Plagioclase weathering across hydrological gradients

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Chemical compositions of drilled well waters from the Vila Pouca de Aguiar region (Northern Portugal) were related to weathering of granite and metasediment plagioclases using a mole balance model. These waters travelled across soils, then saprolites and finally fault zones, before being collected at depths $D = 18–96$ m. The model results indicate that plagioclase weathering along the more superficial paths produces gibbsite. This is justified by a rapid flow of water across the permeable soils and saprolites and by the local precipitation (> 1000 mm/yr). Along the less permeable fault zone path, made of gravity flow fractures in connection with networks of capillary flow micro fractures, the model results indicate that plagioclase weathering produces halloysite and smectite. A correlation was found between dissolved silica concentrations derived from the plagioclase to halloysite reaction and $D$ (Fig. 1), suggesting that halloysite precipitates along the walls of gravity flow fractures because this is a medium where solute transport is advective and therefore concentrations are expected to increase with increasing flow path lengths ($D$). The lack of a correlation for smectite (Fig. 1) suggests that precipitation of this clay mineral occurs at micro fractures adjacent to the gravity flow fractures, where solute transport is diffusive, mediated by local gradients of chemical potential and by the length of diffusion trajectories, and hence not necessarily dependent on $D$. Our results comply with observations made by Meunier et al. [1].

Textural record of metamorphic fluids expulsion during high-pressure deserpentinization

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Although the cyclic nature of metamorphic dehydration events is subduction zones is attested by intermediate-depth seismicity, the hydrodynamics of fluid expulsion during the high-pressure, breakdown of antigorite (atg) in these settings are still barely known. This is due to the complexity of the system and the paucity in the geological record of arrested dehydration fronts. The HP atg-dehydration front in the Cerro del Almirez ultramafic massif (Betic Cordillera, Spain) offers an unique opportunity to investigate the dynamics of expulsion of large amount of deserpentinization fluids (~ 9 wt %) [1, 2]. The prograde assemblage is a chlorharzburgite showing two contrasting textures: granofelsic (with coarse, round olivine) and spinifex-like (dendritic-like, cm-sized olivine and orthopyroxene). Both textures occur as interspersed, m-sized boudins behind the atg-dehydration front. We ascribe these textures to shifts of the growth rate due to temporal and spatial fluctuations of the affinity of the atg-breakdown reaction. These fluctuations are driven by cyclic variations of the excess fluid pressure which are ultimately controlled by the hydrodynamics of deserpentinization fluid expulsion. Crystallization at a low affinity of the reaction, corresponding to the granofelsic texture, may be attained if fluids are slowly drained out from the dehydration front. During the advancement of the dehydration front, overpressured domains are left behind preserving highly metastable atg-serpentinite domains. Brittle failure results in a sudden drop of the fluid pressure, and a displacement of atg equilibrium towards the prograde products that crystallizes at a high affinity of the reaction (spinifex-like texture). This textural bimodality hence witnesses a unique example of the feedbacks between the cyclic dynamic of metamorphic fluid expulsion, the reaction rate and crystallisation of the atg-dehydrating system.


Figure 1: Plot of dissolved silica concentrations resulting from weathering reactions of plagioclase producing smectite, halloysite and gibbsite, as a function of $D$.

Combustion-derived dissolved organic matter in rivers and estuaries of the sugar-cane area of Southern Brazil

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Introduction
Pyrogenic organic carbon (black carbon, BC) has been recognized as a significant component in dissolved organic matter (DOM) in surface waters. Since BC is produced by biomass burning, it is an important source of DOM in South Brazilian catchments where the burning of sugar cane occurs during the dry season. In this study, detailed spatial profiles were sampled along transits of estuarine and coastal areas in southern Brazil. Furthermore, we assessed the export of BC within the rivers draining to the catchments.

Discussion of Results
Black carbon was quantitatively determined as benzene-policarboxylic acids (BPCAs) using high performance liquid chromatography (HPLC). All DOM samples yielded significant amount of BPCAs, ranging from 3 to 29 mM, representing roughly 3 -9 % of dissolved organic carbon (DOC). The concentrations of BC, as well as the relative contributions of BC to the DOC pool, were largest in riverine and estuarine DOM. Qualitative identification of molecular formulas by ultrahigh resolution Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) identified more highly condensed aromatic structures in these same samples. The abundance and composition of combustion-derived DOM from terrestrial sources such as southern Brazil are necessary for a better understanding of global biogeochemical cycles.

Estimates of Earth system climate sensitivity
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Climate sensitivity to CO2 refers to the change in global temperature due to the radiative effects of a doubling of CO2 combined with rapid climate feedbacks such as changes in atmospheric water vapor, sea ice, and cloud/aerosol distributions. Over geologic timescales, the global temperature response, defined here as ‘Earth-system’ climate sensitivity, also includes the effects of other climate responses such as changes in continental ice volume, terrestrial ecosystems, non-CO2 greenhouse gas production, and other parameters. Assessing Earth-system climate sensitivity requires estimates of CO2 concentrations and global temperatures during discreet time intervals in Earth history. While uncertainty persists in these estimates, available temperature and CO2 records provide some constraint on magnitudes of Earth-system climate sensitivity with time. Current records provide evidence that Earth’s climate sensitivity varies with the climate state. Very high climate sensitivities are associated with ice-house conditions, and there is little support for climate sensitivities lower than ~3°C per CO2 doubling during ice-free conditions.
Cryptic metasomatism during exhumation of Franciscan eclogite and hornblende revealed by \textit{in situ} $\delta^{18}$O analysis of garnets

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Garnet-bearing metamafic rocks from the Franciscan Complex and Catalina Island preserve textural evidence of high fluid pressure (veins, vugs) and geochemical evidence of large fluxes of water during their metamorphism. Much of the published geochemical evidence is based on analyses of whole rock samples which homogenize differences that exist between and within grains. Eclogite (Junction School) and garnet hornblendite (Panoche Pass) high-grade blocks hosted by the Franciscan Complex contain volumetrically minor retrograde phases (phg + chl + sph ± ab ± gl). Garnets and zircons from these blocks were analyzed for $\delta^{18}$O by ion microprobe (±0.5‰, 10$\mu$m spot) and matrix phases were analyzed by laser fluorination. Eclogite garnet cores contain prograde cation zoning and inclusion assemblages, but are homogeneous in $\delta^{18}$O (4.0±0.5‰, 2SD) and are not in equilibrium with bulk matrix omphacite (5.8‰). Garnet rims show periods of resorption followed by regrowth (oscillatory cation zoning on a fine scale). Rims contain phg + omph inclusions that yield blueschist-facies P-T, are more variable in $\delta^{18}$O (6.2±1.2‰), and some domains are in equilibrium with matrix omphacite. Garnet cores from the hornblende are homogeneous in both $\delta^{18}$O (11.0±0.5‰) and cation composition, and are also not in equilibrium with matrix hornblende (6.1‰). Garnet rims are compositionally and isotopically (6.6±0.9‰) different from cores, and are in equilibrium with matrix hornblende. The $\delta^{18}$O of metamorphic zircon (7.2±0.5% Eclogite, 8.9±1.1% hornblende) are not in equilibrium with garnet cores, and REE patterns suggest formation in the absence of garnet. Zircons record relatively late ages (~145 Ma) for eclogite and hornblende from the Franciscan, but are similar to garnet blueschist ages. Taken together these data suggest that both samples underwent massive metasomatism during exhumation but were relatively unmodified by fluids during subduction. Similar cation zoning patterns in garnets not in equilibrium with hornblende from Catalina may be indicative of a similar fluid history.

Trace elements in chromite by LA-ICP-MS to constrain the origin of podiform chromitites in the Thetford Mines Ophiolite

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The Thetford Mines Ophiolite (Canadian Appalachians) is a complete ophiolitic sequence consisting of a thick mantle section (5 km), a plutonic crust and a volcano-sedimentary cover dominated by boninitic lavas. This ophiolite is interpreted as a fragment of a fore-arc oceanic lithosphere. It hosts 50 chromitite occurrences and one third of them are of podiform-type and are hosted in a dunitic envelop within the mantle tectonites.

This study presents the concentrations of a complete suite of minor and trace elements (Sc, Ti, V, Mn, Co, Ni, Zn, and Ga) in chromites from podiform chromitites of the Thetford Mines Ophiolite, and from the associated boninite lavas, using laser ablation inductively coupled to a plasmaquadrupole mass spectrometer.

The aim of this study is to use trace elements to constrain the parental melt from which the podiform chromitites have crystallized. The chromites from Thetford Mines Ophiolite podiform chromitite deposits are Cr-rich (Cr$\#$ = 100xCr/(Cr+Al) = 69 to 84), Fe-rich (Fe$^{2+}$# = 100xFe$^{2+}$/Fe$^{2+}$+Mg = 32 to 46), Mn-rich (1081 to 1962 ppm), Co-rich (166 to 386 ppm), Sc-rich (5.5 to 11.3 ppm), and they are Ti-poor (TiO$_2$ = 0.06 to 0.18 wt%), Ga-poor (11.3 to 26.5 ppm), and Ni-poor (441 to 875 ppm) compared to MORB chromite (Cr$\#$ = 35; Fe$^{2+}$# = 23; Mn = 881 ppm; Co = 165 ppm; Sc = 5.3 ppm; TiO$_2$ = 0.22 wt%; Ga = 52.5 ppm; Ni = 1766 ppm). The chromites from Thetford Mines Ophiolite podiform chromitite deposits are similar to chromite in podiform chromitites of the Thetford Mines Ophiolite, and from the associated boninite lavas, using laser ablation inductively coupled to a plasmaquadrupole mass spectrometer.
Intermediate water source variations in the tropical Atlantic from the last glacial maximum to present

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Intermediate water masses are an integral part of the global meridional overturning circulation and play an important role in redistributing heat and nutrients to the global ocean. Antarctic Intermediate Water (AAIW) formed in the Southern Ocean, is the most dominant of intermediate water masses in volume and spatial extent, and recent changes in AAIW properties suggest a swift response of AAIW to global warming [1].

Here we present neodymium isotope ratios (143Nd/144Nd, expressed in ɛNd notation) measured on a mid-depth sediment core from the tropical northwest Atlantic (MD99-2198) that suggest changes in the contribution of AAIW to the mid-depth water column in the North Atlantic over the past 25,000 years [2]. In particular, ɛNd reached values of up to -9 to -8 during meltwater event Heinrich-1 (H1) and the Younger Dryas (YD). These shifts towards more positive ɛNd compared to LGM and Holocene values indicate an increased northward extent of southern sourced AAIW at these times. These results are consistent with radiocarbon evidence from the North Atlantic that suggests increased incursions of old, southern-sourced intermediate water into the North Atlantic during H1 and the YD [3, 4]. Moreover, the observed changes in the source of intermediate waters in the tropical North Atlantic are in line with abrupt benthic δ13C changes in the southwest Pacific [5]. The close correspondence between intermediate water changes close to the formation region of AAIW and a site in the tropical Atlantic that today lies close to the northernmost extent of AAIW, suggests a common mechanism for the observed mid-depth changes. That is, most likely variations in the northward extent of AAIW in response to climate and ocean changes in the Southern Hemisphere.


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Study of gold nanoparticle interactions with humic acid using small angle neutron scattering

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Gold nanoparticles (GNPs) present a wide range of applications in diagnostic imaging, cancer therapy, and semiconductor and sensor technologies. However, the release of gold nanoparticles into the environment has implications for their interactions with environmental entities such as humic acids (HA). Small angle neutron scattering (SANS) offers a unique and very specific window for measuring structural changes taking place at the GNP/HA interface. The current study investigates the interactions of citrate-coated gold nanoparticles (CT-GNPs) with humic acid with the application of SANS. The SANS results suggest that the core size of CT-GNPs (0.6 wt %) did not change significantly in the presence of HA (1.8 mg/mL), therefore the HA may not be having significant interactions with CT-GNPs.
Large exchange through the 660km discontinuity: Evidence from C- and N- isotopes in super-deep diamonds

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Diamond provides a unique opportunity to sample parts of the mantle that remain inaccessible by any other means. Some mineral associations in diamond, such as majoritic garnet, calcic and magnesian perovskite and manganese ilmenite with ferropericlase have been recognised as originated from the transition zone down to the lower mantle (Stachel et al. [1]; Kaminsky et al. [2]). In addition, nitrogen is potentially a good tracer for mantle geodynamics. Exchanges between an inner reservoir (characterised by negative δ15N) via degassing at oceanic ridges with an outer reservoir (characterised by positive δ15N) via recycling at a subduction zones can lead to nitrogen isotopic contrast in a stratified mantle.

Taking advantage of the rather common occurrence super-deep mineral inclusion assemblages in diamonds from Juina (Brazil) and Kankan (Guinea), we carried out a detailed study of C and N-isotopes. There are broadly similar ranges of δ13C and δ15N values with negative δ13C and δ15N of mantle diamonds from 3.8% down to -8.8% and from +9.6% down to -39.4% for respectively Juina and Kankan diamonds. Both sets of results suggests extensive material-isotopic exchange through the 660km discontinuity, this contrast with the existence of isolated lower mantle. Most of δ13C values are negative and in the present upper mantle range with the exception of 3 Kankan diamond values down to -39.4%. These very low δ13C are compatible with primitive material and provide evidence that mantle has kept heterogeneities.

Three zoned super-deep diamonds demonstrate large δ13C variations with parts which are typical of their local transition zone δ13C value. Most likely these diamonds have initiated their growth in the LM and following slow uplift in a convective mantle have equilibrated in the TZ, and in doing so show an evolution in carbon isotopic composition.

Therefore the C- and N- independent isotopic tracers provide evidences that a significant amounts of material are exchanged across the 660km discontinuity.


Biomarkers for methane cycling: From marine to terrestrial settings

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Lipid biomarkers derived from methanogens (e.g. archaeol and other ether lipids) and methanotrophs (e.g. specific bacteriohopanoids) have shown potential in the investigation of methane biogeochemistry. To develop this approach, we have determined these biomarkers’ distribution and isotopic composition in a range of settings, including marine sediments, wetlands and permafrost. Controls on biomarker concentrations are evaluated, and the potential for examining ancient methane cycling is discussed.

Archaeoel and hydroxyarchaeol are common in Archaea and are expected to occur in the diverse settings such organisms inhabit. However, both compounds are absent or undetected in most environments, including surface marine sediments, dry and aerated soils, and shallow peat and permafrost. Instead, significant quantities of ether lipids are limited to ‘classical’ archael settings: extreme environments or hotspots of methane cycling. The latter include water-saturated soils and peat, marginal marine sediments below the sulfate-methane transition zone, and even the faecal material of ruminants. This suggests the potential for using archael lipids to quantify methanogen biomass and interrogate methane biogeochemistry. Indeed, archael concentrations across all settings are apparently dictated by the same environmental controls that govern methanogenesis rates, including for example, water saturation of soils, temperature and the bioavailability of organic matter.

We have explored the potential for applying these compounds as methane-cycling proxies to ancient settings. Archaeol occurs in organic-rich Paleocene sediments and Miocene sedimentary cycles from the Benguela upwelling system, and in both cases its concentration dramatically increases in response to elevated organic matter contents. Archaeol is also present in thermally immature lignites; intriguingly, its concentration is much higher in Eocene deposits suggesting elevated rates of methanogenesis during past warm intervals. Despite this potential, further work must be underpinned by quantification of intact polar lipids, experimental testing of observation-based inferences and integration with other approaches.
Mantle metasomatism in the basement of the Deccan Trap: Stable Carbon and Oxygen isotope compositions of carbonates from the Killari borehole, Maharashtra, India

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The Deccan Volcanic Province, covered by a thick suite of volcanic rocks erupted during the K-T boundary 65 Ma, is one of the largest flood basaltic eruptions on the surface of the earth. There are only few reports available on the nature of the crustal structure, tectonism, thermal characteristics, and chemical composition of the basement of the Deccan Trap [1]. The basement rock is identified as an amphibolitic granulate containing 2 wt % of CO₂ [1]. In order to study the origin of CO₂, we have measured stable oxygen and carbon isotope compositions of the two samples KIL-13 and KIL-20 (499.6 meter depth), having 2.28 and 2.18 wt % CO₂. About 50 to 60 µg of powdered carbonates were used for δ¹³O and δ¹³C isotopic measurements, by using a Delta+ Advantage IRMS coupled with Kiel IV automatic carbonate device. The precision was better than 0.10 ‰ for δ¹³O and 0.05‰ for δ¹³C [2].

The values of δ¹³C and δ¹⁸O obtained for the KIL-13 samples are -6.23‰ and 7.94‰ (relative to v- PDB and v-SMOW respectively) and for the KIL-20 sample the values are -6.22‰ and 8.11‰ indicating that the Deccan Trap basement carbonates are derived from deep mantle carbon reservoir, similar to carbonatite magma [3]. In the Deccan region, alkaline and ultra-alkaline rocks such as the carbonatites of the Narmada zone have been attributed to mantle metasomatism and enriched mantle sources. It has also been proposed that in the northern parts of the Deccan Trap, a variety of mineralogical and geochemical features point to mantle metasomatism, probably due to the complex interaction between the Reunion plume and the lithospheric mantle [4].

Our present study provides an additional evidence for the presence of mantle metasomatism in the Killari region of the Deccan Trap.

References:

δ¹³C of n-alkanes as a new potential proxy for high atmospheric pCO₂

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Published estimates of Phanerozoic atmospheric pCO₂ levels range from 1–10× today’s level, and imply large fluctuations across critical transitions, such as extinction and diversification events. A variety of geochemical proxies have been developed to estimate pCO₂ through geological time, however many of these techniques are fraught with limited applicability and/or large uncertainty, particularly under high pCO₂-scenarios. Thus, as part of our ongoing effort to understand the effect of geologic levels of pCO₂ on plant development, we have tested the potential of n-alkane biomarkers as a proxy at elevated levels of pCO₂. These biomolecules are targeted for study because terrestrial leaf wax alkans were a likely prerequisite for the evolution of terrestrial photosynthesis, and they may be isolated with strategic value from Paleoaozoic rocks, thus providing a window into fluctuating pCO₂ levels during critical periods of land plant evolution. In addition, their lifeform specificity, ease of extraction and routine analysis make these molecules attractive as potential proxy markers. Here we report on growth experiments within which a model angiosperm (R. sativus) was grown under systematically increasing pCO₂ levels from ambient to 4200 ppm (RCO₂ = 14). Hydrocarbon fractions were extracted from above ground plant tissue and analysed by gas chromatography-isotope ratio mass spectrometry (GC-IRMS). An excellent correlation is observed between ε₁₃C (the stable isotope fractionation between ambient δ¹³CO₂ and the aC₃₁ alkane, δ¹³C₃₁) and pCO₂ (r² = 0.99, hyperbolic regression) being most sensitive up to ~1800 ppm. Interestingly, the fractionation between bulk δ¹³Cₚₙₚₚₚ and δ¹³C₃₁ decreased as pCO₂ increases (from ε₁₃ = 6.1 to 3.9), again up to ~2000 ppm. Carbon isotope analysis of individual lipid fractions (i.e., sterols, fatty acids and phytol) will allow us to determine if the dependence on pCO₂ results from gross metabolic shifts affecting all lipogenesis or from specific alterations to n-alkane biosynthetic pathways. We will also speculate as to why the physiologic response we observe appears to stabilize at ~1800 ppm, within the same range where other plant-based proxies lose precision.

References:
[1] Triplicate runs were made to check the reproducability. The values of δ¹³C and δ¹⁸O obtained for the KIL-13 samples are -6.23‰ and 7.94‰ (relative to v- PDB and v-SMOW respectively) and for the KIL-20 sample the values are -6.22‰ and 8.11‰ indicating that the Deccan Trap basement carbonates are derived from deep mantle carbon reservoir, similar to carbonatite magma [3]. In the Deccan region, alkaline and ultra-alkaline rocks such as the carbonatites of the Narmada zone have been attributed to mantle metasomatism and enriched mantle sources. It has also been proposed that in the northern parts of the Deccan Trap, a variety of mineralogical and geochemical features point to mantle metasomatism, probably due to the complex interaction between the Reunion plume and the lithospheric mantle [4]. Our present study provides an additional evidence for the presence of mantle metasomatism in the Killari region of the Deccan Trap.
Zinc isotopic variations in HED meteorites

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The zinc isotopic compositions of 21 HED meteorites were determined by MC-ICP-MS following the technique described in Moynier et al. [1-3]. The $\delta^{66}\text{Zn}$ values for the entire suite of samples ranged from -2.0 ‰ to +2.0 ‰, with a mean value of -0.07 ± 0.37 ‰ (2σ), excluding one anomalous sample (PCA 82502, which has $\delta^{66}\text{Zn} = -7.75$ ‰). The mean $\delta^{66}\text{Zn}$ value for 13 eucrites was +0.13 ± 0.50 ‰; for 4 diogenites, -0.41 ± 0.99 ‰; and for 4 howardites, +0.30 ± 0.49 ‰. Eucrite falls were significantly isotopically heavier (+0.47 ‰) than finds (-0.99 ‰), consistent with previous reports of heavy isotope loss with terrestrial weathering (Luck et al. [4]). There was significant Zn isotopic heterogeneity between different chips from the same meteorite, and even within the same small chips. The mean HED fractionation of approximately zero supports a chondritic origin for Vesta (Luck et al. [4] report $\delta^{66}\text{Zn} = -1.30$ to +0.76 ‰ for ordinary and carbonaceous chondrites). The anomalous eucrite PCA 82502 was significantly isotopically lighter than the others, with a $\delta^{66}\text{Zn}$ value of -7.75 ‰, the largest Zn fractionation reported in the solar system to date. This meteorite may be a sample of the primitive eucritic crust that was spared from mixed with different parent bodies.


