solid igneous objects as well as the accretion of the undifferentiated kilometer-sized carbonaceous chondrite parent bodies must have been complete within +0.91 to -1.17 Ma at 4568 Ma ago. This is currently the best estimate for the stage-I planet formation timescale.


Aerogeophysical, geological and geochemical investigation of the Late Archaean granitoids in the Musoma-Mara Greenstone Belt, NE Tanzania

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The Musoma Mara Greenstone Belt (MMGB), is among the six greenstone belts forming the Archaean Tanzania craton. This belt is intruded by syn-to-post orogenic granitoid suites which range in composition from Tonalite Trondhjemite Granodiorites (TTG) to granite. Based on the analysis and interpretations made on high resolution airborne radiometric data as well as previous geological maps, a geophysical interpretation map was obtained. This map broadly categorized the MMGB granitoids into two types: the first type is characterized by high contents of K, U and Th, whereas the second type is characterized by high K relative to U and Th. The aeroradiometric interpretation map was used as a base map for ground follow-up whereby the granite types were sampled accordingly for geochemical analysis. Geochemical data from the granitoids confirmed the two radiometrically classified granites which are high-K granites and Tonalite Trondhjemite Granodiorite (TTG). The high-K granites were further subdivided into biotite and calcite granites. According to the geophysical interpretation map, biotite-granites and calcite-granites correspond to the aerogeophysical high K, U and Th granite type whereas the TTG precisely correspond to the high K, low U and Th granite type.

Biotite granites showed high content of K2O (mean = 5.1 wt %), low Mg # (mean = 25), low CaO (mean = 1.14) and moderate alkali affinity with an average Na2O+K2O value equals to 8.5 wt %. Similarly, calcite granites are high in K content (K2O, mean = 4.8 wt %), high Mg # (mean = 42), also high CaO (mean = 1.9). TTG showed, high Mg# (mean = 47), Al2O3 > 13 %wt, Yb<1 ppm, La/Yb > 30, Na2O/K2O >1 with both Sr and Ba >500 ppm. Biotite and calcite granites are interpreted to have been generated from re-melting of the TTG and intermediate to felsic volcanic rocks in a subduction related environment whereas TTG were formed by partial melting of garnet amphibolites in a Neoarchaean Andean-type convergent margin.
Importance of colloidal iron in mine waters revealed by differential pulse voltammetry

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Whilst polluted mine waters are of course enriched in iron, we are remarkably ignorant of the iron’s physical state and chemical speciation. This is a problem since the physical and chemical state of iron is central to understanding a range of processes relevant to mine water geochemistry and remediation. Examples include the hydrolysis of dissolved Fe(III) to release protons, the adsorption of trace metals onto iron colloids and the bioavailability of iron within wetlands designed to remediate acidic mine waters.

In this work we have developed Differential Pulse Voltammetry (DPV) as a rapid and robust method of determining the concentration of truly dissolved iron and colloidal iron in 0.45 µm filtered waters from a series of mine water discharges and remediation sites in NE England. The waters have a pH range of 3 to 5 and concentrations of <0.45 µm iron between 30 and 800mg/L across the sites.

The good agreement between the iron concentrations measured in acidified samples electrochemically and by ICP-OES validates the accuracy of DPV as an analytical method for iron. Since DPV measures uniquely dissolved iron, particulate (>0.45µm) and/or colloidal (<0.45µm) iron can then be estimated as the difference between the voltammetric responses of natural samples and samples in which the solid phase iron has been dissolved by the addition of HCl.

Percentage dissolved Fe ranged from 60-90% (in most cases) in unfiltered samples while percentage colloidal iron varied widely across the sites and ranged from 25-45% in unfiltered samples and 50-75% and 35-85% for dissolved and colloidal Fe in the 0.45µm filtered samples. The proportion of colloidal Fe increases with pH.

Atomic Force Microscopy shows that the colloids range in size from nm to µm for lower pH mine waters; at higher pH, particles are mainly aggregates on the µm to mm scale. FT-IR, XRD and TEM show that the most common colloidal phase is poorly crystalline Fe oxi-hydroxide.

Revisiting the oxygen isotopic composition of the Archean ocean

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Recent studies as diverse as of evolution of temperature tolerant proteins, silicon isotope ratios in cherts and climate modeling, have all reinvigorated the 40 year old controversy regarding the $\delta^{18}O$ value of the Archean ocean. All cherts of Archean age have $\delta^{18}O$ at least 10 to 15‰ lower than from the Cenozoic. If not reset, the chert data imply substantially higher seawater temperature or proportionately lower $\delta^{18}O$ seawater. Either alternative has profound implications to evolution, tectonics, metalogeny and climatology.

