

Li in plagioclase: Investigating its rapid diffusion and potential as geospeedometer

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Elemental and isotopic studies with Li as a geochemical tracer for source components and potential tool for geospeedometry have proliferated in recent years. Indeed, the abundance and isotopic fractionation of Li, alongside its rather rapid diffusivity especially in plagioclase, remain topics of interest and importance. In volcanic systems, such Li data may demonstrate processes and timescales that lead up to the extrusion of magma.

To further understand Li diffusion in (and out of) plagioclase, we analyse exceptionally large crystals using the SIMS, to be confirmed by other methods. Our current results involve a heating experiment on a 2cm-long plagioclase phenocryst from a lava flow in Luzon, Philippines. The crystal, partly surrounded by groundmass, was heated in an oven first at 500°C, then at 800°C, both for an interval of 30 hours. Li, Be, B and $\delta^7\text{Li}$ analyses were undertaken before the experiment and after each heating. The Li concentration profile prior to heating, with values that decrease from core to rim, had a range of 12-29 $\mu\text{g/g}$. After each heating, a general drop of 2-5 $\mu\text{g/g}$ was observed. The profile however, was rendered more irregular and the outermost rim displayed an unmistakable increase in Li content after heating at 500°C. Surprisingly, the $\delta^7\text{Li}$ profile did not show any significant modification.

Preliminary as it was, the experiment showed that Li does diffuse within the range of temperatures in a matter of days. How this experiment may be refined, e.g. to constrain the effects of Li escaping into the air, define how it leaves the plagioclase to diffuse into different phases of the matrix, or estimate how fast at which temperature the diffusion occurs, is a matter of continued consideration. Moreover, corroborative analyses, time calculations and diffusion modelling are needed to better interpret our existing data.

Uranium minerals from a Portuguese Variscan granite and its hydrothermal alteration

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Electron microscopy images, X-ray maps and electron microprobe analyses were carried out on uraninite, coffinite, (meta)saleeite, thorite, xenotime, monazite and apatite from unaltered and altered Variscan peraluminous granite and related hydrothermal brecciated uranium-quartz veins. Uraninite occurs mainly in the unaltered granite [1], is rare in the altered granite and was not found in the mineralized quartz veins. Uraninite from the altered granite is fractured and hydrated, has the radioactive damage halos filled with late mineral phases, and its analytical totals are lower than in the uraninite from the unaltered granite. The alteration zones are poorer in U than the unaltered zones and some uraninite crystals are replaced by coffinite, which results from uraninite alteration and only in the altered granite. Its U content ranges between 65.0 wt.% UO_2 in the rims to 84.0 wt.% UO_2 in the cores of crystals. Thorite was found in all the granite samples and its composition is variable from 0.5 to 10.4 wt.% UO_2 , with the low UO_2 contents in fractured crystal zones. Secondary thorite replaces apatite and monazite. Monazite from the altered granite is vacuolated, replaces apatite, and is replaced by secondary thorite. In the altered granite, xenotime is zoned, with cores richer in U than rims. Apatite from the altered granite is dissolved and has lower U and P contents than apatite from unaltered granite.

[1] Cabral Pinto MMS *et al.* (2008) Geochemistry of U-bearing minerals from the Vale de Abrutiga uranium mine area, Central Portugal N. *Jb. Miner. Abh* **185/2**, 183-198

Do preserved mineral compositions reflect peak-pressure metamorphic conditions?

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Chemical zoning established during prograde metamorphic garnet growth is commonly used to infer P - T conditions during orogenesis. Records of specific mineral reactions may be retained as small lengthscale compositional zoning steps. These are characteristic of P - T conditions but are rapidly lost by diffusion during subsequent high- T events. Here we examine several possible exhumation P - T -time paths (from 700°C at 1.5 GPa) in terms of the preservation of both μ m-scale and crystal-scale growth zoning features. The initial crystal zoning profile plays an important role in the rate of chemical re-equilibration, because we calculate composition-dependent diffusivities. However, all but the fastest exhumation paths ($> ca. 5 \text{ mm yr}^{-1}$) result in significant modification of the internal zoning profiles of garnet crystals smaller than $ca. 1 \text{ cm}$ diameter.

Deviation between the growth composition of a garnet crystal and the preserved composition following exhumation clearly changes apparent K_D values between co-existing crystal pairs and can yield inappropriate thermobarometer results (with errors exceeding 100°C and 2 kbars in some cases). We quantify the likely uncertainties associated with common mineral thermobarometers when applied to rocks (i) experiencing one of three exhumation geometries of cooling and decompression, (ii) experiencing exhumation at a variety of rates and (iii) containing a range of crystal sizes. For much of the explored range of exhumation-times (1 to 100 Myrs) and crystal sizes (100 μ m to 1 cm), P - T paths involving significant isothermal decompression result in demonstrably different zoning profiles to those involving monotonic P and T decrease. Such zoning profiles are therefore diagnostic of P - T path type.

Reservoir porosity enhancement by multiple stages of TSR in East Sichuan Basin gas fields, China

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It is well known that high H_2S in East Sichuan Basin gas fields was originated from TSR [1, 2]. However, different from other TSR provinces, dolomite reservoirs in the East Sichuan have been measured to have porosity up to 28.2%, and experienced burial down to $>7000\text{m}$ [3, 2], suggesting that the high porosity in local areas was generated during deep burial, likely during TSR [3], and that dissolved ions must have been migrated out. This is impossible unless there exist multiple stages of TSR because TSR in nature generally occurs in a closed system. The proposal is supported by the following lines of evidence: 1) no anhydrite was found in Upper Permian reservoirs, however, where up to 34.7% H_2S by volume was detected, suggesting that reactant sulfates or resultant H_2S was external; 2) in the Lower Triassic reservoirs, fracture-filling anhydrite has $\delta^{34}\text{S}$ values about +39‰, the value being significantly higher than contemporary seawater. Coexisting with the anhydrite are isotopically light H_2S and elemental sulphur with $\delta^{34}\text{S}$ values of +2.0 to +7.9‰. This suggests that at least part of TSR occurred between excessive dissolved sulphate and limited hydrocarbon, and thus unreacted sulphate is isotopically heavy [4], and precipitated as anhydrite during migration. 3) Based on burial history rebuilding, TSR may have taken place at temperatures $>130^\circ\text{C}$ during the period from Late Triassic to Middle Jurassic, and during Early Cretaceous; lateral and cross formational fluid flow must have taken place during the end of Jurassic to earliest Cretaceous as a result of tectonic activities. 4) Some reservoir bitumen was observed in the centre of pore, suggesting porosity enhancement occurred after solid bitumen filling. Thus, multiple stages of TSR and fluid flow may have resulted in dissolution of anhydrite and dolomite, and thus high porosity for the reservoirs.

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[1] Cai, *et al.* (2003) *Chem. Geol.* **202**, 39-57. [2] Cai, *et al.* (2004) *Mari. Petro. Geol.* **21**, 1265-1279. [3] Ma, *et al.* (2007) *AAPG Bull.* **97**, 627-643. [4] Cai, *et al.* (2008) *Appl. Geochem.* **23**, 2226-2235.

The organo-clay complexes in source rocks—a natural material of hydrocarbon generation

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It is well-known that a kerogen, separated by demineralization from source rocks, is the main material of hydrocarbon generation. However, during this process, the feature of occurrence and the associations of organic matter with clay minerals are destroyed. Therefore, we extract organo-clay complexes ($< 2\mu\text{m}$) from crushed source rocks in depth 1000-3500m, Shahejie Formation, Oligocene, Jiyang sag, east China, and study its characteristics and potential of hydrocarbon generation. The complexes is mainly composed of interstratified illite-smectite (I-S) and illite minerals, and its value of TOC is 2.62-9.78%. Its value of TOC treated by H_2O_2 is still up to 1.23-4.63%, which suggests an enrichment of organic matter in the complexes. The diffraction peak (d001) of complexes is 1.3-1.4nm at 250°C , and move to 1.0nm until heating to 550°C in XRD curves, and the exothermic peaks of complexes with extraordinary stable occur at 350°C in DTA curves. This information is consistent in the XRD and DTA observations, and it is a symbol characteristic that an organic matter can enter in the interlayer space of clay minerals. With PY-GC analysis, the organic matter is released in temperature range $250\text{--}650^\circ\text{C}$, mainly at about 450°C , and the components is consistent with higher content of C_5 and C_{25} in the complexes and source rock. Our findings indicate that organic matter can enter interlayer of clay minerals forming natural and highly stable organo-clay complexes. Also the composition of organic matter in the complexes is similar to crude oil. These results suggest that an organo-clay complexes is a natural material and plays an important role in organic matter preservation and hydrocarbon generation in source rocks.

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Estimating submarine groundwater discharge into Xiamen Bay (China) using naturally-occurring Radium isotopes

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It has been suggested that the submarine discharge of chemical species carried by groundwater has been found to be significant, eventually having considerably impact on coastal biogeochemistry and ecosystems. Chemical tracers of Submarine groundwater discharge (SGD), such as radium isotopes, have the advantage of integrating this process over a wide range of spatial scales from the continental shelf to individual estuaries.

In many coastal regions, SGD is a potentially important process for delivering a wide range of anthropogenic contaminants, including nutrients, to coastal waters. The objective of our study is to quantify SGD into the coastal seawater of Xiamen Island, China, via interpretation of a unique set of radium data spanning nearly several years.

In this paper, concentrations of ^{224}Ra , ^{226}Ra , ^{228}Ra , δD and $\delta^{18}\text{O}$ of seawater and coastal groundwater in the Bay of Xiamen were measured to study SGD.

The δD , $\delta^{18}\text{O}$ data of the coastal groundwater were found to increase from land to the sea, which revealed the coastal groundwater flows into the sea. This is supported by the result of hydrological study in the same area.

Then, based on a Radium isotopes mass-balance model, the advective flux of ^{228}Ra through SGD was calculated to be $3.84 \text{ Bq m}^{-2} \text{ d}^{-1}$ in the studied area, while the rate of SGD (mostly brackish groundwater) was estimated to be about $1.4 \times 10^9 \text{ m}^3/\text{a}$, at least 12% of the input of Jiulong River, which is the second largest river in the Fujian Province, China.

Although there are large uncertainties in this estimate, it is obvious that SGD is potentially an important route in this area. In addition, SGD appears to be important source of N and P (together with other nutrients) in the coastal Seawater of Xiamen Island. This result from such a representative area implies that the N and P flux through SGD may be significant in the large area of the south of China.

Comparative XPS study between experimentally and naturally weathered pyrites

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The comparative study was carried out between the experimentally and naturally weathered pyrites. The naturally weathered pyrites were collected at the Tongling multi-metal deposit, China. The fresh pyrites with an euhedral shape were exposed in a humid environment supplied by an accelerated weathering tester. Both of them shared the similar chemical species of weathering products and weathering mechanism. The X-Ray Photoelectron Spectroscopy (XPS) was used to study the surficial chemical species of the weathered products, and the argon ion etching techniques was used to study the vertically structural profile.

The outmost weathering surficial products could be concluded into sulphur-bearing and iron-bearing groups. The sulphur-bearing group were comprised by sulphate, sulphite, thiosulphate, elemental sulphur (S₈), polysulphide, and mono-sulphide, etc. The iron bearing group was composed by goethite, hematite or magnetite, and iron sulphate. Though the chemical species were same, phases from naturally weathered pyrites differed from experimentally weathered ones in its crystalline degree. Excluded elemental sulphur, most of phases could be detected on the naturally weathered surface by GIXRD. This difference could be attributed to the weathering time scale and environment.

The weathering structural profile was also similar. The structural profile was constructed by surficial layer and transient layer. The surficial layer was made up of the sulphur-bearing and iron-bearing product, the transient layer was comprised by goethite and hematite or magnetite. The inward moving of weathering interface was stimulated by the diffusion of oxygen and moisture. The oxygen was considered to preferably squeeze the iron to form goethite, and ferric of goethite act as a bridge [1-3] of electron transferring between bulk S₂²⁻, Fe²⁺ of pyrite and oxygen. Hence, the weathering rate of pyrite was constrained by the diffusing rate of oxidized moisture, but the weathering degree was constrained by both diffusion rate and mainly the time scale of weathering.

[1] Nesbitt & Muir (1994) *GCA*, **58**, 4667-4679. [2] Knipe *et al.* (1995) *GCA* **59**, 1079-1090. [3] Rosso *et al.* (1999) *Am. Mineral.* **84**, 1535-1561.

Biom mineralization of the iroko tree (*Milicia excelsa*): How does this carbon sink work?

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Biom mineralization in the plant kingdom has been documented since a long time. A particularly interesting example is the iroko tree. CaCO₃ biom mineralization occurs in its plant tissue and unexpected CaCO₃ accumulations are observed in its surrounding soil. We present a conceptual model for iroko tree mineralization and soil CaCO₃ deposition based on a multiscale approach ranging from field observations and laboratory measurements to electron microscopy images and microprobe analyses.

Photosynthesis is the first step by which atmospheric CO₂ is sequestered as large amounts of calcium oxalate and accumulated in the iroko tissues. A flux of oxalate-rich dead Organic Matter (OM) from the tree to the soil (partly increased by termites) has been quantified. Various microorganisms decay soil OM and cause the release of calcium oxalate crystals inside the soil matrix. As demonstrated by Braissant *et al.* [1], soil oxalotrophic bacteria oxydize the release oxalate, increasing complexed Ca²⁺ and carbonate ions in the soil solution, and inducing a pH increase in the initially acidic soil. In the presence of calcium and favourable physicochemical conditions, carbonate ions can precipitate in the soil pores and lead to the formation of large CaCO₃ concretions. Alternatively, carbonate ions can be pumped through the roots and translocated by conductive vessels inside the tree. In the tree tissues, by some yet unknown processes, biom mineralization (e.g. calcitic pseudomorphosis of organic cells) can occur.

In conclusion, the iroko tree ecosystem, with its calcium oxalate-carbonate pathway, represents a carbon sink, which leads to a long term sequestration of large amounts of atmospheric CO₂ into a geologically stable form, CaCO₃.

[1] Braissant *et al.* (2004) *Geobiology* **2**, 59–66.

Volcanic signature of volatile trace elements on atmospheric deposition at Mt. Etna, Italy

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Volcanic volatiles and aerosol emitted into the atmosphere ultimately fall on the Earth's surface as wet or dry deposition, and they can influence the environment and the ecosystems at local and regional scales. Therefore, atmospheric deposition plays a key-role in the geochemical cycles, redistributing volcanogenic elements to the ground. For this reason, estimating the volcanogenic trace element fluxes from the atmosphere to the surface is necessary for a better knowledge of the environmental impact of the volcanic emissions. Nevertheless, from a literature review, we have recognized the scarcity of investigation on trace element deposition in the surroundings of active volcanoes. Here, we present a chemical characterization of bulk deposition around Mt. Etna, Italy, including both major and many trace elements.

Bulk depositions were collected approximately fortnightly, from April 2006 to December 2007, using a network of five rain gauges, located at various altitudes on the upper flanks around the summit craters of the volcano. For most elements highest concentrations have been found close to the emission vent, confirming the prevailing volcanic contribution to rainwater composition close to the summit craters. Comparison with contemporaneously collected plume emissions shows that deposition processes produce no evident element-to-element fractionation. By contrast, comparison with whole rock composition indicates a contrasting behaviour between volatile elements, which are highly-enriched in rainwater, and refractory elements, which have low rainwater/whole rock concentration ratios.

Chemical concentrations in bulk deposition were used to estimate the deposition rates of a large suite of elements. Deposition rates for volatile trace elements like Se, As, and Cd range from 1.7, 1.2 and 0.9 $\mu\text{g m}^{-2} \text{ day}^{-1}$ nearby to the summit vents, to 0.5, 0.3, and 0.1 $\mu\text{g m}^{-2} \text{ day}^{-1}$ at the local background site on the upwind western sector.

Uranium trapping on opals from the Nopal natural analogue : Evidence for complexation on internal surface of opal

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Uranium is an important environmental contaminant. The modeling of uranium mobility, controlled by its chemical behavior, helps understand the migration of transuranic elements, a major concern in nuclear waste management. In the volcanic-hosted uranium deposit of Nopal I (Chihuahua, Mexico), considered to be a natural analogue for the proposed high-level nuclear waste repository at Yucca Mountain (Nevada, USA), uranium occurs under both reduced and oxidized forms [1]. Late opal deposition accompanied the last alteration event, the $\delta^{18}\text{O}$ values indicating that opal formed at around 30°C. This opal contains low amounts of uranium, typically in the 500-2000 ppm range, and corresponds to a late mobilization of uranium. It is then important to determine the form under which uranium occurs in this opal to understand the trapping processes, which may be at the origin of a potential retardation of radionuclide migration.

In order to investigate uranium speciation, we have used fluorescence spectroscopy, a tool well-suited at low-level concentrations. The spectra, recorded at room temperature and 77K, are different of those found in secondary uranium minerals, showing that fluorescent properties of opal do not arise from (nano-)mineral inclusions, despite opal usually covers secondary uranium silicate minerals at Nopal I. In addition, fluorescence is observed at room temperature, as uranyl silicates show short fluorescence lifetimes at room temperature. The position and relative intensity of the vibronic components of the fluorescence spectrum are also different from those found on the spectra of uranyl complexes sorbed on silica. The O=U=O symmetrical stretch frequency, measured from the spacing of the vibronic bands of the fluorescence spectra data, is consistent with aqueous uranyl-phosphate complexes adsorbed as ternary surface complexes on the internal surface area of the colloidal array. They indicate uranium trapping under oxidized conditions and shed light on potential retardation mechanisms.

[1] Calas *et al.* (2008) *Terra Nova* **20**, 206-21.

Low-pressure fractionation of undersaturated alkaline lavas from Cape Verde Islands

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Sub-aerial flows of olivine nephelinites and melilitites (Mg#: 70-73; Ni: 430-560 ppm) from Cape Verde Islands (Sal and Santiago) underwent post eruptive fractional crystallization resulting in granular segregates ('pegmatitoids') of ijolitic to melilititic composition (Mg#: 42-64; Ni: 40-60 ppm). These segregations form discrete clots to sinuous veinlets at the base of the flows, developing in to coarse-grained bands at the central part of the outcrops. Their paragenesis, partially common to the host lavas, includes variable amounts of Ti-augite ($\text{Wo}_{55-28}\text{En}_{40-6}\text{Fs}_{66-9}$), rimmed by aegirine-augite/aegirine, + nepheline + melilite + Ti-magnetite + apatite + aegirine-augite ($\sim\text{Wef}_{61}\text{Ae}_{39}$) + perovskite + rhonite + carbonates + yellowish glass. Late perovskite (average wt%: $\text{Nb}_2\text{O}_5 = 1.22$; $\text{Ce}_2\text{O}_3 = 1.92$; $\text{La}_2\text{O}_3 = 0.43$; $\text{TiO}_2 = 51.85$; $\text{CaO} = 37.96$) in rosary, cruciform or fishbone structures, along well-defined lineaments down cleavage planes and micro-fractures stand out in the 'pegmatitoid' domains. Its orientation in the host minerals strongly suggests crystallization from secondary fluid inclusions under the influence of Ti rich fluids. The host rocks are composed of olivine (%Fo = 82-88) and Ti-augite ($\text{Wo}_{55-51}\text{En}_{40-32}\text{Fs}_{12-9}$), essential to accessory nepheline and melilite, Ti-magnetite (%Usp \approx 42-64), apatite, small crystals of perovskite, and rarely biotite and amphibole. Pyroxenes define a fractionation trend from host rocks to granular segregates with decreasing Mg# and Al_2O_3 and increasing SiO_2 , Na_2O and FeO. Also, whole rock chemistry shows that, when compared with parent rocks, 'pegmatitoids' are highly depleted in Mg, Cr and Ni, largely due to olivine extraction, and are enriched in incompatible elements like Zr, Cu, Nb, Ba, La, Yb, Hf, Th, Pb and U. Incompatible elements and REE contents for the segregations show similar patterns to the parental rocks, typical of alkaline OIB, but with higher enrichment degree ($\Sigma\text{REE}_{\text{peg}} = 561$ to 964; $\Sigma\text{REE}_{\text{host}} = 338$ to 551). This data indicates that the 'pegmatitoid' granular segregations resulted from low-pressure *in situ* crystallization of residual liquids from fractional crystallization of undifferentiated melts of nephelinitic and melilititic composition. However, the abundant fluid and perovskite inclusions in some minerals suggest the influence of late-magmatic fluids into partially crystallized magma. Decreasing $f\text{O}_2$ conditions are deduced from increase in ulvospinel percentage in magnetite with differentiation.

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Contribution of deep groundwater to weathering budget in a rapidly eroding mountain belt, Taiwan

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Weathering processes occurring in the soil zone and shallow bedrock are supposed to provide most of the dissolved load in rivers. However, river chemistry combines weathering products resulting from surface processes such as soil production and erosion, as well as those coming from deeper processes occurring within the underlying bedrock. A straightforward quantification of those different contributions remains difficult from punctual samplings and may require time series samplings. Analysis of a 7-yr time series of water samples from a well-drained, rapidly eroding catchment in Taiwan, the Liwu River, shows that three water reservoirs with distinct weathering signatures systematically contribute to the dissolved load. Whereas the contributions from surface and shallow groundwater increase at high discharge, the deep groundwater component becomes a predominant water source at low discharge and therefore for 75% of time. The longer residence time of water in the deep reservoir enhances silicate weathering implying that deep groundwater provides a large part of the silicate weathering flux because about 50% of the total chemical flux is carried at low discharge. Deep weathering fluxes may therefore be an important component of the global silicate weathering flux even in high rainfall and rapidly eroding environments. This highlights that weathering reactions in soil and shallow reservoirs only provide part of the total dissolved load and studies that focus on the controlling parameters of chemical weathering must take into account weathering fluxes coming from deeper reservoirs.

Dissolution of fluorite (111) cleavage surface in acid pH: VSI, AFM and Monte Carlo simulations

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To enlarge the current understanding of fluorite (CaF₂) dissolution kinetics we have carried out a detailed study of fluorite dissolution, combining fluid-interface experiments (AFM and VSI techniques), as well as Monte Carlo simulations of fluorite cleavage (111) surface dissolution. To our knowledge, these are the first direct observations of etch pit nucleation on the (111) surface of fluorite under low but variable pH conditions.

AFM (Atomic Force Microscope) and VSI (Vertical Scanning Interferometry) were used to measure dissolution in single pass flow-through cells at pH values ranging from 1 to 3.15 in dilute HCl solutions far from equilibrium. Under these conditions, our observations show that dissolution proceeds through the formation of crystallographically-controlled triangular pits, whose coalescence results in overall surface retreat. These observations are consistent with the stepwave model [1], which predicts that at ΔG_r less than a critical value, mineral dissolution is controlled by stepwave generation and movement. Surface retreat was quantified as a function of pH, yielding an intrinsic fluorite dissolution rate constant as well as the dependence of dissolution rate on pH.

The results of Monte Carlo simulations were also found to be entirely consistent with the above observations. These fully parameterized simulations include a lattice-accurate cubic structure with Ca-F bonds and do not require any "strategic" assumptions about reaction mechanism, thus allowing us to explore and compare the changes in virtual surface microtopography and process kinetics with direct observations. Simulation results include the formation of triangular etch pits and their coalescence under far-from-equilibrium conditions.

[1] Lasaga & Lüttge (2001) *Science* **291**, 2400–2404.

The thermochemical structure of the upper mantle as inferred by seismic and gravity data

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We consider a reference mineral physics model based on current knowledge of material properties at high pressure (P) and temperature (T). The phase equilibria and the elastic properties are computed with a recent thermodynamical model covering a six oxides (NCFMAS) system. Anelastic properties are implemented with a P, T and frequency dependent law based on mineral physics knowledge. The model predicts values of physical parameters (e.g., shear velocity, density) as function of pressure (or depth), temperature and composition. Equilibrium compositions or mixtures of different compositions (e.g., MORB and Harzburgite) can be considered.

Starting from this model, we adopt a non-linear approach to obtain the average thermal and compositional structures that are able to fit global seismic data, i.e. normal modes and travel times. Then, we extend our results to 3-D inversion of long period seismic waveforms, which allow us to resolve seismic structure in the whole upper mantle. We produce several T-C models that are able to fit the seismic observations. At the same time, we predict the 3-D density structures related to the inverted T-C fields. Viscosity is evaluated with a similar physical law as seismic attenuation. We compute the synthetic geoid for all the models by using the STAGYY code and thus the misfits with observations. The analysis of the results will give a robust interpretation of the thermochemical structure of the upper mantle, will reduce the trade-off between T and C and it will point out possible problems with uncertain physical properties in the reference mineral physics model used.

Rate of growth of the preserved North American continental crust: Evidence from Hf and O isotopes in Mississippi detrital zircons

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Ninety-six concordant zircons from the mouth of the Mississippi River, which show no age zonation, were selected to represent six time U/Pb intervals previously identified from zircon dating, and analyzed for Lu-Hf and O isotope by laser ablation MC-ICP-MS and SHRIMP II, respectively. ϵ_{Hf} values for the zircons show that the overwhelming majority of the grains crystallized from melted pre-existing continental crust, or mantle derived magmas that were contaminated by continental crust. The average Hf model age, if weighted by fraction of zircons in the river load, is 1.94 Ga, but 2.35 Ga if weighted by area, which compares with equivalent Nd model ages of 1.7 Ga and 2.36 Ga respectively. Our preferred approach is to use the measured O isotope values to constrain variations in the $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of the granitic source region from which the zircons crystallized. This method gives an average Hf model age of 2.53 Ga.

The Halmyrolisis Effects on the mantle derived rocks in productive water on St. Paul's Rocks, Equatorial Atlantic

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Geochemical Remobilization

The sedimentary cycle, the main phenomenon that stimulate the chemical mobility of the elements from the oceanic rocks is the halmyrolisis process [1, 2] and many of these chemical elements show a strong influence on biota [3], principally the elements that participate in the photosynthesis, respiration and nutrition of the livings creatures (e.g: soluble complex of C, N, S, P and Si) and in the electrolytic equilibrium of tissues (e.g: Na, K, Ca, Mg and Cl) or in the catalysis of the aquatic photosynthesis (e.g: P, Cu, Co, Fe, Mo, V, Mn, etc). The phosphorus abundance is an important factor in the aquatic photosynthesis and in the formation of sedimentary phosphorites. That suggests a close relation between halmyrolosis, phosphogenesis and the biota proliferation with the geological evolution [4, 5].