Nanoscale structure of organic matter could explain soil organic matter recalcitrance

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Previous our studies showed that the modification of the ultra-structure of the cell wall influences its degradability in soil [1, 2]. In particular according to the more recent literature it seems that microstructure of the cell wall, limits enzyme activity because these latter has a dimension greater that pores compositing the topography of the cell wall [3, 4]. In a more recent study on energy crop, we have shown that by modifying the cell wall microstructure by removing hemicelluloses via steam explosion, the cellulose availability for enzymatic action increased, such as confirmed by the higher glucose produced by cellulase enzymes when it was dosed on treated plants. These results were ascribed to the enlargement, such as effectively measured, of the pore spaces between cellulose fibrils. Therefore our results attested that effectively there is a ‘steric’ protection of the cell wall polymer to the enzyme attack due to the micro-porous structure. Here we provide new data to support our idea, going insight into mechanistic understanding of cell polymer protection. Doing so, we have selected different biomasses (n=15) such as plant residues, crop energy plants and lignin-carbohydrates complexes (LCC) isolated after acid hydrolysis (core-fraction). These fraction were incubated in soil for 1 year, i. e. agricultural season, dosing an amount of 2 g C kg⁻¹ soil dry matter. CO₂ evolution was detected by using NaOH trap and data reported as cumulative results. Microporosity surface was, also, detected by using the technique of the gas adsorption utilizing a porosimeter (that allow to measure both micro-porosity surface (MiS) (surface of pores of 0.3-1.5 nm of diameter) and corresponding micro-porosity. Incubation experiment revealed that the recalcitrance, i.e. the natural resistance against microbial and enzymatic deconstruction was associated to the MiS. For example, LCC complexes were less degraded and they were characterized by a highest MiS. On the other hand biomasses characterized by young tissues, such as plant residues were largely degraded in soil and showed low MiS values. The relationship between MiS and degradability was confirmed by the good correlation found between these parameters (r=0.85, p<0.01; n=15). Therefore the results of this investigation indicated that protection from enzymatic attack by cell wall topography plays a main role in determining biomass degradability and so its turnover in a short term.

Fluid-deposition of graphite with apatite in an Eoarchean banded iron formation from the Nuvvuagittuq Supracrustal Belt, Québec, Canada

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Banded iron formations (BIFs) are among the oldest sedimentary rock-types on Earth and it has been hypothesized that they may have formed under the influence of microbial oxidation of Fe2+. Biological remains of early microorganisms may thus be preserved in BIFs as mineral associations between graphite and apatite, which can form from the diagenetic oxidation of organic carbon. However in highly metamorphosed BIFs, fluid-deposition of graphite may be an alternative mechanism of graphitization with apatite, although this remains to be documented. In a thin section of an Eoarchean BIF from the Nuvvuagittuq Supracrustal Belt (NSB) in northern Québec, which is at least 3.75 Ga and was metamorphosed at the upper amphibolite facies, we have so far documented 43 apatite grains in their petrographic context and found at least six to be associated with graphitic carbon. In one of these mineral associations, Raman micro-spectroscopic imaging revealed a relatively strong D* band at 2700 cm⁻¹, which may be indicative of curled graphite structures. The Raman spectrum of this graphite is also characterized by sharp and intense D- and G-bands, which suggest a partly disordered graphite structure or partly hydrogenated graphene sheets. High-resolution TEM imaging of a FIB-extracted foil of this graphite revealed that it occurs as a ~300nm thick layer in contact with a grain of chalcopyrite + sphalerite about 300nm in size and enveloped in a thin amphibole layer coating the apatite grain. This mineral assemblage was most likely fluid-deposited under high-temperature hydrothermal conditions. A first survey of carbon isotope compositions of whole-rock powders from a dozen BIF samples revealed a large range of δ¹³Corg values with an average of -34.9 ± 8.9‰, which can be used to assess possible sources of carbon in graphite from NSB BIFs. These new datasets suggest that fluid-deposited graphite associated with apatite can form at high temperatures that can obscure the identification of carbon sources. Combined micro-analytical approaches have provided crucial details to establish the mechanisms of graphitization, which is vital to the search for biological signatures in metasedimentary rocks.

Variations in the osmium isotopes record during the Azolla phase (IODP Expedition 302)

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We report on a preliminary reconstruction of the seawater ¹⁸⁷Os/¹⁸⁸Os ratios in organic-rich and anoxic sediments of the Lomonosov Ridge (IODP Expedition 302) from the Azolla event (49.3-48.1Ma) [1] and compare it with a newly reconstructed ¹⁸⁷Os/¹⁸⁸Os record from an open ocean site (ODP Site 1263). The Azolla phase is a stratigraphic marker in the Arctic and surrounding seas and indicates strong salinity-stratification and limited exchange with the open ocean. If we assume that the Os isotopic composition of the Arctic Ocean is homogenous and represents a mixture of unradiogenic dissolved Os from hydrothermal and extraterrestrial (¹⁸⁷Os/¹⁸⁸Os ~ 0.13) and radiogenic from continental sources (¹⁸⁷Os/¹⁸⁸Os ~ 1.4), the Re-Os isotope system can be used as a proxy to estimate the ventilation of the Arctic Ocean. We have measured Os and Re using both bulk fusion-leachates and Carius Tubes digestion methods to calculate the initial ¹⁸⁷Os/¹⁸⁸Os and compare methods. Significant authigenic enrichment of Re-Os suggests that these organic-rich sediments have the potential to record the Os isotopic composition of the Middle Eocene Arctic Sea. Measured ¹⁸⁷Os/¹⁸⁸Os ratios range from 1.2 to 1.6. This is indicative of significant in situ decay of ¹⁸⁷Re to ¹⁸⁷Os. During the Azolla time interval where multiple analyses yield initial ¹⁸⁷Os/¹⁸⁸Os close to 0.8, with two post-Azolla samples yielding values as high as 1.2. These ratios are significantly larger than contemporaneous values of seawater ¹⁸⁷Os/¹⁸⁸Os ratios measured in Site 1263 (0.45-0.5). Thus we interpret these data as supportive of a highly restricted Arctic Ocean at this time.

Heavy noble gases from the Southwest Indian Ridge: Insights into upper mantle heterogeneity

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Basalts from the ultra-slow spreading Southwest Indian Ridge (SWIR) exhibit remarkable variability in helium isotopic composition: SWIR 4He/3He varies from 51,000 to 120,000 (4He/3He of 14.1 to 6 R A; [1]), spanning half the range observed in mantle-derived basalts. 4He/3He values both higher and lower than the canonical mid-ocean ridge basalt range (4He/3He of 80,000 to 100,000; 4He/3He of 9 to 7 R A) are erupted in close proximity. Low 4He/3He ratios reflect a mantle source that is less degassed than the mid-ocean ridge basalt (MORB) source, while high 4He/3He ratios are commonly attributed to the presence of recycled crust in the source region. Therefore, the SWIR provides a unique window into the nature and distribution of heterogeneities in the upper mantle.

We have measured Ne, Ar and Xe abundances and isotopic compositions, along with He and CO2 abundances, in glasses from the SWIR. There is good correlation between Ne and He: 4He/3He ratios less radiogenic than Ne, while high 4He/3He ratios are commonly attributed to the presence of recycled crust in the source region. Therefore, the SWIR provides a unique window into the nature and distribution of heterogeneities in the upper mantle.

We have undertaken the application of AGNES with screen-printed electrodes (Figure 1), which can be deployed in situ and, thus, avoid problems of contamination [2]. These disposable sensors can also be easily modified to enhance selectivity and/or sensitivity.

First, the area of the working surface of the disposable sensor and the thickness of the mercury film have been optimized, as well as the parameters of AGNES technique. Then, calibration curves were performed in synthetic solutions for Cd (II), Zn (II) and Pb (II). In addition, the free ion metal concentrations were determined in synthetic solutions containing a complexing ligand and compared with results obtained with conventional HMDE. This study shows that sensitivity and repeatability were strongly related to the volume of the mercury film. Lower limits of detection were reached with SPE, due to the possibility of using higher preconcentration factors than with HMDE. Speciation results were consistent with speciation codes.


Disposable sensors for [Zn2+], [Cd2+] and [Pb2+] determination in natural samples

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The knowledge of the free ion concentrations of metals like Zn, Cd or Pb is key to predict the biouptake of trace elements. Electrochemical techniques, such as ion selective electrodes (ISE), are of particular relevance for metal studies, but commercial ISE’s sometimes lack the required sensitivity. The analytical challenge is to develop a technique able to determine free metal ion concentrations at trace levels.

Absence of Gradient and Nerstian Equilibrium Stripping method (AGNES) is an emerging electroanalytical technique typically implemented with the hanging mercury drop electrode (HMDE) [1]. In AGNES conditions, the stripping step leads to a measured charge just proportional to the free metal ion concentration in the solution.

We have undertaken the application of AGNES with screen-printed electrodes (Figure 1), which can be deployed in situ and, thus, avoid problems of contamination [2]. These disposable sensors can also be easily modified to enhance selectivity and/or sensitivity.

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Novel iron-reducing bacterium isolated from Oak Ridge TN

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Dissimilatory iron reduction enables prokaryotes that respire ferric iron to thrive in subsurface geologic environments. Previous studies have shown that microorganisms with such respiratory capabilities play an important role in iron mineral formation, sediment diagenesis, carbon cycling, and contaminant bioremediation. In this study, we report the isolation of a novel spore-forming, strictly anaerobic, iron-reducing bacterium from groundwater sediments in Oak Ridge, Tennessee.

Enrichment cultures were established with sediments collected from the DOE’s Field Research Center in Oak Ridge, TN. An oligotrophic medium was constructed to simulate in situ groundwater chemistry as revealed by on-site monitoring wells, using acetate (10mM) as the electron donor and ferrihydrite (30mM) as electron acceptor. After a pure culture was obtained, the genomic DNA was extracted and the 16S rRNA gene was PCR amplified. Growth experiments were conducted to evaluate the ability of this organism to respire alternate electron acceptors, including solid phase Fe (III) oxides, oxygen, fumarate, nitrate, and sulfate. The cultures were sampled at periodic intervals and the cells were examined using TEM and SEM. Mineral transformation products were analyzed using XRD, and Mössbauer spectroscopy.

Enrichment cultures resulted in the isolation of a pure culture of a spore-forming bacterium designated as FRC-RU4. Its 16S rRNA gene sequence (1509 bp) has the most similarity to that of the Veillonellaceae family at relatively low level (91% identity), thus may represent a new genus among this family. When grown on ferrihydrite and goethite, the formation of secondary mineral products were observed. Electron microscopy, Mössbauer Spectroscopy, and X-ray diffraction analysis revealed FRC-RU4 induces the formation of nano-particulate goethite and magnetite when grown on ferrihydrite. Biogenic magnetite crystals produced by FRC-RU4 are relatively large particulate (>50nm) compared to the magnetite particles formed by iron reducing Gammaproteobacteria such as Shewanella and Geobacter.

Did evaporites record the boron isotopic composition of seawater?

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The secular variations of seawater chemical composition have been investigated through different media among which fluid inclusions in marine evaporites [1]. Boron is an element with a residence time of 10-20 My in seawater [2], longer than the mixing time of the ocean. The boron isotopic composition of seawater (δ11Bsw) is thus homogeneous in the modern ocean. Until then, the variations of the δ11Bsw values have been mainly explored using numerical models based on the modern boron cycle. Such model suggests that the δ11Bsw signal is likely to have changed by 2‰ in the last 20 Ma. In this presentation, we explore the boron isotopic composition of Cenozoic evaporites. Boron isotopes are extracted from salts after dissolution in pure water and analyzed on MC-ICPMS Neptune with a d-DIHEN (direct injection) system [4]. Total external reproducibility including chemical extraction process is better than 0.3‰ (2σ). Strontium isotopes are also analyzed to investigate the origin of the brine.

The δ11B sw values reveal a relative homogeneity for each epoch despite variability likely due to the chemical evolution of the brine during its evaporation. The brine is interpreted as being originally seawater. It is possible to define a seawater component for each studied epoch. Our results suggest that δ11Bsw has significantly changed along the last 40 Ma, in agreement with other parameters of the oceanic chemical composition. The δ11Bsw change amplitude appears to be stronger than suggested by models. Boron isotopic composition of ancient carbonates is broadly used as a seawater paleo-pH proxy and is therefore used to constrain pCO2 in ancient times. Using boron isotopes for paleo-pH reconstruction following the paleo-pH equation [2] relies on the knowledge of δ11Bsw. Constraining the evolution of δ11Bsw is a prerequisite for more reliable determination of seawater paleo-pH.

Understanding the composition and structure of ferrihydrite

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A growing body of evidence confirms a single phase model (SPM) suffices to explain the core (but perhaps not surface) atomic arrangement in inorganically and biologically derived 2- and 6-line varieties of ferrihydrite. The 50 years of effort expended on studying this material produced inconsistent results, probably due to variations in preparation, confusion due to over-fitting information poor (low Q, high incoherence) diffraction and x-ray absorption data with overly complex models, electron beam damage in TEM, etc. Careful large-batch synthesis of hydrogenous and deuterated samples and the use of several analytical probes on synthetic and natural samples provide a consistent picture: 1) there is no need to fit the data with a 3-phase model (TPM) – a SPM fits the PDF derived from the total elastic coherent neutron and x-ray scattering; 2) models claiming water contents of 10% or more, and citations of densities as rebuttal of the SPM that are based on samples that include non-structural water only removed after treatment to 215°C, are at odds with TGA/DSC/in situ scattering data that shows ~2 wt % structural water in ferrihydrite. The results of combined in situ high energy XRD/DSC are particularly revealing, since they show clearly ferrihydrite persists with about 2 wt % water up until transformation to hematite; 3) IR spectroscopy is fully consistent with result; 4) In situ PDF analysis indicates the ferrihydrite bulk structure remained intact up to the direct transition to crystalline hematite, with no intermediate phases, crystalline or amorphous, formed; 5) the recently proposed akdalaite-like ferrihydrite model has 2.2 wt.% H2O-equivalent structural OH, and is consistent with these results. The TPM has an average formula close to FeOOH, containing 10 wt.% H2O-equivalent structural OH, far more than suggested by our experiments. Based on the constraints set by the estimated water content and the PDF signatures, we examined possible anion packing types and local structural motifs in ferrihydrite, and demonstrate that ABAC is the only feasible packing type and that the peak at 3.45 Å in PDF provides indirect evidence for the presence of tetrahedral Fe.

Opportunities at light source and neutron facilities

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X-ray sources and pulsed neutron sources are getting brighter. In the case of x-ray sources peak brightness has risen increasing by several orders of magnitude in the last few years, spot sizes are approaching several nm and beam coherence is increasing. Although the gains in peak power in neutrons are modest by comparison, the coming on stream of SNS (and Japan and Europe sources eventually) in combination with Montel-like focusing optics will allow studies of smaller samples at more extreme and relevant environments at these sources as well. Together these developments in x-ray and neutron beam conditioning are opening up whole new areas of research in scattering, spectroscopy, and imaging studies of earth materials and processes that were not possible a decade ago. Increasingly the expectation is that the study of earth and planetary materials, and their analogues, will be carried out with selectable nm-µm-mm spatial resolution with < 1meV energy resolution and in operando – under the conditions simulating the pressure, temperature, humidity, and other environmental variables under which Earth, the planets (including gas giants and recently discovered exo-planets) operate. For example, at spallation and reactor sources the unique properties of the neutron will enable in situ studies using isotope specific imaging, contrast variation techniques, diffusion studies, derivation of partial structure factors for glasses along with already established studies of structure and dynamics for magnetic and hydrous materials, studied at older neutron sources for over 60 years. X-ray free electron lasers and next generation storage rings such as NSLS-II will provide opportunities for coherent imaging, diffraction microscopy, inelastic studies and a host of techniques previously regarded as 'pre-emergent' and exotic only a couple of years ago. Unprecedentedly small beams will allow imaging and spectroscopy, and possibly diffraction, from interfaces and small sample volumes. The impact of these latest-generation facilities on characterization of the chemistry and atomic arrangements in materials will be profound. In order to take full advantage of the opportunities afforded, earth scientists continue to design, build and operate new sample cells that simulate the conditions existing on Earth and planetary surfaces, and in their interiors.
Microbial precipitation of Se(0) and Au(0) nanospheres

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The metal-reducing bacteria, Haejae-1 and KURT-1, were enriched from inter-tidal flat sediments and groundwater, respectively. Microbial metal reduction and precipitation are expected to eco-friendly and economical methods to immobilize Se(VI) as a pollutant in groundwater and to recover Au(0) as a novel metal in a mine residue. Table 1 shows experimental setup for microbial precipitation of Se(0) and Au(0). Fig. 1 shows Se(0) and Au(0) nanospheres precipitated by the microbial processes.

Table 1: The experimental conditions for Se(0) and Au(0) precipitation via microbial Se(VI) and Au(III) reduction.

<table>
<thead>
<tr>
<th>Bacteria</th>
<th>Haejae-1 (1mL)</th>
<th>KURT-1 (1mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron donors (Carbon source)</td>
<td>Acetate (10mM)</td>
<td>Formate (10mM)</td>
</tr>
<tr>
<td>Glucose (10mM)</td>
<td>Pyruvate (10mM)</td>
<td></td>
</tr>
<tr>
<td>Lactate (10mM)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium selenate (15 mM)</td>
<td>Gold chloride trihydrate (1mM)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1: The TEM-EDS analyses of a Se(0) nanosphere formed by KURT-1 (A) and Au(0) nanospheres formed by Haejae-1 (B).

<table>
<thead>
<tr>
<th>A</th>
<th>Se</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 nm</td>
<td>5 nm</td>
<td></td>
</tr>
</tbody>
</table>

The metal-reducing bacteria reduced Se(VI) and Au(III) and precipitated Se(0) and Au(0), respectively. The bacteria precipitated Se(0) and Au(O) nanospheres extracellularly. This study indicates that reductive precipitation of Se(0) and Au(0) may be useful for Se immobilization and Au recovery in the natural environments.

Aqueous-mineral interfaces toward extreme conditions: The potential experimental approaches with synchrotron X-ray probe

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Aqueous-mineral interface reactions exert a primary control over elemental transport in the near-surface environment. These molecular scale elementary processes have been studied in recent years using synchrotron based surface and interface X-ray diffraction techniques, including X-ray reflectivity (XR) [1], resonant anomalous X-ray reflectivity (RAXR) [2], and X-ray reflection interface microscopy (XRIM) [3]. The XR and RAXR studies revealed layering structure of water near the mineral surfaces [1, 4], strong influence of surface morphology on the layered structure through molecular interactions [1, 5], complex ion adsorption structures with simultaneous inner- and outer-sphere adsorbed species [2, 6], and thermodynamically controlled inner- and outer-sphere partitioning of adsorbed ions in the electrical double layer [7]. The XRIM provides a new capability to obtain a full field image of the surface topography with ~100nm lateral spatial resolution. These previous studies were performed under ambient (or near-ambient) conditions; and high pressure and high temperature interfacial processes have yet to be surveyed. After a brief review of the above results, I will discuss the potential importance of these aqueous-mineral interface processes under extreme conditions, probed by the synchrotron X-ray techniques, in the context of the cycling and sequestration of elements in the sub-surface environment.

Using Sm-Nd garnet geochronology to date mid-to lower-crustal partial melting: An example from Fiordland, New Zealand

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Trace element compositional zoning and Sm and Nd isotope data provide information on the nature, timing, and duration of partial melting in the Cretaceous magmatic arc exposed in Fiordland. Mid-to lower-crustal meta-igneous rocks display evidence for intrusion followed by high-pressure metamorphism and partial melting. These high Sr/Y melts may have facilitated large-scale extension of the crust.

We present ages for peritectic garnet in high Sr/Y trondhjemite leucosomes that constrain the timing of partial melting in the Western Fiordland Orthogneiss (WFO) in the Doubtful Sound area. Garnet compositions were determined by EPMA and LA-ICPMS in order to identify compositional zoning and inclusion phases. HREE: Yb (20-100 ppm), Lu, Y, and Cr show cyclic zoning with sharp boundaries. LREE: Sm (6-8 ppm) and Nd are unzoned, and Tb displays little or no zoning. These patterns are compatible with either cyclic availability of HREE during garnet growth or slow diffusion of HREE and faster diffusion of LREE. Single phase inclusions are: rutile – random and - lattice controlled orientations, apatite, sphene, ilmenite, zircon, clinopyroxene, and plagioclase. Biotite is restricted to garnet that shows retrograde alteration along fractures. Albite, potassium feldspar, and quartz only occur as polyphase inclusions in garnet and are interpreted as melt that was trapped during incongruent melting of the host diorite gneiss. Garnet isotope ratios may be strongly affected by inclusions of REE-rich accessory phases; therefore, inclusions were removed by hand-picking followed by HF leaching which increased garnet Sm/Nd ratios. In one example, multiple splits of a single garnet crystal resulted in an increase from 0.8254 to 1.1867 as inclusions were removed.