All early Archean sub aqueous basaltic rocks from South Africa, W. Australia and Isua, Greenland reflect interaction with the Archean ocean and have $\delta^{18}O$ values within the range (6 - 17‰) now observed on the ocean floor and young ophiolites. The $\delta^{18}O$ of the water had to have had a $\delta^{18}O$ similar to today’s. The alternatively suggested and modeled -13‰ ocean would have left a low $\delta^{18}O$ imprint on any crust. The magnitude of the imprint can be estimated from what is now seen on Iceland at Krafla, in the northern rift zone where geothermal steam is produced from hydrothermal systems fed by low-$\delta^{18}O$ glacial melt waters (ca. -13‰). Several km of basalt recovered by deep drilling are all pervasively altered to $\delta^{18}O$ of -3 to -11‰(1). The data from Iceland show that were the $\delta^{18}O$ of the Archean ocean -13‰, then the hydrothermally altered Archean crust would be similarly depleted of $^{18}O$ irrespective of the elevation of the Archean seafloor.

ChemXSeer: Cyber-tools for environmental chemistry and geochemistry

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Research in environmental chemistry and geochemistry is becoming increasingly collaborative in scope and approach. A main goal of the geochemistry and environmental chemistry research at Penn State (and, indeed, across the world) has been the integration of experimental, analytical, and simulation results performed on systems from molecular to field scales in order to better approximate the complex physical, chemical, and biological interactions controlling the fate and transport of environmental contaminants. E-science or cyberinfrastructure have become crucial for scientific progress. We will report here on our development of the ChemXSeer architecture as a portal for academic researchers in the area of environmental chemical kinetics, which integrates the scientific literature with experimental, analytical and simulation datasets. ChemXSeer offers unique aspects of search not yet present in other scientific search services: for example, we will demonstrate tools for the extraction of tables, figures, equations and formulae from scientific documents. Ultimately, ChemXSeer intends to provide a wide range of features including full text search; author, affiliation, title and venue search; figure search; table search; formulæ search; citation and acknowledgement search; and citation linking and statistics. In this presentation, we will detail our progress to date, and discuss the future goals and implementation of this platform.

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Eruption of discrete magma batches along a normal fault zone: The Poison Lake chain, Caribou Volcanic Field, southernmost Cascades

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The Poison Lake chain of small, monogenetic, calc-alkaline basaltic volcanoes is located east of the Cascade arc 30 km ENE of Lassen Peak. This chain comprises 41 mapped units in a zone 14 km long and 2 km wide trending NNW parallel to nearby Quaternary normal faults. The 41 units fall into 10 distinct groups based on stratigraphy, petrography and comprehensive major-element geochemistry. Petrographic differences among groups are expressed by different assemblages, amounts and proportions of phenocrysts. Many units contain only sparse olivine; a few units are distinctly porphyritic with olivine, clinopyroxene and plagioclase. MgO-SiO2, K2O-SiO2 and TiO2-SiO2 variation diagrams illustrate clear differences in compatible and incompatible elements among the groups. Limited trace-element and 87Sr/86Sr data suggest little if any interaction with the upper crust. Paleomagnetic determinations indicate characteristic directions for each group except the oldest. Dated samples were chosen from stratigraphically constrained units with distinct paleomagnetic directions. Precise 40Ar/39Ar determinations show that the lavas erupted in three separate episodes at 100, 117 and 202 ka. Collectively, the data indicate that each group represents a small, discrete magma batch generated in the mantle and stored briefly in the lower crust. Episodic movement along a NNW normal fault zone provided transitory conduits for these batches to ascend to the surface and erupt as distinct volcanic groups, each aligned along a segment of the Poison Lake chain.
Record of upper mantle evolution beneath Western Alaska as preserved by peridotite xenoliths in the Bering Sea Volcanic Province