Discussion of Results

In this context, we can consider the halmyrolisis of the mantle derived rocks from the St. Peter and St Paul archipelago (SPSPA-Atlantic Equatorial, 0°55'01"N, 29°20'44"W) as a determinative factor in the fertile seawater that surrounds this archipelago. The waters of the deep oceanic layers associated closely to the *new production*; the turbulent or advective entrance of nutrients in the photical layer, will feed the planktons of the most superficial layers, as well as the fishes, seaweed and corals that grow incrustated on the rocks from SPSPA. Our whole rock geochemical data and mass-balance calculations show that the halmyrolisis caused gains and losses in all major elements and induced some remobilization in trace elements.

The redistribution of these elements shows a increase on the water of SiO_2 , $\text{Total Fe}_2\text{O}_3$, MgO, Na_2O , K_2O , Ni, Nb, Y, V, L-REE, Re, Pd.

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Hematite contaminated by heavy metals

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The aim of this project is to use computational and mineralogical techniques to determine the mobility of potentially toxic metallic and metalloid elements such as lead (Pb) and arsenic (As) in pyrite ash wastes.

Contaminated soils and aquifers are often linked with industrial activities or land treatments. One example is the high levels of potentially toxic metallic and metalloid elements on sites associated with old paper mills. To produce cellulose the paper mills used to dissolve wood in sulphite SO_3^{2-} solutions, which were produced on site by oxidizing sulphur-bearing minerals (mostly pyrite) at high temperatures. The remaining ash, so called 'pyrite ash', is now found as fine-grained sand with a characteristic red-violet colour.

Pyrite ash contaminated by lead and arsenic has been found in the south-west of Sweden. Mineral characterization shows that the main components of the pyrite ash are hematite ($\alpha\text{-Fe}_2\text{O}_3$), and quartz ($\alpha\text{-SiO}_2$). The soils contain more than 20000 mg/kg Pb and 10000 mg/kg As. We find that Pb concentrations are independent of soil pH, but As concentrations are highest at $\text{pH} < 2$.

In order to gain a better understanding of the mobility of Pb and As in pyrite ash wastes, we are using quantum mechanic and classical inter-atomic potential calculations to study the 1) bulk structure of hematite contaminated with Pb, As and Mg and 2) Pb and As adsorbed on hematite surfaces under different pH conditions.

Traditional density functional theory (DFT) techniques cannot be applied to study $\alpha\text{-Fe}_2\text{O}_3$. To deal with this problem we are using HYBRID functionals and DFT+U. We have found that the electronic and geometric structures of the hematite can be correctly described using the B3LYP functional. Our simulations show a phase transition into a spinel structure (magnesioferrite, MgFe_2O_4) when hematite is contaminated with higher concentration of Mg. Results for Pb and As will be presented on the poster. Initial calculations indicate that these elements might reduce iron(III) to iron(II) in hematite.

Determination of semi-volatile organic compounds adsorbed on the surface of suspended particulate matter

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Atmospheric particles, with their high surface area to mass ratio, constitute a possible sink for organics. On the other hand, semi-volatile organic compounds (SVOC), because of their molecular size and complexity, tend to become easily attached to aerosol particles. The amount in the adsorbed phase depends on several factors such as volatility and polarity of the organic, and nature of particulate components to which it might adsorb. Organics adsorbed on particles have a different fate with respect to organic compounds in the gaseous phase, as they can be long-range transported, thanks to a lifetime similar to those of aerosol particles themselves, and removed from the atmosphere by wet and dry deposition. In addition, atmospheric particles may have a catalytic role in the reactions between adsorbed VOCs and inorganic gases, leading to the formation of secondary PM. Also, it is probable that the species adsorbed on the external surface of particles are particularly available for the interaction with the human body and the ecosystem. For all these reasons, the issue of organics adsorption deserves an deep investigation.

A few studies, up to now, have been addressed to the determination of SVOC adsorbed on PM; these studies were generally aimed to evaluate the extent of PM sampling artefacts which are the result of the interaction between organics in the gaseous phase and the particles collected on the filter media.

We report in this paper the results of a first series of experiments aimed to develop a reliable procedure for the determination of organics adsorbed on atmospheric PM. Thermogravimetric methods, headspace analysis and thermal desorption of the filter membranes followed by GC-MS determination of the evolved species have been tested on atmospheric PM samples of different composition.

The fingerprint of the organic species thermodesorbed at different experimental conditions has been used also to evaluate the performance of the front + backup filter configuration commonly used for OC determination in atmospheric particulate matter.

Flush-out of evaporitic sulphate salts in the Tinto River: Environmental implications

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The Tinto River drains one of the largest massive sulphide provinces in the world, the Iberian Pyrite Belt (IPB). As a consequence of intense mining activities dating back to the Third Millennium B.C., this river is extremely polluted by acid mine drainage (AMD) and releases a significant contaminant load into the 'Ría de Huelva' estuary [1].

During dry periods, the formation of evaporitic sulphate salts (mainly Fe sulphates) on riverbeds and AMD sources may play a key role in metal and acidity storage in the Tinto system. However, upon dissolution by rainfalls these highly soluble salts may release a high load of metal and acidity to an already polluted environment [2]. Water quality variations were monitored in October 2005 with an autosampler to study these flush-out processes in the Tinto catchment.

First rainfalls recorded in autumn in the Tinto catchment flushed out highly-soluble sulphate salts massively deposited during the summer. This flush-out event in October 2005 provoked a strong increase in sulphate (from 1964 to 8669 mg/L) and metal concentrations (from 199 t 1280 mg/L of Fe, from 88 to 462 mg/L of Al, from 17 to 113 mg/L of Cu, from 20 t 137 mg/L of Zn, etc.). Once these highly-soluble salts were washed out from riverbeds and spoil heaps, concentrations decrease progressively, reaching slightly higher values than those reached before rainfalls. However, elements such as Fe, As, Cr and Pb increased their concentration, being this increase especially significant for As (from 353 to 1885 µg/L). This increase could be due to dissolution of less-soluble salts releasing these elements into the river water. The dissolution of soluble salts with the arrival of the first rainfall after a long dry period provokes a yearly pulse of pollution into the Tinto River that may cause a significant damage to the living biota of the "Ría de Huelva" estuary.

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Overview of the geochemical modeling on CO₂ capture & storage in Italian feasibility studies

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CO₂ Capture & Storage in saline aquifers is presently one of the most promising technologies for reducing anthropogenic emissions of CO₂. In these sites the short-long-term consequences of CO₂ storage into a deep reservoir can be predicted by numerical modelling of geochemical processes.

Unfortunately a common problem working with off-shore closed wells, where only the well-log information are available, is to obtain physico-chemical data (e.g. petrophysical and mineralogical) needed to reliable numerical simulations. Available site-specific data generally include only basic physical parameters such as temperature, pressure, and salinity of the formation waters.

In this study we present a methodological procedure that allows to estimate and integrate lacking information to geochemical modelling of deep reservoirs such as: *i*) bulk and modal mineralogical composition, *ii*) porosity and permeability of the rock obtained from heat flow measurements and temperature, *iii*) chemical composition of formation waters (at reservoir conditions) prior of CO₂ injection starting from sampling of analogue outcropping rock formations.

The data sets in this way reconstructed constitute the base of geochemical simulations applied on some deep-seated Italian carbonatic and sandy saline aquifers potentially suitable for geological CO₂ storage.

Numerical simulations of reactive transport has been performed by using the reactive transport code TOUGHREACT via pressure corrections to the default thermodynamic database to obtain a more realistic modelling.

Preliminary results of geochemical trapping (solubility and mineral trapping) potentiality and cap-rock stability as strategic need for some feasibility studies near to be started in Italy are here presented and discussed.

Trace oil migration using element composition of reservoir diagenetic mineral: A preliminary case study in the Junggar Basin (northwest China)

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In this study, we present a discussion on a new method for tracing oil migration based on a case study in the Junggar Basin (northwest China). Mn abundance of diagenetic calcites was used to trace oil migration. This proxy was preliminarily applied based on the theory of reservoir water rock interaction. The interaction between petroleum fluid, formation water and reservoir rocks is common in petroleum migration, thus the geochemical composition of diagenetic minerals can reflect petroleum migration.

In the Junggar Basin, the diagenetic calcite is widely occurred in hydrocarbon-bearing reservoirs. The calcites were analyzed for element compositions by electronic probe microanalysis (EPMA). Analytical results indicate that Mn-content of the calcites displays a generally good correlation with oil/gas shows. This implies that Mn-concentration has a close relation to the intensity of petroleum fluid charging. Here, mechanism of the positive correlation is discussed. In the Junggar Basin, mudstone source rocks are present with volcanic rocks. Thus, during hydrocarbon generation, acidic petroleum fluid will interact with volcanic rocks. As Mn is a typical element that enriched in volcanic rocks, the petroleum migrate from source sequences will be Mn-rich accordingly. This Mn-rich fluid will have less and less Mn-concentration along migration direction with decreasing intensity of petroleum charging. Consequently, diagenetic calcite formed in the fluid will have the same varying trend of trace element. Then, the Mn-content has a positive correlation with oil/gas shows. This likely provides a possible novel tracer for oil migration. In some case studies, the tracer was successfully applied, showing promising prospects.

Iron and aluminum precipitates as metals and metalloids sinks in a passive treatment system

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Sorption capacity of synthetic or natural iron precipitates from acid mine drainages (AMD) has been widely studied by the use of laboratory batch experiments, while this kind of studies are less frequent concerning aluminum precipitates. However, a better understanding of the removal capacity of iron and specially aluminum precipitates at field conditions is needed.

For this purpose, we have study the different Fe and Al precipitates typically formed after the neutralization of AMD in the field. Monte Romero high monitored passive treatment system (SW Spain) was selected as the best field testing site because inside its reactive material the down flowing of AMD sequentially increases its pH, leading to the formation of two well differentiate Fe and Al precipitation horizons.

Mineral characterization was performed by XRD, Differential-XRD, SEM-EDS, EPMA and sequential extractions. Schwertmannite and goethite were identified as the Fe mineral phases in the studied samples, while the presence of hydrobasaluminite and amorphous Al(OH)₃ as Al mineral phases could only be suggested.

On the light of the sequential extraction results obtained, removed metals and metalloids could be classified in three different groups. The first group, including As and Ti, corresponds to elements completely removed in the Fe horizon. The second group includes elements complete (Cu and Pb) or partially (Zn) removed from the AMD by both Fe and Al precipitates, although Al precipitates removal is always higher than Fe precipitates removal. Finally the third group is formed by the elements completely removed by the Al precipitates (Si and Be). Although some of these elements were obtained after the specific sequential extraction step designed to release the adsorbed elements, only after the complete dissolution of the Fe and Al phases the great majority of the removed elements were released. These results offer a first insight into the stability and specificity of natural Fe and Al precipitates as metals and metalloids sinks.

Uplift and active tectonics of southern Albania inferred from dating of incised alluvial terraces

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The west part of the Balkans is formed by the Albanides convergence zone that produces permanent microseismicity and frequent earthquakes reaching intensities of IX. In Albania, the Osum and Vjose rivers cross the active graben and frontal thrust systems of the Albanides.

The effects of climatic and geodynamic forcing on their development were investigated by the means of field mapping, topographic surveying and compilation of absolute dating of alluvial terraces. We established the chronology of terraces abandonment from new (¹⁴C and *in situ* produced ¹⁰Be) and previously published dating (TL, ESR, U-series [1, 2, 3]).

We identified nine incised terraces units developed since the "Marine Isotopic Stage 6" (MIS 6), up to historic times. Once the climatic effect was identified, the vertical uplift has been quantified on a time scale shorter than the glacial climatic cycle. Regional bulging produces an overall increase of the incision rate from the west to the east that reaches a maximum value of 2.8 m/ka in the hinterland. Local pulses of incision are generated by activation of normal faults. The most active faults have a SW-NE trend and a vertical slip rate ranging from 1.8 to 2.2 m/ka. This study outlines the geodynamic control of the development of rivers flowing through the Albanides and mid-term neotectonic features are in agreement with the present-day NW-SE extension deduced from the GPS network [4].

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The isotopic composition of atmospheric zinc

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Zinc is emitted to the atmosphere by natural (soil erosion, volcanoes, vegetation) and anthropogenic (metallurgy, waste incineration, fuel combustion, fertilizers) sources, with both similar Zn fluxes on a global scale (~50±10 Ktons/yr.). Metal concentrations in aerosols, rain, snow or epiphytic lichens are often well correlated and reflect that of atmospheric fall out fluxes. In some samples, Zn concentration is decoupled from that of other metals, suggesting independent sources or a different behaviour during transport or deposition. Trying to document the various origins of atmospheric Zn, we have analysed the Zn isotopic composition of different biogeological samples having various Zn concentrations.

Samples were collected in an urban area of NE France (aerosols, lichens) and in Eastern Canada (rain/snow from single precipitation events, snow packs from two winter seasons, lichens). Samples yielded few ppb to hundreds ppm Zn with Al/Zn wt. ratios from near 0 to 40. As the average upper silicate crust has a mean Al/Zn > 1000, Zn originated from anthropogenic and/or other natural sources such as vegetation or volcanic material. The overall range in $\delta^{66}\text{Zn}$ values (relative to Zn JMC-Lyon) varies from 0.6‰ to -0.25‰. Lichens and aerosols from the urban area display the same $\delta^{66}\text{Zn}$ values ($0.1\pm0.1\text{‰}$), very similar to the mean composition of ore Zn ($0.16\pm0.2\text{‰}$; [1]). Lichens from remote area in Canada yielded heavier Zn with $\delta^{66}\text{Zn}$ from 0.25 to 0.6‰, towards values reported for Russian lichens ($1\pm0.2\text{‰}$) sampled near a mining/process plant [2]. Zinc retrieved from snow packs (from ca. 40000 km² in the St. Lawrence valley) have very homogeneous $\delta^{66}\text{Zn}$ ($-0.02\pm0.04\text{‰}$, n=9), whereas single precipitation samples have statistically lighter Zn ($-0.18\pm0.10\text{‰}$; n=7). This suggests that dissolved (light) and solid (heavy) atmospheric Zn species may have an overall different isotopic composition. Low $\delta^{66}\text{Zn}$ may originate from th192 input of refined Zn and/or automotive circulation whereas high $\delta^{66}\text{Zn}$ might come from industrial process residual Zn or the contribution of organic aerosols from vegetation.

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Molecular level *in silico* analysis of mass and energy flows in microbial communities

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Motivation

Complex microbial communities drive the Earth's biogeochemical cycles. In spite of their importance, the biochemical interactions within these communities are not yet well understood, nor are many *in silico* methodologies available for studying them.

Results

Three *in silico* methodologies were developed for studying mass and energy flows in microbial communities on the molecular level. Each approach has distinct advantages and disadvantages suitable for analyzing systems with different degrees of complexity and *a priori* knowledge. These methodologies were tested and compared using the extensive data from the phototrophic, thermophilic mat communities at Octopus and Mushroom springs in Yellowstone National Park. The models included three community guild members: cyanobacteria, filamentous anoxygenic phototrophs, and sulfate reducing bacteria. The *in silico* models were used to explore fundamental microbial ecology questions including the prediction and explanation for measured relative abundances of the oxygenic phototrophic primary producer cyanobacteria and the filamentous anoxygenic phototrophic bacteria. The three approaches represent a flexible toolbox which can be rapidly adapted to study other microbial systems with a variety of electron donors and acceptors on scales ranging from individual cells in a pure culture to entire ecosystems represented by metagenomic data.

Asian aerosols: Current and future distributions and implications to air quality and regional climate change

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Asian environments contain high levels of aerosols and these have profound impacts on human health and on climate change. Vast regions (>80%) in Asia have PM_{2.5} concentrations that exceed on an annual basis the WHO guideline of 10 µg/m³, often by factors of 2 to 4. The high aerosol loadings cause a significant dimming at the surface, and mask ~45% of the warming by greenhouse gases. In this paper, we present results using the STEM chemical transport model to help describe the regional distributions and seasonal cycles of Asian aerosols. The seasonal cycles of Asian aerosols are shown to be driven by seasonal variations in emissions associated with combustion processes such as open biomass burning and heating cycles, monsoonal flows that bring strong on-shore flows across large regions, and strong flows across arid and semi-arid regions resulting in large quantities of wind blown dust. We also discuss some of the important impacts of Asian aerosols on human health and the climate system. Finally, we look to the future and discuss the implications for aerosol emissions in Asia, and the opportunities for win-win strategies built upon addressing air quality and climate change together. Throughout the paper we focus special attention on black carbon (BC) because of its unique role as the aerosol that acts like a greenhouse gas and warms the atmosphere, and its importance in human health effects.

Heavy metal (Cd^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+}) uptake from seawater by calcite

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In some coastal areas, the anthropogenic inputs of trace metals to the surface ocean exceed the natural inputs from continental sources. One example is found in the southwestern coast of Spain, where the waters from Rio Tinto, that drain the Iberian Pyrite Belt, transport enhanced concentrations of dissolved metals into the ocean [1].

Several studies have demonstrated that the mobility of divalent metals such as Cd, Co, Ni and Zn, in freshwater environments, is reduced when the metals are sorbed to calcite forming (Me^{2+} ,Ca) CO_3 solid solutions. This sorption was shown to be especially effective in the case of Cd (e.g. [2]). In the oceans, however, calcite is usually not considered to be a significant scavenging phase for these trace elements [3] and there are few experimental studies on the uptake of metals from seawater.

The aim of this work is to determine if these metals could be inorganically removed from seawater by sorption to calcite, thus contributing to a natural attenuation of high metal concentrations in marine environments. To study the effect this uptake might have on the metal concentrations in seawater, sorption experiments were carried out by reacting calcite particles (1-25 μm) with metal-enriched artificial seawater solutions, in continuously stirred vessels at ambient conditions. Experiments for each metal were done in separate, with initial concentrations of ~ 1 ppm in all cases. Samples of the seawater were collected throughout the duration of the experiments, and the concentrations of the considered dissolved metals were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES).

A decrease in concentration in seawater was observed for each metal. Our preliminary experiments suggest that the sequence of metals, from the most to the least sorbed to calcite, might differ from the sequence determined by [2] regarding the preferential partitioning of the metals in freshwater solutions.

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Investigation of nanoparticles and carbon nanotubes toxicity and transfer in bacteria and plants

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If released in the environment, nanoparticles and carbon nanotubes might have devastating effects on ecosystems. This work explores the relative toxicity of TiO_2 , Al_2O_3 nanoparticles and multi-walled carbon nanotubes water suspensions towards two bacterial strains (*Cupriavidus metallidurans* CH34 and *Escherichia coli* MG1655) and three plants species (*Arabidopsis thaliana*; wheat, *Triticum aestivum* and the Indian mustard, *Brassica juncea*). A panel of nanoparticles have been used, the aim of this work being to evaluate the influence of physico-chemical characteristics, *i.e.* size, shape, crystal phase, purity, surface charge, on bacterial and plant response.

Firstly, nanoparticles were precisely characterized. Nanoparticle dispersion and stability was optimized by using biologically-compatible surfactants. Antibacterial properties and seed germination inhibition were assessed on the test organisms. Uptake of nanoparticles was observed by transmission electron microscopy.

In our conditions, nanoparticles display antimicrobial activity on *E. coli* MG1655, but not on *C. metallidurans* CH34. This activity does not depend on nanotubes length and purity, but depends on TiO_2 diameter and crystal phase. It is not linked to nanoparticle uptake, since some TiO_2 nanoparticles are internalized by *C. metallidurans* CH34, where they do not exhibit any antibacterial properties. Seed germination inhibition also varies with nanoparticles physico-chemical characteristics.

Taken together, these results suggest the need for improved understanding of nanoparticles behavior and lifecycle, both in the environment and towards living species, in order to guarantee their safe handling and disposal.

Heavy metals in ice cores from mexican mountains

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The first interest on drilling and analysis ice cores for general chemistry and isotopes was in Antarctica, Greenland and the Alps. Then the interest moved to other major mountain ranges. Since the 1990's several kilometres of ice cores have been drilled in the Himalayas, Alaska, Andes, and even Kilimanjaro [1, 2]. However, no attention had been focused on the Mexican Glaciers. Ground Penetration Radar data indicates more than 30 m of ice in the thickest section of the glaciers. Geographically these glaciers are important because they are the only glaciers between Ecuador and norther USA in North America, and some of the very few at 19-20° north latitude in the world. Low latitud glaciers are unique in various ways since they have archives of past climate and environmental changes on millenial to decadal times escales [1]. We present here preliminary data on heavy metals in the ice from three shallow ice cores (1.6 meters depth) in Iztaccihuatl (5,280 meters above sea level –masl- total altitude; one core at 5,130 masl) and Pico de Orizaba (5, 714 masl total altitude; two cores, one at 5,100 masl and other at 5,200 masl). The data indicates that some concentrations of Cl, NO₃, SO₄, Fe, Ni Cu, Zn, Pb and As very likely are from aerosols and atmospheric dust. However, there are some anomalies in Zn, Co, Cu and Ni that need other sources to explain their concentrations. We also present some correlations between some heavy metals in the Iztaccihualt ice (located relatively close to Mexico City atmospheric influence) and Pico de Orizaba ice (relatively far from any big city). No age dates have been obtained for these glaciirs, but Vazquez-Selem & Heine [3] suggest that the current glaciers in Mexico are the remains of bigger glaciers during the Little Ice Age, so the dephest ice should be, at least a couple of hundred years old. This current investigatios aims to get ice cores from all the depth.

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Degradation and transformation of organic nitrogen compounds in two Swiss lakes—linking biogeochemistry and microbiology

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In order to study the fate of lacustrine organic nitrogen compounds in two Swiss lakes dissolved organic matter (DOM) and particulate organic matter (POM) were sampled. The study sites distinguish themselves in trophic level and redox conditions. Lake Brienz was chosen as an oligotrophic and fully oxic peri-alpine lake. By contrast Lake Zug is eutrophic and under a certain water depth anoxic. Ten different water depths throughout the entire water column were sampled and additionally a core from the underlying sediment was taken. The concentrations of single amino acids and amino sugars which mainly contribute to the DOM and POM in lakes were measured in all samples. To characterize the degradation status of the organic material the pigment based Chlorin Index and amino sugar ratios were applied. Additionally, variations in amino acids patterns related to degradation processes were investigated. One focus of this study is set on biomarkers as the amino sugar muramic acid and D-amino acids which can be synthesized only by bacteria.

In a further step the obtained results will be linked to microbiological data characterizing the microbial communities in the two lakes. Changes in the microbial communities as well as their abundances will be related to organic matter changes. Here we present first results from both lake systems.

Geochemical and isotopes approach on the characterization of groundwater paths in Sintra Massive (Portugal)

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Groundwater from crystalline aquifers developed in the Sintra igneous massive is widely used for drinking water supply. The identification of recharge areas and flow paths are important for the correct definition of aquifer protection areas. Chemical and isotopic compositions of the groundwater samples were examined and water-rock interaction studies have been used in order to elucidate about the origin and the chemical evolution of the groundwater pathways.

Sub-alkaline to calc-alkaline granite dominates the high-level plutonic massif of Sintra, while two overlapping ring complexes recognised within it consist of four distinct alkaline to sub-alkaline quartz-bearing syenitic units, together with intrusions of a remarkable kaersutite- and (titan?) biotite-bearing theralite heteromorph (Mafrate) [1].

The water composition varies from sodium-chloride to calcium-bicarbonate, with a wide range of mineralization; the pH ranges from neutral to slightly acid (7.06-5.79). The Ca and Mg enrichment is observed in waters circulating in syenite and gabro aquifers. The dissolved silica concentration is higher in waters of syenite rocks (up to 45 mg/L), as a result of increased dissolution of plagioclase relative to quartz and feldspars.

Environmental isotope data ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) show an ^{18}O enrichment in waters from the N slope, with average values of -4.09 ‰ and -25.6 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ respectively; while in the S part -4.54 ‰ and -25.0 ‰ were obtained. This isotope enrichment could be related with the first condensation effect of the water vapour masses entering the continent and allowed to separate two main recharge areas.

The water-rock interaction studies have shown that the sea side location, aluminosilicates dissolution (sodium or calcium) and the water residence time in aquifers are the main responsible processes for the groundwaters chemical evolution.

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Geochemistry of soils close to abandoned Sb-Au and As-Au mines from Valongo, northern Portugal

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The Valongo area lies c.18 km at east of Porto, in the Dúrcio - Beirão district, northern Portugal. In this region Variscan folding gave rise to the large Valongo anticline and a syncline to the west. The Valongo anticline is limited at southwest by the Douro Shear Zone and at northeast by the granite. It comprises Cambrian to Carboniferous metasediments. The Cambrian schist-metagraywacke complex predominates in the region. The Sb-Au quartz veins outcrop on the western limb of the anticline, filling faults and shear zones and are hosted by Cambrian phyllites and metagraywackes. There are several abandoned mines, such as Montalto and Tapada. The As-Au quartz veins outcrop on the eastern limb and are hosted by Ordovician quartzites and schists and were exploited at Banjas mine. The Sb-Au quartz veins contain mainly quartz, arsenopyrite, pyrrhotite, pyrite, marcasite, sphalerite, chalcophyrite, galena, gold, tetrahedrite, jamesonite, plagioclase, berthierite, stibnite, antimony and carbonates. The As-Au quartz veins consist of quartz, arsenopyrite, pyrite, pyrrhotite, cobaltite, sphalerite, boulangerite, tetrahedrite and siderite. Soils close to the Tapada Sb-Au mine have the highest Sb and As contents, 21776 ppm and 1116 ppm, respectively, whereas those close to the Montalto Sb-Au mine show up to 767 ppm Sb and 338 ppm As. Soils close to the Banjas As-Au mine contain up to 904 ppm As. Soils have acid to neutral pH (3.8-7.6), low conductivity (0-69 $\mu\text{S}/\text{cm}$), but few samples have 209 $\mu\text{S}/\text{cm}$ and 732 $\mu\text{S}/\text{cm}$ close to Montalto and 818 $\mu\text{S}/\text{cm}$ close to Banjas, low to high organic matter content (17-134 g/kg) and low cation exchange capacity (1.6-9.7 cmol kg^{-1}). The particle size distribution shows a low clay content (2.2-5.3 %). Kaolinite is the most abundant clay mineral in soils. However, soils also contain muscovite, chlorite, smectite, vermiculite and mica-smectite, goethite, ferrihydrite, hematite and lepidocrocite. The BCR shows that Sb and As are not bioavailable in soils, because these metalloids are mostly retained in the residual fraction (71-100%) and only up to 101 ppm Sb and 54 ppm As are in oxyhydroxides. Sb and As are mostly adsorbed by clay minerals. Al, Cr, Cu, Fe, Mn, Ni, Pb and Zn are the most adsorbed in the highest available fractions and are bioavailable.