Garnet isochron ages indicate that partial melting occurred at 109.8 ± 1.3 Ma (4 pts.) in Crooked Arm, below the Doubtful Sound Shear Zone. U-Pb zircon ages from these rocks date intrusion of the WFO between 115.6±2.4 Ma and 114±2.2 Ma [1] indicating a brief interval between emplacement and partial melting. Additional garnet ages of 111.9±3.0 Ma (6 pts.), 115.5±3.0 Ma (5 pts.), and 113.6±2.5 Ma (5 pts.) from E to W along Doubtful Sound require widespread near synchronous partial melting.


Catalytic mechanism of Hg-C bond cleavage by the organomercurial lyase MerB

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The bacterial organomercurial lyase, MerB, catalyzes the cleavage of Hg-C bonds in organomercurial species such as methylmercury ([CH3Hg (II)]+). Two cysteines (Cys196 and Cys159) and an aspartic acid (Asp99) are known to be required for catalysis, but the detailed reaction mechanism has not yet been determined conclusively. We have performed hybrid density functional theory calculations on an active-site model of MerB derived from an X-ray crystal structure of the Hg (II)-bound product complex. Stationary point structures and energies were computed for two mechanisms that have been proposed in the literature. The calculations favor a two-step mechanism in which Asp99 first abstracts a proton from one of the two cysteines and subsequently protonates the organic leaving group. We show that coordination of organomercurials by two cysteine thiolates is sufficient to activate Hg-C bonds. Natural Population Analysis reveals that MerB lowers the activation energy of the Hg-C bond cleavage reaction by redistributing electronic charge into the leaving group and away from the catalytic proton.

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Pervasive replacement in alkali feldspars: A major crustal process

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Microtextural evidence of replacement reactions can be found in most alkali feldspars in salic plutonic igneous rocks. Turbidity, caused by μm-scale micropores, is a familiar feature of feldspars and micropores are one of the hallmarks of replacement reactions. Perhaps because of the familiarity of feldspar turbidity (it is seen as a normal feature of ‘fresh’ rocks) the geochemical implications of the implicit replacement reactions have been largely neglected. There is great potential for correlating microtextural evidence for multiple episodes of fluid–rock reaction with accompanying geochemical changes, including changes in $^4\text{He}$, $^{18}\text{O}$ and trace elements.

Turbidity is associated with the development of sub-grain mosaics within single feldspar crystals, with micropores at their junctions. Regions unaffected by turbidity often contain coherent micro- and crypto-perthitic microtextures, orientated to minimize coherency strain energy. The bulk chemistry of such regions is a robust guide to the chemistry of the crystals prior to coherent exsolution, and very probably (although not certainly) at the solidus.

Replacement reactions take place by dissolution–reprecipitation in an aqueous fluid. Mutual replacement is isochemical with respect to the major feldspar components and is driven by minimization of coherency strain; non-isochemical replacement involves exchange of components via the fluid from local or remote sources. Chemical and microtextural criteria for distinguishing these types of replacement will be illustrated. Some crystals provide evidence of both styles. An important limitation on the scale of non-isochemical replacement in igneous rocks is the relationship between modal mineralogy and thermal minima in Ab-Or-An-Q. Replacement on a scale that implies an isochemical replacement involving exchange of components from the fluid is implausible for most igneous rocks.

As yet too few studies have been carried out using the necessary SEM and TEM methods to make useful generalizations. Examples of evidence for episodic replacement reactions beginning near 500°C and continuing to the solidus will be presented. Recent work on TE partitioning may provide a useful means of distinguishing those pairs of feldspar phases in complex intergrowths that are in equilibrium, and the $T$ of the exchange reaction.

Pedgeochemistry around industrial waste disposal site at Dundigal, Hyderabad City, India

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Waste disposal sites are one of the major sources of elevated levels of metals in the soil environment. In contrast, all soils naturally contain trace levels of metals. The concentration of metals in uncontaminated soil is primarily related to the geology of the parent material from which the soil was formed and is ascribed as background values. An industrial waste disposal site at Dundigal, Hyderabad City, India, spread over 200 acres, receives ~50,000 tonnes of hazardous waste per annum is situated in north-western part of Hyderabad city has been selected for the current study. Soil samples were collected and analyzed using XRF technique for heavy and trace metal concentrations to define the degree of contamination of soil in the study area due to leachate emanating from the industrial/hazardous waste dump. The analytical results reveal that metal intensity varies As (6.15-411mg/kg), Cr (12.26-480mg/kg), Cu (11.6-186mg/kg), Ni (12.55-131mg/kg), Pb (42.9-1833mg/kg) and Zn (27-882mg/kg) and are found to be beyond the background values and Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health. Soil pH significantly affects the solubility of these minerals. Most of the minerals are soluble in acid soils than in neutral or slightly basic soils [3]. Soil pH in Dundigal varies from 5.7 to 8.9 and is slightly acidic to alkaline in nature. The concentration of metals like nickel and zinc are considerably high at pH < 6, and are relatively mobile and enriched in soil. Whereas copper and lead can be figured out as slightly mobile at pH < 6 and P H > 6, however arsenic and chromium are high at pH >7 and are relatively mobile. These metals can bio-magnify in plants and animals eventually making their way to humans through food chain [1, 2]. To evaluate the impact of dumpsites, this study recommends periodic monitoring of soil samples for toxic metals in the study area.

Micro-Raman spectroscopic study on Ararki (L5) chondrite

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We present here the Micro Raman spectroscopic characterization of Ararki (L5) Chondrite. The mineralogical and chemical composition data of the Kaprada meteorite have been discussed elsewhere [1]. Laser–Raman spectra of chromites from Ararki chondrites show characteristic peaks of natural chromites in the region 400 to 800 cm⁻¹ with A1g mode at 700 cm⁻¹ yielding the composition Cr# of about 87, which in excellent agreement with the EPMA data. There is a well known correlation occurs between the A1g mode and the composition of the chromites. Viz., the highest frequency band shifts from 685 cm⁻¹ for high chromium content to 770 cm⁻¹ for Al-rich end in natural chromites. The equilibration temperature is determined by the composition of the few grains of chromite by adopting the method described by Wlotzka [2]. Ararki meteorite showed the chromite composition with Fe # 100 X(Fe/(Fe+Mg)) = 87 to 89 Cr# 100 X {Cr/(Cr+Al)} = 86 to 87, which yielded the equilibrium temperature of be about 730 to 750 °C. Olivine in L6 chondrite is used to determine the residual stress present in the meteorite [3] The residual stress in the olivine is estimated by using the Raman line at 820 cm⁻¹, and is found to be about 300 MPa for the Ararki meteorite.

I am grateful to Professor N. Bhandari for providing me the Ararki meteorite sample for the present study.


Experimental study of solid-state ¹³C-¹⁸O bond reordering in calcite

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The carbonate clumped isotope thermometer is based on the relative abundance of ¹³C-¹⁸O bonds in carbonate minerals, and thus it is important to understand the temperatures and conditions where solid state ¹³C-¹⁸O bond reordering occurs on geologically short timescales. This is relevant to the preservation of primary signals in paleoclimate applications, as well as applications in the intermediate temperature realm (ca. 50 – 300°C) relevant to diagenesis, hydrothermal mineralization, and basin evolution [1]. I present results from heating experiments designed to deduce Arrhenius parameters and ‘closure temperatures’ for the ¹³C-¹⁸O order/disorder process in calcite. Carrara marble heated at 500°C and 600°C under dry conditions is measurably changed in ‘clumped isotope’ distribution on timescales of hours to days (Figure 1). The Δ₁₈O values of CO₂ extracted from carbonate fail to reach equilibrium values predicted by the theoretical temperature scale of Guo et al. [1] (0.26 to 0.25‰), possibly indicating incomplete approach to equilibrium, a non first-order rate law, or other factors. Continuing work will address these questions with additional experiments over an extended the range of temperatures and time durations.

Figure 1: Δ₁₈O values of Carrara marble samples heated at 500 and 600°C in the presence of dry CO₂ gas in sealed quartz tubes. Dashed lines are first order reaction progress models. The mean value for unheated Carrara marble is 0.352‰.

Why do fossil bones and teeth exist?

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Given the readily observable instability of bone in surface environments, the abundance of very ancient fossil bones and teeth is quite remarkable. Although both modern and fossil bones and teeth are composed of the calcium phosphate mineral apatite, the fossil material is enriched in such elements as fluoride. Comparison of Raman spectral trends in natural primary fluoride-rich apatite in shark teeth, secondarily fluoridated modern teeth, and fossil teeth supports a solubility-driven model of fossilization. During interaction with groundwater of even minor fluoride concentration, fossilizing bones and teeth undergo partial dissolution (of original bioapatite) followed by new precipitation (of essentially end-member fluorapatite). The lower solubility of fluorapatite than original bioapatite both induces the dissolution-reprecipitation process (cf. [1]) and preserves the bones and teeth from further disintegration. The driving force to initiate fossilization is chemical disequilibrium between bioapatite and the water in contact with it; the completion of fossilization depends on the maintenance of disequilibrium. The initial requirement is a slow rate of introduction of water that is undersaturated with respect to bioapatite, but that contains an ion (Z) whose activity, together with those of the now-dissolved calcium and phosphate, exceeds saturation with respect to Z-apatite. The latter precipitates epitaxially on the existing apatite. Continued delivery of new aliquots of such water, aided by the enhancement of bone’s porosity and permeability as its 50 volume% of collagen is degraded and consumed by microbes [2], ensures the progress of dissolution-reprecipitation. The fact that, in the examples here, end-member fluorapatite precipitates rather than the equilibrium composition of OH-F-Cl-apatite is another example of disequilibrium processes at work. Depending on the timing and ambient chemistry, this fluoridation-preservation process may preserve important isotopic and trace-element signatures of the original sample.

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Runoff water pollution in India

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Urban runoff water pollution is one of the leading causes of water pollution and becomes worse with population growth and urbanization [1]. The runoff water pollution is one of the major diffuse pollution sources for depleting water qualities [2]. The aim of this work is to describe the runoff water quality during the rainy season (i.e. May – September, 2008) in the most industrialized region: Raipur region (Chhattisgarh state, India).

Two cities: Raipur (21°24’N and 81°63’E) and Korba (22° 21’ N and 82° 40’ E) of central India was selected for the proposed study due to running of several industries by collecting the water samples into 5-l cleaned polyethylene container following the established method. The mean (n = 10) pH value of the runoff water at three sites: Raipur urban (RU), Raipur industrial (RI) and Korba industrial (KI) is 6.9±0.4, 6.9±0.3 and 6.8±0.3, respectively. The annual volume weighted mean value (n=10) of, Cl -, NO3 -, SO4 2-, NH4 +, Na+, K+, Mg2+, Ca2+, Mn, Fe, Cu, Zn, Pb and Hg in the RU site is 120±144, 297±192, 113±63, 12±4, 84±138, 67±87, 42±41, 484±557, 271±122, 995±1187, 190±73, 675±205, 226±96 and 8±3 mg l⁻¹, respectively. In industrial site, higher loading of the pollutants is observed. The variations, correlation, enrichment and removal of the pollutants are discussed.

Sr isotope geochemical studies on rivers of South India: Evidence for high CO₂ consumption rates on chemical weathering of silicates

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Study of silicate weathering has attracted much interest as it sequesters atmospheric CO₂ over geological timescales [1]. Rivers draining volcanic terrains and tectonically active mountain chains were studied extensively as high rates of chemical weathering is observed in these areas which result in more CO₂ consumption [2, 3, 4, 5]. Whereas, this study is focused on Kaveri, Palar and Ponnaiyar rivers draining the Dharwar Craton (DC) and Southern Granulitic Terrain (SGT) of south India to estimate their weathering rates, which experience tropical bimodal monsoonal climate.

The Kaveri, Palar and Ponnaiyar rivers of south India were sampled during NE monsoon of the year 2005 and SW monsoon of 2006. The dissolved major ions, trace elements and ⁸⁷Sr/⁸⁶Sr ratios of river waters were measured. Using average annual flow, total drainage area and major ion concentrations of these rivers chemical weathering rates, annual fluxes of different ionic species to the ocean and CO₂ consumption rates were calculated after deducting atmospheric input. The final specific chemical denudation rate (silicate + carbonate) estimated for these basins ranges from 1.3 to 13 tons/km²/y. During SW monsoon upper reaches draining Archean granitoid gneisses and greenstone belts of DC receive abundant rainfall and result in high ⁸⁷Sr/⁸⁶Sr ratio, whereas, during NE monsoon lower ⁸⁷Sr/⁸⁶Sr ratios were found in the rivers due to weathering of granulites and gneisses of the SGT that are exposed in lower and middle reaches.

The estimated CO₂ consumption rates vary between 3.49 × 10⁹ mol km⁻² a⁻¹ in the main stream of Kaveri. The upper limit of CO₂ consumption rate of the Kaveri basin is close to the area-weighted CO₂ consumption rate for the Deccan basalt, i.e. 0.36 × 10⁶ mol km⁻² y⁻¹ [2]. CO₂ sequestered due to silicate weathering in this basin is 20.00 to 23.13 × 10⁷ mole y⁻¹ which represents 0.22 – 0.26 % of global CO₂ drawdown of 8700 × 10⁷ mole y⁻¹ [3]. Thus, CO₂ drawdown estimated for the Kaveri basin covering 0.044 % global drainage area is ~5.5 times higher than the global average consumption rate per unit area. This could be due to enhanced chemical weathering of silicate rocks under tropical humid climate.

Characterization of reactive ferrous iron in titanomagnetite (Fe_{3-x}Ti_xO_4) nanoparticles for contaminant reduction

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Sediments at the Hanford nuclear processing site, WA, USA contain significant amounts of reactive ferrous iron, which can occur as magnetite containing structural impurities, including a substantial proportion of titanium. Titanomagnetites (Fe_{3-x}Ti_xO_4) have electron equivalents available for reduction of key polyvalent metal contaminants, e.g. pertechnetate. Compositionally controlled Fe_{3-x}Ti_xO_4 bulk powders and nanoparticle suspensions were synthesized to provide pristine materials for development of a molecular-level understanding of rate controlling factors, e.g. surface passivation and Fe (II) resupply, in the heterogeneous reduction of Tc (VII). A solid solution of bulk powders from passivation and Fe (II) resupply, in the heterogeneous 900°C. Fe3-

Microbial community diversity under extreme euxinia: Mahoney Lake, Canada

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Mahoney Lake, British Columbia, Canada, is shallow (15 m), with a stable hypolimnion containing > 400 mM SO_4^{2-} and >30 mM S^{2-}, far more euxinic than the Black Sea. The densest plate of phototrophic bacteria ever detected (10^9 cells/mL, ~10 cm thick) is found at the boundary with the oxic mixolimnion. This layer is reported to contain predominantly the Chromatiaceae (purple sulfur bacteria), Amoebobacter purpureus (98%) and Thiocapsa roseopersicina (2%) [1, 2]. To date, little information has been reported on other members of the Mahoney lake microbial ecosystem, and there is no information about the microbial community residing in the aphotic hypolimnion or in the lake sediments. Suggestions that the deep lake is not active are based on the absence of gradients in SO_4^{2-} and S^{2-} profiles and on a general abundance of fragmented, rather than intact, DNA in sediments [3]. In support of this argument, much of the sulfide appears to be supplied by sulfate reduction from within the phototrophic plate, rather than from the deeper lake [1, 4].

A better understanding of Mahoney Lake could help reveal if or what types of microbes are found in extreme eunxia. Here we profiled distributions of 16S rRNA genes using PhyloChip, a high-density microarray able to detect >10,000 different prokaryotic OTUs [5]. Our results yield a semi-quantitative picture of the Mahoney Lake mixolimnion (5 m), chemocline (7 m), hypolimnion (8 m), and sediments. For comparative purposes, traditional clone libraries (150-200 clones/sample) also were sequenced. Both approaches suggest that microbial diversity is greatest in the hypolimnion and sediments. Diversity is lowest in the photosynthetic plate. Comparison of PhyloChip data with clone libraries reveals the limitations and strengths of each approach, but both are consistent with active sulfate reduction persisting below the chemocline (7 m), hypolimnion (8 m), and >30 mM S^{2-}, far more euxinic than the Black Sea. The densest plate of phototrophic bacteria ever detected (10^9 cells/mL, ~10 cm thick) is found at the boundary with the oxic mixolimnion. This layer is reported to contain predominantly the Chromatiaceae (purple sulfur bacteria), Amoebobacter purpureus (98%) and Thiocapsa roseopersicina (2%) [1, 2]. To date, little information has been reported on other members of the Mahoney lake microbial ecosystem, and there is no information about the microbial community residing in the aphotic hypolimnion or in the lake sediments. Suggestions that the deep lake is not active are based on the absence of gradients in SO_4^{2-} and S^{2-} profiles and on a general abundance of fragmented, rather than intact, DNA in sediments [3]. In support of this argument, much of the sulfide appears to be supplied by sulfate reduction from within the phototrophic plate, rather than from the deeper lake [1, 4].

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Investigation of Hg species binding biomolecules in dolphin liver: Use of isotopic tracers for sample treatment optimization

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Despite mercury being well recognised as an important pollutant in marine animals, the metabolic pathways of this element has not been fully elucidated. It has been suggested that Hg can bind thiol containing proteins/biomolecules [1]. The study of mercury containing biomolecules is essential for the assessment of its biotransformation mechanisms and toxicological impact. In general terms, most of the speciation studies have been carried out in fish muscles because of its consumption by humans and were restricted to the discrimination of an inorganic and monomethyl (MeHg) mercury ‘pool’ in these samples. However, speciation of this heavy metal in vital organs like liver has not been extensively studied. In fact, the main problem is to maintain the original speciation avoiding all possible transformations during the analytical process in order to elucidate the structure of Hg containing biomolecules, which is a great challenge. Multiple isotopic tracers spiking, used in isotopic dilution methodologies, is a powerful tool and its potential to deal with these problematic is investigated.

The main aim of this work is the study of Hg species (i.e. IHg and MeHg) binding biomolecules in the aqueous soluble protein fraction of white-sided dolphin (Lagenorhynchus acutus) liver homogenate (QC04LH4). By using stable enriched isotopic tracers (199IHg and 2°1MeHg), the rate of species transformation during sample treatment steps, such as lyophylization and protein extraction by ultrasonication, was evaluated. IHg and MeHg distribution into pellets and protein soluble fraction was determined. The analysis of the soluble protein fraction by size exclusion chromatography-ICP-MS reveals the association of Hg with biomolecules in a wide molecular weight range. This was followed by the GC-ICP-MS speciation in order to determine the ratio of IHg and MeHg into the different protein fractions. In this work, isotopically labeled Hg species were also used as tracers to optimize the sample treatment to assess Hg species in protein fractions.


Heterogeneity of the lower continental crust beneath southern Jilin Province, NE China: Evidence from geochemical and Sr–Nd–Pb isotopic compositions of Early Cretaceous granitoids

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The spatial variations of geochemical and Sr-Nd-Pb isotopic compositions of Early Cretaceous granitoids from southern Jilin province, China, provide insight into the nature and its variation of the lower continental crust beneath the northeast segment of the North China Craton (NCC). Zircon U-Pb dating results show that the granitoids formed in the Early Cretaceous (119-130 Ma). The Early Cretaceous granitoids have SiO2 = 61.8~76.6%, Mg# =7~55, A/CNK = 0.86~1.12, (87Sr/86Sr)i = 0.7054~0.7107, eNd (t) = -1.93 ~ -13.9, and are characterized by enrichment in large ion lithophile elements (LILEs) and light rare earth elements (LREEs), and depletion in high field strength elements (HFSs), such as Nb, Ta, and Ti and heavy rare earth elements (HREEs). These geochemical features reveal that they could be derived from partial melting of the lower continental crust. Chemically, the spatial variations of their compositions exist among these coeval granitoids. For example, their initial 87Sr/86Sr ratios increase from 0.7054 to 0.7107 whereas their eNd (t) values decrease from -2.33 to -13.9 from the northeast to the southwest in southern Jilin province. The above-mentioned results indicate that the Early Cretaceous granitoids could be mainly derived from partial melting of ancient lower continental crust in southwestern segment of southern Jilin province, whereas the coeval granitoids could chiefly originate from partial melting of the juvenile lower continental crust besides minor ancient basement in northeastern segment of southern Jilin province, which is also supported by their two-stage Nd model ages (TDM2), i.e., the former is 2058 Ma, the latter is 1081Ma. Combined with the coeval mafic-ultramafic intrusive rocks [1], it is suggested that these granitoids formed under an extensional environment in the Early Cretaceous.

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Biogenically formed metal sulfide phases

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The biologically mediated formation of metal sulfide precipitates in anoxic sediments represents a potentially important mechanism for the sequestration of toxic metal elements. Our current knowledge of the structure and reactivity of these biogenic metal sulfides is scarce, limiting our ability to effectively assess contaminant sequestration in, and remobilization from, these solids. In a series of experiments, pure cultures of sulfate-reducing Desulfovibrio bacteria were exposed to growth media amended with dissolved Zn, Fe and/or Pb. The resulting precipitates were characterized using x-ray absorption spectroscopy. Subsequently, these solids were reacted in oxygenated water to assess their reactivity and metal remobilization potential.

Figure 1: \( \chi \)-transformed EXAFS spectra of biologically-mediated metal sulfide precipitates.