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Upper mantle peridotite xenoliths from the volcanic rocks erupted at 6 Ma (Seward Peninsula), 2.5-1.6 Ma (St. George Island), and 0.70-0.15 Ma (Nunivak Island) of the eastern sector of the Bering Sea Volcanic Province (BSVP) have a broad range of major oxide concentrations (MgO = 37.4-45.1%; SiO₂ = 41.0-44.0%; Mg# = 87.0-90.8) and trace-element abundance patterns (La/Yb₀ = 0.3-18; individual REE concentrations = 1-10 times chondrite). Some xenoliths display pronounced U-shaped patterns, and others exhibit depleted or highly enriched patterns. Isotopic ratios have the following ranges: ⁴⁰Sr/⁴⁰Ca₀ = 0.702546 – 1.07311, ¹⁴⁳Nd/¹⁴⁴Nd₀ = 0.512979 – 0.513148, ⁴³Ca/⁴⁰Ca₀ = +6.7 to +9.9, ⁴⁰Ar/⁴⁰Ar₀ = 2.83097 – 2.83364, ⁴⁰Ar/⁴⁰Ar₀ = +11.5 – 20.3). ²⁰⁸Pb/²⁰⁴Pb₀ = 18.36 – 20.56, ²⁰⁷Pb/²⁰⁴Pb₀ = 15.37 – 15.92, and ²⁰⁶Pb/²⁰⁴Pb₀ = 37.81 – 39.79. Together, the data suggest close proximity of numerous compositionally distinct mantle domains, including a primitive mantle-like end-member, refractory mantle variously depleted by melting and melt extraction, and mantle overprinted by metasomatic processes.

Two types of metasomatism have been identified based on peridotite xenolith compositions: (a) those influenced by reaction with melts migrating through fractures, and (b) those completely overprinted by a recrystallization front ascending from a fluid-laden source at deeper levels. Metasomatism by silicate melts appears to have been widespread in the BSVP, was active throughout the eruption period between ca. 6 Ma and ca. 0.70 Ma, when the crust was being extended. Xenoliths from the 0.70-0.15-Ma volcanic rocks on Nunivak Island are the only suite studied in the BSVP that exhibit evidence of both silicate melt- and fluid-induced metasomatism. This suite developed through a series of events, including extraction of some basaltic components and strongly incompatible trace elements, metasomatism by silicate melts, and then finally, overprinting with an ascending recrystallization front. Silicate liquids derived from a garnet-free, peridotite-dominated mantle beneath the BSVP, as represented by the recovered xenoliths, could account for the origin of the Late Cenozoic volcanic rocks observed in the BSVP.

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Dust emission from the Sahara-Sahel region over the past 150 years

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Measurements of atmospheric mineral dust loads at Barbados indicate that dust export from the Sudano-Sahel region of Africa has increased dramatically over the past four decades [1]. The increase in dust export rates is interpreted to be related to prolonged droughts in the Sudan-Sahel region. However, in the absence of longer time records, particularly from regions close to sources of N. African dust, it is difficult to quantitatively constrain the factors responsible for the observed trends in dust export. To better understand the controls on dust generation rates and how climate change would affect dust mobilization in the future, we have reconstructed dust export rates from the Sahara-Sahel region over the past 150 years.

Previous work has shown that ⁴He is an excellent tracer of mineral dust (e.g. [2]). The approach we have taken to reconstruct mineral dust emission at high-resolution (annual to sub-decadal) is to use ⁴He as a tracer of dust and corals as dust archives. The ⁴He-based proxy record of dust, reconstructed from the Red Sea Porites lutea coral, correlates well with instrumental records of 20th century precipitation in the Sahel region. Hence, variations in North African precipitation patterns in the historic past can be reconstructed from dust records. In particular, all major droughts of the 20th century, such as droughts in 1910’s, 1970’s, and 1980’s are characterized by high ⁴He fluxes. The 1950’s, which is the wettest decade in the Sudano-Sahel region in the 20th century, is characterized by low ⁴He fluxes.

The ⁴He-based proxy record of dust suggests that dust export rates from the Sahara-Sahel region at the terminal stages of the Little Ice Age, were a factor of two higher compared to the 20th century average. Additionally, baseline values of dust export decreased from 1840’s to 1900, remained constant between 1900 and 1950’s, but then increased from 1960 to 1990’s. We find that the high dust emission rates from the Sahel during the 1980’s are not unprecedented over the past 150 years. Comparisons between our ⁴He-based proxy record of dust and North African climatology over the past 150 years suggests that if current trends in climate continue, dust export rates in the Sahara-Sahel region are likely to increase during the 21st century.