Geochemical characterisation of hypersaline anoxic brine basins from eastern Mediterranean Sea

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Amongst the most extreme deep marine environments found on Earth are the hypersaline anoxic brine basins in the Eastern Mediterranean. These are characterized not only by their high pressure and density, but also by their distinct redox interfaces, high salt, methane, and sulphide contents. These hypersaline anoxic brine lakes resulted from the dissolution of subterranean late-Miocene salt deposits [1].

Despite these extreme conditions and the limited exchanges between brine and overlying seawater, several microbe communities have developed [2].

Chemically all brine basins are distinguished by elevated methane concentrations ranging from 0.1 to > 10 mM (or 50.000 to >5.000.000 times background seawater methane concentration). In addition, distinct differences occur in sediment composition between the various basins, which may in part be related to differential preservation of suspended matter fluxes, to early diagenetic reactions and the production of minerals, and to different brine composition and density.

Preliminary results from a multidisciplinary study of water and sediment samples collected during the 2008 DOPPIO cruise with RV Pelagia will be presented.

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Geogenic trace elements in groundwaters in the Mt Etna region: Geostatistical, proteomic and epidemiological approaches to assessing human exposure and health risks

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Approximately 1,000,000 people live in the region of Mt Etna and rely upon local groundwaters as their main drinking water source. Volcanic CO₂ in the aquifer is thought to result in leaching of geogenic elements into the groundwater [1] with concentrations of trace elements (TEs) such as Mn, As, V, Fe and Se, often exceeding the National/EU MCL/PV for drinking water [1, 2]; however no comprehensive study of associated health risks has been published to our knowledge.

We present a study of TE hazard in groundwater and exposure assessment as a foundation for assessing TE-attributable human health risks in this population. Hazard distribution was modelled geostatistically from point data. Population characterization, including food and water consumption habits, was determined via questionnaires. To determine biomarkers of exposure, hair, nails and urine have been collected from a small community in Mt. Etna (Linguaglossa) where a possible Multiple Sclerosis cluster has been reported by Nicoletti *et al.* [3]. ICP-MS and AAS is being used to determine total TE concentrations in hair, nails and urine, whilst proteomic analyses of urine (MALDI-TOF and 2D-PAGE) have been performed to reveal new biomarkers of exposure and/or pathology.

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As mobilization and accumulation in topsoils (Chalkidiki, Greece)

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The geothermal field of Chalkidiki prefecture, Northern Greece, is known as an arsenic rich region. Arsenic concentrations range from 300 to 3000 ppb in groundwater within the area. Agriculture is the first economic activity and fields are irrigated during the dry period from May to September (600 mm/yr). A soil sampling campaign conducted in 2008 found As concentrations (HNO₃ digestion) in irrigated topsoil ranging from 5 to 110 mg/kg outside the geothermal area and from 20 to 520 mg/kg inside the geothermal area. Topsoil containing more than 200 mg As/kg is in need of remediation according to intervention values reported by most of the EU countries (EUR 22805-EN, 2007). In the same area, high As concentrations, up to 690 mg/kg, were found in some limestone rocks which may represent a source for arsenic in groundwater. Core soils (50 cm depth) collected in As rich irrigated areas showed a good correlation among As and Ca along the vertical profile.

A selection of 11 soils with different As contents (low <30 mg/kg, medium 30<mg/kg<200 and high>200 mg/kg) was used for column leaching experiments. Synthetic rainwater (no As) and irrigation water (1500 ppb As) were used to simulate 10 rainfall events (50 mm each) followed by 10 irrigation events (50 mm each). The amount of As leached during the rain events varied from 0.5 % to 6.0 % of the initial amount. The amount leached is correlated with the fraction of clay, stressing the importance of the residence time of water in soil to desorb arsenic. The As adsorbed during the irrigation period (12.5 mg/kg added) ranged from 6.3-12.4 mg/kg. Soils with low As content showed almost 100% sorption capacity, but even the soil with high arsenic content could still sorb at least 50% of the As contained in the irrigation water. These results suggest that arsenic accumulates in agricultural topsoils during the summer period and that about 30% is re-mobilized during the winter rainfalls. Risks to food safety and yield are likely to increase with the build-up of As in the soil and further investigation of the As content in agricultural products could be of interest in this region to quantify the soil to plant transfer coefficient. We acknowledge funding from the European Commission (AquaTRAIN MRTN-CT-2006-035420).

⁴⁰Ar/³⁹Ar thermochronology using plagioclase

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⁴⁰Ar/³⁹Ar thermochronometry using plagioclase holds tremendous potential for quantifying thermal evolution on Earth and other planetary bodies. Detailed diffusion experiments on single crystals of plagioclase from a gabbro in the Bushveld Complex yield activation energies of 36-48 kcal/mol, positively correlated with $\ln(D_0/a^2)$, which varies between 5 and 10, corresponding to closure temperatures of 200 to 300°C for a 10°C/Ma cooling rate. Age spectra generally conform to single-domain diffusive loss profiles, which suggests that grain-scale diffusion dominates argon transport in this homogenous plagioclase. The observed diffusion kinetics predict the differences in discordance observed in the age spectra (i.e. the most retentive grains have the least disturbed age spectra) and yield an internally consistent thermal history.

The cause of observed differences in diffusion kinetics between the plagioclase grains is not clear, but the differences appear to be inherent to each grain. ³⁹Ar and ³⁷Ar diffusion experiments on a variety of plagioclase with differing compositions and microstructural characteristics reveal an even larger range of apparent E_a and D_0/a^2 than that observed in the Bushveld gabbro. It appears that natural variations in plagioclase argon diffusion kinetics preclude a generically applicable set of diffusion parameters unless large uncertainties ($\pm 100^\circ\text{C}$) are ascribed to them. However, when argon diffusion kinetics are quantified for each grain of interest, a sensitive thermochronology below 400°C can be attained.

Complexities arise in samples having microscopic exsolution. Arrhenius arrays are consistent with multiple diffusion domains or experimental coarsening of subgrain diffusion domains. Substantial Ca and K zoning also produces irregular Arrhenius plots, although corrections can readily be made if zoning is well characterized. Temperature cycling to lower temperatures often yields irreproducible results if measurements follow heating to ~800-850°C, possibly due a structural transition occurring during prolonged heating. More obvious deviations from linear Arrhenius arrays occur above ~950-1000°C. Taken together, this suggests much previous data acquired under suboptimal laboratory conditions and with multiple grains has questionable reliability.

Melting of subducted mélanges in mantle wedge plumes: Eutectic-like behaviour in the generation of batholiths

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Albeit the relevance of arc magmatism on a global scale, the processes involved in its generation remain controversial. Here we show new experimental data aimed to test a new conception for arc magma generation based on melting of ascending mantle wedge plumes. Partial and near-total melting of composite sources is addressed here using constraints imposed by recently developed numerical experiments on the thermo-mechanical evolution of the suprasubduction mantle wedge. Our results support the generation of large amount of hybrid, calc-alkaline magmas by partial or total sub-lithospheric melting of a mechanically mixed mantle-crust composite source corresponding to a subducted tectonic melange. According to our hypothesis generation of many batholiths is related to formation, ascent and spreading of large compositionally buoyant mantle wedge plumes triggered by hydration, deformation and melting processes atop the subducting slab. Melting experiments on composite MORB-sediment mélanges were run at 1000-1200°C, 1.5-2.0 GPa, which correspond to conditions of final sub-lithospheric emplacement of thermal-chemical plumes within the shallow sub-lithospheric mantle. The composition of melts formed after partial melting of end-members bulk compositions (greywacke and MORB) is not buffered, forming granitic (melting of greywacke) and tonalitic (melting of MORB) melts in high-variance assemblages Melt+Grt+Pl and Melt+Grt+Cpx, respectively. However, the composition of melts formed after partial melting of greywacke-MORB mélanges is strongly "buffered" (i.e stabilized in the binary-eutectic-like fashion for greywacke-MORB ratios ranging from 3:1 to 1:3), producing compositionally stable andesitic-granodioritic liquid in lower-variance phase assemblage Melt+Grt+Cpx+Pl. Our hypothesis may explain satisfactorily the geochemical and isotopic features of arc magmas without implying any hidden process or hidden geochemical reservoir.

Interfacial water ordering and complex oxoanion adsorption on hematite and corundum surfaces

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Development of thermodynamic and kinetic models to predict the behavior of chemical species in environmental and geological systems benefit from a fundamental understanding of mineral-water interface structure and reactivity. Our work in recent years has sought to provide new insight into metal oxide-water interfaces in two areas: the ordering of water and the mechanisms of oxoanion adsorption at these interfaces.

We have explored the structure of interfacial water on a number of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and corundum ($\alpha\text{-Al}_2\text{O}_3$) surfaces. While ordering in this water appears to be a general phenomenon, with the degree of ordering declining away from the surface on the length scale of approximately 1-2 nanometers, quantitative differences in water structure and positional disorder exist among the different surfaces examined [1-3].

We have also recently investigated arsenate (AsO_4^{3-}) adsorption on the (012) surfaces of these minerals and have demonstrated that the accepted conceptual model for this process has been missing a key mechanism: outer-sphere adsorption. We observed that arsenate simultaneously forms inner- and outer-sphere surface complexes at pH 5 and 0.01 M ionic strength on both oxides [4]. We have begun to investigate the dependence of this unexpectedly complex adsorption behavior on pH, ionic strength, and the crystallographic orientation of the sorbent mineral phase. These studies explore how variations in chemical conditions and interfacial water ordering affect arsenate adsorption behavior. Our observations suggest that the molecular-scale arrangement of water near a mineral surface and the chemical properties of that surface are connected.

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A maximum age of the Nuvvuagittuq supracrustal belt, northern Québec (Canada) at 3.77 Ga

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The Nuvvuagittuq supracrustal belt (NSB) is the oldest granitoid gneiss complex so far discovered in Canada's Northeast Superior Province (NESP). U-Pb zircon ages for ortho- and banded gneiss sheets which transect NSB volcano-sedimentary lithologies (banded iron-formation, quartz-biotite schists, and various amphibolites) established a minimum age for these rocks of 3.75 Ga [1, 2]. Mineral-pair thermometry, zircon U-Th-Pb age vs. depth profiles, REE-partitioning and Ti_{Zr} thermometry, shows that the NSB subsequently experienced several episodes of deformation and thermal metamorphism which began at 3.6 Ga with granitoid intrusions surrounding the belt, and culminated with terrane assembly at upper amphibolite facies in the late Archean [3]. NSB rocks preserve abundant cummingtonite-rich amphibolites with unusually low Ca-content [4]; based on field relations they are unlikely to be gabbroic, and geochemistry indicates the protolith may have been an altered tuff. A recent study of the cummingtonite rocks, and a 3.75 Ga granitoid gneiss at Porpoise Cove, reported resolvable deficits in ^{142}Nd relative to the terrestrial standard [5]. Yet, these same rocks also preserve conventional $^{147}Sm/^{143}Nd$ isochron ages of ca. 3.8 Ga [5]; consonant with U-Pb zircon geochronology [1]. If the NSB amphibolites represent ancient crust isolated from the evolving mantle around ca. 4.28 Ga as proposed [5], it makes sense to independently verify the possibility. The amphibolites are characteristically low in Zr (<50 ppm), and no igneous zircon has so far been found. Our fieldwork (July 2008) identified four candidate detrital quartzites (Qtz+Fuch+Po±Mag±Zirc) in the NSB, including one sample from within the ^{142}Nd -deficient cummingtonite reported in [5]. We find that the oldest, most concordant zircons which also have igneous Th/U compositions and Ti_{Zr} temperatures in these samples is 3.77 Ga. Based on these results, we propose that the maximum age of the NSB is ca. 3.8 Ga and that earlier ^{142}Nd deficits may have been inherited by isolated remelting of some remnant of Hadean crust.

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Evidence that barely-contained nearly-explosive venting of large volumes of magmatic volatiles initiated porphyry Cu formation

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Conversion of hornblende to biotite through the addition of K at high temperature is the earliest, most extensive alteration in porphyry copper deposits. In the Butte deposit in Montana a 7 x 4 x 2 km deep rock volume is altered by the addition of ~1 wt% K at ~600°C. The transition to fresh quartz monzonite occurs over a distance of only ~230 m. The pre-main stage porphyries and the main stage veins sit within a small portion of the K alteration.

The volume of magmatic volatiles vented is measured by the K altered rock volume; the rate of volatile expulsion by the width of the transition zone. Division gives the duration of venting. The most likely parameter values at Butte indicates that the alteration occurred in ~900 years when ~100 x 10⁹ m³ of magmatic volatiles were expelled from an ~8.3 km diameter magma body. Uncertainties in matrix porosity, pore tortuosity, and fracture spacing and the fraction transmitting fluid at any one time suggest range of 1/3rd to ~50 times the 900 year estimate.

The K alteration requires 22 times the volatile volume needed to heat the rock to 600°C. Thus the Butte system started by heating a rock volume ~3 times larger than that potassically altered, and the K alteration occurred under isothermal conditions. The two pre-main stage porphyry deposits formed as the venting waned and the system cooled to ~450°C, allowing SO₂ to disproportionate to H₂SO₄ and H₂S. System life was ~500,000 years- the conductive cooling time of the heated volume. This is a reasonable estimate provided weak venting did not significantly prolong nor convection accelerate the cooling. The spectacular 3 m wide main stage chalcocite veins formed ~1.8 Ma after the pre-main stage as a consequence of a less contained venting of volatiles from a second intrusion.

Porphyries are susceptible to explosive eruption (Mt Pinatubo, sector failure, pebble dikes). The evolution from rapid to slower, cooler venting with mineralization and acid attack matches geological observations. Rapid initial venting requires rapid magma crystallization and it is challenging to understand how this might occur.

Proof of biogenic origin of marine aerosol by ^{13}C and ^{14}C analysis

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A contribution of various sources to aerosol organic matter has been notoriously difficult to discern due to the poorly resolved organic matter speciation, but is of paramount importance to global carbon budget. Carbon isotope analysis can offer a powerful tool, because different sources have unique isotopic signatures [1]. Carbon isotope measurements of marine aerosols have been very rare [2] mainly due to technical and analytical challenges. By combining stable carbon isotope (^{13}C) and radiocarbon (^{14}C) analytical methods we were able to prove biogenic origin of marine aerosol over the North Atlantic. During MAP project submicron aerosol was sampled during 2006 and analysed for ^{13}C and ^{14}C . ^{13}C ratio of marine aerosol was between -21 and -23‰, while polluted aerosol exhibited much lower ratios between -25 and -27‰ with significant seasonal pattern. By using isotope mixing equation it was possible to discern marine and continental organic matter using ^{13}C data only. ^{14}C analysis enabled to discern continental natural and anthropogenic sources by separating 'modern' and 'fossil' carbon [3]. ^{14}C analysis revealed the dominant fraction of non-fossil carbon in marine aerosols and still substantial fraction of non-fossil carbon in polluted (continental) aerosol. An even more detailed picture is emerging if organic and black carbon fractions can be separated for isotope analysis. By combining ^{13}C and ^{14}C data one can calculate regional aerosol carbon budget.

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Influence of sulfide mineralogy on oxygen and sulfur isotope ratios of sulfate generated via oxidation

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An important source of terrestrial sulfate is oxidative weathering of sulfide minerals. Mineralogical data indicate that the structure of pyrite (FeS_2) is unique and that this mineral is oxidized by different mechanisms compared to sphalerite (ZnS), galena (PbS) and S^0 [1]. In order to test if the oxidation of distinct sulfide minerals produces sulfate having different $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values, we carried out metal sulfide oxidation experiments (biological vs. abiotic) at pH 3.0 and 2.7 under aerobic and anaerobic conditions, with water having different $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values. Pyrite, sphalerite, galena and S^0 were used in the experiments. Biological experiments were conducted in the presence of Fe(II)-sulfur oxidizing bacterium, *Acidithiobacillus ferrooxidans*. The $\delta^{18}\text{O}_{\text{SO}_4}$ values from aerobic biological S^0 & ZnS and anaerobic ZnS experiments indicated that H_2O was the sole source of O_2 for sulfate with an oxygen isotope enrichment factor ($\epsilon_{(\text{SO}_4\text{-H}_2\text{O})}$) of ~ 9 ‰. $\epsilon_{(\text{SO}_4\text{-H}_2\text{O})}$ for the aerobic/anaerobic biological FeS_2 experiments was ~ 4 ‰. These results suggest that $\delta^{18}\text{O}_{\text{SO}_4}$ values from aerobic and anaerobic sphalerite and the aerobic S^0 experiments were ~ 5 ‰ higher compared to those from FeS_2 experiments. The $\delta^{34}\text{S}_{\text{SO}_4}$ from aerobic & anaerobic FeS_2 experiments closely reflected the parent $\delta^{34}\text{S}_{\text{FeS}_2}$ value (<1 ‰) whereas the $\delta^{34}\text{S}_{\text{SO}_4}$ values from anaerobic ZnS experiments were ~ 3 ‰ lower than the $\delta^{34}\text{S}_{\text{ZnS}}$ value. Our experimental results compared well with the $\delta^{18}\text{O}_{\text{SO}_4}$ values observed at different acid mine drainage sites, suggesting that $\delta^{18}\text{O}_{\text{SO}_4}$ values may be used to elucidate the mineralogy of the oxidized minerals.

[1] Crundwell (1988) *Hydrometallurgy* **21** 155-190.

Allanite *in situ* dating in mylonite: Case study at the Mt Mucrone, Italy

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Allanite occurs in meta-granodiorite showing different amounts of strain, from undeformed (a) to mylonitic (f). This body intruded the polycyclic Sesia basement at Permian times and underwent HP metamorphism during the Alpine convergence. We study the effects of deformation on allanite U-Th-Pb apparent ages.

Relics of Permian magmatic monazite are found exclusively in the undeformed samples where the magmatic textures and minerals are largely preserved. Coronas of allanite, thorite and apatite surround monazite relics indicating the reaction: monazite + plagioclase + fluid → allanite + apatite + thorite.

In the mylonite, allanite forms mm-size grains in a strongly recrystallised matrix, whereas it is restricted to tiny (ca. 50 µm) rims around monazite in the undeformed samples. Allanite is generally associated to the HP assemblage garnet + phengite. Its chemical zonation patterns are not altered in the deformation profile (a)-(f).

Preliminary LA-ICPMS dating of allanite does not indicate the expected metamorphic Alpine age based on petrographic and structural observations. All allanite grains show Permian ages independent of the degree of mylonitisation, recrystallisation and grain size. Despite drastic textural variations, allanite isotopic composition is uniform!

Allanite is a robust chronometer. A deeper look into textures and structures – that can be misleading at a first glance – is necessary to understand the significance of U-Th-Pb *in situ* ages in polycyclic rocks.

Effect of pyroclastic atmospheric fallout on YREE distribution in human bronchial washing solutions

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The eruption occurring during the 2001 on Mount Etna was characterised by the largest production of pyroclasts in the last 300 years. The fall out affected the urban area of Catania where YREE contents in bronchial alveolar wash solutions have been investigated to assess bioavailability of these elements in body fluids of people exposed to pyroclasts inhalation.

Obtained results evidence high YREE contents, Y-Ho decoupling and HREE enrichments in bronchial alveolar wash solutions. Y/Ho decoupling usually occur in F-rich hydrothermal fluids [1] due to the different dissolved behaviour of yttrium and holmium during complexation. At the same time increasing stability of REE dissolved complexes with several ligands, apart from Cl⁻, along the lanthanide series is a suitable explanation for observed HREE enrichment [2-3]. Furthermore, pyroclastic products are formed by a solid silicate fraction and soluble salts coating silicate surface. The last fraction has high trace element contents being formed during ash uprising inside the volcanic plume where trace elements are enriched as high temperature volatile complexes. Salt coating is highly soluble and quickly dissolves when exposed to aqueous media. Such features suggest dissolution of labile YREE-rich sublimates can provides large YREE bioavailability to body fluids. A comparison with YREE pattern in leaching solution from interaction between ash and seawater [4], excludes a contribution of YREE from leaching of silicate fraction.

[1] Bau (1996) *Contrib. Miner. Petrol.* **123**, 323-333.

[2] Wood (1990b) *Chem. Geol.* **88** 99-125. [3] Haas *et al.* (1995) *GCA* **59** 4329-4350. [4] Censi *et al.* (2007) *GCA* **71**, 5405-5422.

SEM-EDS applications in mineralogical phases study of oil well cements attacked with H₂S/CO₂ mixtures

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Ordinary Portland cement (OPC) is the main component in cementitious materials used in oil wells construction. The mineralogical changes caused by chemical interactions between this material and acid gases (H₂S and CO₂), has been studied [1, 2]. The behavior of some mineralogical species, that constitute the main OPC phases, can indicate the integrity of this material in terms of compressive strength. Particularly, Ca(OH)₂ transformation in CaCO₃ caused by carbonation process. This study shows the influence of gas mixtures, at different pH₂S/pCO₂ ratios, on the chemical, mineralogical and mechanical properties of cement samples (class G and H) exposed to high pressure (total pressure = 1500 psi) and temperature (160°C) in well bore real conditions, based on the exposure time (t = 20, 40 and 80 days). In-closed system conditions (Parr reactor type), partial pressure of pCO₂ = 38 atm, and pH₂S = 4, 8 and 16 atm, for 0.1, 0.2 and 0.4 pH₂S/pCO₂ ratio, were used in this work. Mineralogical phases composition was determined by X-Ray diffraction, and scanning electron microscope and energy dispersive spectrometer (SEM-EDS). These techniques can be used to track resulting changes in the cementitious material microstructure (i. e. porosity) as intensity of carbonation, and estimates can be made of possible effects that these changes may have on the performance of the cementitious material. Compressive strength measurements were made after controlled time exposures. The results indicate important changes in mineralogy. The most important H₂S effect is test tube leaching. CaCO₃ formation (vaterite, aragonite and calcite) is the principal effect of CO₂. Both processes affect cementitious materials integrity. For pH₂S/pCO₂ ratios around 0.2, the maximum value of compressive strength is reached. In conclusion, an important relationship between the compressive strength and the pH₂S/pCO₂ quotient was determined, therefore, the integrity of cementitious materials can be estimated according to previous parameters.

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Determination of source and transfer-time of river sediments in alluvial plain from U-series nuclides: Evidence from the Ganges River System

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²³⁸U-²³⁴U-²³⁰Th radioactive disequilibria were analysed in different granulometric fractions of Himalayan sediments from the Ganges river and one of its main tributary: the Narayani-Gandak river. Such a study was performed by taking advantage of the natural mineralogical sorting done by the river, that is by analysing coarse and suspended sediments collected at different depths of the water column.

The results highlight that U-series disequilibria of river sediments carried by the different rivers depend both on their grain size and on their location in the basin. This dependence is explained by a mixing scenario between a coarse sedimentary end-member and a fine-grained one, which transit with different time constant within the alluvial plain. The river coarse sediments are Himalayan sediments, which transit rather slowly through the plain (>100ky) due to long period of storage driven by avulsion processes, and are modified by chemical weathering and pedogenetic processes within the alluvial plain [1]. By contrast, the fine-grained end-member of the suspended materials is marked by recent U-Th fractionations processes most likely occurring in plain soil horizons, which could indicate a much more fast transfer for this fine sedimentary end-member from the high range to the Bay of Bengal.

These results highlight that sediment U-Th characteristics are strongly size-dependent, outlining therefore that studying the whole granulometric fractions of the sediments is of prime importance for a correct use of the U-Th disequilibria to perform mass balance calculations and to assess the steady-state nature of erosion at the scale of a watershed.

[1] Granet *et al.* (2007) *Earth and Planetary Science Letters* **261**, 389-406.

Microbialites from Rincon de Parangueo in the volcanic complex of Central Mexico

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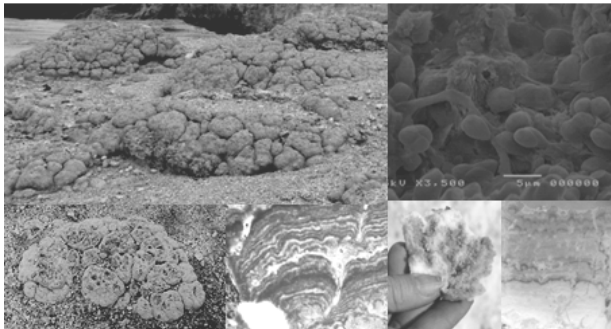
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Rincon de Parangueo (RP), a recently dissected crater lake from the volcanic complex of Central Mexico, represents an extreme environment where microbialites distribute irregularly along the external facies of the former crater lake. A previous short report [1] showed extreme geochemical conditions as a high pH (10) and high salinity in which only special microbial life could inhabit. These stromatolitic mounds pile up in regular groups varying in their individual sizes. They show a fine lamination within the first 2 mm of surface, followed by a coarser texture, exhibiting a typical stromatolitic microfabric in thin section.



Discussion

Preliminary results derived from different analysis under progress suggest both, a biogenic and abiogenic inputs in the construction of these carbonates. The microbialites from RP offer an intriguing example of recent microbialites from fresh-water settings that may help to clarify the role of microorganisms in the construction of ancient and recent microbialites.