Biogenically mediated Zn and Fe sulfides showed significantly more short range crystallographic order than abiotically prepared amorphous precipitates. Lead sulfide, however, formed only in samples containing dissolved sulfide species prior to Pb addition, due to competition from dissolved Pb sorption to the Desulfovibrio cells. These results indicate that, for some metals, sulfide phases precipitated directly proximate to cell surfaces may be relatively ordered. This finding could have implications for precipitate stability in systems that cycle between oxic and anoxic conditions.

Causes and consequences of ecosystem retrogression

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In the long-term absence of rejuvenating disturbances, ecosystem properties such as NPP, decomposition, and pedogenic processes undergo substantial declines termed ecosystem retrogression. Here we review and synthesize the findings from studies of long-term chronosequences that include retrogressive stages. Studies on retrogressive chronosequences in contrasting regions provide unparalleled opportunities for developing general principles about the long-term feedbacks between biological communities and pedogenic processes, and how these control ecosystem development.
Meridional advection of Southern Ocean intermediate waters during the last deglaciation from Nd Isotopes in foraminifera

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The Southern Hemisphere plays a key role in the global ocean thermohaline circulation and the climate system, particularly during the glacial-interglacial transitions [1,2]. In particular, the advection of Southern Ocean intermediate waters like Antarctic Intermediate Water (AAIW) and Sub-Antarctic Mode Water (SAMW) towards the tropics is a means for rapid transfer of climatic signals from high-to-low latitudes, channeling heat, freshwater, salt, and chemical species, including dissolved CO₂, through a so-called ‘oceanic tunnelling mechanism’ [3]. We will present new results for Nd isotopes (¹⁴⁶Nd/¹⁴⁴Nd) in foraminifera shells (N. dutertrei) at ODP Site 1240 (0° 01.31’N, 86° 27.76’W, 2921 mbsl) in the Eastern Equatorial Pacific. N. dutertrei preferentially dwells in the lower thermocline, at the core of the Equatorial Undercurrent (EUC). Therefore, changes in the Nd isotope ratio of cleaned samples will reflect the isotopic composition of the EUC, which in turn reflects changes in the composition of the Southern Ocean end-member and in the advection of SAMW-AAIW.

The Nd isotope ratios indicate the following LGM-to-Holocene history for the EUC. The LGM shows lower εNd values than the late Holocene, consistent with more intense glacial advection of SAMW-AAIW from the Southern Ocean to the EUC. These values increase with the onset of deglaciation, reaching the highest εNd (~1) at ~15 kyr, coinciding with the Antarctic Cold Reversal (ACR), and implying weaker SAMW-AAIW advection to the tropical thermocline. Following the ACR, the advection initially strengthens, reflected by lower εNd, but then transitions to the weaker Holocene mode as reflected by higher εNd values.


Research on geological features and characteristics of inclusions of Zhongqu Gold Deposit in Maqu, Gansu, China

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Zhongqu Gold Deposit in Maqu, Gansu which was found in west Qinling mountain area was a type of gold deposits with extremely unique mineralization characteristic. The tectonic location of the deposit belonged to Qin-Qi-Kun orogenic belt, south of west Qinling orogenic belt. Gold mineralization was strongly related to the silicification and hematitization. The ore was red, brown and very poor in sulfides. Currently the study level on this type of gold deposit was low; researching the geological and fluid inclusions characteristics would bring significant meaning on discussing ore-forming fluid sources and forming mechanism of this type of gold deposit.

In this article freezing method, homogeneous and Laser-Raman and so on were used to measure various geochemical characteristics of fluid inclusions and discuss the source of ore-forming fluid and deposit genesis. The results showed that the ore-forming fluid was low temperature, low salinity and low-density system. The gas phase in the inclusions contained a certain amount of organic ingredients that were supposed to be involved in the mineralization. The inclusions of Zhongqu gold deposit might suffer the later thermal power effects during the ore-forming process. The depth of mineralization in this area was shallow, belonging to the hypabyssal-shallow causes.
The study on the equilibria of the system NaVO₃ - NaH₂PO₄ - (NH₂)₂CO - H₂O at 298 K

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Vanadium has strong transfer ability in environment. This ability related to the solubility of vanadium in soil solution. In this article, the solubility of the metavanadate coexists with sodium, nitrogen, phosphorus has been determined. The phase equilibria of the quaternary system NaVO₃ + NaH₂PO₄ + (NH₂)₂CO + H₂O were studied at 298 K using an isothermal dissolvable method.

Figure 1: The solubility isotherms of the quaternary system NaVO₃ + NaH₂PO₄ + (NH₂)₂CO + H₂O at 298K

The phase diagram is shown in Figure 1. There are three crystallization fields, three univariant curves, and one invariant point. No double salt was found at research temperature. The crystallizing field of urea is the smallest, which indicates urea is of a high solubility. The salting-out effect lies in the salts of NaVO₃ and NaH₂PO₄. The aggregative species of metavanadate change with the acidity of solution. In this weakly acid system, crystallization form of metavanadate is polyoxovanadate.

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Highly siderophile elements as tracers of mantle-crust interactions in subduction zone metamorphic rocks: Evidence from the Franciscan Complex, CA

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The substantial differences in ¹⁸⁷Os/¹⁸⁸Os and abundances of highly siderophile elements (HSE: Re, Os, Ir, Ru, Pt, Pd) in mantle peridotites compared to subduction zone oceanic crust means that this suite of elements may prove useful in assessing mantle-slab material transport. There is currently, however, limited information regarding the mobility of the highly siderophile elements (HSE) in aqueous fluids in subduction zone environments. To explore this issue further, we measured HSE abundances and Os isotopic compositions of high-grade m-scale blocks of metabasite and related rocks from subduction-related mélangé within the Franciscan Complex, CA. Rinds of actinolite-chlorite-phengite observed in high-grade blocks have been previously interpreted to be metasomatic features that formed when fluids that serpentinized the surrounding ultramafic matrix interacted with the outer portions of the basaltic blocks.

The cores of the blocks have low abundances (<0.05 ppb) of Os, Ir and Ru, and modest concentrations (<1 ppb) of Pt and Pd. Cores are variably radiogenic, with initial ¹⁸⁷Os/¹⁸⁸Os ranging from 0.200 to 2.94. These are characteristics consistent with little-modified basaltic presursors. In contrast, HSE concentrations (except Re) in all of the rinds are much higher, with absolute and relative abundances approaching values typical of peridotites. Initial ¹⁸⁷Os/¹⁸⁸Os are also typical of upper mantle peridotites, ranging only from 0.126 to 0.132. Both HSE concentrations and isotopic ratios suggest efficient and rather uniform transference of mantle HSE to the block rinds, if the mass transfer was produced by fluids. If the result of fluid transport, these results suggest that HSE can be highly mobile in the fluids that serpentinized the ultramafic matrix and interacted with basaltic blocks. Alternatively, the rinds may have been produced by mechanical mixing of material derived from blocks with mélangé matrix in a shearing environment. Experiments are underway to allow discrimination between these possibilities.
Mineral transformations and contaminant release dynamics under wetting-drying cycles in simulated Hanford sediments

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In order to successfully predict waste plume migration and understand possible mechanisms of radionuclide release after removal of the caustic waste source at the Hanford Site, the impact of background pore water (BPW) on impacted sediments and transport processes have to be elucidated. Using Hanford sediments (HS) weathered by synthetic tank waste leachate (STWL) and co-contaminated with Sr, Cs and I, we investigated mineral transformation and sorbate speciation over a matrix of field-relevant gradients in contaminant concentration, $P_{CO_2}$, and reaction time. Further, we monitored the elemental release induced by BPW infiltration through HS packed columns.

Characterization of STWL reaction products using EM and quantitative-XRD indicate the importance of STWL reaction conditions on the kinetics of mineral transformation during contact with STWL (native silicates $\rightarrow$ zeolite $\rightarrow$ sodalite $\rightarrow$ cancrite). Additionally, we found that $P_{CO_2}$ affects calcite weathering such that elevated Ca$^{2+}$ release in absence of CO$_2$ promotes strätlingite formation.

Sediments reacted for 12 months with various STWL solutions were subjected to both continuous flow and four 24h dry/wet leaching cycles with BPW. After each drying event, large NO$_3$ pulses were observed in effluents, but these were not accompanied by corresponding Si pulses that would signal zeolite/feldspathoid dissolution. Wetting-drying increased NO$_3$ desorption 4-5 fold over continuous flow experiments. Sr and Cs desorption is diminished in the wet/dry cycle experiments relative to continuous saturated or unsaturated flow, except for Sr in cases where CO$_2$ was eliminated from the STWL weathering reaction.

Our results indicate that STWL composition, $P_{CO_2}$, and reaction time strongly influence contaminant sequestration mechanisms and, therefore, the rate and extent of subsequent re-mobilization and transport in Hanford vadose zone sediments.

Environmental geochemistry of Argemela Mine area (Barco, Central Portugal)

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Mining and mineral-processing activities affect relatively small areas, but they can have a large local impact on the environment. The Argemela mining area is located at Central Iberian Zone, central Portugal. The mineralized veins intersect the Cambrian schist-metagraywacke Complex and is situated at about 13 km, to the east of the famous wolfram Portuguese producer, Minas da Panasqueira. Argemela and Panasqueira mines are included in the metallogenetic Sn-W province of Portugal. The Sn veins contain mainly quartz, albite, moscovite, lepidolite, cassiterite, columbite group minerals, ambylygonite-montebrazite, pyrite, arsenopyrite and pyrrhotite.

At Argemela mine, the underground exploration of cassiterite was dominant and ceased since fifty years ago. The tailings and rejected materials were deposited on the ground and are exposed to the air and water that can change the environmental geochemistry of the area.

The geochemical soil data show anomalies in the dependency of the mineralizations and mining activities. Representative soil samples of the local geochemical background and soils collected inside mine influence were analysed. Soils inside mine influence present higher electrical conductivity (62 $\mu$S/cm; Cd = 28 mg/Kg; Pb = 2 mg/Kg; Cu = 4990 mg/Kg; Zn = 1168 mg/Kg) than soils collected outside mine influence (EC= 29 $\mu$S/cm; Cd = 0.3 mg/Kg; Pb = 2 mg/Kg; Cu = 35 mg/Kg; Zn = 51 mg/Kg). Most of soils are contaminated in Cu and Zn and must not be used for agriculture and human residences. Plants growing on the abandoned mine area have been study for their biogeochemical indication and mine remediation potential.

The obtained results indicate that Erica cinerea L., Cytisus striatus and Cistus Ladanifer are adapted to enriched Cu, Zn and Ni soils. Erica cinerea roofs tend to accumulate Cu (27 mg/Kg), while leaves from Cytisus striatus (9 mg/Kg) presents the highest Cu content of this species. Leaves from Erica cinerea L. and Cytisus striatus contain higher Zn, Cr, Ni and Pb contents than respectively roofs and stalks. The informations obtained for these species allows biogeochemical delineation of areas from similar soil anomalies.
Towards an improved IMS 1280 model: The IMS 1280-HR

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SIMS technique provides direct in situ measurement of elemental and isotopic composition in selected μm-size areas of the sample. The CAMECA IMS 1280 is a ultra high sensitivity ion microprobe that delivers unequaled analytical performance for a wide range of SIMS applications: isotope ratio measurements [1], geochronology applications (U-Pb dating in Zircon) [2], trace element analyses [3].

In order to optimize the performance at high mass resolution conditions, both in monocollection and multicollection modes, a new model of the CAMECA IMS 1280 is introduced: the IMS 1280-HR.

Main targeted applications are the K/Ca and Rb/Sr dating, in monocollection mode at Mass Resolving Power (MRP) > 20,000, as well as Mg and metal isotope analysis in multicollection mode at MRP > 5,000.

The IMS 1280-HR combines the well-proven features of the standard IMS 1280 with new developments oriented towards high mass resolution capabilities:

1) redesign of the coupling section for minimizing second-order aberrations, which are known to limit the MRP capabilities
2) low noise electronics, new Hall probe and associated pre-amplifiers for an improved magnetic field stability
3) modification of the magnet pole piece in order to minimize the off-axis aberrations and improve the peak shape in multicollection mode
4) magnet flight tube with new baking system for a better abundance sensitivity.

Data obtained on the IMS 1280 will be presented. Transmission tests performed for the 40K in Adularia sample show that a transmission of 75 c/s/ppm/nA can be achieved at MRP (10%) > 32,000 in monocollection mode. In multicollection mode, a reproducibility of < 0.3 permil (1σ) could be obtained for the δ²⁰Mg and δ²⁶Mg ratios measured at MRP (10%) > 6,000 in Olivine San Carlos.


Chemical variations in multicoloured “Paraíba”-type tourmalines from Brazil and Mozambique: Implications for authentication and provenance determination

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Chemical profile analyses by LA-ICP-MS and EMPA analysis revealed characteristic chemical differences between different colour zones in copper-bearing tourmalines from Mozambique and Brazil. From the core to the rim of the tourmaline crystals chemical variations were found for the elements Be, F, Mg, Ti, Fe, Cu, Zn, Mn, Sb, Nb, Ta, U, Th, Pb and REE [1].

Cu-isotope ratios have been measured in tourmalines using femtosecond LA-MC-ICP-MS as an additional critical test for provenance and authentication. The samples from Paraíba that were analyzed for copper-isotopes showed very similar δ⁶⁵Cu/⁶³Cu ratios, positively biased to NIST610. The additional potential of this method [2] for future identification of treatments of tourmaline is discussed.

It was possible to create a flow chart for different methods useful for origin determination of copper-bearing tourmaline. The EMPA and LA-ICP-MS generated database allows using commonly applied gem-testing methods (ED-XRF- and LIBS-analysis) to measure critical Cu/Ga-ratios, Be- and Mg-concentrations for origin determination of copper-bearing tourmalines.

Reactions of Tc with Fe(II) and O₂ in Hanford redox-sensitive sediments

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Technetium-99 is a fission product of uranium-235 and plutonium-239 and has been introduced in Hanford site as a result of disposal of spent nuclear fuel and tank waste leakage. Under oxic conditions, Tc exists as the pertechnetate anion which is weakly sorbed. The reduced form of technetium, Tc(IV), is stable in anoxic environments, and often forms a sparingly soluble precipitate TcO₂·nH₂O. Therefore, Tc redox transformations are crucial in controlling its migration in subsurface environments. The objective of this work was to investigate abiotic electron transfer reactions of Fe, O₂, and Tc in mineralogically heterogeneous sediment obtained from a subsurface redox transition zone including their reaction products and kinetics. Technetium (VII) reaction experiments were performed with anoxic sediments collected from Hanford’s unconfined aquifer (~18 to 55 m bgs). Wet chemical, X-ray diffraction, Mössbauer, X-ray absorption and electron microscopy measurements were performed to identify the ferrous minerals that might control Tc (VII) reduction. The results revealed complex Fe (II) mineralogy, including Fe (II)-smectites, pyrites, magnetites and still unidentified Fe (II) discrete phases. Batch experiments with 10 µM Tc (VII) and six different sediments demonstrated that all anoxic sediments reduce Tc (VII), but with different rates. All Tc (VII) was reduced to Tc (IV) and immobilized as TcO₂·nH₂O. The residual Tc (IV)-containing sediment suspensions were used in stirred flow reactors to study their reaction with dissolved O₂. Ongoing experiments reveal that O₂ reacts preferentially [over Tc (IV)], albeit slowly, with sediment Fe (II). Effluent Tc solution is at nanomolar concentration level and consists of Tc (VII) and up to 5% Tc (IV). The data suggest that both non-oxidative and oxidative dissolution of TcO₂·nH₂O occur.

Geochemical dispersion of weathered copper mineralised dolomitic rocks in tropical environment, Dos Parecis Basin, Amazon Craton, Brazil

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The Dos Parecis basin is located in the south-western part of the Amazon Craton, Brazil. The Dos Parecis Basin is composed of two parallel sub-basins: Basin of Colorado in the north and Pimenta Bueno Basin in the south. A dolomitic layered unit is exposed in the northern limit of the Colorado Basin and hosts copper sulphides, which are mainly chalcocite. Chip samples from outcrops, samples of drainage sediments and pan concentrates of heavy minerals were collected. All samples were analyzed with acid digestion and ICP finish. Chemical analysis was undertaken on the fine fraction (-270# and +400#), on the coarse fraction (+35# and +65#) and on whole-pan concentrates.

The highest copper concentrations are found in white dolomites (4, 137 ppm Cu on average). The dolomitic unit also has the highest concentrations of manganese (0.56% to 2.6% MnO). Basement rocks contain high local copper concentrations (1, 529 ppm maximum). This unit locally has copper sulphides and oxides.

Weathering has produced oxidation of rocks. Anomalous concentrations of copper in soils in the B horizon range from 51 ppm to 98 ppm, up to 2, 580 ppm. Barium and manganese anomalies are also found within 40 m to 160 m of the mineralised outcrops.

Sediments in creeks cutting the non-mineralised sedimentary rocks contain low copper concentrations: 7 ppm to 17 ppm in the coarse fraction; 21 ppm to 25 ppm in the fine fraction and variable concentrations between 34 ppm and 108 ppm in the whole-pan concentrates. Anomalous values for stream sediment samples containing detritus with copper oxides range from 51 ppm to 145 ppm in the fine fraction and 44 to 830 ppm in the pan concentrates. Copper concentration in the coarse fraction varies from 19 ppm to 39 ppm, up to anomalous values of 193 ppm and 290 ppm.

The observed copper concentrations in the fine fraction, related to the distance downstream from the mineralised outcrops, is 39 ppm to 77 ppm between 0 and 500 m; 99 ppm to 135 ppm between 500 and 1000 m; 90 ppm between 1000 and 2500 m and less than 53 ppm at distances greater than 2500 m.
δ¹⁸O and Mg/Ca temperature in Brazil margin foraminifera species

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Oxygen isotopes (δ¹⁸O) and Mg/Ca ratio observed in foraminiferal tests can be used to establish the ocean temperature from organism habitats.

Temperature values obtained from δ¹⁸O (T₁⁸O) and Mg/Ca (Tₐ₈Ca) in seven different planktonic and benthic foraminiferal species were compared in order to evaluate differences among these results in each species. Holocene samples were collected in two cores from slope of the Brazil margin in the Western Atlantic Ocean between 21° and 24°S (KF-D, 1503 m and KF-12, 1568 m).

Salinity (WOA 05, Locarnini et al. [1]) and δ¹⁸O seawater (South Atlantic equation, LeGrande & Schmidt [2]) were used to estimate the mean calcification depth, δ¹⁸O values were corrected from disequilibrium as described by Niebler et al. [3]. Local temperature was obtained from WOA05 (Antonov et al. [4]). We selected the paleotemperature equation that provided the best fit to each species.

In general T₁⁸O showed lower deviation from local temperature (-0.40 - 0.02) than Tₐ₈Ca (-9.20 - 9.48).

In planktonic species (“G. ruber” and “G. sacculifer”) both proxies present a good relationship with the local temperature; meanwhile in benthic species “Uvigerina sp” presented the best fit.

C. corpulentus showed deviation of -9.20 °C and 0.03 °C for Tₐ₈Ca and T₁⁸O, respectively. These results suggest that T₁⁸O from this species could probably be used to reconstruct temperature, but the mechanism that control Mg/Ca relationship could not be the same observed in other Cibicidoides species of this work (C. wuellerstorfi and C. kullenbergii).

Tₐ₈Ca in H. elegans was expected to present the best fit as it is an aragonitic species. Although, the deviation was 9.48 °C, much more than the temperature deviation observed in T₁⁸O (0.11 °C). H. elegans are not commonly used in δ¹⁸O analyses, but the result show a good relationship between δ¹⁸O and temperature.


Controls of H incorporation in pyroxenes and garnets from FTIR data on Kaapvaal craton xenoliths

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Pyroxene (Px) and garnet (Grt) accommodate hydrogen (H) as defects bonded to structural oxygen. The present study aims at characterizing the control on incorporation of water (H contents calculated as H₂O ppm) in orthopyroxene (Opx), clinopyroxene (Cpx), and Grt using Fourier transform infrared spectrometry (FTIR). We want to test on natural peridotites from the Kaapvaal craton [1, 2] experimental results which suggest that H partitioning is controlled mainly by Al in px, and Si, Ti, and pressure (P) in Grt [3-7].

Garnets

Grt water contents range from 0 to 19 ppm H₂O, with 6 out of 19 samples having no detectable H. In Lihobong xenoliths, Cpx H₂O may increase with increasing Ti and decreasing oxygen fugacity. No correlations with Si content, P, or any other parameters are evident.

Pyroxenes

Opx water contents correlate negatively with Opx Al⁴⁺ indicating that H incorporation is charge coupled with Al⁴⁺. Cpx water contents correlate negatively with Cpx Ca contents and positively with Cpx Al⁶⁺ and Fe³⁺/ΣFe (Mössbauer data [8]), suggesting that substitutions on the M1 and M2 sites can control H. These correlations are most evident when examining xenolith locations individually. The intake of water by Px consequently appears to depend on the Px composition and the local mantle water conditions. In particular, Px from P > 3 GPa have a narrow range of H₂O contents (Opx: 119-251; Cpx: 149-398 ppm) compared to those from lower pressures (mainly off-craton; Opx: 5-460 ppm; Cpx: 5-957 ppm), and this corresponds to a narrow range of low px Al contents at P >3 GPa [9]. For a similar Px major element composition, water contents increase in Px from Lihobong, through Finsch Mine, Jagersfontein, to Kimberley xenoliths.