Preserving high $^3$He/$^4$He ratios in a convective mantle

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Many Ocean Islands Basalts (OIBs), such as at Hawaii and Iceland, have $^3$He/$^4$He ratios that are a factor of 4-6 higher than in Mid Ocean Ridge Basalts (MORBs). The high $^3$He/$^4$He ratios in OIBs are usually viewed as evidence for the existence of a $^3$He-rich primitive mantle reservoir. In contrast to Hawaii and Iceland, some OIB have $^3$He/$^4$He ratios lower than MORBs (HIMU OIBs such as the Cook-Austral Islands). Our high-precision neon and helium isotopic measurements indicate that even in HIMU OIBs, $^3$He and the primordial isotopes of neon originate from the same $^3$He-rich and high $^3$He/$^4$He reservoir sampled at Hawaii, Iceland, and Samoa.

Helium is a highly incompatible element. During mantle melting helium strongly partitions into the melt phase leaving the residue severely depleted in helium. Thus, the simplest explanation for preserving high $^3$He concentrations and high $^3$He/$^4$He is to convectively isolate the reservoir over Earth history. However, geophysical and geochemical observations suggest whole mantle convection and imply that most, if not all, of the Earth’s mantle has been processed through melting. Consequently, preserving a primitive mantle reservoir over Earth history is challenging.

We propose a new explanation for preserving high concentrations of primordial volatiles (and high $^3$He/$^4$He) in the Earth’s mantle. We will show that convective mixing inhibits mantle degassing and a mantle reservoir can undergo extensive melting over Earth history but still retain significant primordial volatiles. The degree to which volatiles can be preserved is a function of how efficiently subducted slabs, devoid of $^3$He, are mixed back into the mantle reservoir. For example, if mixing is efficient, ~40% of the original budget of primordial volatiles can be retained in the mantle reservoir even after the whole mass of reservoir has been processed through the melting column once. We find no need to invoke the presence of a convectively isolated mantle reservoir for preserving high $^3$He/$^4$He ratios. Neither is U and Th depletion, relative to $^3$He, required to explain the high $^3$He/$^4$He ratios in OIBs. The differences in $^3$He/$^4$He ratios between MORBs and OIBs can be explained within the framework of plate tectonics and mantle convection.

Study of processes involving selenite immobilization in a soil-plant-microorganisms system

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Radioactive selenium (Se) is produced in fission reactors in the form of several isotopes including $^{79}$Se, which is a long-lived fission product with a half-live of about $1 \times 10^6$ years. Over time, the long-term radioactive waste disposal sites may represent sources of long-lived radioactive contamination of the environment. Indeed, Se migration can occur via groundwater and reach the soil, thus affecting the rooting zone of vegetation. In most of soils, the species selenite $\text{SeO}_3^{2-}$ and selenate $\text{SeO}_4^{2-}$ are the most frequent. These anionic forms are very soluble, mobile, biouavailable and potentially toxic.

This study aims at determining quantitatively the processes involved in radioactive $^{75}$Se (selenite) transfer in rye grass grown in two soils located on the surface of two eventual sites studied for radioactive waste geological disposal. The role of microorganism was studied by sterilizing the soils with a gamma source and rye grass seeds with $\text{H}_2\text{O}_2$. Volatilization of selenium was studied using activated carbon cartridges in a closed system. The results will be presented in term of chemical budget of selenium and transfer factors to the plant.
A conceptual model of kinetically controlled isotope fractionation during diffusion-controlled magmatic mineral growth

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The crystallization history of magmatic mineral grains is recorded in its chemical and isotopic composition, which is commonly used to constrain parental magma compositions and temperature of crystal formation. While this approach inherently implies that crystal growth took place under equilibrium conditions, an increasing number of studies find evidence indicating non-equilibrium crystal growth.

We present a conceptual model of kinetically controlled element uptake and isotope fractionation during diffusion-controlled mineral growth. The multi-component and multi-dimensional numerical modelling approach assumes a spherical grain growing under the assumption of local equilibrium on its surface in a spherical matrix of given size and composition. It is shown that the time-dependent ratio between mineral growth and near-surface diffusion in the matrix controls the uptake of an element into the crystal lattice. Modeling results reveal that under conditions of fast mineral growth highly compatible or incompatible elements will be depleted or accumulated near the growing mineral surface forming a compositional boundary layer in apparent disequilibrium with the matrix. Equilibration of the boundary layer and the reservoir will depend on the diffusivity of an element if the effect of free and forced convection can be assumed to be sufficiently small. As a result, significant isotope fractionation is predicted to occur during progressive mineral growth since diffusion rates of isotopes of the same element depend on their masses. Consequently, this fractionation is then “recorded” in the resulting isotope profile of the crystal.