[1] Chacon *et al.* (2003) *Origins of Life Proceed.* **32**, 592 pp.
Aranda-Gómez *et al.* (2009) *Proceed. IAS 3MC Conference.*

Petrogenesis of the Early Devonian metarhyolites in the Kelang basin at the southern margin of the Altay, Xinjiang: Implications for tectonic evolution

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The Chinese Altay is an important part of the Central Asian Orogenic Belt (CAOB). The Paleozoic tectonic evolution of the Chinese Altay has been controversial. The Early Devonian metarhyolites from the Kangbutiebao Formation in the Kelang basin at the southern margin of the Chinese Altay are wonderful examples to constrain its geological evolution history.

Geochemical data of these metarhyolites show that they have high SiO₂ (72.46% to 80.07%) and total alkali (Na₂O+K₂O) (6.38% to 11.34%) content, and low Al₂O₃ (9.68% to 12.19%), TiO₂ (0.17% to 0.35%), MgO (0.08% to 0.48%), CaO (0.14% to 0.73%) and TFeO (0.34% to 0.55%) content, which defines as calc-alkaline volcanic rock series. They are characterized by enrichment in light rare earth elements (LREEs) and high strength elements (HFSEs, e.g., Th, U, Pb, Zr and Hf), depletion in large ion lithophile elements (LILEs, e.g., Sr and Ba) and HFSEs (e.g., Nb, Ta, Ti, P) relative to primitive mantle. In addition, they have noticeable negative Eu anomalies ($\delta\text{Eu}=0.5-0.71$) and high Yb content relative to Chondrite. These geochemical characteristics indicate that the rhyolites were derived from the partial melting of the lower crust, and the residual minerals were plagioclase, amphibole and apatite. The primitive magma was likely resulted from the underplating, and underwent fractional crystallization and minor wall-rocks assimilation during the ascending of magma. These rhyolites formed in an active continental margin environment during the Early Devonian at the southern margin of the Altay.

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Silicon isotopic variability in Proterozoic cherts

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Biological fractionation of Si isotopes in the Phanerozoic marine realm has been well documented (e.g. [1]). In the absence of any known silica-secreting organisms, however, the Si cycle must have been very different in earlier oceans [2]. Cherts, which are common in the rock record of all ages, can provide important clues into states and processes of Earth's early Si cycle. However, the use of cherts as a direct proxy of the composition of Precambrian seawater (e.g. [3]) has its limitations because most cherts have formed during diagenesis of precursor sediments. In addition, while younger Proterozoic cherts are typically found in a peritidal environment, many Late Archean and Paleoproterozoic cherts precipitated along with Fe-bearing minerals in deepwater settings [4].

Keeping in mind the above mentioned complexities, we have analyzed Si-isotopes ($\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$) in well characterized Proterozoic cherts of varying ages (750-2500 Ma) deposited in different water depths. HF-free sample dissolution was performed using an alkali flux; Si was chemically purified using ion chromatography and isotope ratios were measured using a GV Isoprobe-P MC-ICPMS by sample-standard (NBS28) bracketing in high resolution.

$\delta^{30}\text{Si}$ of the cherts of the present study range from -4.36 to +1.84 ‰ (w.r.t. NBS28). The heaviest values obtained so far are from the 1.5 Ga old peritidal cherts of the Yushmanakh Formation, Siberia, while the lightest values are from Fe-associated basinal cherts from the 1.8 Ga Duck Creek Formation. Cherts associated with BIFs show systematically lighter Si-isotopic compositions consistent with fractionation of Si-isotopes during adsorption of silica on Fe-hydroxide particles [5]. The large range in $\delta^{30}\text{Si}$ (-2.6 to +1.26‰) in peritidal cherts from a single basin (Neoproterozoic Akademikerbreen Group, Spitsbergen) suggests that source variability as well as diagenesis must be taken into account when interpreting the Si isotopic compositions of Proterozoic cherts.

[1] De La Rocha *et al.* (1997) *GCA*, **61**, 5051-5056. [2] Siever (1992) *GCA*, **56**, 3265-3272. [3] Robert & Chaussidon (2006) *Nature*, **443**, 969-972. [4] Fischer & Knoll (2009) *Bull. GSA*, **121**, 222-235. [5] Delstanche *et al.* (2009) *GCA*, **73**, 923-934.

Spectroscopic investigations of uranyl reduction by Fe-bearing clays

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Ferrous iron in clay is a potential natural reductant in anoxic environments. The reduction of U^{VI} by Fe^{II} is an important pathway for the immobilization of uranium in subsurface as well as in high-level nuclear waste (HLW) repositories. In the present study, we employed three dithionite-bicarbonate-citrate (DCB) treated, Ca-exchanged Fe-bearing clays viz. montmorillonite (FeSM), Fe-rich smectite (Swa-1) and nontronite (NAu-2) with varying Fe content and studied the reactivity of structural and readsorbed (surface complexed) Fe(II) species in sorption-reduction of U at pH 6 under CO_2 -free anoxic atmosphere (<1 ppm O_2 (v/v)) by using XPS, EXAFS and ^{57}Fe Mössbauer spectroscopies. The surface complexed Fe(II) species on untreated, Ca-exchanged clays were not found to be reactive in uranyl reduction. All three partially (17-45%) reduced, Ca-exchanged clays remove U from solution with a fast rate (minutes-hours), followed by a slow (in months) reduction step. The EXAFS analysis showed that U forms a mononuclear bidentate surface complex with Fe in the untreated Ca-exchanged clays at near-neutral pH which is the pre-requisite for heterogeneous reduction of U by their analogue in DCB treated clays. The adsorbed U was present as partially reduced mixed valence state (U^{VI} and U^{IV}) in 15 days and 30 days. After 3 months, XANES spectra showed a substantial increase of U^{IV} (20-50%) at the expense of U^{VI} in case of reduced (DCB treated) FeSM, Swa-1 and complete reduction occurred (100%) in case of reduced NAu-2. The $\text{U}4f_{5/2}$ XPS spectra were deconvoluted into two components, a higher binding energy (393.2 ± 0.2 eV) for U^{VI} and a lower binding energy (391.5 ± 0.2 eV) for U^{IV} . Despite the presence of abundant structural Fe(II) species, the slow reduction of U might be due to (1) the stabilization of Ca in the clay interlayer inhibiting the cation release into solution linked to the electron transfer process, (2) the fewer number of potentially reactive Fe(II) in clays are accessible to uranium.

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How mountains are made out of molehills: The link between geological episodes and events as revealed by kinetic studies

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Rates of reaction and diffusion measured in the laboratory are increasingly being used to determine the durations of a variety of processes ranging from evolution of plumbing systems under volcanoes, through partial melting in the crust to stages of exhumation of metamorphic rocks and mountain ranges. The results are often unexpectedly short timescales of days to millenia, rather than millions of years. More conventional bulk isotopic data from these same rocks often date events separated by millions of years. However, confidence in the modern kinetic rates measured in the laboratory, combined with other geological observations, now indicate that the shorter timescales obtained from kinetic modelling relate in many cases to durations of individual episodes that make up the larger events that were more conventionally demarcated. The short duration of episodes are consistent with time scales of thermal relaxation and other physical processes. Indeed, the durations determined from kinetic modelling can be used as an added fingerprint to identify the nature of processes that produced particular chemical and textural features recorded in rocks. Examples from igneous as well as metamorphic systems will be discussed.

These improvements in the temporal resolution of geological processes have been made possible in part by advances in analytical methods that allow us to manipulate and measure concentration gradients over scales of a few nanometers. Scaling laws, such as the relation $x^2 \sim Dt$ for diffusion, allow us to translate the enhanced spatial resolution (x) to increased resolution of time (t), or duration of processes. These analytical advances allow us to (i) reliably determine smaller diffusion coefficients and other rate constants in the laboratory and (ii) measure rates at conditions close to those at which processes occur in nature, so that the large source of uncertainty that arose from extrapolation is largely eliminated. Some examples of such experimental studies will be shown from our recent works.

Two (nearly) single-mineral monitors of the activity of rutile, 2: Applications

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We have recently calibrated two exchange reactions involving Ti in micas that have equilibrated with rutile and quartz [1]. These calibrations allow estimation of:

- (1) $a(\text{Rt})$ in rutile-absent rocks, if pressure and temperature are known and SiO_2 (either quartz or coesite) is present;
- (2) Ti contents of mica coexisting with rutile and SiO_2 , if pressure and temperature are known;
- (3) temperature, if rutile and SiO_2 are present and pressure is known.

Although Ti in mica can serve as a thermometer in rutile-bearing assemblages, it is much less sensitive to T than Ti-in-Qtz, Zr-in-Rt or Ti-in-Zrc (assuming Zrc is present). Rather, we anticipate that the main application of this equilibrium will be for estimating $a(\text{Rt})$ in conjunction with Ti-in-Qtz and Ti-in-Zrc thermometry in rocks that lack rutile, and especially in high-variance or inclusion assemblages which limit the use of traditional geothermometers. For example, Hopkins *et al.* [2] calculated Ti-in-Zrc temperatures of $\sim 700^\circ\text{C}$ for Hadean zircons that lack rutile, but contain inclusions of muscovite (~ 0.4 wt% TiO_2) and quartz. When combined with our Ti-in-Ms calibration, $a(\text{Rt})$ for the Ms-Qtz inclusions is estimated to be ~ 0.85 . Iterative solution of T from Ti-in-Zrc and $a(\text{TiO}_2)$ from Ti-in-Ms increases the best-fit calculated temperature by $\sim 15^\circ\text{C}$. This result further supports the key conclusion that Hadean zircons formed in relatively low-T magmas.

The Ti content of mica can also serve as a useful check on equilibrium mineral compositions and assemblages. Our literature search uncovered several discrepancies in HP and UHP micas: the measured Ti content was 2-3 times lower than predicted from the inferred P-T conditions. These results imply that most phengite in HP and UHP rocks forms at low-T on the prograde path, and that many measured phengite compositions are not in equilibrium with the peak mineral assemblage.

In summary, while Ti-in-mica may not become a widespread thermometer, it can be used to diagnose chemical disequilibrium where T is already known, and refine temperatures determined using trace element thermometers for all mica + quartz-bearing assemblages.

[1] Kohn & Chambers (2009) *GCA*, this volume. [2] Hopkins *et al.* (2008) *Nature*, v. **456**, p. 493-496.

Australia's high heat producing granites: Importance, distribution and genesis

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Valuable new insights into the distribution and geological settings of U, Th and K rich (HHP) granites in Australia have come from interrogation of national datasets, supplemented by recent regional studies [1]. Within Australia, such granites have been implicated in the formation of U mineralization and are actively being investigated for geothermal energy potential.

The oldest HHP granites in Australia are late Archean (2.85 and 2.65-2.63 Ga) K-rich I-types in the Pilbara and Yilgarn Cratons [2]. These were produced on a large scale, cutting across terranes, by melting of tonalite-trondhjemite-granodiorite (TTG)-rich crust.

I- and A-type granites with high K and, locally very high U and Th are widespread in the Proterozoic in Australia. These also formed by crustal reworking particularly in the 1.8-1.5 Ga period [3].

Both I- and S-type HHP granites occur within the Paleozoic. The majority of these appear to have been derived by crustal melting, largely in late syn-tectonic, to post-collisional and back-arc extensional settings [2].

The high Th and U reflect both crustal reworking and fractional crystallisation, though enriched lower crustal sources are important for the Archean and most Proterozoic granites. The necessary high crustal geothermal gradients were possibly linked to crustal thinning, mantle inputs and thermal blanketing by sediments. Fractional crystallisation was dominant in the Palaeozoic high HHP granites.

[1] <http://www.ga.gov.au/minerals/research/oesp/index.jsp>

[2] Champion & Smithies (2007). 6th Int. Hutton Symp., Univ. Stellenbosch, S Africa, 2-6 July (2007). [3] Budd *et al.* (2001) *Geoscience Australia Record* 2001/12. 152pp.

Visualizing cell surfaces and biominerals in 3D: Cryo-electron microscopy and tomography of iron-oxidizing bacteria

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Prokaryotic microorganisms are small and abundant, representing an enormous amount of surface area available to interact with minerals and solutes in the environment. Despite much research on cell walls, membranes, and extracellular polymers, we are still learning about the variety of microbial surface configurations. Recent years have seen the development of cryotechniques for electron microscopy, which can eliminate traditional fixation and dehydration methods that severely damage cell components. With cryoTEM and tomography, more realistic, detailed, hydrated, 3D views of ultrastructure have been obtained, beginning a revolution in our understanding of cell organization and processes. In particular, delicate surface and extracellular structures are preserved, finally giving accurate images of surfaces exposed to the environment.

We focus on aerobic iron-rich systems because of their abundance in terrestrial and marine environments (e.g. iron seeps and hydrothermal vents), and because the constant mineral precipitation poses particular challenges to cells. We have been studying two iron-oxidizing bacteria: the terrestrial FeOB *Gallionella ferruginea* and marine FeOB *Mariprofundus ferroxydans*. While not closely related, they are remarkably similar in morphology and metabolism, making them an ideal pair for comparison. Both excrete abundant extracellular polymers in the form of twisted stalks, which appears to be a mechanism to rid the cell of ferric iron and nucleate further iron mineralization. Our previous work on culture and environmental samples (by scanning transmission x-ray microscopy and TEM) has shown that the cells escape encrustation. Thus, we hypothesize that they have developed surfaces designed for this task. We will present our results of live-cell time lapse microscopy, showing mineral formation processes of both microbes. We will also present cryo-transmission electron microscopy and tomography images, movies, and analyses, showing novel surface structures exhibited by both *Gallionella* and *Mariprofundus* cells. To our knowledge, these structures have not been documented in other microbes, and may represent a particular adaptation to highly mineralizing environments.

Magnitude of Precambrian impact experienced by native iron sample through High-pressure Mössbauer Spectroscopy

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Native Iron sample obtained from Proterozoic Mica schist of Chaibasa Shingbhum craton of Eastern India was studied by Mössbauer spectroscopy at ambient conditions. The Mössbauer parameters – isomer shift and magnetic hyperfine field, both correspond to the Fe⁰ ions present in the sample. To study the nature of the impact on the sample, high-pressure Mössbauer spectroscopic studies were carried out on the sample using Diamond anvil cell with 4:1 methanol:ethanol mixture as hydrostatic pressure medium up to 10 GPa [1]. Isomer shift remains almost constant up to ~5 GPa then shows continuous decrement. At ~9 GPa, onset of an extra peak is visible. Detailed study on the metallic iron (BCC structure) under high pressure using Mössbauer spectroscopic technique indicated continuous decrease in the isomer shift up to 13 GPa at which a sudden change corresponding to BCC→HCP transformation associated with appearance of an extra peak is observed [2-4]. Comparison of this parameter of native iron with metallic iron suggests the magnitude of the Precambrian impact experienced by the sample is about 6 GPa. The onset of extra peak at 9 GPa also confirms independently the impact origin of the sample, representing the Precambrian impact in the studied region.

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Terminal Ediacaran oceanic anoxia: Evidence from framboidal pyrites in the cherts of Laobao Formation (South China)

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The terminal Ediacaran strata at the deep-water facies along the southeast margin of Yangtze Block are composed of black rock series which are dominated by cherts and siliciclastic sediments. The suite of chert rocks, correlated with the contemporary Dengying Formation (ca. 551 ~ 542Ma) on the carbonate platform, widely spreads into a 1600-km belt in South China.

Laobao Formation at Silikou section, North Guangxi is composed of ca. 169-meter thickness of chert rocks with thick bedded cherts in the lower part and with bedded cherts increasing mud components into the upper part. Framboidal pyrites are prevalent in these chert rocks, and ten samples from the lower and upper unit were investigated for their sizes and distributions. Results show that these framboidal pyrites are dispersed and mainly in small sizes. The maximum framboid diameters in these samples are generally between 7.7 to 18 µm and are no more than 20 µm. The mean values of framboid diameters are less than 5 µm for the seven samples from the lower unit and around 6.5 µm for the three samples from upper unit. In addition, of framboids, more than 85% in the seven samples from the lower unit and ~65% for the three samples in the upper unit are less than 7 µm; only < 4% framboids in most chert samples are >10 µm.

The small grain sizes of these framboidal pyrites preserved in the Laobao cherts together with their narrow size range are well consistent with that they were formed in an euxinic water column, implying that the deep water in the Nanhua (South China) Basin was probably euxinic in the terminal Ediacaran. Mean and median values of framboid diameters and maximum diameters increased gradually upward the section, probably implying that the deep water of the basin was gradually oxidized when entering into the beginning of the Cambrian.

Exploring the relationship between molybdenum and organic matter through experimental approaches and XAS and NMR characterization

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Although used widely in studies investigating the evolution of biospheric oxygenation, mechanisms of secondary molybdenum (Mo) fixation in settings rich in organic matter and hydrogen sulfide remain unclear. A key micronutrient playing a particularly important role in nitrogenase metalloenzyme systems, Mo is the most abundant transition metal in the modern ocean and is conservative with a residence time of ca. 700,000 years. Mo is soluble under oxic conditions as the molybdate ion (MoO_4^{2-}) but becomes insoluble in anoxic settings. Based on these redox properties, many studies have used Mo to trace the extent of euxinia in the ancient ocean. When $[\text{H}_2\text{S}]$ approaches a threshold value of ca. 10 μM , the molybdate ion is converted to particle reactive tetrathiomolybdate (MoS_4^{2-}) through a series of oxythiomolybdate ($\text{MoO}_x\text{S}_{(4-x)}^{2-}$) steps [1]. Surprisingly, we know little about the direct role of organic matter in sequestering Mo, although many studies suggest a dominant linkage to organic delivery and burial [2]. This gap limits the utility of the Mo paleoproxy.

Here, we present preliminary results that speak to the binding relationship between highly reactive MoS_4^{2-} and different varieties of bulk organic matter. Specifically, we emphasize two types of allochthonous natural organic material isolated via reverse osmosis and three forms of pure autochthonous organic matter produced from pure bacterial cultures (cyanobacteria, green algae, and heterotrophic bacteria). The nature of the Mo – organic matter relationship was analyzed via EXAFS and XANES techniques to identify Mo oxidation state, chemical structure, coordination environment and nearest neighboring atoms. To refine our investigations, experimental products were also analyzed with ^1H , ^{13}C and ^{95}Mo NMR and ESI-MS. Collectively, these data should illuminate the long-elusive details regarding organic-Mo coupling, including the dominant types of organic matter, the critical functional groups and the possible role of organic sulfurization.

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Mineral trapping in Deccan Basalt Province India: Implications for geological sequestration of CO_2

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Atmospheric accumulation of CO_2 has drastically increased due to excess usage of fossil fuels in order to meet the ever increasing energy demands the world over. An option to mitigate the hazardous consequences of the above is the deep underground sequestration of CO_2 in suitable geological formations. Laboratory simulation experiments and field studies carried out here towards geological CO_2 sequestration are aimed at the feasibility of underground retention of CO_2 as a trapped solid phase stable over geological time scales. This study has shown that the injected CO_2 has reacted with the host rocks leading to the formation of secondary carbonate minerals due to mineral trapping. This study on the mafic-ultramafic rocks constituting the Deccan Continental Flood Basalt Province (DCFBP), India has shown appreciable concentration of iron, magnesium, calcium and suitable mineralogy, which make the DCFBP a potential reservoir system for underground geological sequestration of CO_2 . Most of the lava flows in the DCFBP have amygdular flow tops and bottom as well as interflow features, imparting the required porosity and permeability for CO_2 diffusion and storage. Under suitable conditions of temperature and pressure and local formation water's pH, the dissolved CO_2 interacts with iron, magnesium and calcium released due to reaction with primary pyroxene, olivine, plagioclase and glass especially at low pH, to form geologically stable ferrous, calcium and magnesium carbonates, as confirmed by laboratory experiments. The causative exothermic reactions are: (a) $2\text{Mg}_2\text{SiO}_4$ (Olivine) + CO_2 + $2\text{H}_2\text{O}$ = $\text{Mg}_3\text{SiO}_5(\text{OH})_4$ (Serpentine) + FeCO_3 (Ankerite) + MgCO_3 (Magnesite) and (b) $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Plagioclase) + $2\text{H}_2\text{O}$ + CO_2 = CaCO_3 (Calcite) + $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})$ (Clay). Laboratory experiments over 5 months duration at a temperature and pressure of 100° C and 60 bars of CO_2 , have shown growth of secondary Fe-, Ca- and Mg-bearing carbonates over the surface and in fractures of picritic basalts reacted with water and carbon dioxide in its supercritical condition. These secondary carbonates characterized by Infrared Spectroscopy and SEM techniques show (a) signatures which match well with ankerite (Iron carbonate), calcite (Calcium carbonate), magnesite (Magnesium carbonate) and (b) that they are made up of porous ankerite cores covered by fibrous calcite rich crusts with minor magnesite, serpentine and released silica.

Interaction of prion protein, pentapeptide and lysine with soil clays

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Pathogenic prion protein-scrapie (PrP^{Sc}) may contaminate soils for decades, providing infection pathways for animals through inhalation or ingestion.

Sorption of Lysine and PrP(92-96)

NMR and XRD investigations of simple amino-acid (lysine) on synthetic montmorillonite show that lysine adsorption at most leads to a 6 nm expansion of the interlayer, compared to 12 nm expansion observed by [1]. These results indicate the importance of surface charge density, which is lower in the present synthetic montmorillonite and the importance of organic molecule geometry sorbed onto smectites. ESR investigation of the pentapeptide (PrP(92-96)) complex formed with -Cu²⁺ demonstrates a change of Cu²⁺ coordination in the complex upon adsorption to the synthetic clay from, at neutral pH, a N₄ type coordination in bulk water [2] to a NO₃ one in the interlayer).

MD Simulations of the PrP-clay System

MD simulations were performed for the PrP(92-138) peptide [3] adsorption on clay. The peptide anchored to the clay surface via up to 10 hydrogen bonds from lysine and histidine residues to oxygen atoms of the siloxane cavities, and a total adsorption energy of 3465 KJ.mol⁻¹ was obtained. Our results provide insight to the mechanism for strong association of prion protein on clay surfaces.

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The Lesser Antilles subduction factory

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In subduction zones, crustal material consisting of oceanic basalts overlaid by sediments is recycled into the mantle but part of the subducted material is immediately recycled into new crust during the formation of island arc volcanics. The proportion of subducted material involved in the genesis of this crust varies depending on factors such as the amount and type of subducted sediments or the speed and angle of the subducting plate.

Here we concentrate on the chemical budget of the Lesser Antilles Arc, which is famous for having the most "continental crust-like" geochemical signature. Its location perpendicular to the South American continent and the vast amount of sedimentary material present on the subducting oceanic plate in front of the southern part of the arc certainly play a major role in this signature.

We establish the average chemical and isotopic compositions of sediments located at three different latitudes in front of the arc and show that major differences exist along the north-south axis. The presence in the south of high proportions of continental detrital material leads to very continental-like Nd, Hf and Pb isotopic compositions, but more interestingly, to a decoupling of the Nd and Hf isotopic systems with very low Hf relative to Nd isotopic ratios. In addition, because the oceanic crust subducted in the south is older than in the north, thick layers of black shales created during two major oceanic anoxic events are present only in the south. They are characterized by extremely radiogenic Pb isotopes and their occurrence in the southern sedimentary pile contributes to large diversity of Pb isotopic compositions in the subducted material.

The north-south chemical and isotopic variation defined by the sediments is mirrored in the arc lavas and the clear correlation suggests that most of the arc characteristics are inherited from subducted sediments rather than acquired through the melting processes producing the arc magmas.

Chemical compositions of the arc magmas also change through time at the same location. Detailed chemical and isotopic analyses of 25 Ma of magma genesis in Martinique shows that the subducted sediments always contributed to the source of magmas but that their proportion varied through time, most probably in relationship with the thickness and geometry of the subducted sedimentary pile.

Fluid circulation in the oceanic crust: The case of the alkaline springs of the Oman Ophiolite

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The Oman ophiolite is a very well preserved section of the oceanic lithosphere that has been thrust onto the Arabian continental margin during the Cretaceous. The role of fluids in the oceanic crust has been well documented by observations and data of high temperature fluid discharges at seafloor spreading centers collected during cruises over the last 30 years. The recent discovery of peridotite-serpentine outcrops at the Lost City site on the Mid-Atlantic ridge has shed light on a new type of hydrothermal activity producing high pH and low temperature fluids as well as large quantities of hydrogen. Similar alkaline waters are also found at springs located in the Oman ophiolites. The hydrothermal fluids of Oman originate from rain waters rather than seawater.

The aims of our project are the characterization of fluids reacting with peridotites exhibiting various degrees of serpentinization and the investigation of low temperature water rock interaction processes taking place at the springs (changes in fluid pH, formation of Ca and Mg hydroxides, carbonization reactions, fate of trace elements, etc).

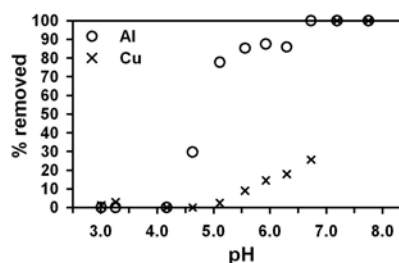
A first exploratory field trip in December 2008 allowed us to collect samples of spring waters and precipitate at about twenty distinct locations over the entire Oman ophiolite. Most sites show evidence of degazing (hydrogen; A. Prinzhofer pers. com.). The precipitate samples analyzed by DRX and MEB analyses are composed of calcium carbonates (calcite or aragonite) and magnesium hydroxide (brucite). The springs waters are characterized by pH values and temperatures ranging from 6.6 to 12.2 and 20.2° to 65.5°C, respectively. The total alkalinity values vary between 0.9 to 5.9 mmol.kg⁻¹ compared to seawater at 2.3-2.4 mmol.kg⁻¹. Sr isotope compositions range between 0.705797 and 0.713106, and vary according to the fluid temperature. This is a first step toward an exhaustive geochemical and isotope study of the Oman ophiolite fluids discharge at the surface.