Phase equilibria controls on mass transfer reactions in the rainbow hydrothermal system

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In July 2008, high temperature hydrothermal fluids (~365°C) were sampled from the Rainbow vent field (36°13.8'N at 2300 m depth) on the Mid-Atlantic Ridge during cruise KNOX18RR. Rainbow, located at the intersection of non-transform and ridge-related faults, is characterized as an ultramafic system. Considering the temperature and reducing nature of the Rainbow fluids, end-member dissolved sulfate concentrations must be near zero. Extrapolation of dissolved Mg data to zero sulfate suggests Mg values as high as 1.5-2 mmol/kg. Measureable concentrations of Mg provide new insight into the mineral phases that buffer fluid chemistry in ultramafic systems. In combination with other select species (Fe, Si, Al, Ca and H2), these data permit calculation of the pH and redox dependent solubility of minerals. We speculate that the moderate (measured) dissolved silica values result from alteration of plagioclase and olivine to chlorite + magnetite ± talc. The available data for activity-composition relations of chlorite solid solutions indicates that in spite of the high Fe/Mg ratio in the vent fluids, the mole fraction of chamosite is ~0.22. The coexistence of chlorite solid solutions with magnetite provides a redox buffer that helps to maintain the characteristically high H2 concentrations in Rainbow fluids. Furthermore, the pH of chlorite saturation is similar to that required for both magnetite and talc. These data strongly suggest the existence of gabbroic intrusions within the Rainbow system and the existence of talc may influence strain localization with implications for the tectonic evolution of detachment fault shear zones.

Linking temperature to time in retrograde metamorphism: Ti-in-quartz + Rb/Sr of muscovite in preserved Ms + Qtz symplectite

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Symplectites are arrested metamorphic reaction textures that are preserved when falling temperature and/or other factors limit grain boundary diffusion rates such that the transport of chemical components to the reaction interface cannot keep pace with the rate of grain boundary migration. Analysis of symplectites provides a unique opportunity to use preserved phase relationships to better assess how crustal conditions evolved after the formation of peak-grade mineral assemblages. For example, in batholithic settings, symplectites can be analyzed to determine the timescales for re-equilibration of the geotherm following the heat input associated with massive intrusion. To answer first-order questions of this type, both temperature (T) and time (t) data must be extracted from symplectites.

Muscovite + quartz and plagioclase + quartz symplectites (myrmekite) that form at the expense of K-feldspar + sillimanite-bearing assemblages are widespread phenomena in deeply exhumed arc crust that provide the essential mineralogy to constrain T-t history. We have performed Ti-in-quartz thermometry with the ion microprobe and have used back-scattered electron (BSE) imaging to guide focussed ion beam (FIB) sampling of the symplectites to perform Rb/Sr geochronology via TIMS and ICP-MS methods. Previous muscovite, biotite, and K-feldspar 4°Ar/39Ar results revealed that the 15 km deep exposures we have studied cooled from > 600°C to 450-400°C over a 15 m. y. interval that followed massive intrusion at 95-91 Ma. Preliminary Rb/Sr results from the symplectites indicate that the geotherm decreased from > 40°C/km to ca. 30°C/km over a < 2 m. y. interval post-intrusion. These results demonstrate our ability to collect data directly from µm-scale metamorphic textures to determine the timing and rates of tectonic processes. It also highlights the rich record that symplectites preserve regarding the retrograde evolution of orogens.
Preliminary report on the experimental measurement of trace-element partitioning between zircon and hydrothermal metamorphic fluids at High/Ultra-High Pressure conditions

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Zircon (ZrSiO₄) is one of the most important minerals available to study the geochemical and geodynamic evolution of the Earth. Recent developments in micron-scale in situ zircon geochemical and isotopic (U-Pb and Lu-Hf) analysis have caused an exponential growth in its use for understanding geodynamic processes during High and Ultra-high pressure (HP/UHP) metamorphism. Geochemical and textural evidence suggests that zircons in HP/UHP metamorphic terrains grew at sub-solidus conditions in the presence of a hydrous metamorphic fluid. However, to date no experimental studies have been performed to characterize the geochemical behavior of zircon in equilibrium with hydrous metamorphic fluids. Here we present preliminary experimental results aimed towards characterizing the trace-element partitioning behavior of zircon in hydrothermal fluids at High/Ultra-High Pressure (1.5 to 3.0 GPa) conditions.

An exploratory zircon growth experiment yielded D (zircon/fluid) increasing from light to heavy REE, typical of REE substitution favoring HREE incorporation in the Zr lattice site, and a D (Th)/D (U) ratio of ~2.5. Favorable partitioning of Y, Sc, Nb, Ta, and Hf into zircon is also observed. These measurements should aid in identifying zircons that have grown from a hydrous metamorphic fluid. However, to date no experimental studies have been performed to characterize the geochemical behavior of zircon in equilibrium with hydrous metamorphic fluids. Here we present preliminary experimental results aimed towards characterizing the trace-element partitioning behavior of zircon in hydrothermal fluids at High/Ultra-High Pressure (1.5 to 3.0 GPa) conditions.

In our experiments, the akaganéite to hematite transformation was completed in 100, 20 and 4 minutes at temperatures of 150°C, 175°C and 200°C, respectively. Refined unit-cell parameters for each phase followed the same general trends at all temperatures. Lattice parameters of akaganéite did not significantly change throughout the reaction. The hematite a parameter decreased with increasing particle size, but the c parameter increased until all akaganéite had transformed, after which it decreased. Our results demonstrate that in situ structural and kinetic data of low-yield hydrothermal reactions can be successfully captured using our experimental design and TR-XRD.

Time-resolved X-ray diffraction study of the in situ hydrothermal phase transformation from akaganéite to hematite

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Akaganéite nanoparticles commonly form when chlorine-rich fluids alter metallic Fe, and recently they have been discovered as a biogenic product. Although the precipitation of akaganéite (β-FeOOH) and its subsequent transformation to the stable phase hematite (α-Fe₂O₃) are well documented, the mechanism and the kinetics of this reaction are debated. The difficulty in characterizing the transformation can be attributed in part to the poorly crystalline nature of most natural akaganéite. Additionally, in situ analysis is challenged by the low precipitate yield in hydrothermal experiments within the Fe-Cl-H₂O system.

Here we present new observations from in situ heating experiments using time-resolved synchrotron X-ray diffraction (TR-XRD) conducted at the Advanced Photon Source (APS). Starting with ferric chloride solutions (0.45 M FeCl₃ + 0.01 M HCl), we have collected TR-XRD data of the hydrothermal precipitation of akaganéite and transformation to hematite. Design of a new heater and experimental protocol facilitated our collection of in situ data by precipitate sedimentation at the base of a sealed 0.7 mm quartz capillary. XRD data were collected every 30 seconds at temperatures ranging from 80-200°C. Rietveld refinements using the General Structure Analysis System (GSAS) allowed for quantitative measurements of reaction rates as a function of temperature. Moreover, we determined the dependence of unit cell parameters on temperature and particle size.

In our experiments, the akaganéite to hematite transformation was completed in 100, 20 and 4 minutes at temperatures of 150°C, 175°C and 200°C, respectively. Refined unit-cell parameters for each phase followed the same general trends at all temperatures. Lattice parameters of akaganéite did not significantly change throughout the reaction. The hematite a parameter decreased with increasing particle size, but the c parameter increased until all akaganéite had transformed, after which it decreased. Our results demonstrate that in situ structural and kinetic data of low-yield hydrothermal reactions can be successfully captured using our experimental design and TR-XRD.
Microbiologically-catalyzed cementation of modern gypsum-dominated thrombolites

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Large gypsum-dominated microbialites coated by well-developed and stratified microbial mats have been found growing in the shallow waters of a restricted hypersaline lagoon on the Archipelago Los Roques, Venezuela. The overlying hypersaline water is characterized by temperatures in excess of 30°C and elevated total alkalinity (164 meq/L as CaCO3), pH (~9.1), and Mg/Ca ratio (6.1). In the organic mud- and gypsum-dominated basin the environmental conditions promotes bacterial growth and abundant production of EPS matrix forming a microbial mat which in the shallow areas (to a depth < 1 m) can be linked to the development of unusual subaqueous microbialites, cemented by Mg-carbonates. These microbialites have a crudely laminated to clotted internal fabric and thus can be morphologically regarded as thrombolites [1]. Results from various analytical approaches, including standard and fine-scale petrography, C and O stable isotope analysis, and laser-ablation ICP-MS, suggest that carbonate cementation of these thrombolites is an early diagenetic process, catalyzed by the breakdown of gypsum by SRB. The thrombolites no longer occur at water depths > ~1 m, and in deeper parts of the lagoon (max. depth = 1.6 m), sedimentation consist of gypsum nodules growing in a gelatinous organic matrix without any carbonate cementation. The carbon and oxygen isotopic composition of the carbonate phases within the thrombolic fabric reflect the timing of precipitation and the interplay of organic and inorganic carbon reservoirs; early-diagenetic carbonate cements (δ13C = -2‰) are close to equilibrium with respect to inorganic carbon, while deeper in the thrombolites, gypsum-replacing carbonates are relatively enriched in 13C (δ13C = -5‰), likely incorporating carbon released by SRB heterotrophy of organic matter. The oxygen isotopic composition (δ18O = -0.6 to -0.1‰) results from equilibrium mineral precipitation from evaporated seawater (δ18O = +2.0 to +4.0‰); the uniformity of the δ18O values, as compared with allochemical grains in the basin (aeolian-transported Halimeda flakes, δ18O = -3.0‰) suggests that authigenic precipitation exceeds trapping and neomorphism within the microbial mat. This thrombolite-rich lagoon thus serves as an unparalleled field site for the study of chemical and isotopic processes influencing early diagenetic gypsum microbialite formation.

**Isotopic evidence of possible Cr(III) oxidation in an early contaminated site from NE Italy**

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Trivalent chromium [Cr (III)] is an essential human and animal nutrient at the proper amount of ingestion; hexavalent chromium [Cr (VI)] is toxic and causes a wide range of health effects. Under the redox and pH conditions usually found in nature, Cr (VI) has the tendency to be reduced to Cr (III), e.g. in the presence of aqueous Fe (II), and is scavenged from solution by adsorption, in particular onto clay mineral surfaces. Only few oxidants are present in natural systems which can oxidize Cr (III) to Cr (VI). It has been demonstrated that Cr isotopes fractionate during the Cr (VI) to Cr (III) conversion under reducing conditions [1]. In the present study, preliminary $^{53}$Cr data were obtained on groundwaters draining a phreatic aquifer in the High Friuli Plain (NE Italy), an area which underwent extensive Cr (VI) contamination from manufacturing during 1985, creating a plume of Cr (VI)-contaminated groundwaters. Later, the industrial activity was made environmentally protective and a natural reduction of contamination occurred over the years. Recently, new spikes in the Cr (VI) content, reaching 1600 µg/L, have been observed in a number of wells, with concentration generally decreasing downgradient from the original site of contamination. The measured $\delta^{13}$Cr on the Cr (VI) contaminated waters ranges between -0.50 and -2.96. These data are tentatively interpreted, within a Rayleigh distillation model, as possible evidence of the oxidation of the trivalent chromium originated by reduction of the anthropogenic Cr (VI), released during the ‘80s, which accumulated onto alluvial sediments.


**LA-(MC-)ICP-MS element and isotope ratio analysis of fluid inclusions in minerals**

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Element concentration and isotope ratio data for individual fluid inclusions revolutionize our understanding of fluid-mediated element transfer and enrichments in geologic systems down to subarc depths. Here, we focus on LA-ICP-MS analytical strategies and progress.

Average fluid solute concentrations can be determined down to 0.0X µg/g for a given fluid inclusion assemblage. Uncertainties can be as good as ± 5 % 1 SD, while counting statistics uncertainties raise to ± X0 % 1 SD for elements nearing their LOD. Accuracy is limited by internal standardization for quantification and, for metals heavily enriched in micronuggets, by representative recording of short transient signals. A jump routine in which the metal of interest is recorded every other time in a sweep (recording cycle) mitigates the latter problem [1] as will be illustrated by simple modeling. But quadrupole instruments measure strictly with increasing mass in a sweep, even if at least one instrument suggests the opposite; thus rendering it impossible so far to benefit from using the jump routine.

Precise and accurate isotope ratio measurements for Pb and Sr on an individual inclusion are possible using LA-MC-ICP-MS and within-run mass bias correction. Limitations are the small dynamic range of detectors and uncertainties in faraday - multiplier cross-calibration, and settling time issues for faraday amplifiers. The latter require either complete, controlled ablation of the entire inclusion and bulk signal integration, or implementation of Tau correction schemes, which we have adapted for fast transient signal analysis. Inclusion-to-inclusion accuracy can be as good as ± 0.8 ‰ (±1 SD) for $^{203}$Pb/$^{206}$Pb for as little as 0.01 ng Pb present in an individual inclusion. Ratios normalized to $^{204}$Pb are less precise due to limitations in recording Faraday detectors.

Inclusion-to-inclusion accuracy can be as good as ± 0.8 ‰ (±1 SD) for $^{206}$Pb/$^{204}$Pb for as little as 0.01 ng Pb present in an individual inclusion. Ratios normalized to $^{204}$Pb are less precise due to limitations in recording Faraday detectors.

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The analysis of Sr isotope ratios is currently explored using synthetic fluid inclusions with known Sr isotope and Rb/Sr ratios. Proper interference correction (Kr, Ca-argides. $^{87}$Rb) is essential and shows that the limiting parameter for accuracy is a high Rb/Sr ratio in the fluid, thus suggesting that potential applications of the Sr isotope tracing approach may be limited to fluids with low Rb/Sr ratios.

Visualizing organic matter biogeochemistry at the microaggregate scale: Lessons from STXM-SIMS

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Advancing our understanding of soil organic-mineral interactions requires disentangling the complex interactions between soil mineral surfaces, decomposed organic compounds, and soil microbial activity/biomass in both the rhizosphere and bulk soil. To visualize these interactions in intact soil aggregates with limited physical or chemical disruption, we proposed a combination of high-resolution spectroscopy (STXM/NEXAFS), electron microscopy (SEM/TEM) and imaging mass spectrometry (NanoSIMS). By combining these techniques, we have mapped organic carbon (OC) distribution, and imaged associations of organics with specific minerals in soil. Using these approaches with soils has required the development of new preparation techniques for complex organic-mineral samples, along with new ways to navigate and re-locate analysis points. Following isotope labelling experiments, we use both STXM and SIMS to image the same soil microaggregates, thereby generating coherent data on organic matter type and source. This approach allows us to measure role of microorganisms in the formation of protective microaggregates, and examine how differences in organic matter source and environmental controls affect microorganisms and their effects on protected C in microaggregates. These approaches are complementary to more traditional bulk analyses (14C dating, NMR, density fractionation) and ideally will yield mechanistic explanations for the C saturation behaviour of soil fractions crucial to long-term soil C stabilization.

Zircon U-Pb geochronology and trace element chemistry of lower crustal xenoliths, western Churchill province of the Canadian shield

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Here we describe the age and trace element geochemistry of zircon from lower crustal xenoliths, recovered from kimberlite drill core from the Rankin Inlet region, Nunavut, Canada. This is the first stage in a broader effort to characterize the age and petrogenesis of the deep lithosphere beneath the western Churchill province.

We report preliminary results for zircon obtained from four garnet-bearing, mafic granulite xenoliths. In colour SEM-CL, zircon exhibits a wide range of growth morphologies and textures. Mottled to sector-zoned, dark grey metamorphic cores are commonly mantled by uniformly zoned, light grey metamorphic rims. These textures are prevalent throughout the sample suite, with the light grey rims recognized in all samples. Only a small fraction of the suite comprises primary igneous zircon, as determined by the presence of oscillatory, planar growth banding in cores.

U-Pb geochronology and trace element analyses of zircon were conducted using a SHRIMP II at the Geological Survey of Canada, with ages reported here as 207Pb/206Pb. Primary igneous cores from two samples yield ages of ca. 2.7 Ga and older, while mottled to sector-zoned, metamorphic cores commonly have ages of ca. 1.9 to 2.0 Ga. Uniformly zoned, light grey (in CL) metamorphic zircon rims have ages of ca. 1.7 to 1.8 Ga. Trace element compositions of ca. 1.7 to 1.8 Ga zircon differs significantly from those of older zircon, and are characterized as relatively REE-depleted, with low (Lu/Gd)_N and low HREE. The low (Lu/Gd)_N ratios and relative HREE-depletion suggests garnet crystallization occurred syn- to pre-zircon growth at ca. 1.7 to 1.8 Ga. Throughout the sample suite, the wide range of SEM-CL textures, and U-Pb and trace element results, suggests multiple zircon recrystallization and growth events in the lower crust. This interpretation is consistent with tectonic models for the Churchill province based on bedrock exposures, which indicate a prolonged, complex tectono-thermal history in the Paleoproterozoic [1].

Flux and $^{87}\text{Sr}/^{86}\text{Sr}$ of land-derived Sr to seawater – Interpreting the marine Sr isotope record

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Temporal variations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ are very well documented throughout the Phanerozoic, but are difficult to interpret. Palmer and Edmond [1], Davis et al. [2] and more recently Vance et al. [3] have used assessments of present-day river, diagenetic and hydrothermal fluxes to argue that the marine Sr system is currently not at steady state. This view is supported by combined stable and radiogenic Sr isotope analyses [4]. In contrast, Allegre et al. [5] argue that the missing flux of unradiogenic Sr to seawater results from weathering of volcanic arcs and ocean islands.

A critical, comprehensive review of available (more than 200 analyses) river fluxes of Sr to the oceans [6] indicates that the flux from young volcanic terrains has been underestimated [7]. However, this unradiogenic land-derived flux is likely insufficient to fully account for the missing unradiogenic Sr. The biggest unknowns regarding the land-derived Sr flux are the subterranean contributions and the fact that contributions from near-coast areas have been under-sampled in most previous studies. A few examples from well-studied river systems in North America, Europe and Asia illustrate this point. As coastal areas are typically geologically younger than the continental interiors, and dissolved riverine $^{87}\text{Sr}/^{86}\text{Sr}$ correlates well with bedrock ages of drainage basins, present-day assessments of riverine Sr fluxes may be biased to more radiogenic values [6]. The present-day riverine $^{87}\text{Sr}/^{86}\text{Sr}$ is thus likely less radiogenic than the best empirical global estimate of 0.7111 [6]. Temporal variations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ likely reflect variations in the flux and $^{87}\text{Sr}/^{86}\text{Sr}$ of land-derived Sr to seawater caused by tectonic, lithologic and climatic changes of Earth’s surface.


Zircon and titanite geochemical and age constraints on ore-related magmas

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Accessory minerals are recognized as ‘small but important’ geochemical tracers of petrological processes. The range of minerals to define the temperature or oxidation state of the magma/fluid is wide (e.g. rutile, magnetite, ilmenite, etc.) but zircon, titanite, and occasionally apatite and rutile are preferred due to the opportunity of reconstructing the time succession of the geochemical evolution. In present study we focus on the behaviour of zircon and titanite during processes which are important for ore-deposits: (i) magma mixing, as it can lead to magmatic volatile saturation and potentially trigger volcanic eruptions and/or the formation of magmatic-hydrothermal ore deposits, and (ii) deposit scale evolution of the magma from a single source magma chamber.

Zircon and titans from the complex gabbro-to-granite Petrochyan pluton in W Bulgaria are both dated precisely by ID-TIMS in the range 303-307 Ma. Mixing and mingling affect both accessory phases (LA-ICP-MS and EMP data): the zircons in the hybrid gabbro are typically rich in REE, U and Th; REE in titanites reflect late magmatic concurrent growth with the apatites and zircons in the hybrid varieties and a growth as an reaction phase (1.5-2 orders lower content of the LREE and one order lower HREE) in the cross-cutting lamprophyre (feeder?) dykes. Insitu tHf values of the zircons (MC-LA-ICP-MS) range from +1 to +11 with the highest values in some mafic magmatic enclaves and the gabbros.

In a Variscan granite hosting an ‘intrusion related’ Au (-Ag-W) mineralization (Trun region, W Bulgaria) zircons and titanites are both U-rich. The zircons show common lead rich inclusions and lead loss that hamper age determinations. After applying the ‘chemical abrasion’ technique and the new double spike solutions of the Earth Time project they are dated at 352.57 ± 0.60 Ma by ID-TIMS. The late magmatic titanites yield concordia age of 334.1 ± 1.2 Ma. Both minerals reveal a trace and REE-distributions that are typical for a differentiated crustal dominated magma.

In the Cretaceous magmatic belt of Bulgaria, which hosts world-class Cu-(Au)-porphyry deposits the titanite can be used complementary to the zircon as geochronometer when its radiogenic lead/common lead ratio Pb*/Pb < 0.5.
Micromorphology and mineralogy of interbasaltic palaeosols at Giant’s Causeway, Northern Ireland

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Past Humid Tropical to Sub-Tropical Environment

Interbasaltic palaeosols formed from intensive chemical weathering of Tertiary basalts during a period of volcanic inactivity in Northern Ireland (NI) [1]. The composition and palaeolandscape of these palaeosols indicate that they formed in a humid tropical to sub-tropical environment [2].