The maximum amount of fractionation and the shape of the resulting isotope profile are shown to be sensitive to the applied growth and diffusion rates as well as the effect of free and forced convection on the size of the boundary layer. Thus, application of this model potentially provides an additional key tool to decipher crystallization histories of magmatic mineral grains.

Magmatic history of the Ice River Alkaline Complex, British Columbia (Canada)

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The 368±4 Ma [1] Ice River Alkaline complex of southern BC is hosted in Cambro-Ordovician limestones and shales. The intrusion is exposed over an area of 29 km², and comprises three major units, an early ferrocarbonatite phase located near the centre of an older layered alkaline mafic complex, and a younger zoned syenite complex. The feldspar-poor, mafic complex comprises rhythmically layered urtite, ijolite, and jacupirangite; the feldspar-rich, zoned nepheline syenite complex has a range of lithologies that grade from leuco- to melanocratic nepheline syenite, natrolite- and sodalite-rich syenite. Two phases of late carbonatite veins crosscut the syenite complex. One is highly enriched in Ba-Sr-REE (>140000 ppm Ba), whereas the other has Ba contents of <3000 ppm. A 2-3 m wide, coarse-grained alkaline lamprophyre occurs between the limestone of the Ottertail Formation and a nepheline syenite dyke. This lamprophyre is unrelated to the finer-grained lamprophyres that are present throughout the intrusion. Several generations of fine-grained to pegmatitic, nepheline syenite dykes cut both the nepheline syenite and layered mafic alkaline complexes and their associated rocks. These dykes are interpreted to be the result of periodic tapping of a deep-seated fractionating magma chamber. One of the most REE-enriched dykes gives an EPMA U-Pb monazite age of 155±17 Ma, suggesting that at least some of the dykes may be from a magmatic event that is temporally distinct from the 368±4 Ma Ice River Intrusion.

Pseudosection and thermobarometry constraints on the P-T-t evolution of Ribeira Belt, SE Brazil

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Pseudosection analysis, combined with geothermobarometric data and petrographic observations of gneissic migmatites and granulites from the central area of Neoproterozoic Ribeira Belt, SE Brazil is used here in order to quantify the tectonometamorphic P-T evolution during prograde and retrograde metamorphism of the Braziliano Orogeny.

Results establish a prograde metamorphic trajectory from amphibolitic to metamorphic peak granulite facies at T=850±50°C and P=8±1kbar, consistent with 30 to 40% dehydration-melting (involving significant melt loss) of the gneissic protoliths. After reaching peak metamorphic conditions, migmatites underwent cooling and decompression (∆T=-200 to -350°C and ∆P=-2 to -2.5kbar) to T~500°C and P~5kbar; the retrograde P-T path was associated with water influx (increasing a\(\text{H}_2\text{O}\), with replacement of the high grade garnet-plagioclase-K-feldspar paragenesis by biotite-quartz-sillimanite-muscovite.

Regional high grade conditions were sustained from ~570 to ~480Ma [1]. The intrinsic long-term high-heat flux induced further dehydration and (~10 %) biotite-amphibole-garnet bearing, restite, re-melting at deeper crustal levels, giving rise to widespread development of granulites and associated aplititic intrusions. Thus, granulites can be envisaged as lower crust highly dehydrated restites. During this period, granulites were slowly (nearly isobarically) cooled with ∆T=100 to -340°C and ∆P=0.1 to -1.8kbar, this tectonothermal regime ceased with the tectonic collapse of the orogenic belt, when granulites were rapidly cooled and decompressed (∆T=-100 to -200°C and ∆P=-1 to -3kbar) during exhumation (~470 Ma). Retrograde P-T evolution and hydration, induced replacement of early plagioclase-hyperstene-garnet granulate assemblages by biotite-k-feldspar-quartz simpletites, being consistent with a general P-T-t metamorphic path that comprised initial (long-term) isobaric cooling followed by decompression and cooling.