Mixing experiments of acid mine drainage and seawater

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High concentrations of yellowish and trace metal-bearing suspending nanoparticles of schwertmannite and non-crystalline Fe,Al oxyhydroxysulfate compounds occurring in the surface layers of estuarine and shoreline seawaters adjacent to the Chinkuashih acid mine drainage (AMD; pH = 2.8) area, northern Taiwan actuated our interest to investigate AMD-seawater interaction processes. Experimental products of laboratory mixing of Chinkuashih AMD and fresh seawater (pH = 8.0) at volume ratios up to 1 were analyzed by ICP-OES, ICP-MS, XRD, SEM, TEM and FTIR. The principal precipitates were identified to be schwertmannite and amorphous hydrous oxides of iron and aluminum (HFO & HAO) with increasing proportions of seawater during the transition of pH values from 3.0 to 7.8 in the mixed solutions. Three principal types of metal-element behaviors were observed in association with the precipitation during the mixing experiments including (1) rapid removals of Fe, As, Cd, Cr, and Pb at pH < 4-4.5 at high AMD/seawater ratios, (2) gradual and/or relatively small attenuations of Mn, Co, and Zn with increasing pH values, and (3) virtually no changes at low pH values and gradual or rapid removals of Cu and Al at pH > 4-4.5. The first phenomenon can be attributed to rapid crystallization and/or sorption of Fe, As, Cd, and Pb associated with the formation of schwertmannite. The third type of behavior can be ascribed to co-precipitation and/or sorption of Al and Cu in connection with the precipitation of the non-crystalline HFO-HAO compounds, while the second mode of actions might be simply a result of elemental sorption onto the solid precipitates. The results suggest that the precipitation/sorption of Cu and Al are greatly enhanced under conditions favorable for the formation of amorphous HFO instead of schwertmannite, concordant with the findings obtained from the Chinkuashih AMD-seawater mixing area.



The isotopic and chemical characteristics of groundwater from Shihongtan uranium deposit and its surrounding area

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Isotopic and Chemical Characteristics of Groundwater

Hydrogeochemical study shows that the groundwater from Shihongtan uranium deposit is classified as the Cl-SO₄-Na type water which is highly mineralized with TDS ranging from 8g/L to 12g/L. For the high TDS, high Ca²⁺ and SO₄²⁻ concentration, the calcite and gypsum in the groundwaters are over saturated. The δD and $\delta^{18}O$ values of the groundwater are in the range of -85.5 ‰ to -20.8‰ and -9.3‰ to -7.9‰ respectively [1]. The water from the surrounding area of this deposit is much less salinity than those from the deposit area. Its TDS ranges from 0.2 to 1.7 g/L. The δD values are in the range of -56 to 60 ‰ and the $\delta^{18}O$ values are in the range of -8.7 to 9.2‰.

Discussion of Results

The waters from the deposit area have significant difference of chemical properties from the waters from its surrounding area. High TDS is one of the main characteristics for the groundwater in this uranium deposit area. The exceeding evaporation does great contribute to the high ionic content for the groundwater in the area.

Stable isotopes of $\delta^{18}O$ and δD are used to trace and determine the origin and movement of groundwater. All waters samples both in Shihongtan uranium deposit area and its surrounding area follow a local meteoric water line, indicating that the waters are of meteoric origin (come from melting of snows in mountains). We obtain the correlation line between altitude and isotopic composition of local precipitation in this area, defined as $\delta D = -0.036H - 7.46$. According to this correlation, the recharge altitudes are calculated as around 1348m~1460m for the groundwater in the surrounding area of this deposit.

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Multistage and heterogeneous uplift of the Tibetan Plateau implicated by the multi-episode post-collision lava

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Uplifting history of the Tibetan Plateau since continental collision between the India and Asia is still a contentious issue. It is generally believed that eruptions of post-collision lava were related to uplift of the plateau [1, 2], therefore their erupted times may be used to trace uplifting history. This study reports new-episode volcanic rocks in Qiangtang block of the central Tibetan Plateau, which erupted between 7-3Ma, and geochemical characteristics show that they were derived from a lower crust source.

Cenozoic post-collision lavas are widely distributed in several blocks of the Tibetan plateau. Combining published age data with our dating results, we find that eruption of the post-collision lava is discontinuous and heterogeneous in the plateau. The multi-episode magmatic activities occur in different blocks of the plateau, i.e., the earliest episode lava are only exposed in Qiangtang block of central Tibet. Then 26-10Ma and 18-10Ma lava occur in Lhasa block of south Tibet and Songpan-Ganzi block of north Tibet, respectively. Finally, 7-3Ma volcanic rocks erupted again in Qiangtang block of the central Tibet.

According to above temporal-spatial distribution of the post-collision lava, we suggest that the Tibetan plateau has experienced a discontinuous and heterogeneous uplift process. Earliest uplift took place in central Tibet (Qiangtang block) during 45-28Ma, then the elevation seems cessation in the central Tibet instead of south and north Tibet (Lhasa and Songpan-Ganzi blocks) started uplifting during 26-10Ma. It is in 7-3Ma that the central Tibetan plateau experienced new elevation. In addition, uplift of the Tibetan plateau may not be interpreted by a single tectonic model, it is more likely that the multi-geodynamic processes [3], e.g., break-off of the north-dipping subducted Indian slab in south [4] and the south-leaning of Euro-Asian plate [5], as well as the delamination of lower crust or lithosphere below the central Qiangtang [1], resulted in construction of the Tibetan plateau.

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Volumetric properties of CO₂-rich mixed fluids near critical regions

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The application of supercritical CO₂ (SC CO₂) is crucial for the Carbon Capture and Storage (CCS) big problem in earth environment science [1]. The physical and chemical properties of CO₂-rich mixed fluids are significantly different from that of pure CO₂ near critical regions. One of the important mixture's parameters is the excess volume [2]. It can be used to reflect the mutual dissolvability of components in the system. Acetone is a polar solvent while pentane is a non-polar one and they are typical organic co-solvents in supercritical CO₂ applications. Unlike high-pressure vapor-liquid equilibrium data, the densities and volumetric properties for CO₂-rich fluids with acetone and pentane mixtures near critical regions are very limited.

We have studied phase behavior and local density enhancements in CO₂ mixtures in various phase regions [3-7]. In this work, we focus on the comparison of volumetric properties for CO₂-rich binary and ternary mixed fluids with polar and non-polar co-solvent near critical regions where the most character of mixture is changeful. It shows that the excess molar volumes are all negative under pressure from the phase separation point to 15 MPa and become less negative with increased pressure. At fixed temperature and composition, the densities of CO₂-rich fluids with more acetone are bigger than with pentane and the excess molar volumes are more negative. At the same temperature, the excess molar volumes of mixtures with different critical composition are almost the same. The excess molar volumes of mixtures with different compositions have the similar behavior and become more negative with decreased CO₂.

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Stable isotopic composition of Zn in hydrothermal spring waters

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Recent studies have demonstrated the interest of Zn isotopes for investigating water-rock interactions. Speciation-related fractionation as well as source-related fractionation between its isotopes (about 2‰ in $\delta^{66}\text{Zn}$ unit) make Zn isotopes a promising tracer for studying the mobility of metals during weathering, hydrothermalism and ore formation. Although previous studies have focused on the processes fractionating Zn isotopes in hydrothermal solid deposits and seafloor vents, the Zn isotopic composition of hydrothermal waters in continental arc setting have not been investigated so far.

Hydrothermal springs from nine main rivers of the La Soufrière de Guadeloupe volcanic area (French West Indies) have been collected for Zn isotopic measurement. These samples display generally low dissolved Zn concentration (from 1 to 33 µg/L) despite their enrichment in iron and sulfate concentrations. We have developed a new one-step protocol for direct ion-exchange separation of Zn from thermal spring waters. The protocol is proven to be reproducible by tests on synthetic solution, with an average yield close to 100% and no isotopic fractionation.

$\delta^{66}\text{Zn}$ values of spring samples show a big variation range (from -0.43‰ to 0.80‰), being 70% of total variation of $\delta^{66}\text{Zn}$ data reported to date (from -0.43‰ to 1.33‰) for hydrothermal system, and an interesting correlation with Zn concentration for these samples. Isotopic characterizations of Zn in hydrothermal spring waters provide important information for studying hydrothermal processes and island arc weathering.

Dust as main sources of preanthropogenic lead in central Pacific deep water

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The dominating factors controlling preanthropogenic Pb isotopes in central Pacific deep water over the Cenozoic are still controversial. The debate mainly focused on whether regional eolian dust or volcanogenic aerosol is the dominant source for seawater dissolved Pb budgets. The latest research surmised that soluble Pb released from eolian dust in the seawater was originated from atmospheric deposition of globally well mixed volcanic aerosols from the stratosphere and further suggested that this kind of volcanic aerosol dominated the sources of dissolved Pb in the central Pacific over the Cenozoic.

In this study we found two difficulties faced by the volcanic aerosol model: 1) Lead flux from aerosol may have been too low to be a dominant flux over the local dust inputs in central Pacific deep water so that 2) Pb isotopic compositions were actually not homogenous but recorded very localized signals in all ocean basins. Moreover, evidences from patterns of trace elements leached together with Pb from Fe-Mn oxides (e.g. particle reactive elements enrichment, relative depletion in HFSE and highly soluble elements) are consistent with their derivation from chemical weathering of mineral dust. Mass balance consideration also precludes a predominantly volcanogenic Pb source for the leachable phase of loess. The less radiogenic Pb of the leachates than the bulk loess can be fully explained by a time-integrated effect of lower U/Pb and Th/Pb of the leachable phases. Furthermore, Pb isotopic evolution of the eolian silicate fraction of central Pacific core GPC3 actually reflects the local eolian signal rather than the global stratospheric volcanic aerosol imprints. Pb isotopes in central Pacific deep water also did not correspond to any main change of volcanic activity or continental sediment flux to the Pacific marginal seas, suggesting that both Pb from volcanic aerosol and Pb advected from the marginal Pacific may be insignificant compared with the regional eolian input via dust deposition. We thus propose that dust input should be the dominant source for the Cenozoic Pb in central Pacific deep water.

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The Ar-Ar geochronological study of the shear zone-type gold deposit of East Tianshan, Xinjiang, NW China

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The Ar-Ar isotope geochronological study of the Kanggur, Hongshi and Hongshan, three typical shear zone-type gold deposit located in Qiugemingtashi-Huangshan large-scale ductile shear zone in the middle of the East Tianshan orogenic belt, NW China, shows that the time of the gold deposit mineralization is in agreement with that of the strike-slip shear deformation of the shear zone in its late period. The main shear deformation time of the Qiugemingtashi-Huangshan ductile shear zone is between 262.9Ma-242.8Ma [1], while the gold mineralization time of the shear zone-type gold deposit is between 261.0Ma -246.5Ma. This high concordance proves that the late right-lateral strike-slip shear deformation is the main reason for the gold mineralization.

The agreement between the gold mineralization time and the right-lateral strike-slip shear deformation time shows diversity in different part of the shear zone. The fast uplift of middle-western part of shear zone happened in 261.5Ma-262.9Ma while the main mineralization time of the Kanggur gold deposit is between 261.0Ma -252.5Ma, which indicates that the mineralization of the Kanggur gold deposit began just after the fast uplift of the middle-western shear zone. In the eastern part of shear zone, the fast uplift happened in 247.1Ma-246.9Ma while the main mineralization time of the Hongshan gold deposit, situated in the north area of the eastern shear zone, is between 246.9Ma-246.5Ma, which indicates that the mineralization of this gold deposit also began after the fast uplift of the eastern part of shear zone.

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Modeling of formation of uranium ore deposits related to granitoids

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We modeled leaching, transport, and deposition of uranium during filtration of water through a granite massif at gradients of temperature (800-100°C) and pressure (3000-700 bar). The modeling was carried out for the 14-component system O-H-Si-Al-K-Na-Mg-Mn-Fe-C-Cl-F-Ti-U. The computer simulation technique [1] was used, which allows to develop a model of ore formation based on geological and geochemical constrains [2]. Input data for modeling were based on geological and mineralogical [3], and fluid inclusion [4] studies. It was shown that leaching of uranium from granite takes place in high temperature zones. Further moving of hydrothermal fluid to colder zones is accomplished by re-deposition of uranium. As the mass of filtrating fluid increases, the stronger leaching takes place. It results in increase of quartz and mica amounts, formation of kaolinite and other secondary minerals. Consecutive change of mineral assemblages, including U-ore minerals, takes place. At the same time the fronts of uranium mobilization and re-depositions moves in the line of T and P decrease (Fig. 1). The dominant uranium aqueous species are fluorine complexes of U(IV) at high temperatures, and $\text{UO}_2(\text{CO}_3)_2^{2-}$ и $\text{UO}_2(\text{CO}_3)_3^{4-}$ at lower temperature.

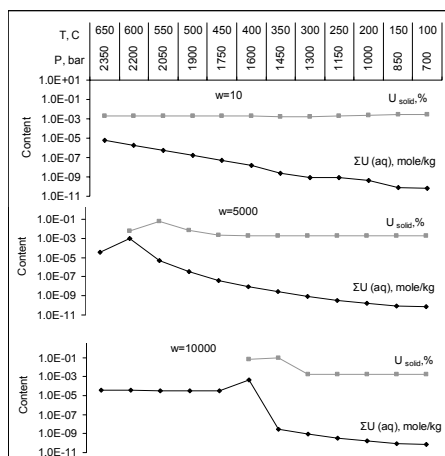


Figure 1.

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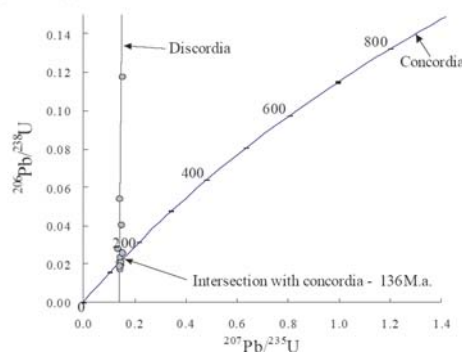
The case of continuous redistribution of intermediate ^{238}U daughters radionuclides migration and exotic U-Pb age discordance

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U-Pb ID-TIMS study of multicomponent macrosamples (4-10 cm³) set drawn along 3.5 m profile within uranium hydrothermal mineralization zone in Streltsovskoye deposit (E.Transbaikalia) showed that their age relationships are distinguished fundamentally from age discordance pattern which is well known for the majority of U-Pb systems as a result of radiogenic lead loss.

The data points displaying great variation by $^{206}\text{Pb}/^{238}\text{U}$ lie along discordia (see figure) which is parallel to $^{206}\text{Pb}/^{238}\text{U}$ axis. When occupying such position the discordia intersect a concordia at the point 136 M.a. corresponding to the age of uranium mineralization - 135 ± 3 M.a. [1]. By this it meant that: 1) ^{235}U - ^{207}Pb isotope system remained closed in individual samples while ^{238}U - ^{206}Pb was significantly broken down; 2) this set of data is inexplicable in the context of lead/uranium migration. The scatter of T(206/238) values have resulted from continuous long-term (tens of M.a.) migration of intermediate ^{238}U daughters radionuclides (RD ^{238}U).



It is believed that RD ^{238}U have lost from mineral volumes containing fine-grained uranium oxides with high Si, OH⁻ contents and $^{238}\text{U}/^{235}\text{U}$ ratio and have deposited in neighbouring volumes containing sulfides. The last have played role of geochemical 'barriers' for the most long-lived RD ^{238}U . The main factor have provided a closeness of ^{235}U - ^{207}Pb system lies in very short half-lives RD ^{235}U . The later had no time to leave U mineral volumes before ^{207}Pb formation.

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Fate of mercury entering lakes and ponds in the Canadian High Arctic: Role of biological and geochemical drivers

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Mercury is a contaminant of concern in the High Arctic because of intense atmospheric deposition events in spring and elevated levels in some top predator organisms. We investigated the influence of geochemical and biological factors on the methylmercury (MeHg) content of aquatic invertebrates (chironomids and zooplankton) in 22 lakes and ponds in the Canadian Arctic Archipelago. Total mercury (THg) is delivered to fresh waters primarily by snowmelt, and we tested the role of mercury supply by sampling water bodies with a range in drainage basin size. We found that THg concentrations in sediment (after correcting for organic matter content) increased with drainage basin size, suggesting our study sites represented a gradient in mercury loading. MeHg concentrations in sediment and water were low and generally similar despite a gradient in THg supply. We suggest that bacterial production of MeHg in High Arctic lakes is weakly coupled to the supply of inorganic mercury because of poor environmental conditions for methylation. Biological processes were key drivers of invertebrate MeHg content while environmental mercury levels, drainage basin size and habitat characteristics were secondary explanatory variables. *Daphnia*, an efficient filter feeder, had elevated MeHg content compared to other zooplankton species in the water column, and its abundance best explained mercury levels in this invertebrate community. *Daphnia* densities in High Arctic lakes were related to aquatic productivity, and we suggest that climate warming may increase the presence of these mercury-rich zooplankton. For bottom-dwelling invertebrates, specifically chironomids, metamorphosis concentrated MeHg in adults up to 3 times more than in immature stages. Landlocked Arctic char inhabiting our study lakes primarily consume chironomids, and differential consumption of immature and adult stages may affect MeHg uptake by fish. We conclude that biological and food web processes play a greater role in MeHg transfer to fish than atmospheric mercury deposition in the extreme environment of High Arctic fresh waters.

Isotopic data (Sr-Nd-Hf-O) of intrusive rocks from the Kerguelen Islands (Indian Ocean)

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The Kerguelen Archipelago (Indian Ocean) is the emergent part of the northern Kerguelen oceanic Plateau. When the Kerguelen Mantle Plume started to build the Kerguelen Islands about 30 million years ago, it was situated near the South East Indian Ridge that then moved away, leaving the Plateau in its present intraplate setting. The early magmatism was transitional-tholeiitic and changes to alkaline to highly alkaline over time [1, 2] with some underplating [3] to create thickened oceanic lithosphere (15-20 km thick). The nature of the intrusive rocks and related cumulate ultramafic-mafic xenoliths is unravelling the different stages of lithospheric differentiation in this unusual thickened oceanic crust.

Studied samples (phenocrystic basalts, dolerites and ultramafic-mafic cumulates) mainly consist of the minerals plagioclase and clinopyroxene. Accessory minerals are oxides, alkali feldspars, sulfides and apatites. Results show that several types of gabbroic (intrusive and cumulates) rocks can be distinguished on the basis of the rare earth element (REE) composition of their clinopyroxene. Isotopic data (Hf-Sr-Nd) show that the gabbroic rocks mostly have the same range of isotopic signatures as the basalts and that they mostly vary between two end-members corresponding from the inferred sources for the Kerguelen plume and oceanic basalts. The $\delta^{18}\text{O}_{\text{cpx}}$ values for gabbroic samples are relatively homogeneous (5.0-6.0‰SMOW) and show equilibrium at high temperature in mantle conditions. However the $\delta^{18}\text{O}_{\text{WR}}$ values indicate that subsolidus interactions with crustal fluids have taken place.

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Studying gold solubilities using fused silica capillaries

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Solubilities of metals in geological fluids at elevated temperatures and pressures were conventionally studied with autoclaves. With the advance of analytical technology, new methods are being developed, e.g., synthetic fluid inclusions coupled with LA-ICP-MS analysis [1]. Here we report a new method using fused silica capillaries [2] to study gold (Au) solubilities. We inserted a gold wire into a silica capillary and fused the tube at one end. We then injected a fluid of known composition into the capillary and fused the other end. Four types of samples were prepared: 1) CO₂, 2) CO₂ + H₂O, 3) CH₄ + 10N H₂SO₄ solution, and 4) S (solid) + CH₄, each with a gold wire in the capillary. The samples were then placed into autoclaves and heated to 400-600°C for 3-38 hr. After being examined by Raman spectroscopy for fluid composition, the samples were opened and the gold wire removed. The capillaries were analyzed for Au content (assumed to be on the inner wall of the capillaries) with the LA-ICP-MS and ICP-MS methods. The analytical results were then used to calculate Au solubility in the fluid.

Preliminary experiments indicate that dissolution of Au occurred at least in type 3 and 4 fluids as described above, where H₂S was generated after the heating as indicated by Raman inspection. Gold dissolution is indicated by the change of the gold wire color and reflectance and by the formation of dark coating on the inner wall. Gold solubilities up to 86 ppm have been obtained in some of the runs. Gold solubilities up to several hundred ppb have also been observed for fluids without H₂S, and further analyses need to be done to verify these results. On-going research aims to resolve problems related to the heterogeneous distribution of precipitates on the capillary wall and analytical procedures associated with ICP-MS analysis of very small sample volumes.

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Metallogenic ages of the Shaxi porphyry Cu-Au deposit, Anhui Province

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Yangtze valley is one of the most important metallogenic region in Jurassic-Cretaceous period in East China, where more than 200 polymetallic Cu-Fe-Au, Mo, Zn, Pb, Ag deposits resident [1-3, 8]. Among them, the Shaxi porphyry Cu-Au deposit was one of the importance discoveries of the Cu-Au exploration in the middle-lower Reaches of River in China in 1970's. Its geochemical studies are extensive investigated [4-7]. However, the metallogenic ages are still unknown.

In this study, we hire Le-Os dating method on sulfides. Both pyrite and molybdenite samples from the sulfide ore were collected. These samples were analyzed by the ICP-MS method in National Research Center of Geoanalysis, Chinese Academy of Geological Sciences. The ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os values by the ICP-MS. One isochron age calculated is c.a. 130 Ma with an initial Os ratio of 1.30 or so. We believe that this age represents the ore-forming time of the Shaxi Cu-Au deposit, which is also with accordance with the intrusive Ar-Ar ages from Yang *et al.* [6]. Our study indicates that the Yanshanian magmatism is of great significance for Shaxi Cu-Au mineralization in central Anhui, east China.

This study is supported by The Public Geological Survey Management Center of Anhui Province, China.

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Molecular-based Simulation of Liquid-vapor equilibrium isotopic fractionation of water

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Liquid-vapor equilibrium isotopic fractionation of water is determined via Gibbs Ensemble Monte Carlo and isothermal-isochoric molecular dynamics simulations of two radically different but realistic models, the extended simple point charge (SPC/E) and the Gaussian charge polarizable (GCP) models. The predicted temperature dependence of the liquid-vapor equilibrium isotopic fractionation factors for $\text{H}_2^{18}\text{O} / \text{H}_2^{16}\text{O}$, $\text{H}_2^{17}\text{O} / \text{H}_2^{16}\text{O}$, and $^2\text{H}^1\text{H}^{16}\text{O} / ^1\text{H}_2^{16}\text{O}$ are compared against the most accurate experimental datasets [1, 2] to assess the ability of these intermolecular potential models to describe quantum effects according to the Kirkwood-Wigner free energy perturbation \hbar^2 -expansion [3].

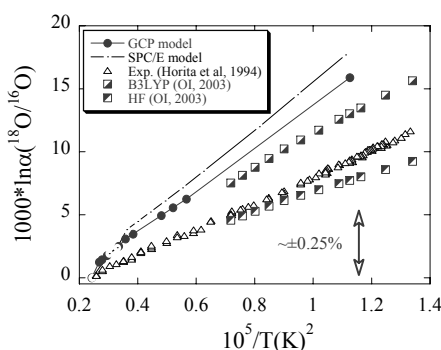


Figure 1: Liquid-vapor $\text{H}_2^{18}\text{O} / \text{H}_2^{16}\text{O}$ fractionation.

Representative results in Figure 1 illustrate the agreement between the model predictions and the experimental data; they are within $\pm 3\%$ even though the GCP model appears more accurate. In contrast, the experimental data are sandwiched between the two sets of *ab initio* predictions [4] whose deviations from each other are similar in magnitude to that between our simulation and experiment. Predictions of the corresponding vapor-pressure isotopic effect are also given in comparison with experimental data and two recently proposed thermodynamic modeling approaches. Extensive discussion on the other fractionation pairs, including the mechanism underlying the rule of the geometric mean for the H/D substitution and its relation to roto-translational coupling, are given in [5].

Copper behaviour in andesitic magmas evolving at high $p\text{H}_2\text{O}$ (Pilavo volcano, Ecuador)

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Formation of porphyry-type deposits results from the positive coincidence of several geodynamic, tectonic and magmatic factors. Magmatic evolution may play an important role in sequestering chalcophile metals (e.g., Cu, Au) into early crystallizing mineral phases or leaving them available until later stages when a fluid phase exsolves from the magma. In this study we investigate the behaviour of Cu in andesitic lavas of the Pleistocene Pilavo volcano, Western Cordillera of Ecuador, through LA-ICP-MS analyses of amphibole, the most abundant phenocrystic phase in these lavas. Pilavo lavas result from magma mixing between two end-members: (i) a low Ni (<10 ppm) mafic magma that has undergone abundant fractional crystallization of olivine, clinopyroxene \pm amphibole at subcrustal or lower crustal depths and (ii) a felsic magma that has evolved through extensive amphibole fractionation under high $p\text{H}_2\text{O}$, probably at mid-crustal levels. Mixing resulted in a wide range of incompatible element contents for a limited range of major elements, correlations between elements and radiogenic isotopes, and inverse zoning in amphibole phenocrysts.

Copper (and to less extent also Zn and Co) contents decrease steadily from a maximum of 220 ppm in amphiboles of the least evolved lava to a maximum of 40 ppm in amphiboles of the most evolved lava. The Cu decrease in amphibole does not correspond to a Cu decrease in the host rocks (which remains the same ~ 45 ppm). This is because in the most evolved lavas Cu occurs in abundant droplets (few micrometers in size) of Cu-Fe sulfides hosted by magnetite micro-phenocrysts in the matrix of the lava, whereas in the least evolved lavas Cu-Fe sulfides are absent. These data suggest Cu sequestration by amphibole in the mafic end-member at high pressure and Cu partitioning into a non-silicate melt/fluid during fractionation of the felsic end-member under high $p\text{H}_2\text{O}$ conditions at lower pressures. This is supported by positive correlations between Cu and Li in amphiboles. The association of Cu-Fe sulfides with magnetite might suggest sulfide saturation due to Fe subtraction by magnetite crystallization or direct partitioning of Cu into a Fe-O-S melt at some stage of the magmatic evolution.