Micromorphology and Mineralogy of the Palaeosols

Thin section and x-ray diffraction (XRD) analysis of palaeosols from Giant’s Causeway, NI revealed iron oxides (Fig. 1), hematite [Fe₂O₃] and magnetite [Fe₃O₄], in very red zones. Gibbsite [Al(OH)₃] and titanium oxides, anatase [TiO₂] and ilmenite [FeTiO₃], were also detected in these sections. Kaolinite [Al₂Si₂O₅(OH)₄] was detected by XRD throughout the soils, while tubular kaolinite (halloysite) was identified in more highly weathered zones. In some sections of the palaeosols, there are small segregated areas of iron oxides surrounded by green and grey zones (relic reduced conditions) which indicate past hydromorphic conditions.

Biogeochemical consequences of changes in root-derived carbon inputs to soil in a forest exposed to CO₂ enrichment

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The release of organic compounds to soil by plant roots strongly influences soil biogeochemistry by stimulating microbial activity, acidifying soil, complexing metals and promoting redox reactions. We sought to better understand the ecosystem consequences of changes in carbon (C) supply from roots to soil in a 28 year-old loblolly pine stand exposed to elevated atmospheric CO₂ (ambient + 200 ppm) and nitrogen fertilization (11 g m⁻² yr⁻¹) at the Duke Forest FACE site, NC. Over a two-year period, trees exposed to CO₂ enrichment increased the release of root exudates by ~50% in nutrient-poor soils, resulting in a doubling of microbial activity in the upper mineral soil (p < 0.05). Fumigated trees that received nitrogen (N) fertilizer did not exhibit any significant increases in exudation or microbial activity. We then sought to examine how changes in C supply may influence rhizosphere biogeochemistry by adding model root exudates to soil via artificial roots. Increases in C supply stimulated microbial respiration in all soils (p < 0.05), with the largest changes occurring in nutrient-poor soils. Moreover, increased C supply induced significant changes decreases in N and increases in P availability as a result of changes in microbial activity and to a lesser extent, changes in soil pH. Collectively, our results suggest that dynamic processes occurring at fine spatial scales (e.g. in the rhizosphere) may disproportionately influence biogeochemical responses to global environmental change.

Figure 1: Iron oxides in the matrix and as branched formations in voids. (scale: micrograph 500 µm wide)

Microbial selenium and iron reduction under high pressure

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The Earth’s subsurface is characterized by hostile conditions for life in terms of temperature, pressure and nutrient availability. Among the factors governing microbial dissimilatory metal reduction and thus carbon oxidation in the subsurface, pressure may have a broad impact on reaction rates and yields. The understanding of metal reduction in natural environments, especially in the subsurface, can be first comprehended thanks to studies of metal reduction in pure cultures.

We investigated the effects of pressure on the reduction of Se (IV) and Fe (III) to Se (0) and Fe (II), respectively by the bacterial model Shewanella oneidensis MR-1. This strain is a mesophilic and piezosensitive counterpart of psychrophilic and piezophilic Shewanella representatives that have often been isolated from deep-sea environments. Kinetics of Se (IV) and Fe (III) reduction were monitored in situ under high hydrostatic pressure by X-ray Absorption Spectroscopy (XAS) in an autoclave. Most measurements were performed at the BM30B beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Experiments were conducted from 0.1 MPa to 150 MPa at MR-1 optimal temperature of 30°C. The effects of pressure on cell survival were evaluated by comparing the Colony-Forming Units (CFU) before and after pressure incubations.

Metal reduction occurs in cultures of MR-1 at pressures in excess of 100 MPa. This shows that the metabolic activity of a microbe, despite being piezosensitive, extends far beyond its pressure limits for growth at 50 MPa. Consequently, considering only the ability to grow in the conditions of the deep subsurface as a proof of metabolic activity may lead to an underestimation of the impact of the biosphere in deep environments. Although the experimental conditions may not match exactly environmental subsurface conditions, we show here that the metabolic activity of a surface microbe potentially brought to the deep subsurface can affect significantly biogeochemical cycles such as those of selenium, but more importantly those of iron and carbon.

Effect of B/Al ratio on the dissolution of nepheline glass, Na3(Al, B)1-4Si4O16

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The dissolution kinetics of five glasses along the NaAlSiO4-NaBSiO4 join were used to evaluate how the structural variations associated with boron-aluminum substitution affect the rate of dissolution. The composition of each glass varied inversely in mol% of Al2O3 (5 to 25 mol%) and B2O3 (20 to 0 mol%) with Na2O (25 mol%) and SiO2 (50 mol%) making up the remaining amount, in every case Na/(Al+B) = 1.0. Single-Pass flow-through experiments (SPFT) were conducted under dilute conditions as a function of solution pH (from 7.0 to 12.0) and temperature (from 23° to 90°C).


Results from SPFT experiments suggest a forward dissolution rates, based on Na and Si release, for homogeneous glasses are independent of the B/Al ratio, whereas dissolution rates based on Al and B release are not. Normalized dissolution rates based on B release increase with the molar fraction of [3]B (ring).

Finally in accord with previous studies, these data suggest rupture of either the Al-O or Si-O bonds as the rate-limiting step controlling the dissolution of these glasses.
PGE distribution in the Aguablanca Ni-Cu sulfide deposit, Spain: Evidence from LA-ICP-MS

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The concentrations of PGE have been determined in magmatic sulfides (pyrrhotite, pentlandite and chalcopyrite) and hydrothermal pyrites from the Aguablanca Ni-Cu sulfide deposit (SW Spain) [1] by LA-ICP-MS at the University of Quebec, Chicoutimi, Canada. The whole-rock PGE contents, the PGE concentrations in the sulfides and the PGE mineralogy [1] suggest that the PGE distribution among the sulfides is primarily controlled by their partitioning behaviour during the fractional crystallization of a base metal sulfide liquid.

With the exception of Pt, all PGE have been identified in the sulfides. The PGE contents vary as a function of the sulfide host and the ore-type. Os, Ir, Ru and Rh are present in Po and Pn and are much more abundant in those sulfides of semi-massive ore than in those of disseminated and chalcopyrite-veined ores. Pd is, by far, the main PGE found in Pn (> 85% of the PGE in Pn) and is relatively more abundant in Pn of disseminated and chalcopyrite-veined ores than in that of semi-massive ore. These data are in agreement with the initial hypothesis that semi-massive ore represents a mss cumulate and has preferentially concentrated IPGE, whereas the disseminated ore represents an original, unfractinated sulfide liquid or a more evolved sulfide liquid [1]. Mass balance calculation indicates that IPGE mostly occur as solid solution in the exsolution products of mss (Po and Pn). Whole-rock analyses indicate Pd is incompatible with the semi-massive ore (mss cumulate) and concentrates in the Cu-rich ore (fractionated liquid). Surprisingly, it is not concentrated in Ccp, but rather in Pn. Pd contents in Pn from Sudbury and Noril’sk Ni-Cu deposits have been attributed to Pd diffusion into Pn from the surrounding sulfides during cooling [2]. At Aguablanca, since chalcopyrite veins are interpreted as a Cu- and Pd-rich fractionated sulfide liquid [1], this diffusion mechanism would explain the high Pd content of the Pn in this ore-type.


24Mg/26Mg Isotope fractionation in silicate minerals through first principles calculations

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Understanding the partitioning of Mg within planetary bodies can help to constrain their histories of accretion and differentiation. Mg is an abundant element and with its intermediate volatility should help in understanding the origin of the planet. Nevertheless the constraints on the Earth’s Mg isotope composition are still only poorly understood. Fractionation factors are also important in recognising open-system exchange of Mg isotopes in mantle rocks [1]. We have used first principles atomistic calculations to study the structure, dynamics and thermodynamic properties of the silicate minerals forsterite, enstatite and diopside. Advances in the calculation of free energies allow prediction of fractionation factors under conditions of thermodynamic control. Thus we have extended this study to the fractionation of 24Mg and 26Mg isotopes in silicate minerals as a function of temperature and pressure. Here we show orders of fractionation for 24Mg/26Mg of 0.05‰ between olivine (forsterite) and the orthopyroxene (enstatite) with fractionation slowly decreasing with pressure. As expected partitioning becomes negligible at very high temperatures. We have also explored the partitioning effects between orthopyroxenes and clinopyroxenes where we have seen that 26Mg/26Mg partitioning is slightly enhanced with an approximate fractionation of 0.1‰.

Source area processes and the regional distribution of orogenic gold deposits

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Orogenic gold deposits have provided over 25% of the World's gold, but our understanding of their formation is poor. Recent research in the Otago Schists of New Zealand has shown that the metals may be sourced from within the metamorphic rocks that host the ore deposits through leaching by metamorphic fluids produced during prograde devolatilisation. The ‘Otago model’ provides a fantastic opportunity to identify the controls on the regional and global distribution of orogenic gold deposits. The ‘Otago model’ has been tested in two different orogenic belts, the Dalradian metasedimentary belt in Scotland which represents a very poorly mineralised belt, and the Victorian goldfields, Australia which contains extremely abundant mineralization.

Results will indicate whether gold and associated metals are commonly mobilized during prograde metamorphism or whether specific hydrothermal and tectonic conditions are required. This has significant implications for the distribution of orogenic gold deposits and will elucidate the relative importance of factors such as tectonic setting, source-rock composition, timing of deformation and hydrothermal fluid flow, and efficiency of chemical and structural trapping mechanisms in the formation of large orogenic gold deposits.

Effect of physical reworking and bioturbation on sedimentary reactive iron within a microtidal estuary

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Iron redox cycling in surface sediments can enhance the remineralization of sedimentary organic carbon. In part this may occur because easily reducible iron oxides can be used by heterotrophic bacteria to remineralize the organic carbon. This phenomena has been observed in bioturbated sediments and in areas where physical factors (such as strong bottom currents) constantly rework the sediments. To specifically determine the effects of physical reworking and bioturbation on concentrations of easily reducible iron oxides, reactive iron concentrations were measured in surface sediments taken from two contrasting sites in the York River, a Chesapeake Bay tributary. Box core samples were collected between March 2007 and December 2007.

Operationally defined iron fractions as well as total iron concentrations were measured using chemical extraction methods. A selection of sediments were also further analyzed using X-ray diffraction (XRD) and Mössbauer Spectroscopy (MBR).

Concentrations of easily reducible iron oxides and total iron at the site experiencing physical reworking were higher than those at the bioturbated site. XRD analysis did not indicate the presence of iron oxides due to interferenceby the high concentrations of major mineral species such as quartz. Preliminary results from room temperature MBR indicate the presence of paramagnetic iron minerals with iron spectra patterns similar to those observed by van der Zee et al. [1] in Canadian boreal lake sediments. Further analysis of sediments at 4.2 K will be performed using MBR, a temperature at which crystalline iron oxides such as 2-line and 6-line ferrihydrite and nanogoethite become magnetized. MBR results will be compared with results from the chemical extraction sequence to better define the relationship between the concentration of iron in different chemical extracts and the concentrations of individual iron minerals determined by MBR.

Enhanced primary productivity in the aftermath of the rise of atmospheric oxygen
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Carbonates from ~2.3-2.1 Ga have markedly positive carbon isotope values, commonly reaching +10‰. If these values capture the primary composition of marine dissolved inorganic carbon, this event, referred to as the Lomagundi excursion, represents the most severe and long-lived perturbation of the Earth’s global carbon cycle and may reflect greatly enhanced organic carbon burial. Other researchers attribute these values to widespread methanogenesis within the sediments, possibly linked more broadly with Earth’s redox evolution. We have found that there is a narrow range of moderate $^{34}$S values from carbonate-associated sulfate (CAS) of Lomagundi age, which is inconsistent with carbonate formation in the methanic zone. Instead, CAS $^{34}$S values that closely match those from coeval sulfate evaporites suggest that the carbonates record primary seawater signals and that C-S isotope systematics can be used to track the global C and S cycles.

In the falling limb of the carbon isotope excursion there is an up-section increase in the $^{34}$S of CAS. We propose that this enigmatic relationship reflects a decrease in the extent of spatially widespread environments with nearly quantitative sulfate reduction. When sediment organic carbon loading was high, and therefore not limiting for bacterial sulfate reduction, H$_2$S production and burial would be expected to have little net effect on the $^{34}$S value of seawater sulfate. In this light, the inverse relationship between carbonate-C and CAS-S isotopes can be understood in terms of varying extents of sediment organic matter delivery. The Lomagundi excursion appears to be linked with high levels of sediment organic matter loading rather than methane-related overprints.

The oxidation state of magmas from melt inclusions and olivine hosts
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Debate continues on the extent to which the oxidation state of magmas reflects the oxidation state of the mantle vs. confounding processes in the crust, such as degassing, crystal fractionation or diffusive exchange. Part of the debate stems from complexities that plague one approach over another, or from measurements in degassed, evolved volcanic rocks. Here we circumvent both of these issues by examining several heterovalent elements in undegassed melt inclusions, with examples from pyroclastic samples from the Aleutian volcanic arc and Basin and Range. One method is based on the sulfur content of magmas at sulfide saturation [1], which increases exponentially as a function of $f_{O_2}$ due to the addition of sulfate species to the melt. Least degassed melt inclusions from both regions vary strongly in their sulfur content, from 1200 to 5000 ppm total sulfur, placing lower limits on $f_{O_2}$ of FMQ to FMQ+1.8, respectively. Total sulfur is a particularly robust measure of high-$f_{O_2}$, given that it is difficult to envision crustal processes that lead to increases in the sulfur content of a magma; it also avoids the artifacts associated with measuring sulfur species directly in glasses [2]. In the same samples, we have also measured the vanadium concentrations in the olivine population and melt inclusions or host basalts in order to calculate the ol/liq partition coefficient of V, which decreases strongly with increasing $f_{O_2}$ [3, 4]. The V-based estimates of $f_{O_2}$ are concordant with the sulfide saturation model, and also consistent with the high Fe$^{3+}$/Fe$_T$ (~ 30%) measured by micro-XANES [5] in the most sulfur-rich Aleutian melt inclusions. Within each dataset, $f_{O_2}$ correlates not with H$_2$O, but with La/Sm and other source features of the magmas. The concordancy of the different redox-sensitive species, the primitive nature of some of the melt inclusions (i.e., in Fe$_{86-90}$ olivines), and the correlation with incompatible trace element ratios all point to intrinsic variations in $f_{O_2}$ of the primary melts, and not late-stage modification.

Thermal analysis of organo-mineral complexes with increasing carbon loadings

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Thermal analysis techniques (i.e., thermogravimetry (TG) and differential scanning calorimetry (DSC)) have recently been proposed as rapid methods to assess the quality continuum of soil organic matter. An experiment was designed to test the hypothesis that the energy density (J mg⁻¹ OM) of organo-mineral complexes changes as carbon loading (mg C m⁻² mineral surface area) increases.

Methods

Surface soil samples were collected from a long-term manure addition experiment located at Lethbridge, AB Canada. Soils were dispersed and sieved to isolate a fraction consisting of silt- and clay-sized organo-mineral complexes. Total organic carbon concentrations and mineral specific surface area were determined, and used to calculate carbon loading (mg C m⁻²).

Using a Netzch instrument, organo-mineral complexes were heated from 25 to 700 °C at a rate of 10 °C min⁻¹. Energy content of the organic matter was determined using the area of the DSC peak in the exothermic region (180-600 °C). Energy density (J mg⁻¹ OM) was calculated by dividing the energy content (J) by TG mass loss (mg) over the same temperature range.

<table>
<thead>
<tr>
<th>Manure addition rate (Mg ha⁻¹ yr⁻¹)</th>
<th>Carbon loading (mg C m⁻²)</th>
<th>Energy Density (mg C m⁻²)</th>
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<tbody>
<tr>
<td>0</td>
<td>1.29 ± 0.47</td>
<td>9.52 ± 0.53</td>
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<td>60</td>
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<tr>
<td>180</td>
<td>7.46 ± 1.39</td>
<td>16.04 ± 0.09</td>
</tr>
</tbody>
</table>

Table 1: Carbon loadings and energy densities of organo-mineral complexes.

Discussion of Results

Results indicate that increasing manure addition rates increased carbon loadings of organo-mineral complexes. Thermal analyses show that energy density was correlated with carbon loading, suggesting that decomposability may increase as soils approach their protective capacity.
The molecular characterization of dissolved organic nitrogen by APPI FT-ICR MS

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Previous mass spectrometry studies of dissolved organic matter (DOM) have largely focused on the refractory carbon component [1, 2]. Dissolved organic nitrogen (DON) is largely uncharacterized at the molecular level, likely due to the inefficiency with which nitrogen species ionize in complex DOM mixtures. Water Quality Treatment Areas treat agricultural runoff and are often engineered specifically to reduce total nitrogen levels. Currently, the only parameter available to determine the effectiveness of WQTAs is total DON, which does not account for differences in the biogeochemistry of individual organic nitrogen compounds.

Tandem mass spectrometry has identified common fragments in DOM [3]. Here, we report the isolation and fragmentation of nitrogen-containing DOM ions of a single mass-to-charge ratio to elucidate structural information.

Atmospheric Pressure PhotoIonization (APPI) has advantages for FT-ICR MS characterization of dissolved organic matter (DOM) because, unlike electrospray ionization, APPI ionizes both polar and nonpolar compounds simultaneously. In this study, we were able to efficiently ionize N-containing DOM species that contain nitrogen with APPI.

Due to the efficiency of APPI to ionize N-containing DOM compounds, we were able to isolate DON ions of a single mass-to-charge ratio and fragment by infrared multiphoton dissociation. The results show neutral losses (e.g. H2O and CO2) similar to those from dissociation of CnHmOq species. We did not observe the loss of N-containing constituents, an indication that nitrogen may be incorporated into ring structures. Work supported by NSF DMR-06-54118, OCE-07-26754, EAR-08-19811 and the State of Florida.


Mercury stable isotopes fractionation in cryogenically archived specimens from the Arctic marine environment

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Mercury impacts are enhanced at high latitudes with record concentration levels in Arctic marine wildlife [1], posing a health risk for northern people who consume these subsistence resources [2]. Whereas a cascade of processes might ultimately link atmospheric Hg emissions to Hg concentrations in Arctic biota, the different temporal trend series in the Western and Eastern Arctic sectors [3] suggest that other factors may be underpinning these trends. To study these questions, we explored Hg mass dependent fractionation (MDF) and mass independent fractionation (MIF) signatures in marine mammal liver sample collections archived at the US Marine Environmental Specimen Bank. These samples were collected as part of the Arctic Marine Mammal Tissue Archival Project (AMMTAP) initiated in 1987. Mercury stable isotope measurements were conducted in beluga whale (Delphinapterus leucas), ringed seal (Phoca hispida) and polar bear (Ursus maritimus) liver samples collected over several years in different Alaskan regions.

Preliminary results in beluga whale showed that Alaskan Arctic and sub-Arctic regions were characterized by unique Hg MIF signatures, confirming earlier results obtained in seabird eggs collected in the same regions [4]. These results suggest that Hg-MIF may be used as a robust geographical tracer for describing habitat utilization and food webs connectivity. Significant variations in Hg MDF and MIF existed between species and between individuals at the colony, group or stock level. Since Hg concentrations and speciation in marine mammal livers tend to be influenced by several ecological factors and species-specific metabolic processes, we investigated the influence of these factors on Hg MDF and MIF variations.

Ilmenite ultrabasite UV162/09: The role of deep metasomatism in the rock formation

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Ilmenite ultrabasite from the Udachnaya pipe (Yakutia) was studied with the help of a scanning electron microscope. The following mineral phases have been found and analyzed: olivine, ilmenite, orthopyroxene, phlogopite, garnet, clinopyroxene, sodalite, calcite, jerfis herite, hematite, spinel. The first five minerals are the rock forming minerals. The following mineral phases have been found and analyzed: ilmenite, phlogopite, garnet, clinopyroxene, sodalite, calcite, jerfis herite, sodalite, hematite, spinel.

The role of deep metasomatism in the evolution of composition of the Siberian craton lithosphere roots: Evidences from the Udachnaya xenoliths

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Udachnaya kimberlite pipe contains a unique complex of upper mantle xenoliths including practically all known types of the lithospheric mantle rocks [1]. The most deep-seated xenoliths representing lithosphere roots and carrying clear signs of secondary enrichment up to changes of initial mineral parageneses are of special interest [2, 3].

We studied a series of mantle peridotites from the depth a diamond stability field: a) megacrystalline Cr-pyrope harzburgites and dunites including diamondiferous varieties; b) initially extremely depleted peridotites carrying clear signs of secondary enrichment up to changes of initial mineral parageneses; c) fresh sheared Cr-pyrope lherzolites.

Obtained results show that ultra depleted peridotites including their diamondiferous varieties were secondary enriched in different scale by metasomatic agents having geochemical features close to carbonatic melts. This caused enrichment in LREE and Ca, and in rare xenoliths up to appearance of CPX prohibited in initial rock. Enrichment of initial ultra depleted peridotites by basanitic components was fixed in rare samples, and obviously this process was synchronous to the protokimberlite melts generation.

Sheared pyrope peridotites have a complex character of a composition evolution. Initially these rocks were depleted as a result of extraction from them melts of high degree of partial melting. Then depleted rocks were enriched by agent with high content of incompatible elements (probably carbonatic melts) that caused significant increase of La/Yb ratio. And finally these rocks were intensively enriched by basanitic components, and their initial composition and geochemical features were significantly changed. Processes of deformation textures formation, secondary basanitic enrichment and generation of protokimberlitic melts were synchronous and an effect of the same reasons.