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Formation of the lunar magma ocean constrained from high field strength element systematics in lunar rocks

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The compositional diversity of lunar rocks is commonly explained by melting of cumulate layers formed during crystallisation of a lunar magma ocean. Whereas lunar highland rocks and KREEP basalts originate from a trace element enriched layer, lunar mare basalts are inferred to tap trace element depleted cumulate layers. The petrogenesis of high-Ti mare basalts involves either direct melting of, or, alternatively, assimilation of ilmenite-rich cumulate layers by depleted melts. HFSE ratios in lunar rocks, determined by high-precision measurements ([1] and new data) employing isotope dilution, confirm this model in that highland rocks display Nb/Ta and Zr/Hf above the bulk lunar value (ca. 17), whereas mare basalts display lower ratios. Notably, high-Ti mare basalts display lower Nb/Ta and Zr/Hf than low-Ti basalts, consistent with an ilmenite assimilation model. Melting of ilmenite- and clinopyroxene-rich cumulates could not explain this pattern, as ilmenite exhibits similarly low D Nb/DTa (ca. 0.6-0.7, [2]) as clinopyroxene (ca. 0.3-0.4). Combined modelling of W abundances with those of other HFSEs provides additional evidence that high-Ti mare basalts are hybrid melts formed by the interaction of low-Ti basaltic melts with ilmenite- and clinopyroxene-rich cumulate layers. Assimilation of such ilmenite-rich layers is also a viable mechanism capable of buffering the Lu/Hf ratios of mare basalts at relatively low values, thus partially explaining the dichotomy between low Lu/Hf ratios in the magmas and high time integrated source Lu/Hf ratios that were previously inferred from Hf isotope compositions.

Role of garnet and amphibole fractionation in the genesis of high Mg# granitoids

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In this contribution we examine experimental phase equilibria relevant for the differentiation of primary and derivative arc magmas of the deep roots of island arcs to test the role of amphibole and garnet on the genesis of high Mg# granitoids. Contrary to differentiation at relatively shallow pressures (below ~ 0.7 GPa), where fractionation of Fe-Ti oxides plays an important role on the Mg# of derivative liquids, high pressure experimentation on H2O undersaturated liquids demonstrate that oxide fractionation is less important compared to the role of amphibole and garnet. Garnet has a rather high Fe/Mg solid/liquid partition coefficient (0.78-0.92 at 0.8-1.5 GPa) and tends to produce ‘high-Mg’ liquids unlike amphibole that has considerably lower Kd’s (0.32-0.45 at 0.8-1.5 GPa), comparable to olivine and pyroxenes and, thus, extracts Mg more efficiently leading to higher FeO*/MgO liquids at a given SiO2-content. Bulk rock data from the plutonic rocks from the Alps and the Kohistan batholith indicates that high Sr/Y granitoid rocks display lower FeO*/MgO at a given SiO2 than comparable rocks with low Sr/Y ratios, supporting a potential role of garnet in producing “high-Mg# granitoids”. New experimentally determined trace element partition coefficients on garnet and amphibole, and straightforward trace element models using these partition coefficients demonstrate that fractionation of garnet and amphibole exert an important control on geochemical ratios (e.g. La/Yb, Sr/Y and Nb/Ta) on derivative liquids. We will discuss possible processes where amphibole and/or garnet are involved (e.g. lower crustal dehydration melting of amphibolite, amphibolite melting in subduction zones, high pressure fractionation) and propose that the physically most plausible explanation are fractionation processes in the roots of island arcs, either in the lowermost crust or the uppermost mantle. We thus concur with Annen et al. (2006) that the bulk of the major and trace element signatures of island arc plutonic rocks is acquired in ‘arc hot zones’.

Atmospheric oxygen rise in the Paleoproterozoic revealed by weathering model

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It is widely accepted that the atmospheric oxygen level increased between 2.5 and 2.0 Ga. However, the exact quantitative pattern of the increase has remained highly elusive. Paleosols, containing records at the time of weathering, can be a powerful tool to estimate atmospheric oxygen levels quantitatively. The behavior of Fe during weathering was modelled and the model was applied to Fe(II) and Fe(III) concentrations in paleosols to estimate atmospheric oxygen levels between 2.5 and 2.0 Ga.

The model considers the factors affecting dissolved Fe(II) concentrations in a weathering profile which are: i. dissolution rates of Fe(II)-bearing primary minerals, ii. oxidation rates of dissolved Fe(II), and iii. flow rates of ground water. The assumptions for the model are: (a) a weathering profile is formed horizontally and weathering proceeds normal to the surface, (b) ground water and thus Fe(II) flow one-dimensionally and horizontally, (c) Fe(II) dissolved from primary minerals remains in the profile as oxidized and instantaneously precipitated Fe(III) or flows out of the profile as dissolved Fe(II), and (d) rate-controlling factor of the formation of Fe(III) secondary minerals is the oxidation of dissolved Fe(II).