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Compound-specific nitrogen isotope analysis of amino acids: Implications of aquatic food web studies

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Nitrogen isotopic composition ($\delta^{15}\text{N}$) of amino acids has recently been employed as a potential tool for estimating the trophic level of organisms inhabiting aquatic environments [1]. During the metabolic processes, a group of amino acids (e.g., phenylalanine) has little change in their nitrogen isotopic composition, whereas the other group (e.g., glutamic acid) has large isotopic fractionations up to ~ 8 permil. Such a fractionation could be associated with the cleavage of carbon-nitrogen bond during the metabolic processes of amino acids [2]. Here we have established an equation for estimating the trophic level (TL_{AA}) of aquatic organisms by analyzing nitrogen isotopic composition of amino acids from a number of natural and laboratory grown organisms in the following equation:

$$\text{TL}_{\text{AA}} = (\delta^{15}\text{N}_{\text{glutamic acid}} - \delta^{15}\text{N}_{\text{phenylalanine}} - 3.4)/7.6 + 1$$

A key advantage of this “amino acid method” is that trophic level is estimated based on the $\delta^{15}\text{N}$ values of amino acids from a single organism; consequently, unlike the bulk method, it is not necessary to characterize the $\delta^{15}\text{N}$ values of primary producers in the food web. In the presentation, we will overview this method and show its applications to various natural organisms in marine environments (Fig. 1.) (e.g., [3]).

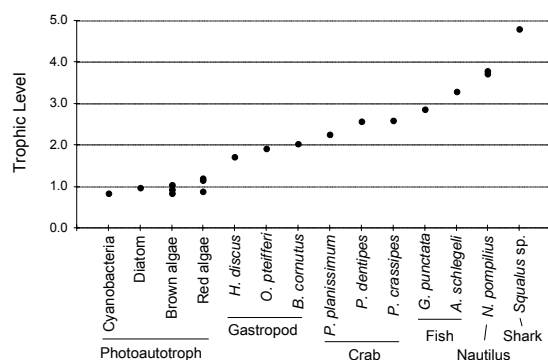


Figure 1. The trophic level estimated by the amino acid method for natural organisms in marine environments.

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Possibilities and challenges in using satellite aerosol data for surface air quality studies

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Surface concentration of aerosol particles, also known as particulate matter (PM), is a key component determining air quality, especially with small particles (diameter less than 2.5 μm , or PM_{2.5}) which are known to cause respiratory diseases. Local emissions and long-range transport can both contribute to the PM_{2.5} levels at the surface. In the past decade, satellites remote sensing measurements of global aerosol distributions have become available, continuously providing large-scale ‘chemical weather’ pictures, which can be potentially useful for estimating surface PM_{2.5} levels. In this presentation, we discuss the possibilities and challenges in using satellite data for air quality applications, in particular, we will address the following questions: (1) What is the relationship between column aerosol optical depth (AOD), which is the quantity measured by satellite, and surface PM_{2.5} concentrations? (2) How and why this relationship varies with time and location? (3) What is the optimal approach to use model and satellite data for air quality studies? We will present case studies over the U.S. using the Goddard Chemistry Aerosol Radiation and Transport (GOCART) model, satellite data from MODIS and MISR, and surface PM_{2.5} concentration data from the U.S. EPA and IMPROVE monitoring networks.

Carbon dioxide emission in Italy: Shallow crustal sources or subduction related fluid recycling?

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Anomalous 'non-volcanic' CO₂ release in central and southern Italy has been highlighted by ten years of detailed investigations on Earth degassing processes. Two regional degassing structures are located in the Tyrrhenian sector where more than 200 emissions of CO₂ are located and has been recently included in the first web based catalogue of degassing sites (<http://googas.ov.ingv.it>). The total amount of CO₂ released by the two structures were evaluated to be $> 2 \times 10^{11} \text{ mol a}^{-1}$ ($>10\%$ of the estimated global volcanic CO₂ emission). The anomalous flux of CO₂ suddenly disappears in the Apennine in correspondence of a narrow band where most of the Italian seismicity concentrates. Here, at depth, the gas accumulates in crustal traps generating CO₂ overpressurised reservoirs. These overpressured structures are, in our opinion, one of the main cause of Apennine earthquake activation processes. The results of these investigations suggested that Earth degassing in Italy may have an active primary role in the geodynamics of the region. What is the origin of gas? The large extension of the degassing structures and petrologic data suggested that the main source of gas is a mantle metasomatised by the fluids produced in the subducted slabs. However, has been also hypothesised the presence of localised crustal source of the gas. This matter will be discussed on the base of unpublished isotopic data of the main gas emissions.

Electrochemical study of FeS corrosion in acid solutions in the presence of benzothiazolic compounds

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Iron monosulfide (FeS) exposed to acidic solutions containing oxidants can dissolve oxidatively [1, 2]. This corrosion releases toxic elements (heavy metals and arsenic) present in the FeS matrix. However, this corrosion may be altered by interaction with organic molecules. 2-(cyclohexylaminomercapto)-benzothiazole (CMB) and 2-mercaptobenzothiazole (MBT) are known to inhibit corrosion of steel [3]. The present study investigated the effect of these molecules on FeS.

The behaviour of synthetic FeS in acid solutions at 25°C in the presence and the absence of CMB or MBT was investigated using electrochemical measurements and microscopic analysis. The corrosion currents (i_{corr}) were obtained from Tafel polarization plots [3]. The polarization resistance in absence and presence of inhibitors (R_p^0 and R_p , respectively) were determined from electrochemical impedance spectroscopy. It was observed that both CMB and MBT reduce the oxidative (anodic) dissolution of FeS. For example, in 0.1 mol L⁻¹ HCl i_{corr} decreases from 342 $\mu\text{A cm}^{-2}$ (in the absence of inhibitors) to 65 $\mu\text{A cm}^{-2}$ ([CMB] = $5 \cdot 10^{-4}$ mol L⁻¹) and to 95.8 $\mu\text{A cm}^{-2}$ ([MBT] = $5 \cdot 10^{-4}$ mol L⁻¹). Instead R_p increases from 33.4 $\Omega \text{ cm}^2$ in the absence of inhibitors to 175.4 and to 119.3 $\Omega \text{ cm}^2$ in the presence of CMB and MBT, respectively. These results indicate that CMB is a more efficient inhibitor than MBT. It was also found that the FeS surface coverage [$\theta = 1 - (R_p^0/R_p)$] increases when inhibitor concentration augments from $2 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ mol L⁻¹. This is in good agreement with microscopic images that indicate the formation of a protective film on the FeS surfaces corroded in presence of inhibitors.

All these findings suggest that FeS corrosion can be substantially reduced by the formation of organic layers that may modify the electronic properties of FeS/water interface.

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The compositional zonation in mafic dykes of the Kestiö Island, Finland

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Detailed sampling across three dolerite dykes of different size (small, 7 cm; middle, 75 cm; and thick, 675 cm) of the Åland-Åboland dyke swarm [1] has revealed an internal zonation of an anomalous nature. The small, almost glassy dyke exhibits a systematic inward decrease in whole-rock MgO and Mg# (indicating a normal fractionation trend) together with a simultaneous increase in normative An and decrease in whole-rock Zr, Y, TiO₂ (indicating a reverse fractionation trend). The middle dyke shows similar compositional trends across its narrow margins, but in the more crystalline interior whole-rock MgO and Mg# gradually but steadily increase inwards. The thick, almost totally crystalline dyke exhibits an internal zonation similar to that of the middle dyke, with fractionation trends becoming only much more pronounced in the centre of the dyke. The almost glassy nature of small dyke suggests that its anomalous compositional zonation most likely resulted from temporal changes in the composition of magma as it formed the dyke. The mechanism(s) responsible for such systematic changes in composition of inflowing magma remains, however, unknown. The margins of middle and thick dyke form in a similar way whereas their interiors formed by *in situ* cumulate growth against dyke sidewalls. The compositional zonation of these dolerite dykes is thus produced by two independently operating mechanisms: successive changes in composition of inflowing magma and an *in situ* cumulate growth on dyke sidewalls.

[1] Ehlers & Ehlers (1977) *Bul. Geol. Surv. Finland* **289**, 31.

Determination of the ¹⁰Be half-life by Multi Collector ICP-mass spectrometry and liquid scintillation counting

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Over the past decades the number of studies using the rare cosmogenic nuclide ¹⁰Be have increased, mainly for geologic, oceanographic, and climate studies. Yet no consensus exists on a reliable value for half-life of ¹⁰Be. Several determinations of this half-life have been done in the past, leaving a discrepancy of 14% between different measurements, and splitting the community of users. While some studies used 1.34 My the others used 1.51 My (see Granger [1] and Nishiizumi *et al.* [2] and references therein).

One fundamental requirement of this determination is an accurate mass-spectrometric measurement of the ¹⁰Be/⁹Be ratio, where the unknown number of atoms of ¹⁰Be present in a sample can be calculated from such a ratio and from the known amount of ⁹Be added gravimetrically. However, the unknown instrumental mass discrimination inherent to most isotope mass-spectrometric methods prevented all previous estimates to measure precisely this ratio. We used a new approach, based on MC-ICP-MS. A ¹⁰Be-rich solution obtained from G. Korschinek at TU München was spiked with various additions of a carefully prepared ⁹Be solution. The mass bias produced by the so-called space charge effect of the ICP source was well-constrained by bracketing the Be ratio measurement with stable isotope ratio measurements of other elements of well known isotope ratio. The ¹⁰Be/⁹Be ratio of the mother solution has been precisely determined as well as the total Be concentration. The activities of several dilutions have been measured by LSC. The ¹⁰Be amount of the solution measured via isotope dilution has then been combined with the results on activity to calculate a ¹⁰Be half-life of 1.39My with an analytical error of roughly 1%. This new half life agrees with that determined at TU München by ERD [3].

[1] Granger (2006) *Geol. Soc. Of America*, special paper **415**, 1-16. [2] Nishiizumi *et al.* (2007) *Nuc. Instr. And Methods in Phys. Res. B* **258**, 403-413. [3] Korschinek *et al.* (2009) *GCA*, this volume.

Comparison of heavy metal removal using adsorbing agents for acid mine drainage

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This study investigated the potential for utilizing 6 adsorbing agents for acid mine drainage (AMD) wastewater. These materials, with a high capacity for heavy metals, can be obtained and employed as alternative low-cost limiting substitutes. For investigating the neutralization capacity, the change in pH, Eh, and EC as a function of time was quantified. Results of column studies demonstrated that the removal rate of Fe and Mn by the tested agents was influenced by their chemical compositions. The results suggest that concrete can be used successfully in the treatment of acid mine drainages with mixed metal-contaminated wastes.

Heavy metals discharged by abandoned acid mine drainage (AMD) are one of the major causes of contaminated subsurface environments [1]. After release of low pH AMD, the geochemical behavior of metals released from the acidic tailing minerals depends on a number of different physiochemical parameters. The mobility of metal ions then is often determined by potentially forming particulate and colloidal species being stabilized and dispersed in the water.

Column experiments were conducted at room temperature. Adsorbing agent filings were then uniformly mixed with sand and packed into polyvinylchloride (PVC) columns. A total of 100 liters AMD were passed through each column for 90 days. The columns were slowly flushed from the bottom and mixed heavy metal solutions were introduced to each column with a specific discharge rate of 4.3 ml h⁻¹. Effluent samples were collected with small vials once a day for 10 min at the same time to measure pH, redox potential (Eh), electric conductivity (EC), and metal concentrations.

Of the agents, concrete showed the highest neutralization efficiency for AMD. The presence of such strongly reducing conditions is consistent with the chemical reduction of not only oxygen, but also iron and manganese [2]. The EC decreased as a function of time since metals in the system may precipitate due to high pH values, which enhances hydroxide precipitation.

With respect to Fe and Mn, Fe removed from the AMD was very high, above 90% for concrete. It should also be noted that limestone and starfish had a much higher affinity for removing Fe than Mn. While manganese can theoretically exist in numerous oxidation states, only the +2 and +4 valences are commonly found in natural waters [3]. Oxidation of the manganous ion (Mn²⁺) is pH dependent, being quite slow below pH 9 even though it is thermodynamically favorable.

[1] Akcil & Koldas (2006) *J. Clean. Product* **14** 1139-1145.

[2] Sposito (1989) *The Chemistry of Soils*. [3] Stumm & Morgan (1996) *Aquatic Chemistry*.

Dissolution of anorthite under supercritical CO₂ – water – mineral reaction system at a CO₂ sequestration site

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The objective of this study is to investigate the dissolution of Ca-feldspar (anorthite) when the mineral reacts with supercritical CO₂ and water at the CO₂ sequestration site. The dissolution of anorthite caused by the reaction with supercritical CO₂ and water at high pressure condition (100 bar and 50°C) was simulated in the high-pressure cell. Cleaved anorthite crystals from a fresh-single crystal (purchased from Hansol fossil & mineral specimens Inc.) were polished and cut a few millimeters. The stainless steel cell (104 ml in capacity; purchased from Thar Inc.) was used to simulate the subsurface condition for CO₂ sequestration. Several crystal samples were glued on a stainless steel plate, which was fixed in the high-pressure cell. Experiments for anorthite dissolution were performed in two different methods. At first, an anorthite was reacted with supercritical CO₂ and distilled water and its dissolution in water was investigated at different time intervals. For the next experiment, anorthite samples were exposed to only supercritical CO₂. For both experiments, the inside of the high-pressure cell was maintained at 100 bar and 50°C for 30 days and the surface of each sample was visualized by SEM(Scanning Electron Microscope) and the roughness of the sample was also measured by SPM(Scanning Probe Microscope) every 10, 20, and 30 days in the experiment. The main compounds dissolved in water were also analyzed on ICP/OES(Perkin elmer(U.S.A.), Optima3300XL) for the experiment. Results from the first experiment showed that the average roughness of sample surface was 0.155 nm before the reaction. It maintained for 20 days, but considerably increased to 2.493 nm after 20 days. In the second study, the average roughness of sample surface slightly decreased from 0.559 nm to 0.217 nm for 10 days, and maintained about 0.285 nm for the next 20 days.

Identification of green rust in groundwater

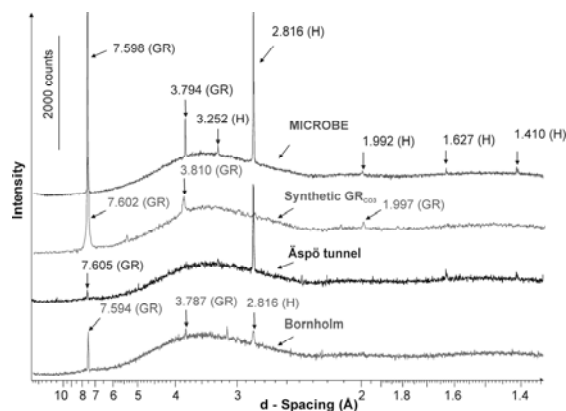
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Green rust, an Fe(II),Fe(III) layered double hydroxide (LDH), is believed to be present in environments close to the Fe(II)/Fe(III) transition zone. Identification of green rust (GR) in natural environments has proven difficult because the material is quickly oxidised with exposure to air. We developed a preservation method for capturing green rust so it is not oxidised during sampling and then we used it to identify the compound in groundwater samples taken below the water table, from fractures in granite 350 m below surface in the Äspö Hard Rock Laboratory tunnel and from an artesian well in a sand aquifer. X-ray diffraction patterns were weak, but clearly identical to those of synthetic GR_{CO3}, the green rust family member where carbonate and water occupy the interlayer between the iron-hydroxide layers. GR particles are colloidal in size and they are very reactive with many contaminants, including actinides and heavy metals. Currently, transport models for predicting the behaviour of contaminants in groundwater do not include parameters for green rust. This work demonstrates they should.



XRD patterns from the natural samples and a synthetic GR_{CO3}. The peaks representing reflections from the basal plane have d-spacings ~7.6 and ~3.8 Å are characteristic for the carbonate form of green rust. H marks halite reflections (from [1]).

[1] Christiansen *et al.* (2009) ES&T, in press.

A Pb (and Sr) isotopic return address for trans-Pacific transported aerosols

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Far-traveled aerosols (including soil-derived dust and industrial pollutants) can affect air quality, atmospheric radiative forcing and cloud formation. Principal component analysis of elemental data for aerosols collected over California has identified a persistent Asian soil dust component that peaks with Asian dust storm events [1]. Isotopic fingerprinting can provide an additional and potentially more discriminating tool for tracing and apportioning sources of aerosols. In particular, because of contrasts between North American and Asian sources [2], we use Pb isotopes to identify and apportion Asian sources of Pb emissions and associated pollutants in distant receptor regions such as the western US.

Here we present time series of the proportion (and mass concentration) of trans-Pacific transported Pb based on Pb isotopic data for aerosols (PM_{2.5}) collected in California during 2008 at two sites, Mt Tamalpais and Chabot Observatory (Oakland Hills), as well as for selected spring 2008 samples from the Eastern Sierra. We compare these records of trans-Pacific Pb transport to the elemental compositions of the collected PM_{2.5} determined by XRF. In addition we use Sr isotopic analyses to discern sea spray and mineral dust (Chinese Loess) components.

From March through May 2008, four episodes of trans-Pacific transport are evident in the trans-Pacific Pb time series. The first three peaks correlate well with mineral dust while the fourth episode has separate arrivals of Pb (with associated S) and Asian dust. Analyses of archived PM_{2.5} samples indicate that at times up to 98% of the aerosol associated Pb at inland California sites can be of Asian origin.

[1] VanCuren *et al.* (2005) *J. Geophys. Res.* **110**, D09S90.

[2] Bollhöfer & Rosman (2001) *GCA* **65**, 1727-1740.

Water mass properties and circulation in the Cape Basin – A multiproxy approach

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Highly resolved profiles of Th/U-isotopes and CaCO₃ concentrations from the southern Cape Basin (ODP Leg 177, Site 1089, 4620 m) are presented covering the past 310 kyr. The ²³⁰Th-profiling method is applied to quantify sediment focussing, and to calculate vertical ²³²Th-fluxes and preserved fluxes of calcium carbonate. The flux of ²³²Th is used as a proxy for dust input [1]. The ²³²Th based dust record from the Sub-Antarctic South Atlantic shows a good covariation with Antarctic dust data [2] although a different signal dynamics points to a non linear amplifier affecting the dust transport to Antarctica. The preserved flux of CaCO₃ at Site 1089 shows a clear variability on glacial interglacial timescales documenting significant changes in the corrosiveness of bottom/deep waters. Authigenic U is commonly present at Site 1089. Since this site is located in an open Ocean area (low productivity) and sediment focussing was high but constant, we interpret the authigenic U signal at Site 1089 as a proxy for the oxygen content of bottom waters. A combination of our results with other proxies (benthic $\delta^{13}\text{C}$ and fragmentation index [3], and mineralogical parameters [4], allows a congruent reconstruction of water mass properties and circulation in the Cape Basin on glacial/interglacial timescales. Based on this multi proxy approach we conclude that that during glacial times the conveyor circulation was weak, and the abyssal Cape Basin was filled with less corrosive and aged deep waters. A correlation/phase analysis suggest the following see-saw scenario: benthic $\delta^{13}\text{C}$ values increase (decrease) first, then the Agulhas Current strengthens (weakens), the fragmentation index of forams rises (falls) before the preserved CaCO₃ flux decreases (increases), and finally authigenic Uranium is not accumulated/released (accumulated).

[1] Winckler *et al.* (2008) *Science* 320, 93. [2] Lambert *et al.* (2008) *Nature* 452, 616. [3] Hodell, Gersonde, & Blum (2002) *Proc. ODP, Sci. Results*, 177. [4] Kuhn & Diekmann, (2002) *Palaeogeography Palaeoclimatology Palaeoecology* 182, 287.

Distribution and potential impacts of biological ice nucleators in the atmosphere

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At subzero temperatures warmer than -40°C, aerosol particles in clouds initiate freezing through the heterogeneous nucleation of ice, which can trigger the processes leading to precipitation. A diverse range of natural and anthropogenic particles are capable of initiating the ice phase, but the most active naturally occurring ice nuclei (IN) are biological in origin and have the capacity to catalyze freezing at temperatures near -2°C. The abundance and distribution of the most active IN in the atmosphere (i.e., biological IN) have been described in only a very limited way, their diversity and ecological/biological sources have not been systematically investigated, and their role in precipitation generation and the global climate remains speculative. However, biological particles have been shown to be abundant in atmospheric aerosols and there is evidence that some bacteria may serve as IN in clouds. Species of ice nucleating bacteria or biological IN in general have been detected in snow and rain from a variety of global locations, and ~95% of the immersion IN active at temperatures warmer than -10°C are inferred to originate from bacteria and/or biological cells. Based on the widespread distribution of biological IN in the atmosphere, they are likely to encounter the appropriate conditions to affect processes leading to precipitation. Aerosol-cloud simulation models imply that high loads (10 per liter at -20°C; under conditions of water saturation) of biological IN may influence the average concentration and sizes of crystals in clouds, horizontal cloud coverage in the free troposphere, precipitation at the ground, and incident solar insolation at the surface. Unearthing a 'weak feedback' between sources of biological IN (e.g., plants and surface ecosystems) and cloud atmospheric processes has implications for deciphering functional biological mechanisms which influence the climate system and understanding global dissemination strategies of phytopathogens and other microorganisms.

Variations of $^{107}\text{Ag}/^{109}\text{Ag}$ isotope ratio in ore deposits by high-precision MC-ICP-MS

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We present results of a $^{107}\text{Ag}/^{109}\text{Ag}$ isotope study for different Au and Ag hydrothermal deposits. Analyses were performed using a NEPTUNE multi-collector -ICP-MC with 3% HNO_3 solutions spiked by Pd. The measured $^{107}\text{Ag}/^{109}\text{Ag}$ ratio were on-line corrected for mass-discrimination using $^{108}\text{Pd}/^{106}\text{Pd}=0.97533\pm 7(\pm 2\text{SD})$ as an "internal" standard isotope ratio. The precision of the method ($\pm 2\text{SD}$) was assessed by replicate analyses ($n=23$) of the SRM 978a Ag standard as $\pm 0.007\%$ ($\pm 0.7\epsilon_{\text{Ag}}$) at a mean $^{107}\text{Ag}/^{109}\text{Ag}$ value of $1.07634\pm 8(\pm 2\text{SD})$.

We studied native Au and Ag from well known deposits: the Precambrian Kidd Creek (Canada), Kolar (India) and Maiskoe (Russia), the Paleozoic Sukhoi Log (Russia), Karabash (Russia), Kongsberg (Norway), Aktepe (Uzbekistan), the Mesozoic Ducat (Russia) and the Cenozoic Hodrusha and Kremnica (Slovakia). The revealed isotope variations in $^{107}\text{Ag}/^{109}\text{Ag}$ is up to $5.3\epsilon_{\text{Ag}}$ which is similar to a variation range of $7.5\epsilon_{\text{Ag}}$ presented for some terrestrial objects – Hawaiian basalts and Ag-deposits [1, 2]. Among our data the lowest ϵ_{Ag} value of (-5.8) was obtained for the Karabash Au-deposit, and the highest ϵ_{Ag} values $(-0.5$ and $-0.4)$ were measured in the Kongsberg Ag-deposit and Kremnica Au-Ag deposit. All other deposits under study show a narrow range of ϵ_{Ag} values (from -1.9 to -4.0).

The obtained ϵ_{Ag} values do not correlate with the geological position, genesis and age of deposits. The latter varies from 2700 to 12 Ma. The most probable reason for $^{107}\text{Ag}/^{109}\text{Ag}$ variations is Ag isotope fractionation in ore-forming processes. Its leading mechanism is connected with changes in Ag valency state during mineral formation. These processes will be a topic of future studies.

The study was supported by the Division of Earth Sciences of the Russian Academy of Sciences (Basic Research Program No. 8).

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Preeruptive conditions and dynamic processes in magmatic systems: The example of Unzen 1991-1995 eruption

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The compositional and morphological characteristics of rocks produced during volcanic eruptions provide constraints on the magma storage conditions prior to eruption and on the dynamic processes occurring in magma chamber and during magma ascent. However, the quantitative interpretation of chemical and morphological variations in terms of eruptive dynamics requires an accurate calibration via experimental approaches. In the particular example of the Unzen eruption in 1991-95, a variety of experimental studies (phase relations, solubility of volatiles in melts, viscosity and decompression experiments) have been combined with petrological, geochemical and geophysical approaches for the erupted rocks as well as for rocks in magmatic conduit drilled by the ICDP (Unzen Scientific Drilling Project), leading to a general overview of the magmatic processes prior to and during the eruption. The eruption was triggered by the mixing/mingling of a low-temperature ($\sim 770^\circ\text{C}$) rhyolitic magma with a high-temperature ($\sim 1050^\circ\text{C}$) andesitic magma at pressures of 300-400 MPa. The rhyolitic magma was rich in H_2O (7-8 wt%) and Cl (up to 0.1 wt%) while andesite was a main source for CO_2 and S (0.04 wt%). The mixed dacitic melt ($T=930^\circ\text{C}$) might have contained about 6 wt% H_2O , 0.09 wt% CO_2 , 0.02 wt% S and about 0.05 wt% Cl. The interpretation (and experimental calibration) of zoning of amphiboles indicate that influxes of volatiles and degassing events occurred in the magma chamber prior to mixing. Experiments aimed at understanding the rheology of Unzen magmas indicate that the viscosity of the two end-member melts (water-poor andesite and water-rich rhyolite) were nearly identical, leading to an effective mixing. Using decompression experiments modelling the magma ascent and the concomitant degassing (exsolution of H_2O - or $\text{H}_2\text{O}+\text{CO}_2$ -bearing fluids), it is demonstrated that microlites can only form at decompression rates <0.1 MPa/s. The size and shape of plagioclase microlites in Unzen rhyodacitic groundmass could be reproduced at decompression rates of 0.0002 MPa/s, corresponding to an average magma ascent rate in the Unzen conduit of ~ 20 m/h.

Impact of mining on aquatic systems: Lessons from Sardinian surveys

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Abandoned mine sites pose environmental hazards and risk to the human health. Mining in Sardinia (Italy) dates back to pre-Roman times. Base-metal ore exploitation and processing lasted several centuries, ended in 1980-1997, and left 169 abandoned mines, $71 \cdot 10^6$ m³ of residues (50% flotation tailings and slag that show high reactivity) spread over a 19 km² surface (RAS, 2003. Piano regionale di gestione dei rifiuti - Piano di bonifica siti inquinati. Regione Autonoma della Sardegna. 255 pp, in Italian). Most of these mines lay with non-identifiable responsibility and this has led to non-action after their closure. Only recently the Regional Government has recognized the need of actions for reducing the environmental risks.