**Geodynamic evolution of the Mesoarchean Fiskenæsset anorthosite complex, SW Greenland**

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The Mesoarchean Fiskenæsset Complex, southern West Greenland, consists of an association of ca. 550-meter-thick layered anorthosite, leucogabbro, gabbro, and ultramafic rocks. The complex was intruded by tonalite, trondhjemite, and granodiorite (TTG) sheets (now orthogneisses) during thrusting that was followed by several phases of isoclinal folding. Despite polyphase deformation and amphibolite to granulite facies metamorphism, primary cumulate textures and igneous layering are well preserved throughout the complex. Trace element abundances of the Fiskenæsset Complex and associated volcanic rocks are consistent with a supra-subduction zone geodynamic setting.

The Fiskenæsset anorthosites, leucogabbros, gabbros and ultramafic rocks yield a Sm-Nd isochron age of 2973±28 Ma (MSWD=33), with an initial εNd = +3.3, consistent with a long-term depleted mantle source. Regression of Pb isotope data defines an age of 2945±36 Ma (MSWD=44); and the regression line intersects the average growth curve at 3036 Ma.

Complex internal structures in zircon from TTGs reveal several episodes of zircon growth and recrystallization between ca. 3200 and 2650 Ma. Zircon ages peak at about 3200, 3100, 3000, 2950, 2820, and 2750 Ma. The 3200-3000 Ma zircon cores are interpreted as inherited xenocrysts from older reworked crustal rocks. The 2950 Ma is considered as an approximate intrusion age of TTGs. The 2940-2650 Ma ages are attributed to metamorphic overgrowth and recrystallization in response to multiple tectono-thermal events that affected the Fiskenæsset region.

On the basis of recently published trace element data, and new Nd and Pb isotope and U-Pb zircon age data, a three-stage geodynamic model is proposed to explain the evolution of the Fiskenæsset Complex. Stage 1 represents the formation of depleted shallow mantle source > 3000 Ma (εNd = +3.3) for the complex. Stage 2 corresponds to the development of an intra-oceanic island arc between 3000-2950 Ma. Stage 3 is characterized by the collision of the island arc with either a passive continental margin or with an older arc between 2950-2940 Ma.

**Evolving conditions of quartz cementation: In situ microanalysis of δ18O across single overgrowths**

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Stable isotope ratios of the basal Cambrian Mt. Simon sandstone in the Illinois basin have been analyzed in situ and reveal information about the evolving chemical and thermal conditions of post-depositional mineral growth and thus of porosity and permeability. Recent studies show a correlation of depth of burial and δ18O in quartz cements from samples that have been buried as deeply as 4000 m [1], but little variability in cements from near surface samples [1-3]. While basin-wide trends may provide information about broad-scale processes such as burial history or fluid migration, the variability of δ18O in single overgrowths has not been studied previously.

Traverses across individual syntaxial quartz overgrowths were analyzed for δ18O using 10 µm and 3 µm spots on an IMS-1280 ion microprobe. δ18O zonation was measured in 71 individual overgrowths from 17 rocks. The variability within a given 100 µm overgrowth is up to 10.4‰; most samples decrease in δ18O with continuing growth. Deeper samples have larger gradients and have wider ranges of δ18O values (δ18O=15-25‰ VSMOW) than more shallowly buried samples (δ18O=20-25‰). The fine-scale zonation measured within single overgrowths yields information about how conditions changed and also the relative timescales over which these changes occurred. Because direct measurements of age and growth rate are not possible in quartz, we examine changes in δ18O of quartz with normalized distance in the overgrowth. The slope of these curves of δ18O versus distance allows estimation of the relative durations of varying quartz forming conditions. Assuming a fluid-dominated system with δ18O (H2O)=1.5‰, equilibrium calculations indicate that cements grew from 80-150°C at depths of ~4000 m, consistent with published [4] temperatures from fluid inclusions and vitrinite reflectance in the Illinois Basin.

**Theoretical investigation of the solvated corundum surface**

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For the reliable long-term modelling of the actinide migration in geological formations, the adsorption/desorption properties and the reactivity of mineral surfaces must be understood at the molecular level. The adsorption of contaminants at mineral surfaces of the aquifer is an important process which leads to the retention/retardation of radio nuclides such as actinide ions. Methods of theoretical chemistry developed to reliable tools in recent years and are of great help to improve the understanding of experimental results and provide data experimental not accessible.

Here we present two completely independent theoretical approaches for this task. In our first approach we used Al$_{17}$O$_{33}$H$_{10}$ or Al$_{31}$O$_{60}$H$_{21}$ clusters as model systems for the corundum (110) and (001) surfaces, respectively. We found, that calculations on these clusters with Density Functional Theory (DFT) using the BP86 functional and the cc-pVDZ basis set provide accurate results in good agreement with ab initio methods. Experimental results at the INE (vibrational Sum Frequency Spectroscopy Generation and Time Dependent Laser Induced Fluorescence) and others (Crystal Truncation Rod Diffraction) experiments are reproduced very well by our calculations.

(1) The determination of the orientation and vibrational frequencies of the alumino groups (Al-OH) at the corundum (001) and (110) surface.

(2) The interaction of bulk water with the surface. We study the accuracy of the model concerning the interlayer spacing between the first water layer to the corundum (0001) surface as well as the vibrational frequencies of the alumino groups.

(3) Inner sphere complexes of trivalent lanthanide and actinide ions on the (001) surface. This is studied with the clusters mentioned above and, additionally, with Al$_{17}$O$_{33}$ (OH)$_{18}$ (H$_2$O)$_{12}$ Keggin clusters as a model system for the (001) surface.

In an independent completely different theoretical approach, we use the plane-wave, supercell density functional theory (DFT) framework as implemented in the Vienna ab initio simulation package (VASP) to study the solvated corundum surface. The Perdew-Burke-Ernzerhof (PBE) functional is used together with the projector augmented wave (PAW) ansatz.

With this ansatz we study the surface alumino groups (bond length, tilt angle) as well as their vibrational frequencies. These calculations complement the theoretical information already available from the cluster calculations.

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**Endolithic habitats in shocked gneisses from Haughton impact structure, Devon Island, Canada**

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Meteorite impacts are rarely thought of as agents promoting microbial growth: generating extreme temperatures and pressures, an impact may cause the target substrate to undergo deformation, vaporization, melting and shock metamorphism. These processes, however, can favourably change the availability and habitability of the substrate for lithophytic organisms, which are then able to (re)colonize microfractures and pore spaces created during the impact [1]. This study shows how shocked gneisses from the 39 Ma, 23 km diameter Haughton structure, Devon Island, Canada, offer significant refuge for lithophytic communities.

Macroscopic observations highlight an increase in the spatial distribution of the endolithic communities with shock level, up to approximately 50 GPa. As gneiss undergoes shock-metamorphism, porosity levels increase, as does the translucence of the rock [2]. These changes increase available surface area and allow in greater levels of photosynthetically active radiation (PAR), while simultaneously acting as a buffer against environmental stressors such as temperature, ablation and ultraviolet radiation. At shock levels greater than 50 GPa, subsequent growth decreases, correlating with the collapse of pore spaces and the creation of glass flows under such high pressures. Similarly, at low shock levels (< 20 GPa), porosity is low, restricting growth to near surface environments. Examination of these endolithic mm-scale habitats using scanning electron microscope has highlighted the presence of a diverse community of microorganisms, including fungi, and organic coatings on mineral surfaces including evidence for bacterial growth as microcolonies. Culturing aerobic, heterotrophic bacteria using contact plates with R2A agar produced limited growth but highlighted the endolithic habitat as the dominant heterotrophic zone within the ecosystem. The increase in porosity created by this shock event appears to have created ideal physical and chemical endolithic habitats, where space and trace nutrients via weathering of glass, respectively, has enhanced the growth of microorganisms.

**Mineralogical and trace element characteristics of noble gas carrier phases of interplanetary dust particles and impact debris in a Central Pacific sediment core**

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We examine mineralogy, trace element and noble gas chemistry of deep ocean sediments from LL-44 GPC-3 including Cretaceous/Tertiary (K/T) and Eocene/Oligocene (E/O) boundaries. Bulk sediment and magnetic isolate extractions were analyzed by noble gas-MS, SEM, and cryogenic LA-ICP-MS (CLA-ICP-MS). Noble gas analysis reveals ET He and Ne throughout the entire sampling interval. $^{3}$He/$^{4}$He ratios of $3.1 \times 10^{-4}$ and $^{22}$Ne/$^{21}$Ne ratios of 9.96-12.62 are consistent with the SEP signatures in c. Pacific zero-age magnetic grains and stratospheric IDPs. Magnetic extracts typically constitute <1% of the bulk sample while accounting for 3-10% of total $^{3}$He. The magnetic isolates reveal no significant differences of $^{3}$He/$^{4}$He, $^{22}$Ne/$^{21}$Ne, or $(^{3}$He/$^{22}$Ne)$_{air}$ from bulk GPC-3 sediments or Z-MAG grains. SEM and CLA-ICP-MS analysis determine the mineralogy and trace element signatures of the magnetic isolates respectively, to distinguish between the carrier phases of the continuous flux of IDPs and the flux associated with major impact events. SEM reveals stark contrasts in composition and morphology of (K/T) and (E/O) boundary samples. It remains unclear if these grains are capable of retaining ET noble gases, but do provide a resilient method of locating impact boundaries in deep ocean sediments. Identifiable ET grains are not observed in a survey of “background” samples leading to a less certain mode for the mineralogical carrier phase of the continual flux of IDPs. We report trace element and mineralogical markers for individual grains, magnetic and bulk separates, which provide insights into the carrier phases of ET noble gas from the continuous flux of IDPs in non-impact boundary related samples.

**Aromatic carboxylic acids are anaerobically transformed in Guaymas basin sediments**

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Guaymas Basin in the Gulf of California is a geologically active region characterized by thick layers of sediment, through which hydrothermal fluids percolate and pyrolyze organic material to form petroleum hydrocarbons. We hypothesize that natural in situ exposure will enable enrichment of microorganisms from Guaymas Basin sediments that are able to degrade hydrocarbons, such as naphthalene, under sulfate-reducing conditions. Hydrocarbon-laden sediments were sampled from 2000 m below the sea surface and were used as inocula to establish anaerobic sulfate-reducing enrichments. While there was little sulfate loss in cultures amended with naphthalene, there was activity in cultures supplemented with an anaerobic metabolite of naphthalene in the form of 2-naphthoic acid. There was significant sulfate loss in active cultures incubated at 30°C as compared to unamended background controls, but sulfate disappearance occurred more rapidly in cultures incubated 60°C. Disappearance continued over several transfers and amendments with new substrate.

DNA was extracted from both frozen, unenriched sediment samples and active cultures, and then probed for functional genes. A clone library was produced from unenriched sediment for dissimilatory sulfite reductase genes (dsrAB), and is being compared to those sequences obtained from active cultures. Cultures were also screened for benzylsuccinate synthase (bssA), a gene involved in the anaerobic degradation pathway of many hydrocarbons. Primers were used to amplify DNA from 2-naphthoic acid-degrading cultures incubated at 30°C, and the resulting product had sequence similarity to the related gene naphthylmethylsuccinate synthase (nmsA). Primers that target nmsA are being used to screen DNA extracts from active enrichment cultures. Further analysis, including nucleotide sequence analysis of clones from active cultures, as well as HPLC measurements of 2-naphthoic acid and sulfate concentrations, can support that the reduction of sulfate coincides with the disappearance of substrate.
River/groundwater mixing study using major and trace elements

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As a part of a hydrogeochemical study of the watershed of the Var River (southeastern France), we focused on groundwaters on the downstream alluvial area providing tools for water management. This resource concerns more than 600,000 inhabitants of the Côte d’Azur.

In order to detect and estimate proportions of water mixing, we use a simple graphical method to plot in a same diagram several major and trace elements. For a single mixing of two components, concentrations ratios of conservative elements fit along a linear plot in a C1/C3 vs. C2/C3 diagram where Ci is the concentration in the component i, #1 and 2 are the origin waters and #3 is the mixture. The intercepts with X and Y-axis give proportions of mixing. By using both major and trace elements, we generally obtain a more precise linear regression than with major data only, because of higher variations of trace elements concentrations. On the given example, Cs and As do not fit at all, suggesting their non-conservative behavior. Very low Pb level induces analytical problems, which can explain its shift from the linear plot.

![Figure 1](image)

Figure 1: Plot of concentration ratios to study the local infiltration of the Var River into the alluvial aquifer.

This method (i) allows to elucidate recharge processes of the alluvial reservoir from the river or a deeper aquifer when concentrations did not give enough information to define the origin and (ii) gives an example of useful utilization of trace elements in groundwater studies.

Lead isotope variations and tectonic terranes in southern Mexico

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New TIMS (Thermal Ionization Mass Spectrometry) Pb isotope analyses of various crustal units and ores from distinct subterranes of the Guerrero terrane are presented in order to trace metal sources in these deposits and infer source reservoirs. Lead isotope data for ores and the associated igneous rocks from deposits located in the Sierra Madre terrane are also presented to examine whether ore metal sources differ among the proposed tectonostratigraphic exotic terranes of Mexico.

Ores from La Verde and La Esmeralda porphyry copper deposits (Guerrero terrane) yield isotopic ratios between 18.678 and 18.723 for 206Pb/204Pb, 15.569 and 15.618 for 207Pb/204Pb, and 38.423 and 38.602 for 208Pb/204Pb, defining a narrow field just below the average Pb crust evolution curve of Stacey and Kramers [1]. Minerals from Zimapan and La Negra skarn mines (Sierra Madre terrane) yield values varying from 18.775 to 18.975 for 206Pb/204Pb, 15.593 to 15.844 for 207Pb/204Pb, and 38.553 to 39.404 for 208Pb/204Pb, plotting above the Stacey-Kramers reference line. The current and previously published [2, 3, 4] data support the hypothesis that subducted crustal material, which might represent pelagic sediment, supplied substantial amounts of Pb to porphyry copper deposits situated in the Zihuatanejo-Huetamo subterrane. The trend is not similar for epithermal deposits situated further inland (Teloloapan and Zacatecas subterranes), where ores show higher radiogenenity; this pattern is compatible with assimilation of radiogenic compositions of Mesozoic metamorphic rocks of the Guerrero terrane by magmas derived from a MORB-type mantle. Comparison between the isotopic signatures of ores from the Sierra Madre terrane and distinct subterranes of the Guerrero terrane supports the idea that there is no direct correlation between the distinct suspect terranes of Mexico and the isotopic signatures of the associated ores. Rather, these Pb isotope patterns are interpreted to reflect increasing crustal contribution to mantle-derived magmas as the arc advanced onto a progressively thicker continental crust toward the east.

Hillslopes are considered asymmetric when one side of a hill or drainage is steeper than the other. In the absence of lithologic and structural controls, differences in slope angles may be due to the influence of insolation-induced microclimates on rates and processes of weathering, soil formation, and hillslope erosion. This appears to promote steeper southern aspects in some areas [1], but steeper northern aspects in others [2]. Despite being studied for more than a century [3], we have been unable to explain the processes responsible for microclimate-induced slope asymmetry.

We hypothesize that in the absence of tectonic and lithologic controls, hillslope asymmetry varies spatially due to climatically-driven feedbacks among insolation, evapotranspiration, soil moisture, vegetation, weathering, erosion, and slope stability. To better understand this spatial variability, we systematically map the distribution of asymmetry across the western U.S.. The asymmetry within a given area is quantified by an asymmetry index, which is the log-transformed ratio of average slope angles for northern and southern aspects. Hillslope asymmetry has significant spatial variability throughout the mountain West, but manifests itself within distinct regions with clearly defined transitions.

While a map at this scale is critical for studying the distribution of asymmetry, more information is needed to separate microclimate from tectonic and structural controls. To isolate the influence of microclimate, we select study areas within the tectonically quiescent and mostly homogenous granite Idaho Batholith. Dry Creek watershed, in the southwestern batholith, has northern aspects which are ~8° steeper than southern aspects. The watershed receives ~50-90 cm of annual precipitation, and has ~80% forest cover on northern aspects, but only ~15% forest cover on southern aspects. Alternatively, the Lochsa River watershed in the northern batholith displays no asymmetry, receives ~75-180 cm of precipitation annually, and has nearly homogenous forest cover, despite similar variations in insolation. In the absence of tectonic and lithologic controls, hillslope asymmetry appears to occur in semi-arid areas along ecotonal boundaries, where vegetation is sensitive to microclimate.

Modeling actinide interactions with minerals and microbes

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Actinide geochemistry is extremely complicated primarily due to the presence of multiple oxidation states, and actinides’ varying tendency to form ligand complexes, sorb to sediments, and precipitate from solution. This work describes ongoing efforts to develop simplified models of actinide interactions with environmentally relevant surfaces such as mineral and microbial surfaces. Our goal is to capture the inherent complexity of actinide interfacial reactions in simplified thermochromically based models which can be easily incorporated into speciation and transport calculations.

Previous work has demonstrated that redox sensitive actinides like Pu undergo surface mediated reduction from the highly mobile pentavalent state to the relatively immobile tetravalent states [1, 2]. Modeling these interfacial processes requires consideration of redox chemistry, surface complexation, and ion exchange processes. This has been demonstrated through modeling studies of Np (V) and Pu (V) sorption to montmorillonite and metal oxides. Further experiments examining Pu sorption in the presence of dissolved organic ligands indicate that highly functionalized ligands such as citric acid and humic acid may increase sorption of Pu relative to a binary (Pu-mineral) system. To aid ligands such as citric acid and humic acid may increase a discrete pKa model of Pu binding with humic acid has been developed.

Recent experiments indicate that similar reduction of Pu (V) may occur in the presence of microorganisms. Sorption of Np (V) to Pseudomonas putida cells increased with increasing pH and was quantified using the discrete pKa, ligand binding approach described previously [3]. However, similar sorption trends between initially Pu (V) and Np (V) systems were not observed. Sequential filtration steps (200-nm followed by 4-nm filtration) indicate that sorption of Pu is drastically influenced by exuded organic ligands. Reduction of Pu (V) to Pu (IV) is inferred from this behavior.


Modern thrombolites from an asbestos open pit pond

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Modern thrombolites were discovered in an open pit pond at an abandoned asbestos mine near Clinton Creek, Yukon, Canada. These thrombolites are extremely young given that they presumably began forming soon after the mine closed in 1978. Detailed characterization of the periphyton and thrombolites using light and scanning electron microscopy (SEM) were coupled with mineralogical and isotopic analyses. The thrombolites have a columnar morphology (cm-scale), internal clotted fabric (mm-scale), and are almost entirely made of aragonite, which is supersaturated in the sub-saline pond water. The maximum accretion rate was determined to be ~5.2 mm per year. Initial precipitation is seen as acicular crystals nucleating onto microbial biomass and detrital particles. Continued precipitation entombs benthic diatom species (e.g. Brachysira vitrea) that are particularly abundant and well preserved, but also filamentous algae (e.g. Oedogonium sp.) and dinoflagellates are easily recognizable. Acid-etching to expose biomass followed by traditional preparation for examination of microbes using SEM was particularly effective for imaging cyanobacteria trapped in the aragonite. The presence of phototrophic microbes at clot centers strongly suggests that these microbes play an important role in aragonite precipitation and thrombolite formation. Clots continue to grow abiotically through periodic precipitation of aragonite that forms concentric laminations around clot centres. Pauses in clot growth allow for re-colonization of the clot surface by microbes. Aragonite more closely associated with microbial biomass has an average $\delta^{13}C$ composition of -4.6% or 0.8‰ enriched relative to milky white aragonite that has no microbial biomass (-5.4‰), suggesting a modest removal of isotopically light dissolved inorganic carbon by phototrophs. The low sedimentation rate, high calcification rate, and noticeably low microbial growth rate appear to result in the formation of microbialites with a thrombolitic texture. The formation of thrombolites in a mining environment demonstrates that an anthropogenically formed environment can foster microbialite formation.
uranium accumulation in the plants of the old mine of sevilha (central portugal)

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the old uranium (u) mine of sevilha (tábuas, central portugal) is one of several small mines exploited by portuguese uranium company. we decided to evaluate the u accumulation potential of the endemic species. samples of soil, water and terrestrial and aquatic plants were collected in the vicinities of the study area. the plant survey did not follow a regular pattern to take into account the dispersion of the species and to sample all the units of the plant community. it was intended to obtain a global view of the response of the vegetation to the accumulation of u. this implied sample collection in the biogeochemical background and within the anomaly. as a result 82 different species we identified and sampled. these species belong to 32 families, five of which are aquatic. all samples were processed at the chemistry laboratory of the earth sciences department of university of coimbra. for determination of mass concentration of u in samples of natural water, soils and plants, it was used the ‘fluorat-02-2m’ analyzer.

current u soil contamination on the sevilha mine ranges from 8 to 560 ppm. in the most abundant families of terrestrial plants, the results show that the compositae and ericaceae families have the highest concentrations. for the compositae, an average of 4.91 ppm and a maximum of 13.12 ppm was found in helchrysum stoechas and an average of 4.07 ppm and a maximum of 10.52 ppm was recorded in hypochaeris radicata. in erica umbellata an average of 1.70 ppm and a maximum of 7.50 ppm maximum were obtained. even though the concentrations obtained in this later species are not high it is particularly interesting because it has a high bio-productivity. the water contamination in the vicinities of sevilha mine results from the natural lixiviation of the wastes used to fill the open pit. although the u concentrations in waters did not surpass 13 ppb (epa limit: 30ppb). four of the analysed aquatic species proved to be u accumulators. the measured average concentrations were: riccia fluitans (29.19 ppm), lemma minor (15.47 ppm), callitriche stagnalis (9.97 ppm) and lythrum portula (15.52 ppm). for these species, the observed maximum values were 50.59 ppm, 52.98 ppm, 55.53 ppm and 32.93 ppm, respectively.

molecular quasi-chemical theory applied to liquid water

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we implement and test a molecular quasi-chemical theory of liquid water. the quasi-chemical perspective is that several physically transparent contributions are involved in a sensitive balance. network-liquid contributions are precisely defined, and long-ranged interactions are characterized by a conditional distribution of binding energies. for simulated liquid water network-liquid contributions are small (even zero), and the free energy is dominated by long-ranged interactions. the binding-energy distributions for liquid water are observed to be unimodal, and a gaussian model can be accurate. a broad distribution of interactions remains as the essential difficulty of the molecular theory liquid water.
Seeking signs of Martian life and caching samples for potential return to Earth

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If life emerged and flourished on Mars then recognizable textural and chemical evidence likely can be recovered from fine-grained clastic or well-cemented chemical sedimentary units known to be exposed at the surface. The presence of rhythmic depositional systems were sensitive to climate change, increasing the inventory of sedimentary and diagenetic materials available for sampling along an exploration transect. Building on the technical and operational heritage of Spirit and Opportunity, a mission is proposed for a new generation of Mars rover capable of exploring, sampling, and caching a diverse suite of rocks from outcrops [1]. The name Mars Astrobiology Explorer-Cacher (MAX-C) reflects the dual purpose of conducting in situ science and making concrete steps towards the future return of samples to Earth. MAX-C would enable scientists to evaluate paleo-environmental conditions, to characterize the potential for preservation of physical and chemical biosignatures, and to examine multiple sequences of geological units in a carefully orchestrated search for evidence of past life and/or prebiotic chemistry. It is critical that samples addressing the life questions be taken from strata crosscut or bounded by datable igneous units so as to constrain the timing of tectonic, magmatic, and climatic processes evolving in tandem with putative biogeochemical cycles.