A change in Fe(II) concentration in a weathering profile is expressed by d[Fe(II)]/dt = f + g + z (f: oxidation term, g: ground water flow term, z: dissolution term) (1). The total amounts of Fe(II) dissolved and flowing out were calculated based on equation (1), and then, the relationships between phi values and atmospheric oxygen levels were derived where phi was defined as a ratio of a total amount of oxidized Fe(III) from dissolved Fe(II) to that of Fe(II) dissolved from primary minerals. The calculated relationships were applied to those observed in laboratory (Sugimori, 2007), which verified the validity of the model. Then sensitivity analysis of the model by changing the parameter values was carried out, which reveals that pH and ground water flow rate are the main factors that affect Fe behavior during weathering. The model applied to the phi-age relation obtained from paleosols reveals that the atmospheric oxygen levels increased gradually, linearly on the logarithmic scale, from about 10^-6 to 10^-3 atm between 2.5 and 2.0 Ga.
Reconstructing intermediate watermass variability in the Southeast Pacific during the past ~30ka: A multi-proxy study

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Three high sedimentation rate cores from the SE Pacific, which sample three different intermediate waters, provide a means to reconstruct past variability of these climatically-important yet poorly studied watermasses. ODP Site 1233, at 41°S, sits in the core of Antarctic Intermediate Water (AAIW) at 838 m depth. Site 1234 (1015m), at 36°S, is located between AAIW and the underlying southward-flowing, low-oxygen Pacific Central Water (PCW) mass. Site 1235 (489 m) is located close to Site 1234, but is between AAIW and the overlying, southward-flowing, low-dissolved-oxygen Gunther Undercurrent (GUC) water mass.

To understand the history of this region we use redox-sensitive authigenic metals (Mo, U, Re, Cd) to characterize sedimentary redox conditions; C, N, and opal to characterize biogenic production; and Ti and Al to characterize lithogenic inputs. At site 1233 the redox-sensitive elements remain close to detrital levels throughout the record, while these elements show enrichment at sites 1234 and 1235 beginning at about 12 ky and extending through the Holocene. This Holocene dissimilarity in elemental distributions can be explained by a reduced penetration of AAIW; greater influence of northern-sourced, lower-oxygen waters (PCW and GUC); a constant influence but a decrease in oxygenation of these water masses; an increase in biological production at sites 1234 and 1235 over pre-Holocene levels; or as an artifact of changing sedimentation rates.

Records of sedimentary organic carbon and biogenic silica show that the enrichment of the redox-sensitive metals at sites 1234 and 1235 was not accompanied by an increase in biological productivity. It is also unlikely that the oxygenation of both PCW and GUC would covary, given that they come from different source regions. At this point it is difficult to unequivocally separate the possibility of changing watermass influence from the change in sedimentation rates during deglaciation, but our data does seem to suggest that some of our observed changes may be ventilation-driven rather than being an effect of dilution from lithogenic sources.

Secondary consequences of Uranium concentration limits for geologic isolation of high-level nuclear waste

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Although the radioactivity of uranium isotopes is low in high-level nuclear waste compared to that of fission products and other actinides, uranium geochemistry exerts important secondary controls on geologic isolation of radioactivity. At the proposed nuclear waste disposal site at Yucca Mountain, Nevada, the UO$_2$ matrix of spent nuclear fuel will oxidize, and uranyl mineral alteration products will dominate near-field uranium chemistry. Other radionuclides (e.g. $^{237}$Np) can coprecipitate in uranyl minerals, and uranyl mineral stability may control source term concentrations of these radionuclides. Using reversed solubility data for uranophane at low temperature [1], total equilibrium uranium concentrations are calculated to be near $10^{-7}$ M in Yucca Mountain groundwater. This value is consistent with model calculations of uranium concentrations for the Nopal I natural analog system [2]. Models for groundwater in the Yucca Mountain environment at equilibrium with uranophane containing 0.001 mole fraction Np-uranophane yield aqueous Np concentrations that are low compared to values used in Yucca Mountain performance assessment calculations [3].

Ingrowth and release of uranium decay series radionuclides (e.g. $^{226}$Ra and $^{222}$Rn) constitute principal natural environmental radiation hazards. In a steady-state scenario relevant to the period of geologic stability at Yucca Mountain, uranium concentration limits in the waste emplacement environment would control aqueous uranium concentrations along flow streamlines to the accessible environment, which would in turn control decay series isotope radioactivities. Natural analog data for groundwater that is conditioned by long term contact with uranyl minerals provide realistic values for aqueous concentrations of decay series isotopes including those of Ra and Rn.