Hydrogeochemical surveys carried out since 1996 comprised about 200 sampling sites located in mined areas. Results of these surveys showed the outflows from flooded mines and drainages from mining wastes to be the main sources of contamination to the aquatic and soil systems. Relevant contaminants are Zn, Cd, Pb, As and Sb, depending on the composition of ore deposits at specific sites. Repeated sampling under different seasonal conditions showed that the mining residues release high concentrations of contaminants to surface waters; extreme contamination has been observed after storm events. The contamination level at some streams is high even during drought periods because they are only supplied by highly polluted mine drainages. The risk to human health is enhanced by the proximity of abandoned mines to water resources and cultivated land. Taking into account the results of geochemical and mineralogical studies, different actions are proposed for specific sites. These can be summarized as follows: 1) stabilization of the impoundments and waste piles (allowing low rates of erosion processes); 2) runoff diverting and drain systems at the waste dumps (minimizing contact between water and polluted materials); 3) treatment of mine drainage before discharge into streams (reducing downstream dispersion); 4) construction of artificial ponds and/or wetland (favoring precipitation and/or sorption processes); 5) treatment and/or removal of those materials highly contaminated.

Lessons learnt by past mining in Sardinia indicate that a correct disposal and management of the mining residues should be mandatory at the active mines. This would allow to reduce the environmental risks and the cost of rehabilitation.

Reconciling models of the solar nebula with the chondritic record

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Protoplanetary disks are dynamic objects, through which mass and angular momentum are transported; the net motions are inward, with much of the disk mass accreted by the central stars during their final stages of pre-main sequence growth. During this evolution, a disk is heated by dissipation effects within the gas as it loses mass and grows in its radius to conserve angular momentum.

Chondritic meteorites record a dynamic history of our own solar nebula, as they contain materials that formed in a variety of chemical and physical environments. Specifically, the refractory CAIs are the oldest objects in these meteorites and appear to have formed in a gas of solar composition, whereas chondrules, which also formed under high temperatures, were exposed to a gas with a range of oxidizing conditions and are enriched in heavy oxygen isotopes relative to CAIs. Further, within chondrite matrix are pre-solar grains, which had to escape high temperatures altogether. Despite these different histories, these materials were mixed together such that they are located within centimeters of one another on chondritic meteorite parent bodies.

To date, it is unclear how the dynamic evolution of a protoplanetary disk would give rise to the different environments sampled by chondritic meteorites and their components. However, recent work has shown that many of the general properties of chondritic materials can be explained within the context of an evolving solar nebula. For example, the high temperatures needed to form CAIs would be prevalent during the earliest, most rapid stages of nebular evolution. The dynamic environment that would be created at such a time would result in the large-scale redistribution of CAIs, allowing them to be transported outwards tens of AU. Declining mass accretion rates through the disk would prevent the CAIs from forming at later times, and would also allow those that were scattered outward to drift inward at rates that depended on their size. During this time, the properties of the inner solar nebula would have evolved, allowing the conditions needed to form chondrules to have developed [1]. Similar evolution is seen in disks around other stars [2]. Further development of these nebular models may provide a context within which to understand the formation of our solar system.

[1] Ciesla & Cuzzi (2006) *Icarus* **181**,178-204. [2] Carr & Najita (2008) *Science* **319**,1504-1507.

Collisions among porous planetesimals and the water content of planetary embryos

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N-body simulations of planet formation have advanced in recent years to predict the bulk composition of the final products as well as their orbital properties. Such studies (e.g. [1]) track the provenance of each planetary building block, and based on an assumed initial compositional gradient for the planetesimals and embryos with distance from the star, the final compositions of the planets are determined as being the sum of each of its individual components. It is generally found that planets that form in what are assumed to be initially 'dry' regions are often able to acquire significant amounts of water through the accretion of planetesimals that originate much further from the star. Often, these models predict very water-rich worlds, sometimes in disagreement with the current inventory of water in our terrestrial planets.

Recently, it has been argued that the growth of planetary embryos proceeds not by direct accretion of planetesimals, but rather by the accretion of fragments produced during planetesimal collisions [2]. In fact, planetesimals are more likely to be destroyed in collisions with one another than by direct accretion by a growing embryo. The orbits of collision fragments are then circularized by the gas in a protoplanetary disk, allowing them to easily be accreted by embryos.

We have developed a model to examine high-velocity impacts between planetesimals [3]. We find that if young planetesimals were porous, which is expected given the low velocity collisions by which these objects accrete, shock heating in subsequent high-velocity, disruptive collisions can lead to temperature increases of the fragments by hundreds of Kelvin, which would drive off volatiles such as water. Embryos that formed from those heated and dried fragments would be volatile-depleted compared to current accretion models, and may reconcile the discrepancy between those model predictions and the actual water abundance of Earth.

[1] O'Brien *et al.* (2006) *Icarus* **184**, 39-58. [2] Chambers (2006) *Icarus* **180**, 496-513. [3] Davison *et al.* (2008) *LPSC* abstract #2008.

Volcanic SO₂, atmospheric photochemistry, and climate on early Mars

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Small terrestrial planets, such as Mars, have significant problems in maintaining habitability. One major hurdle presented by the lower Martian gravity is that significant volcanic outgassing is required to form a dense atmosphere, a seeming necessity for clement conditions. Despite the widely-held hypothesis that there were oceans on early Mars, no self-consistent climate scheme has yet been shown to be fully compatible with this hypothesis [1].

Recently, an SO₂-based geochemical cycle has been proposed for early Mars [2, 4]. SO₂ is undoubtedly a good greenhouse gas, provided that it can be photochemically and geochemically stabilized, and provided that the formation of reflective sulfate aerosols, which are known to act as powerful coolants on Earth and Venus, can be suppressed. We will show results from two modeling studies which cast doubt on the ability of SO₂ to act as a warming agent for terrestrial planets.

First, we describe an extension to a recent 1D photochemical model for the Martian atmosphere [6]. We expand this model to include sulfur chemistry including the formation of sulfate/polysulfur aerosols, along with self-consistent radiative transfer with aerosol mie-scattering. We show that enhanced volcanic sulfur fluxes drive the Martian atmosphere to a more reduced state. In our most reducing Martian atmospheres, SO₂ persists in the gas phase, but it is very difficult to maintain partial pressures greater than ~1 ppm. Furthermore, these atmospheres also feature significant sulfate aerosol formation. We next describe results from a 1D radiative-convective climate model [3], which we have modified to account for sulfate aerosols. Using the atmospheric profiles created by the photochemical model, we show that the net effect of enhanced sulfur fluxes to the Martian atmosphere is likely to be net cooling, not warming, due to the anti-greenhouse effect of the sulfate aerosols.

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Agent-based modelling of Archean biogeochemistry and the Great Oxidation

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Recent work has suggested the delay between the emergence of oxygenic photosynthesis and the Great Oxidation may be explained by a bistability in atmospheric oxygen [1]. The origin of the bistability relates to a nonlinear increase in the lifetime of atmospheric oxygen when levels exceed $\sim 10^{-5}$ present atmospheric levels (PAL). At this point, ozone becomes effective at shielding the troposphere from ultraviolet radiation, permitting oxygen levels to rise. However, the trigger that might have caused the system to flip from the low oxygen state into the high oxygen state (~ 0.01 PAL) remains uncertain. Here we expand upon the work of Goldblatt *et al.* [1] by building an agent-based model of marine life in the Archean. The model is a three-box representation of the ocean-atmosphere system. Into it are placed a number of microbial guilds, containing species that perform similar metabolic transformations, e.g., photoautotrophy, methanogenesis etc. The growth of organisms is modelled as a balance between anabolic and catabolic processes, and includes an explicit representation of energetic yields from various forms of metabolism. Within each guild, multiple species may coexist and compete on the basis of various physiological traits.

Each organism possesses an artificial genome that specifies physiological traits that ultimately determine the organism's competitiveness within the environment. Mutations, prescribed as chance events at the point of reproduction, introduce variability into emergent populations, and supply handles upon which selection may act. Early simulations show organisms evolving with their environment, resulting in a relatively well oxygenated surface ocean, populated by aerobic lifeforms, while an anoxic deep ocean plays host to a small population of anaerobic methanogens. Despite possessing a completely different architecture, the model is able to reproduce a similar transition in atmospheric oxygen as observed by Goldblatt *et al.* [1]. This work represents initial progress made in utilising agent-based models to study the co-evolution of life and its environment.

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Aerosol and ocean-atmosphere processes over the Pacific Ocean

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The flux of gas and particles across the ocean surface in either direction has significant influence on both atmospheric and oceanic processes. These effects are often studied and described for the "local" scale in the vicinity of the ocean surface, marine boundary layer and/or for the air mass to which they are related. There are also larger scale couplings between ocean and atmosphere within which these processes are active, including large convective systems, oceanic gyres, upwelling regions, Hadley circulation etc. that are also coupled to transport regimes, cloud coverage, precipitation processes etc. Aerosol properties responsible for local direct and indirect radiative effects, can influence and be influenced by these larger scale systems. Some of these may give rise to teleconnections where source regions or scavenging regions can have influences over thousands of kilometers, often when transport in the free troposphere is involved.

For 15 years we have participated in numerous NASA and NSF aircraft campaigns over diverse Pacific oceanic regions and continental margins (see Figure below). These allowed us to explore processes active over hemispheric scales. Here we will illustrate aerosol microphysics and chemistry linked on these scales including: nucleation; sea-salt production; long range transport of dust, pollution and biomass burning; boundary layer CCN and relations to cloud scavenging; entrainment and deposition.

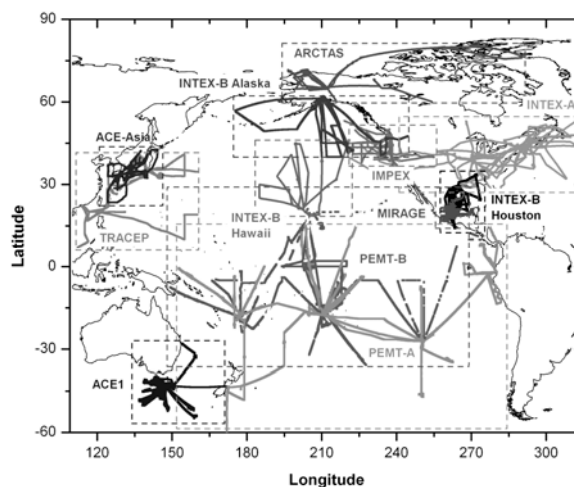


Figure 1: Pacific airborne missions over past 15 years.

Shona and Discovery seamount chains, South Atlantic: Superplume source constraints

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The effectively un-sampled major bathymetric anomalies of the Shona Ridge – Meteor Rise – Agulhas Ridge – Cape Rise and Discovery seamounts in the South Atlantic have been attributed to the activity of the Shona and Discovery mantle plumes based solely on geochemical signatures measured in Mid-Ocean Ridge basalts from the adjacent Mid-Atlantic Ridge and a single Discovery Seamount sample. Here we present new Sr-Nd-Pb-Hf isotope data on dredge samples from these seamount chains collected by the ANT XXIII/5 cruise of the FS Polarstern.

The new Discovery seamount data form endmembers to the so-called Discovery and LOMU geochemical anomalies on the southern Mid-Atlantic Ridge (MAR), suggesting that the latter are formed from the same plume source through plume-ridge interaction.

Some samples from the Shona Ridge – Agulhas Ridge and Cape Rise Seamounts have isotopic compositions forming an endmember to the geochemically enriched basalts of the southern MAR, previously attributed to the influence of the so-called Shona plume. The occurrence of this signature in dredges from each of these bathymetric anomalies suggests that it might represent a long-lived Shona plume component. Overall the samples from the purported Shona plume track are very heterogeneous and range from EMI- to HIMU-type. A Gough-like component is present in the Shona and Agulhas Ridge and combined with its presence in the Discovery Seamounts and Discovery geochemical anomaly on the MAR suggests that this component is an important and common source composition in the South Atlantic mantle. A shallow component from recent continental breakup seems to form an additional but minor component in the Shona plume track.

The new data demonstrate a strongly heterogeneous source region for South Atlantic intraplate volcanism, including DUPAL, HIMU and possibly sub-continental lithospheric mantle components. Combined with the abundance of hotspot tracks lacking initial plume heads, the new data support similarly heterogeneous source characteristics and dynamics to the hotspots developed from both the Pacific and African superplume regions.

Uranium-lead dating of speleothems: Prospects and limitations

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In recent year several studies have shown that U-Pb isotopic dating is a promising option for dating speleothems from the early Pleistocene and earlier which has otherwise presented a difficult challenge.

The integrity of the U-Pb system has been confirmed by comparison of U-Pb and U-Th data on a speleothem from the Spannagel Cave in the Austrian Alps. Disequilibrium-corrected U-Pb ages date growth from 340 ka to 267 ka. High resolution sampling of one short growth interval yielded U-Pb and U-Th ages in close agreement at 266 ka with ± 1 ka error on the U-Pb age. These results confirm closed system behaviour throughout the uranium decay chain even in such U-rich samples.

Speleothems from the Wilder Mann and Wildmahd caves in the Allgäu Alps, western Austria encapsulate a detailed history of environmental variations at the time of speleothem growth. High uranium concentrations have led to the development of highly radiogenic lead compositions by the present day, giving the potential for dating of samples that are well beyond the reach of U-Th disequilibrium dating. Ages are in the order of 2 Ma and for samples of this age 'normal' residual levels of excess ^{234}U are no longer detectable. To incorporate the uncertainty of the unknown initial ^{234}U excess a range of possible values was estimated from a log-normal distribution and incorporated into a Monte Carlo error propagation of the analytical data. One of the stalagmite samples shows significant age variation along its length with a well-resolved growth hiatus separating a younger growth period at $2.04 \pm 0.02/-0.07$ Ma from an older period for which three groups of subsamples give ages of $2.11 \pm 0.03/-0.07$, $2.14 \pm 0.02/-0.06$ and $2.16 \pm 0.04/-0.07$ Ma, in the correct stratigraphic order.

Future applications of this approach depend critically on how well we can correct for the effects of excess ^{234}U . Even with precisions $<0.5\%$ residual excess is undetectable in many samples of interest. It would assist greatly if other persistent geochemical parameters could be identified that correlate with initial excess ^{234}U ; such parameters could then be used as a proxy for initial excess in older samples in which residual excess ^{234}U can no longer be detected.

The role of island arc collisions in building the continental crust: Evidence from Tyrone, Ireland

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Large volumes of continental crust are lost back into the upper mantle via sediment subduction, tectonic erosion of forearcs, subduction of passive margins and gravitational loss of lower crustal material. These losses are balanced largely by arc magmatism. Although oceanic arcs account for only 31% of the total active margins in the world, mass budgets suggest that 40% (ca. 1.2 km³/yr) of global arc melt production occurs along these margins. As a result their preservation is essential to maintaining the volume of the continental crust. New work from the Cambro-Ordovician Tyrone Igneous Complexes (TIC) in Northern Ireland adds to our understanding of how oceanic arc crust is transformed during its accretion to continental masses. U-Pb dating of zircons from primitive arc gabbros shows that subduction was active at least by 493 ± 2 Ma, but that the arc had started to collide with the passive margin of Laurentia by 475 ± 10 Ma based on U-Pb zircon dates from tonalite (possibly as early as 490 Ma; Chew *et al.* 2007). LREE enrichment in volcanism and silicic intrusions of the TIC exceeds that of average Dalradian continental material, that would have been thrust under the colliding forearc and potentially recycled into arc magmatism. This implies that substantial crystal fractionation, in addition to magmatic mixing and assimilation, accompanied the formation of new crust in the Grampian-Taconic Orogeny. Our new data support earlier suggestions that although arc crust is too mafic and depleted to be a good analog for the construction of continental crust it is the injection of enriched material during accretion that helps modify the bulk composition to more continental values, especially if accompanied by loss of lower crustal ultramafic cumulates. Tectonic evolution of the Palaeozoic Caledonides show close parallels with those observed in modern day Taiwan.

Large mantle heterogeneities in H₂O and δD below the Southwest Indian Ridge (35-70°E)

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The concentration and isotopic composition of hydrogen in the upper mantle depend on exchanges during subduction, melting at ridges and interaction with a possible lower mantle. The δD of the present-day upper mantle is assumed to be -80±10‰, and its H₂O/Ce ratio 175±30, but most of the measurements were done on basaltic glasses from the Middle Atlantic Ridge and the East Pacific Ridge. The Southwest Indian Ridge (SWIR), known to be heterogeneous in chemical and isotopic composition is key to understand the processes affecting the variability of the water in the mantle and shed light on the global water cycle.

We present new δD and H₂O measurements on 45 basaltic glasses from the SWIR (35-70°E). Large heterogeneities are observed in H₂O/Ce and δD in the different ridge segments. The δD values range from -44 to -78‰ and H₂O/Ce ratios range from 101 to 435. The δD distribution is bimodal, with most segments being D-enriched with an average δD of -55±5‰ and two D-depleted segments with an average δD value of -70±8‰ (the 39-41°E and the 57-61°E segments). Most of the H₂O/Ce ratios are under 200, except for segments around 50°E and east of the Melville fracture zone (62°E).

All these glasses are undersaturated in water, indicating that degassing is negligible. Crystal fractionation, partial melting of an homogeneous source or contamination by either seawater or a brine cannot explain the observed variations. Thus, both δD and H₂O/Ce variabilities mostly reflect source heterogeneities in the southwest indian upper mantle.

The influence of the nearest hotspots is highly unlikely according to previous data in Sr-Nd-Pb compositions. Our results calls for the existence of a general deuterium enrichment of the SWIR mantle compared to the Atlantic and Pacific oceanic mantles.

Zn isotopic variation in human hair and finger nails

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Zn is an essential microelement for plants and is also a component of many proteins. The isotopic composition of Zn in human blood and red blood cells displays very little variation (the total range reported is limited to 0.2‰). In contrast to Fe, no difference in Zn isotopic composition between male and female blood was yet reported. However, exploratory work did reveal that the isotopic composition of Zn in hair is lighter than that of blood. A first goal is now to ascertain that this observation is not due to the use of Zn-containing beauty products, such as shampoo or dye, although first literature results excluded these as the source of isotopic variations. The second aim was to determine if other parts of human body have fractionated Zn and finally to investigate any seasonality of the measured Zn isotopic variations.

In this study, hair, finger nails and shampoo samples from and used by the same subject have been investigated for their Zn isotopic composition. 4 hair samples and 3 finger nail samples have been analysed to date, covering a one year period. The hair reference material CRM 397 was also measured in order to control the reproducibility of the entire procedure. Two aliquots digested twice give the same results within uncertainties with values of -0.01‰ and -0.09‰ in terms of $\delta^{66}\text{Zn}$ relative to JMC Lyon. Hair samples from the subject revealed overall variation of 0.20‰ in $\delta^{66}\text{Zn}$ ranging from -0.06 to +0.14‰. This value is significantly different from the 0.24‰ obtained for the shampoo, suggesting that the shampoo is not governing the Zn isotopic composition in the hair. Moreover, finger nails present a variation similar to the hair from -0.04 to 0.24‰. Both hair and finger nails sampled between July and October are enriched in ^{66}Zn by 0.2‰ relatively to the rest of the year.

These results together with the hypothesis that the blood value ranges between 0.3 and 0.5‰ point out a real biological fractionation in the human body of up to 0.6‰ along with a seasonal Zn isotopic variation. The origin of the seasonal variation could be linked to the diet but this is still to be confirmed.

¹³C-enriched bacterial lipids in the modern ocean: An analogue to the Proterozoic record

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We have isolated organic matter from bacterioplankton in the modern oligotrophic surface and mesopelagic water column of the North Pacific gyre, and have observed an enriched ¹³C content of *n*-alkyl lipids in relation to total organic carbon. We postulate that this signature may be the natural outcome of carbon dynamics in a mixed, but bacterially-dominated marine community. This phenomenon has been rarely recorded in the Phanerozoic due to the bias of the sediment and sedimentary rock record toward preserving highly productive, eukaryote-dominated shelf environments instead of bacterially-dominated open ocean environments. A similar enrichment in ¹³C of *n*-alkyl lipids as compared to total organic carbon has been a persistent challenge in interpreting the Proterozoic record. We thus suggest that modern oligotrophic, bacterially-dominated water columns may serve as our best observable analogue to the Proterozoic ocean, and that the reversal of the *n*-alkyl—TOC isotopic relationship with the onset of the Phanerozoic might derive from a fundamental change in marine communities to a higher proportion of eukaryotes. It also suggests that Proterozoic surface oceans were organic carbon-limited as a result of nutrient deficiency, perhaps in association with severe trace-metal limitation and/or episodic periods of bottom water euxinia. Here we begin to explore the environmental dependencies of the ¹³C-enriched bacterioplankton signature by comparing results from the oligotrophic North Pacific gyre and the productive Eastern Tropical Pacific. The 0.2-0.5 μm size class was filtered from surface and mesopelagic depths at both sites. We couple compound-specific carbon isotopic analysis of fatty acids by GC-C-IRMS with genetic profiling by Phylochip in order to elucidate the relationship between the dominant living communities and the dominant contributors to lipid biomarkers, and to reveal details of organic matter transfer from the surface ocean to mesopelagic depths. We have derived a preliminary model of carbon export in a bacterially-dominated water column in order to test whether the Proterozoic-Phanerozoic switch in the organic carbon record could be the result of increased eukaryotic dominance, and what environmental constraints would be necessary for this interpretation.

The behaviour of dissolved Pt in the North Atlantic Ocean

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Rationale

The behavior of Pt in the oceans is still controversial since the data presently available for Pt are not oceanographically consistent with respect to their basin-to-basin variation [1]. Accordingly, a recycled-type behavior in the Pacific [2], a scavenged-type profile in the Indian [3] and concentrations invariant with depth in the North Atlantic [4] were reported.

Besides, the environmental emission and long range transport of Pt due to its use in catalytic converters in cars for more than two decades now Pt [5] indicated the need for a new insight on the distribution of dissolved Pt in the North Atlantic Ocean.

Results and Discussion

Water column samples at Bermuda BATS station (31°45.92' N; 64°04.95' W) were taken during the GEOTRACES intercalibration cruise in June 2008 [6]; Pt was analyzed by means of catalytic DPCSV, and was in the range of 0.1-0.4 pM and showing no trend with depth. These results support the invariant depth profile concentrations (0.28 ± 0.07 pM) reported around two decades ago near Bermuda [4]. Also, the impact of the use of Pt in the catalytic converters in cars seems to be negligible on dissolved Pt in the North Atlantic.

We are grateful to G. Cutter, K. Bruland, and R. Sherrell and the people who attended the GEOTRACES cruise, and to the Spanish MICIIN for financial Support (CTM2008-01792-E).

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Microbially-mediated anaerobic redox cycling of iron and nitrogen in sediments

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The ability of some dissimilatory NO_3^- and Fe(III) reducing microorganisms to catalyze the oxidation of Fe(II) with NO_3^- expands the potential for coupled Fe-N redox interactions in sediments. Microbial redox metabolism and community structure associated with either NO_3^- reduction, Fe(III) reduction, or multiple cycles of Fe(III) reduction and NO_3^- dependent Fe(II) oxidation were examined in three fed-batch reactor systems inoculated with iron-bearing, river floodplain sediment. NO_3^- and acetate were strategically added to the Fe redox cycling systems to facilitate four complete cycles of reduction and oxidation.

NO_3^- , Fe(II), NH_4^+ , and acetate concentrations were monitored to follow biogeochemical redox processes. Addition of NO_3^- under low-carbon conditions resulted in rapid Fe(II) oxidation and accumulation of NH_4^+ . Examination of sediment from Fe redox cycling reactors using selected-area electron diffraction and high-resolution TEM revealed the formation of amorphous coatings on the goethite nanocrystals that was not observed in reactors operated under either sustained nitrate- or iron-reducing conditions.

Microbial community dynamics associated with NO_3^- reduction, Fe(III) reduction, and Fe redox cycling systems were assessed using a combination of culture-based and molecular phylogenetic techniques. Results indicate that the NO_3^- -reducing cultures were dominated by *Betaproteobacteria*, Fe(III)-reducing cultures were dominated by *Deltaproteobacteria*, and the Fe redox cycling cultures were more diversely populated than anticipated including members of the *Alpha*-, *Beta*-, *Gammaproteobacteria* and *Clostridia*. The results suggest that sediments where repeated iron-cycling occurs will develop a diverse and well-adapted microbial community to take advantage of the energy available. Such cycling may also notably affect the surface area and crystallinity of sediment (oxy)hydroxides.

Common-Pb correction in laser U-Pb geochronology using MC-ICPMS and a multi-ion counting system

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Prior to measure common-Pb in zircon when using laser ablation, two external sources of common-Pb must be eliminated: one is present on the surface of the mount and the second is in the Ar gas. The pre-ablation procedure makes the effect of surface contamination negligible [1]. The measurement of the blank from the gas before and after each spot analysis is also supposed to allow this contribution to be subtracted. Finally, the remaining common-Pb is mainly originated from the sample.

Similarly to ion probe [2], when using our LA-MC-ICPMS system, three methods can be employed for correcting measured isotopic ratios for common-Pb. (i) The ^{204}Pb method requires no assumption except the knowledge of the common-Pb composition at the time of zircon crystallisation. However, it requires correcting for ^{204}Hg interference by using ^{202}Hg peak. In addition, the precision on $^{206}\text{Pb}/^{204}\text{Pb}$ ratio becomes critical for “young” samples (e.g. < 600 Ma). (ii) The ^{207}Pb method is based on TW’s representation [3] which only requires precisely measured $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{238}\text{U}/^{206}\text{Pb}$ ratios. This method is efficient through the Phanerozoic times and becomes the unique method for Quaternary zircons [4]. (iii) The third method, ^{208}Pb , is much less commonly used. It requires the measurement of both $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{232}\text{Th}/^{238}\text{U}$ ratios, and it works well if the Th/U ratio is low (e.g. < 0.5).

We selected the UQ-Z1 zircon [5] already dated by conventional TIMS (1142±1 Ma). A set of 16 spot analyses were measured using LA-MC-ICPMS equipment and corrected for common-Pb according to the three methods. It was demonstrated, for that sample which shows low Th/U ratio (~0.25), that the best precision and accuracy are achieved by applying the ^{208}Pb method.