High-fidelity contextual interpretation of data from MAX-C relies on integration of meter to submillimeter texture (optical imaging), mineral identification, and major element content with possible supplementation by organic carbon detection. Arm-mounted instruments are the means to investigate abraded rock surfaces using co-registered 2-D maps of visual texture, mineralogy and geochemical properties. If microbial life was manifest at some time on Mars then evidence at sub-millimeter scales is highly desirable to facilitate complex decisions related to sample acquisition, encapsulation, and caching. Ultimately, a cache could be placed on the ground or retained on the rover for recovery by a possible future sample return mission.


Molecular simulations of electrokinetic phenomena at the solid-liquid interface

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In the last 10 years we have been studying by molecular dynamics (MD) the structural and dynamic properties of aqueous solutions in contact with metal-oxide surfaces, mainly rutile [1-3]. We will present the results of our equilibrium and non-equilibrium MD simulations focusing on the molecular level origin of electrokinetic phenomena - electroosmosis and electrophoresis. We will comment on the asymmetry of the density profiles of cations and anions at positive and negative surfaces, discuss the properties of the diffuse and shear layers, if definable at all on the molecular scale, and present our zeta potential predictions from molecular simulations. Our results of zeta potential are in qualitative agreement with experimental data [5]. However, our molecular explanation is rather contradictory to at least some of the commonly used theories of the solid-liquid interface including the common double- or triple-layer models. We observe that the composition and structure at the interface, influenced by the surface charge, are the key factors, while the electrostatics of the aqueous solution is rather independent of the surface charge.

This debate is an important step in validating/challenging the theories of the solid-liquid interface and making as close link as possible between molecular simulations and experiments, which will ultimately lead to a deeper understanding of the solid-liquid interface.

A nested watershed study of streamflow, suspended sediment, and contaminant sources in the urbanized Coastal Plain

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The fate of trace metals (Pb, Zn, Cd, Cu,) that are introduced as airborne contaminants into watershed systems depends upon the pathways that water takes from precipitation to stream channels, sediment mobilization and deposition, and changes in pH, biogeochemical processes and redox state that affect the partitioning of metals from solutes to sediment. We examined these processes in an urban-suburban watershed. We monitored stream flow, conductivity, pH, and turbidity in a nested watershed design (5 sampling locations, ranging from 10-150 km²) in the urbanized Anacostia River Watershed. Electrical conductivity was used as a continuous tracer to separate hydrographs into new and old water sources. Suspended sediment was sampled during storm events along with measurements of flow velocity and shear velocity that are used to define transport conditions. Suspended sediment samples were used to convert continuous turbidity measurements into suspended sediment loads. Samples of water and sediment collected during storms were filtered in the field and analyzed for trace, minor, and major element composition by ICP-MS.

The hydrograph separation results indicate that the upper tributaries generated new water in excess of the amount of impervious surface, and trace metals are transported both as solutes and on sediment. Sediment fingerprinting analysis indicates upper tributaries receive sediment from both surface erosion and bank erosion. Suspended sediment concentrations are significantly higher in the tributaries than at the river mouth. At the mouth, total new water runoff was lower than in the tributaries although impervious cover was greater. Suspended sediment sources change from street sediment sources to bank erosion over the duration of a storm. Sediment contamination with trace metals is highest at the mouth and trace metals are transported with the sediment, not in the aqueous phase due to the high pH (7-9) of urban runoff conveyed in cement-lined channels to the lower watershed.

An infrared study of modern and paleo-filamentous bacteria from Rio Tinto, Spain

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The Rio Tinto River Basin in southwestern Spain is a natural acidic (pH ~2.3) drainage system that supports a diversity of acid tolerant bacteria and eukaryotes with iron- and sulfur-oxidizing prokaryotes performing chemolithotrophy and supporting anaerobic respiration [1, 2]. River terrace deposits formed over the past 2 Myr have preserved remnants of this unique biosphere, particularly microbial filaments, which provide templates for iron sulfate and iron oxide precipitation [1, 2]. This process of permineralization causes organic material to become trapped within a mineral matrix and preserved over geological time.

This study analysed cultured filamentous bacteria, modern biofilms and sediments, and river terrace deposits spanning 2.1 Myr to assess the preservation of organics in this extreme environment over time, and the ability to correlate them with a contemporary culture.

Filamentous bacteria are preserved within optically translucent nanophase to crystalline jarosite and goethite within all samples. The cultures contained 1 µm diameter filaments, some partially encrusted with iron oxides with visible cell walls, and others completely free of iron oxides, that are morphologically comparable to those preserved in the Rio Tinto rock record. Organic compounds (e.g. aliphatic hydrocarbons, amides and carboxylic acids) were detected at various levels within the culture and river terraces using mid-IR spectroscopy.

Rio Tinto is a natural laboratory allowing living cells to be studied and correlated to morphological and biomolecular fossils in the geological record. These deposits will provide predictive tools for biomarker studies that may be extended to analogous environments on ancient Earth or even Mars.

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Dawn’s GRaND to map the chemical composition of asteroids Vesta and Ceres

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The NASA Dawn spacecraft is approaching the main asteroid belt, where it will acquire data needed to understand processes underlying the formation and evolution of the terrestrial planets [1]. Using ion propulsion, Dawn will explore asteroid 4 Vesta, arriving in 2011, followed by the dwarf planet 1 Ceres in 2015. Vesta and Ceres are complementary: Vesta is dry and underwent igneous differentiation to form a crust, mantle, and core [2]; whereas, Ceres underwent aqueous differentiation, and may contain subsurface liquid water [3]. Dawn will acquire remote sensing data to determine shape, gravity field, mineralogy, geochemistry, and surface morphology. Dawn’s payload includes framing cameras, a visual-infrared spectrometer, and a gamma ray and neutron detector (GRaND).

GRaND will determine the abundances of rock forming elements, such as Fe, Si, and Mg, and the abundances of light elements, including H, C, and N, found in ices and products of aqueous alteration and space weathering. GRaND will test the widely accepted theory that Vesta is the source of the achondrites, measure compositional layering to determine how Vesta differentiated (fractional crystallization of a magma ocean vs. serial magmatism), and search for remnants of the primitive crust. In this prospective study, we use modeling, validated with data acquired during cruise and Mars Gravity Assist, to describe how GRaND will constrain the geochemistry of Vesta and Ceres.


Carbonate clumped-isotope paleothermometry of sub-Arctic early Cretaceous fossils

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Here we present estimates of sub-Arctic marine temperatures from Cretaceous belemnites using ‘carbonate clumped-isotope’ paleothermometry. The early Cretaceous (Valanginian) material is from the Yatria River, sub polar Urals, Siberia, paleolatitude of ~60-65°N. The △13C-18O bond enrichment in these shells ranges between 0.64 and 0.67‰ (Δ13C), implying shell growth temperatures of 20-26°C. Present temperatures at this latitude are typically less than 5°C, and our data are consistent with independent evidence of a warm ‘greenhouse’ world featuring a shallow latitudinal temperature gradient, and possibly the absence of ice in the high latitudes. However, there are important issues to be addressed in our use of this relatively new isotopic system. The combined temperature and △18O-carbonate data imply average seawater △18O values of 0.5 to 1.5‰. This is higher than the expected range for high latitude Cretaceous seawater, although such values are plausible and may point to unexpected basin- or global-scale hydrologies in the early Cretaceous. However, we also consider 1) diagenetic reordering of △13C-18O bonds in a closed system, 2) belemnite body fluid in isotopic disequilibrium with seawater, and 3) intercalibration issues and the existing Δ13C-temperature calibration for these measurements. Of these, (2) should not influence clumped isotope paleotemperatures, and we estimate the effects of (3) as less than a few degrees. The combined Δ13C and △18O data rule out isotopic exchange with high temperature fluids in deep burial environments, as well as late diagenesis in the presence of meteoric waters. The isotopic data are consistent with primary marine environments, or early diagenesis in shallow burial environments. We suggest that actual marine temperatures can be conservatively bracketed between traditional △18O-in-carbonate temperatures (assuming δ18Owater = -1.0‰) and carbonate clumped-isotope temperatures. This translates to ca. 5-23°C for samples with the highest △18O (carb) values, and 15-26°C for those with the lowest values.
Silicate weathering and the apparent Arrhenius activation energy of CO₂ consumption at Coweeta Hydrologic Laboratory, western North Carolina, USA

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The weathering of silicate minerals is a natural mechanism by which atmospheric CO₂ is consumed over geologic timescales. This study provides detailed calculations of atmospheric CO₂ consumption (ØCO₂) by the weathering of silicate minerals (ØCO₂min) for seven small forested watersheds underlain by granitic bedrock at Coweeta Hydrologic Laboratory, North Carolina, USA. Relatively accurate mineral weathering rates have been determined for each watershed using stream flux-based mass balance methods to correct for each watershed using stream flux-based mass balance methods. 

For comparison, ØCO₂ has been determined using 2ØSi and ØTZ’, which are widely used in studies of large rivers. The 2ØSi values are consistently higher than ØCO₂min values by up to nearly a factor of four. ØTZ’ values of measured stream water fluxes are typically lower than the ØCO₂min values as biomass is not included in the ØTZ’ metric.

Apparent Arrhenius activation energies (E_a) have been calculated for both ØCO₂min and ØCO₂Ca+Mg at Coweeta. The ØCO₂min E_a range is 73-78 kJ mol⁻¹, and the E_a ØCO₂Ca+Mg range is 50-55 kJ mol⁻¹. The lower ØCO₂Ca+Mg E_a relative to that of ØCO₂min reflects that at Coweeta the influence of temperature on Ca²⁺-Mg²⁺-silicate is lower than that for total silicate weathering. This differs from previous work [1]. This apparent disparity may reflect that the weathering of Ca²⁺-Mg²⁺-silicate minerals in felsic rocks are less sensitive to temperature effects than those found in mafic rocks. The Coweeta ØCO₂Ca+Mg E_a is also lower than that of 63 kJ mol⁻¹ derived from laboratory experiments and utilized in the GEOCARB III model [2]. However, field-based E_a values are likely minimums because the watershed temperature used is ambient air temperature determined from the mean free atmospheric thermal lapse rate.

Molybdenum content and isotopic composition of the Buzzard Coulee Meteorite

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The Buzzard Coulee meteorite fall on November 20, 2008, was observed from three Canadian Provinces with immediate findings in Saskatchewan [1]. First petrographic analyses have classified the Buzzard Coulee Meteorite as a H3/4 chondrite [2]. With the first pieces found only 7 days after the fall, giving the meteorite the weathering grade W0 [2], the Buzzard Coulee meteorite constitutes outstanding material for isotopic analyses.

In this study we investigate the molybdenum (Mo) concentration and isotopic ratios of the Buzzard Coulee Meteorite. Molybdenum has seven stable isotopes: ⁹²Mo, ⁹⁴Mo, ⁹⁶Mo, ⁹⁷Mo, ⁹⁸Mo, and ⁹⁹Mo. Isotopes of Mo are synthesized by p-process (⁹², ⁹⁴Mo), s-only process (⁹⁶Mo), r-only process (⁹⁹Mo) and a combination of s- and r- process (⁹⁷, ⁹⁸Mo). Molybdenum isotopes have been recently found to be indicators of not only biogeochemical processes but also of isotopic heterogeneity in the early solar nebula [3]. With improving analytical techniques, small molybdenum isotopic anomalies have been found in e.g. iron meteorites as a result of nucleosynthetic effects.

We apply ion exchange and double spiking techniques [3] followed by the Mo analysis using multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) to realize measurements with high accuracy and precision. Bulk Mo concentration and isotopic ratios will be presented as well as the Mo content and isotopic compositions of different fractions and grains to further constrain the Mo heterogeneity within the Buzzard Coulee Meteorite. This will allow us to explore changes in Mo content and isotopic composition as a result of heating or other processes.

Highly siderophile elements in the early Earth: A story told by Barberton komatiites

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High-precision highly siderophile element (HSE) data for Archean komatiites afford unique information regarding the early history of the Earth. In this study, we obtained, using state-of-the-art Carius tube digestion technique coupled with isotope dilution thermal ionization mass spectrometry and inductively coupled plasma mass spectrometry techniques, high-precision HSE abundances and Os isotopic data for representative sets of well-preserved samples from three temporal groups of komatiites from the early Archean Barberton Greenstone Belt (BGB) and, using a previously established protocol, calculated relative and absolute HSE abundances in their respective mantle sources. The absolute HSE abundances progressively increase from the ca. 3.6 Ga Schapenburg through the ca. 3.5 Ga Komati, to the ca. 3.3 Ga Weltevreden sources, which contain, e.g. ~30%, 45%, and 70%, respectively, of Os abundances in the projected sources for the 2.7 Ga Abitibi and Belingwe komatiites. Further, the degree of fractionation of the relative HSE abundances in the projected sources, as compared to Primitive Upper Mantle, progressively decreases with decreasing age. These new data may be reconciled within several scenarios. (1) Involvement of different mechanisms of formation for these komatiites, such as hydrous melting of a mantle wedge in an early Archean subduction zone, re-melting of a majorite-enriched mantle domain formed during solidification of a terrestrial magma ocean, and anhydrous batch melting of ambient mantle in deep, extremely hot mantle plumes. (2) Substantial heterogeneity of the terrestrial mantle with respect to HSE abundances, during the early Archean, caused by incomplete vertical and/or lateral homogenization of large planetesimals accreted to the Earth as late veneer after the last major interaction between the core and the mantle. (3) Failure of our protocol to accurately gauge source concentrations. None of these mechanisms alone can fully explain the available geological, geochemical, and isotopic data for the BGB komatiites.

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pH dependent proton reactivity of rough LPS on live cells

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The surface charges of soil particles including bacteria can affect the mobility and retention of metal ions in solution. The pH dependant charges of the proton reactive groups (PRGs) in rough lipopolysaccharides (LPS) of live bacteria were evaluated using a non-ideal competitive adsorption (NICA) model. This was done by titrating suspensions of the model organism Shewanella putrefaciens CN32 between pH 4 and pH 9. A plot of the titration pH as a function of the change in pH resulted in two peaks, indicating the presence of two PRGs with adsorption coefficients consistent with phosphoryl and carboxyl groups. The parameters of the NICA model provide insight into the relative site occupancy of PRGs [1]. We observe that there exists a continuum of bonding arrangements to the PRGs. Unlike the planar and discrete charge distribution of mineral faces, the carbon-carbon single bonds of membrane molecules extending into the solution are flexible. They contain both positive and negative charges. There is also a strong electrostatic effect on total membrane charge indicating the importance of swarming protons in the Donnan phase.

Charged surfaces can facilitate adsorption of cells to mineral nutrients [2] and can be important for metal sequestration. This research provides a fresh perspective on the reactivity of the whole cell with metal ions.

Xenon isotope evidence for UV irradiation in the Hadean and the Archean

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Stable isotope (H and N) systematics of documented cosmochemical reservoirs indicate that volatile elements of Earth and Mars were supplied from a cosmochemical reservoir which vestiges are found in chondrites [1]. However, this possibility faces the long-standing problem of the xenon paradox: the isotopic composition of this element is neither solar nor chondritic, and is under-abundant relative to chondritic volatile elements. Any supply of water and nitrogen by a chondritic source should have resulted in the addition of chondritic Xe in abundance much higher than presently seen in the atmosphere and the mantle, and with an isotopic composition drastically different from that of air Xe. Martian atmospheric Xe is elementally and isotopically similar to air Xe, which casts doubt on the possibility to fractionate Xe by terrestrial processes. Instead we propose that the xenon paradox is the result of atmospheric processing. Xenon has the lowest ionization energy compared to other noble gases, N₂ or O₂. Recent experiments indeed show significant Xe isotope fractionation in xenon by 1.4 % per amu during UV irradiation and trapping in condensed matter [2]. The non radiogenic, non fissionogenic Xe isotopic composition of xenon trapped in Archean barite and quartz is intermediate between Chondritic and Atmospheric [3], suggesting that the process that fractionated atmospheric Xe lasted for long periods of geological time. Tests of this possibility will include further ionisation experiments with other volatiles, and analysis of noble gases in sedimentary rocks from different epochs.


Solid core as relic of protocore

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We suggest that the Earth’s solid core has never been formed from liquid core crystallization, but represents the protocore relict on which accretion has begun. The minimal initial mass of the protocore is equivalent to about 0.5 that of the whole modern core and can be estimated on the basis of Earth’s iron excess in comparison with its chondrite content. According to this estimation the protocore have to be dissolved. It results in increasing the mass of the liquid core. It is possible to suggest that the protocore is heterogeneous in composition and along with some admixture of such light elements as P and S contains a material of a chondrite silicate component. Floating-up of this component in liquid core during protocore decomposition is accompanied by release of energy and causes concentration-induced convection providing geodynamo. If the concentration of chondrite component in modern solid core exceeds critical value ~ 8% then energy of such process is enough for the magnetic field generation. If the content of a light admixture is well below this critical value the dissolution of protocore stops and the liquid core crystallization can begin. Distribution of this admixture in liquid core during protocore decomposition is accompanied by release of energy and causes concentration-induced convection providing geodynamo. If the concentration of chondrite component in modern solid core exceeds critical value ~ 8% then energy of such process is enough for the magnetic field generation. If the content of a light admixture is well below this critical value the dissolution of protocore stops and the liquid core crystallization can begin. Distribution of this admixture in liquid core during protocore decomposition is accompanied by release of energy and causes concentration-induced convection providing geodynamo. 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Beryllium hydration in aqueous solution. II. Correlation consistent basis set calculations

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The structures, energies, and vibrational frequencies of Be$(\text{H}_2\text{O})_n^{2+}$, $n=0-6, 8, 12, 18$ have been calculated at the Hartree-Fock (HF), second-order Moller-Plesset (MP2), and density functional (B3LYP) levels of theory using the correlation-consistent basis sets [1]. Comparisons to the literature Raman spectra of aqueous beryllium solutions will be made [2].


Uralian eclogites as exhumed ultrahigh-pressure paleoproterozoic rocks

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In the Urals, the majority of dates obtained on eclogites falls within the interval 390-240 Ma. Taking this fact as a basis, many scientists limit the time of formation of eclogite-bearing rock associations (from the stage of high-pressure paragenesis crystallization in deep-seated zones till eclogite exhumation during the collision and post-collision stages of fold-orogenic belt development) by the above period.

However, there are more ancient dates on the objects to be studied. That is why, not denying the theoretical possibility of eclogite formation and exhumation during a single geodynamic cycle, we consider more realistic the models, which allow for a long time break between the eclogite formation and exhumation of the high-pressure associations out of the deep zones.

On the ground of the geochronological data yielded by Uralian eclogites, three age levels of the high-pressure metamorphic rocks formation (and alteration) can be distinguished: over 1560, 720-550, and 390-240 Ma.

Nowadays most researches think that conditions for metamorphic eclogite crystallization can occur only in subduction zones. We could agree to this hypothesis, however, repeated manifestation of high-pressure metamorphism in the same complexes in the course of more than 1 bln years seems unlikely. It appears that only the oldest eclogite ages (over 1560 Ma) point to the crystallization time of these rocks in subduction zones. Neoproterozoic and Paleozoic dates indicate the time of collision and post-collision processes at younger stages of geodynamic development. The dislocation of eclogite-bearing complexes to the lower levels of the Earth’s crust is connected with them.