From N₂ to NHₓ groups in silicate melts governed by f_H₂ at high pressure and temperature

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Characterization of the processes that govern the behavior and budget of volatiles in the Earth’s interior is fundamental to our understanding of the formation and evolution of the solid Earth, its oceans, and atmosphere. To this end the behavior of volatiles in the NOH system in magmatic liquids is of central importance. The solubility and solution mechanisms of N-bearing species in silicate melts have been, therefore, examined via nitrogen analyses and vibrational spectroscopy with pressure (P=102.5 GPa), temperature (T=1300°-1500°C), hydrogen fugacity (f_H₂=MH+H₂O), and silicate melt composition as independent variables.

The nitrogen solubility ranges from about 1 to about 5 mol % calculated as N with dX_N/dP>0 and dX_N/df_H₂>0. The d²X_N/df_H₂² is also positive. Two f_H₂ ranges are identified within which the solubility relations with f_H₂ differ. Under oxidizing conditions, the solubility can be fit to a straight line that passes through the origin (Henry’s Law). However, at higher f_H₂ such linear extrapolation through the origin is not feasible.

Raman and FTIR spectroscopic data are consistent with solution mechanisms that involve gradual reduction of nitrogen with increasing f_H₂. In the low f_H₂ range [near f_H₂(MH) – Fe₂O₃/Fe₃O₄+H₂O] there is evidence only for molecular N₂ in the melts. At f_H₂(NNO) (Ni/NiO+H₂O) and f_H₂(MW) (FeO/Fe₂O₃+H₂O), there is partial reduction of nitrogen to form N₂, NH₂⁻ complexes and molecular NH₃ in the melts. At the highest f_H₂(IW) (Fe/FeO+H₂O), only molecular NH₃ and NH₂⁻ groups can be identified in the melts. OH groups are also formed whenever there is reduction of nitrogen from N₂. Solution in silicate melts of reduced, (NH) bearing species results in silicate melt depolymerization. At f_H₂(NNO) and f_H₂(MW), depolymerization occurs via H⁺ interaction with oxygen and NH₂⁻ groups serving as network-modifier. Under more reducing conditions, oxygen is replaced by NH₂⁻ groups.

Degasging models of the Earth depend rely on solubility and solution behavior of volatiles (including nitrogen) in magmatic liquids in the Earth’s interior. The f_H₂-dependent behavior of nitrogen species in melts implies the redox conditions in the Earth also affect these processes.

Excess interfacial force induced by oxide nanostructures on rhodochrosite

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Rhodochrosite (MnCO₃) is an important component of anoxic soils and sediments. At the oxic-anoxic interface, a rhodochrosite surface can be oxidized by dissolved oxygen and form oxide structures of a few nanometers high. The patchwork of exposed rhodochrosite surface and oxide nanostructures results in a map of surface-potential heterogeneity, as previously demonstrated, and suggests that differences in chemical composition and structure at nanoscale can induce dramatic local variations in surface properties and consequently remarkable local variations in the interaction with the surrounding environment. In aqueous solution, the interaction of a surface with ions, molecules, and cells is often manifested as the interfacial force between them, which strongly influences surface adsorption. Nanoscale heterogeneity of the interfacial force is therefore an important regulator of the immobilization of metal contaminants and bacterial attachment.

In this study, we map out the interfacial-force heterogeneity of reacted rhodochrosite to demonstrate that the formation of oxide nanostructures can potentially induce significant changes in surface adsorption in aqueous solution. Using a miniature probe to represent an adsorbate, the interfacial force over reacted rhodochrosite was characterized using force-volume microscopy.

The interfacial force of oxide nanostructures is dominated by electrostatic repulsion at probe-surface distances greater than ca. 2 nm and overtaken by van der Waals attraction at shorter distances. Across the investigated pH range of 5.0 to 9.7, the interfacial force of oxide nanostructures has a repulsive maximum that occur at a separation distance of 2.4±1.1 nm. The pH dependence of nanostructure interfacial force indicates that oxide nanostructures have a point of zero charge around pH 6.5. In comparison to oxide nanostructures, the rhodochrosite substrate exerts little interfacial force to the probe in the same pH range, indicating that the substrate has minimal surface charge. Mapping interfacial-force heterogeneity provides a basis for more sophisticated and accurate modeling of processes affecting contaminant immobilization and bacterial attachment on mineral surfaces under natural conditions.