Nevertheless, using a LA-MC-ICPMS equipped with a multi-ion counting system, one of the three methods can be selected according to the age and the chemistry of the zircon.

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Microbial geomorphology – The role of a biota in coastal erosion

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Microbes are known to play an important role in rock weathering. This work investigated the hypothesis that microorganisms contribute to coastal erosion and are agents in shaping the Earth’s coastlines through weathering activity. The geobiology of the surface of weathered shale on the coast of North-East England, which dislodges during weathering, leading to large-scale cliff wastage, was examined.

The bacterial community is dominated by Proteobacteria, with phylotypes closely associating with *Methylocella* and the γ -subdivision. The second largest number of phylotypes corresponded to *Nitrospira*. Acidobacteria are also abundant. Archaea most closely associated with the crenarcheota SAGMA group and phylotypes previously associated with coal seams. Their putative metabolisms suggest biogeochemical cycling of gases and organic material at the rock-gas interface within the cliff fractures.

The organisms populate a thin (1-10 μm) iron-rich layer on the surface of the weathered shale which XRD shows is formed by conversion of silicates to clays. XAS at the Fe-K edge, Raman (532 nm) and SEM analysis shows the surface to be heterogeneous at the micron scale and Fe to be primarily in the form of disordered iron oxides with some goethite.

NanoSIMS reveals the spatial distribution of organisms in relation to weathered silicates and trace gypsum. The data may either be interpreted as a random distribution of organisms in relation to shale mineralogy or representing specific microbe-mineral interactions caused by different metabolisms.

We propose that through their metabolic activity organisms contribute to surface weathering, rock weakening and coastal geomorphological changes that have been measured at the kilometre scale.

Constraints on hydrothermal fluid fluxes from Tl geochemistry

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Hydrothermal circulation of seawater is a fundamental process in the formation and aging of the ocean crust. This hydrothermal activity has a major impact on ocean chemistry, which in turn may be used to investigate past and present variations of the Earth's climate. The hydrothermal contribution to ocean chemical budgets depends on the composition and flux of hydrothermal fluids.

Thallium (Tl) exhibits distinct behaviour in axial and off-axial hydrothermal systems [1]. During on-axis high-temperature hydrothermal circulation, Tl is leached from the sheeted dikes with no fractionation in Tl isotope composition ($\epsilon^{205}\text{Tl}$). In contrast, isotopically light Tl is added to the upper crust from seawater during low-temperature off-axis circulation. A simple Rayleigh fractionation model can be used to account for the decreasing extent of Tl-enrichment and isotopic fractionation with depth [1].

We present new MC-ICPMS measurements of Tl concentrations and isotopic compositions of ocean crust produced at slow- (Macquarie Island), intermediate- (Ocean Drilling Program Holes 504B and 896A, and the Juan de Fuca Ridge), and fast- (ODP Hole 1256D) spreading rates. These data allow us to constrain the axial and off-axial hydrothermal fluid fluxes required to produce the observed shifts in Tl concentration and isotopic composition, using simple mass balance.

The uppermost basement from ODP Hole 504B displays $\epsilon^{205}\text{Tl} = -20$. Since seawater is characterized by $\epsilon^{205}\text{Tl} = -6$, the off-axis uptake of Tl by the ocean crust is associated with a fractionation factor of 0.9986. We evaluate which minerals are responsible for Tl-uptake from seawater using analyses of samples that exhibit different styles of alteration.

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Geochemical and biotic records of marine anoxia: Disentangling local and global signals

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The widespread accumulation of marine organic carbon has been very uncommon during the Phanerozoic, but the occasions on which this did occur (Oceanic Anoxic Events, OAEs) are of great importance because they are inferred to represent times when the oxygen minimum zone expanded greatly. OAEs were also associated with other expressions of environmental change such as global warming, seawater acidification and large-scale species extinctions. How these episodes developed, and quantification of their duration and effects, are goals that are central to a full understanding of the Earth System not least because of their close similarities to some aspects of present-day environmental change. This study presents new and published geochemical and biotic data from the Toarcian OAE, the Tithonian and the Paleocene-Eocene Thermal Maximum in order to assess how and why large-scale seawater anoxia developed in the past.

The Toarcian OAE was a relatively brief interval *c.* 183 Ma ago when levels of organic carbon accumulation were unusually high worldwide [1]. The OAE was associated with a pronounced global carbon isotope excursion (CIE) and with a range of geochemical proxy data that are consistent with a global increase in the areal extent of marine anoxia [2]. Robust and complete records of the Toarcian CIE from many locations worldwide show a regular structure in both marine carbonate and organic carbon that bears a remarkable resemblance to the CIE that characterises the PETM [3]. Species distributions across the Toarcian OAE are closely allied to the pattern of the CIE and to the fluctuating environmental conditions that are implied by geochemical proxy data [4]. Widespread accumulation of marine organic carbon also occurred in the Tithonian (Late Jurassic), but the patterns and timescales of C- and Mo-isotope variations that are associated with the Tithonian deposits differ greatly to those of the Toarcian, and to the PETM CIE.

[1] Jenkyns (1988) *AJS* **288**, 101-151. [2] Pearce *et al.* (2008) *Geology* **36**, 231-234. [3] Cohen *et al.* (2007) *JGS* **164**, 1093-1108. [4] Caswell *et al.* (2009) *JGS* in press.

Properties of minerals and other things from fundamental physics: From DFT to DMFT and QMC

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We now have a wide range of methods and community codes to study minerals, molecules, and fluids computationally, and to increase our understanding of Earth's constituents throughout the pressure, temperature, and composition. Challenges remain as many problems of interest are barely computationally tractable, and fundamental issues remain for iron- and other transitional metal bearing systems. For systems without transition metal ions, and for metallic transition metals like iron and its alloys, we can accurately compute most thermodynamic and transport properties of interest to geochemistry with sufficient accuracy for application. A range of techniques are available, varying in speed and accuracy. Kinetics and rheology remain challenges. For transition ion bearing systems are among the forefront problems in solid state physics.

I will talk about applications of density functional theory (DFT), dynamical mean field theory (DMFT) and quantum Monte Carlo (QMC), and will review examples from our work ranging from MgO, MgSiO₃, and Fe where density functional computations allow accurate predictions of thermal equations of state, elasticity, and thermal and chemical diffusivity, to transition metal oxides such as FeO which require many-body techniques such as DMFT and QMC to obtain accurate results. Problems also sometimes arise in unexpected places. The local density approximation (LDA) predicts good properties for SiO₂ quartz and stishovite, but incorrectly gives stishovite as the ground state. The generalized gradient approximation (GGA) fixes this problem, but is less accurate for elastic properties. We have been applying quantum Monte Carlo (QMC) combined with phonons computed using density functional perturbation theory (DFPT) to silica, and obtain experimental accuracy in the thermal equation of state and phase transitions. For FeO we are using correlated methods based on LDA, such as LDA+U and DMFT, as well as QMC. DMFT has the advantage of giving the spectral density (electronic structure) as well as the total energy, but still contains approximations. QMC is an exact computation under the constraint of the many-body nodes which comes from a trial wave function.

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Iron in minerals under pressure

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We are using a variety of first-principles methods ranging from density functional theory [1, 2], LDA+U [3], dynamical mean field theory, and quantum Monte Carlo to understand the behavior of iron-bearing minerals under pressure. There are a number of possible phase transitions in iron-bearing minerals under pressure, including structural phase transitions, high-spin low-spin transitions [1, 2], magnetic ordering transitions (e.g. antiferromagnetic to ferromagnetic or paramagnetic) [4], and insulator to metal transitions. Some of these may occur together, such as a structural transition from an insulating to a metallic phase. We have been studying the behavior of pure FeO, iron-bearing perovskite, and iron-bearing post-perovskite, as well as other transition metal oxides in order to better understand the behavior of iron.

LDA+U predicts a low-symmetry, monoclinic, ground state for pure FeO, with a very high-pressure high-spin to low-spin transition. It predicts that FeO will remain high-spin through mantle pressures. Dynamical mean field theory (DMFT) within the simplest Hubbard I approximation predicts FeO to undergo a metallization transition under pressure, where essentially Fe²⁺ loses an electron, which becomes itinerant, similar to the behavior of EuO. We will use more advanced DMFT methods to see if this predicted behavior is robust.

LDA computations predict an antiferromagnetic to ferromagnetic transition in FeO under pressure [4]. Preliminary QMC computations are consistent with this prediction. The spin state of iron in perovskite and post-perovskite will also be discussed.

This work is supported by NSF.

- [1] Cohen, Mazin & Isaak (1997) *Science* **275**, 654 (1997).
- [2] Cohen, Gramsch & Mukherjee *et al.* (2002) in *Proc. Intl. School Physics "Enrico Fermi"*, Vol. CXLVII, "High Pressure Phenomena", eds Hemley, Bernasconi, Ulivi *et al.*, IOS Press, pp.215. [3] Gramsch, Cohen & Savrasov (2003) *Am. Mineral.* **88**, 257. [4] Cohen, Fei & Downs *et al.* (1998) in *High-Pressure Materials Research*, eds Wentzcovitch, Hemley & Nellis *et al.*, MRS, Vol. 499.

Experimental studies on $\text{Th}(\text{OH})_{4(\text{am})}$ solubility in presence of ISA, gluconate or EDTA

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The effect of Low Molecular Weight (LMW) organic compounds (as isosaccharinate (ISA), gluconate (GLU) and ethylenediaminetetraacetate (EDTA)) on the mobilisation of radionuclides has been proven to be important. There is a lack of data regarding the stoichiometry and stability of the species formed, especially under alkaline to hyperalkaline conditions [1].

The present work aims at assessing the effect of ISA, GLU and EDTA on the solubility of thorium. Experimental results at pH=12 indicate that ISA, GLU or EDTA concentrations lower than 10^{-3} M have no effect on the solubility of Th. At higher ligand concentrations there is a clear solubility increase with the concentration of organic ligand (see Figure 1). In this case, the formation of 1Th:1L and 1Th:2L complexes (depending on the ligand studied) is suggested.

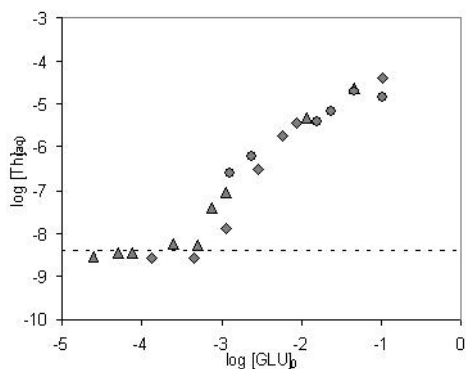


Figure 1: Experimental solubility (symbols) of $\text{Th}(\text{OH})_{4(\text{am})}$ at different Gluconate concentrations (pH=12), and calculated solubility (dotted line) in the absence of organic ligands.

[1] Hummel *et al.* (2005) *Chemical Thermodynamics* 9, OECD Nuclear Energy Agency.

Structure and dynamics of fluids in nanoporous earth and engineered materials determined from neutron scattering and MD simulations

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The behavior of fluids in confined geometries (pores, fractures) typically differs from their bulk behavior in many ways due to the effects of large internal surfaces and geometrical confinement. Phase transitions (i.e., freezing and capillary condensation), sorption and wetting, and dynamical properties, including diffusion and relaxation, may be modified, with the strongest changes observed for pores ranging in size from <2 to 50 nm. Important factors influencing the structure and dynamics of confined fluids include the average pore size and pore size distribution, the degree of pore interconnection, and the character of the liquid–surface interaction. The confining matrices of interest to earth and materials sciences usually contain oxide structural units and thus are hydrophilic. The pore size distribution and the degree of porosity and inter-connection vary greatly amongst porous matrices. Rocks typically possess irregular porous structures, whereas zeolites, and layered systems, for instance clays, have high degrees of internal order. In clays, the interlayer distance may depend on the level of hydration. The properties of neutrons make them an ideal probe for comparing the properties of bulk fluids with those in confined geometries. In this presentation, we provide an overview of research performed on fluids confined in materials of interest to the earth and material sciences (silicas, aluminas, zeolites, clays, rocks, etc.) emphasizing those techniques that assess both structural modification and dynamical behavior such as small-angle (SANS) and quasielastic neutron scattering (QENS). Molecular dynamics (MD) simulations will be described that provide atomistic characterization of the confined fluid behavior as well as aid in the interpretation of the neutron scattering results.

A study of degassing at mid-oceanic ridges by bubble-by-bubble analyses

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Using crushing to study relative He-Ar-CO₂ contents of MORB glass vesicles can give information on magma degassing processes and primary volatile composition as there are large variations in both solubility ($\text{He} \geq \text{CO}_2 \gg \text{Ar}$) and diffusivity ($\text{CO}_2 \ll \text{Ar} < \text{He}$). But using bulk vesicle composition averages different stages of degassing. To improve knowledge of earliest stage of degassing, we ameliorate the method of [1], namely the analysis of individual vesicles by laser ablation. Previous results [1] show that there is a correlation between vesicle size (and so maybe bubble age) and vesicle composition, consistent with equilibrium-driven degassing processes, suggesting some early-nucleated bubbles are preserved in the glass and do not completely reequilibrate with the more evolved magma. But this study was limited to small vesicles due to difficulties imaging thick basaltic glass sections. In contrast, [2] investigated larger vesicles by randomly ablating large pieces of basalt but this method is tedious and doesn't provide knowledge on the size of the vesicle which has been analysed.

We present here analyses of individual vesicles in MORB glasses having a large size range (100 μm to 800 μm of diameter). The samples were imaged tomographically at the Mateis laboratory, Lyon and at the SLS synchrotron facility with 5 and 3.7 μm resolution respectively. For opening bubbles, we used a 193nm laser to avoid noble gases diffusion by local heating. CO₂ contents were estimated by pressure measurement in the laser cell using a sensitive manometer. We analysed ⁴He, and Ar isotopes (36, 38, 40) in order to calculate ⁴⁰Ar* (⁴⁰Ar corrected from atmospheric contamination) on a VG 5400™ mass-spectrometer.

Some MORB glass samples from different ridges have been investigated in order to link degassing process to geodynamic context. We observe systematic variations in composition between bubbles consistent with equilibrium degassing, but surprisingly, it is not automatically the largest bubbles that preserve the least fractionated gases. Models of magma degassing including tomographic observations (vesicle volume and pressure inside the bubbles recalculated from CO₂ content) and volatile composition evolution (He-Ar-CO₂) will be presented.

[1] Burnard (1999) *EPSL* **174**, 199-211. [2] A. Raquin, PhD thesis, 2008.

Mineral studies on Earth and Mars: Chemical evolution approach

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Introduction

Life on Earth could have been originated by abiotic synthesis and accumulation of organic compounds, through physical and chemical processes known as chemical evolution [1]. Chemical evolution processes should not be privative of Earth, the process could have accomplished in other terrestrial planets, like Mars. On Earth and Mars, minerals should have participated actively in chemical evolution, acting as catalyst of reactions and as protective agents against degradation of molecules. In chemical evolution studies, the production of key molecules is as important as the decomposition of them. On these planets, UV and ionizing radiation were a very abundant source of energy. The purpose of this study is to test the role of minerals, like olivine, have on the decomposition induced by radiation (radiolysis) of hydrogen cyanide (HCN), a key compound on chemical evolution.

Results and Discussion

Samples with HCN (0.1 M) in aqueous solution and HCN-olivine were prepared according to [2], and then were irradiated at different doses in a gamma-ray source. The decomposition of the molecule was followed by gas-chromatography. Results show that the decomposition of HCN is modified in presence of olivine: this mineral enhance the decomposition. So, olivine is acting as a catalyst. HCN is not just a very reactive species, but also a parent molecule whose transformation can yield biological important molecules such as: amino acids, carboxylic acids and amines besides others [3]. So, the fact that olivine augments the breaking up of HCN leads to the possibility of the formation of new compounds. This is the first of a series of experiments, in which we are planning to evaluate the role of other minerals such as: silicates, ferrous oxides, etc.

[1] Negrón-Mendoza & Albarrán (1993) in *Chemical Evolution: Origin of Life*. Ponnamperna & Chela-Flores. (eds), 235-237 [2] Draganić & Draganić (1988) *J. de Chim. Phys.* **85**. [3] Colín-García *et al.* (2009) *Astrobiology*, in press.

Impacts of nanosilver on microbial activity in wetlands and streams

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Due to its antimicrobial properties, nanosilver is becoming increasingly common in consumer goods ranging from clothing and children's toys to supplements and cosmetics. Through the use and cleaning of these products, nanosilver enters the waste stream, and may ultimately end up being discharged as treated wastewater into aquatic ecosystems, or applied as biosolids from wastewater treatment plants to terrestrial ecosystems. In both types of ecosystems, microorganisms are essential to decomposition and nutrient turnover. Given the importance of microbes and the antimicrobial properties of nanosilver, we pose the question: what are the effects of nanosilver on microbes in natural ecosystems? To answer this question, we have added different preparations of nanosilver to streamwater, sediments, and soils and examined several indexes of microbial activity including microbial respiration, microbial biomass, and enzyme activities.

Our results suggest that the impact of nanosilver depends on the form in which it is added and the environment to which it is added. While Choi *et al.* (2008) [1] found that 1mg/L nanosilver reduced *E. Coli* respiration by 86%, our work in wetland soils showed 250 mg/L of nanosilver did not cause decreases in biomass or respiration. However, nanosilver did cause an increase in phosphatase enzyme activity, and an increase in phosphorous concentrations rose from 0.12 µg/L to 0.27 µg/L in proportion to the concentration of nanosilver added. Our work shows that the form in which nanosilver is added, the complexity of the physicochemical environment to which it is added, and the nature of the microbial community drive the response of environmental microbes to nanosilver.

[1] Choi *et al.* (2008) *Water Research* **42**, 3006-4074.

Is it possible to access to the dissolution rate constant of soft minerals?

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In standard dissolution experiments of soft minerals (rotating disk, batch, AFM, ...), the studied mineral is dissolving in flowing water. Therefore, convection is present in addition to dissolution and diffusion and the dissolution kinetics is hindered by the diffusion and convection kinetics, all three being of the same order of magnitude. As a proof, we have exhaustively collected the dissolution rates of gypsum in water, measured by various techniques, reported in the literature. These results show absolutely no consistency. By analysing the hydrodynamical details of each setup, we explain quantitatively the origin of this inconsistency and deduce from all these measurements the real pure dissolution rate constant of gypsum in water, which is much smaller than expected. This value compares within experimental error with the value measured unambiguously by holographic interferometry, a technique enabling to work with a non-flowing liquid (cf. Fig. 1)

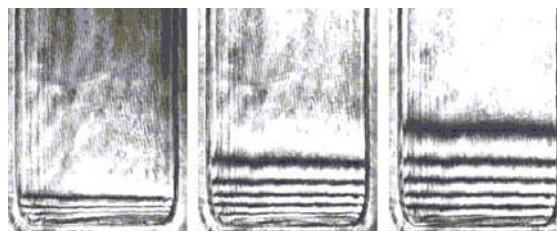


Figure 1: Evolution with time of the holointerferograms of the dissolution of a gypsum sample in still water.

[1] Colombani & Bert (2007) *Geochim. Cosmochim. Acta* **71**, 1913–1920. [2] Colombani (2008) *Geochim. Cosmochim. Acta* **72**, 5634–5640.

Deep lithosphere processes recorded for the West Antarctic Rift System

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Two suites of mantle xenoliths from Baker Rocks (BR) and Greene Point (GP) from Northern Victoria Land (Antarctica) were investigated. These two localities are less than 100 km apart, but the respective xenolith suites show very different petrographic and geochemical features.

Amphibole-bearing lherzolites occur at BR showing amphibole both as disseminated grains and in veins, commonly associated with glass, and growing at the expense of clinopyroxene (cpx). Accordingly, cpx compositions become richer in TiO₂, Al₂O₃ and REE contents and poorer in SiO₂, approaching the amphibole boundary. A Na-alkaline Ti-Nb-HREE-rich melt is inferred to be responsible for this metasomatic reaction. Thermobarometric data indicate a T-P range between 800°C and 1000°C and from 5 to 16 kb, respectively. Anhydrous lherzolites and harzburgites are equally represented at GP. Orthopyroxene is the most reactive phase, possibly producing the abundant SiO₂-alkalies-rich and Ti-Nb-HREE-poor glass. GP primary cpx appears more depleted, sometime recording re-equilibration from a garnet stability field. Thermobarometric data indicate a slightly higher T (1000-1100°C) at similar P (8-16 Kb).

In situ Re-Os age determinations, together with Rb-Sr, Sm-Nd and Lu-Hf pseudo-isochrons, show that at BR, several main events were recorded from Archean to Mesozoic, in contrast to those from GP that are mainly Proterozoic.

Petrological features and isotopic data suggest that BR and GP represent two different mantle domains which evolved separately and were most probably juxtaposed during the Ross Orogen through the Tinker-Campbell Discontinuity. These two domains were finally re-activated and percolated by different fluids during the development of the West Antarctic Rift System (WARS). This complex history emphasises the likely role and the evolution of subcontinental lithospheric mantle during rifting processes.

Water speciation in Anatolian Obsidian: Quenched magmatic Water vs low temperature hydration

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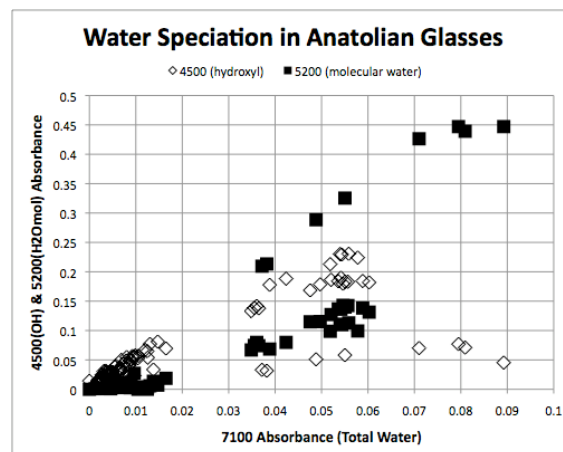
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Rhyolitic volcanism in present-day Turkey, Azerbaijan, Armenia, Georgia, and Iran document widespread felsic magmatic activity throughout the last 10 My. Understanding the role of water in these systems is critical for deciphering the origin and eruptive history of these magmas. In addition, the rhyolite flows were the source of obsidian glasses that were manufactured into flaked stone tools as well as carved items like bowls and beads from hunter-gatherer times into the metal ages. Obsidian has long been utilized by archaeologists for the study of ancient trade networks for two important reasons: (1) their geochemistry identifies the particular volcanic flow from which they came, and (2) the amount of time that has elapsed since the glass was re-worked can be determined by measuring the rim thickness associated with the diffusion of water into knapped surfaces.

We have conducted micro-FTIR analyses on a suite of 30 obsidian flows from Anatolia. Our measurements delineate two series of glasses which reflect that two distinct processes were involved in hydrous species equilibration. One series, with total water contents > 5 wt% and H₂Omol > OH, shows equilibration temperatures ranging between 150-250°C. The second series, all with H₂Omol < OH and total water < 2.5 wt%, show an average equilibration temperature of 490°C. These data are consistent with the high-water glasses having experienced low-temperature hydration and the low-water glasses having experienced little, if any hydration after eruption; their water contents reflect the quenched magmatic water content. Future H and O stable isotope measurements will test our conclusions. Our results have implications for both sourcing and hydration rim dating of obsidian artifacts.



A new perspective on the 2.7 Ga event on Earth

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Of the many changes that have been proposed to occur in the late Archean centered around 2.7 Ga, only seven are well documented: 1) a decrease in the Eu anomaly in hydrothermal cherts and BIF; 2) a large decrease in the proportion of komatiites in greenstone belts and in the Mg# of komatiites; 3) a decrease in the average degree of melting in the upper mantle as recorded by such incompatible element ratios as La/Yb and Nb/Yb in tholeiitic basalts; 4) an increase in the volume of preserved juvenile continental crust; 5) an increase in the volume of depleted mantle as recorded by such geochemical indices as $\epsilon\text{Nd}(T)$ and Nb/Th in non-arc related basalts; 6) production of a thick depleted ultramafic root beneath late Archean cratons; and 7) an increase in the proportion of sediment in sources of granitic magmas as recorded by $\delta^{18}\text{O}$ in detrital zircons.

These changes might be related to the onset of widespread subduction at about 2.7 Ga. This subduction regime could have increased the rate of production of continental crust to such an extent that arcs collided with each other *before* being recycled into the mantle, forming the first volumetrically significant cratons. Likewise, the 'capture' of juvenile felsic crust in stable cratons reduced the recycling rate of this crust into the mantle accounting for the first significant growth of a depleted reservoir in the mantle in the late Archean. The widespread onset of subduction at 2.7 Ga has three effects on the mantle: 1) it produces new continental crust that partially blankets the mantle from losing heat, 2) it leaves the mantle depleted in radiogenic heat-producing elements, and 3) for the first time, a large volume of dead slabs begin to accumulate in the lowermost mantle. This results in a decrease in mantle potential temperature, possibly responsible for changes 1 through 3 listed above. Our geodynamic modeling is consistent with a relatively small drop in global mantle potential temperature and in mantle heat flow ($\sim 20^\circ\text{C}$ and 18 mW/m²) for production of 20-30% of the volume of existing continental crust over a time interval of 150 My at 2.7 Ga. This reduces effective melt fraction in the upper mantle by 4-20%, depending on depth of melting.

Although either of the current ideas for the origin of thick late Archean lithospheric roots remains viable (plume head restite or incompletely subducted oceanic plates), incompletely subducted plates are consistent with geophysical data beneath Archean cratons and with geochemical data from Archean basalts that suggest shallow sources of magma production. An increase in the volume of continental sediments, some of which contribute to sources of granitic magmas, is also an outcome of the production of volumetrically significant cratons in the late Archean.

A model explaining ²¹⁰Pb-excesses observed in magmatic enclaves and segregation veins

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We propose a simple model, involving a magma column, filled with a magma having homogeneous Ra concentration and losing Rn from the deeper part, due to degassing of major gas species that accumulate in the shallower part and generate ²¹⁰Pb-excesses. In such a model of internal Rn redistribution, the whole magmatic system (Rn-degassing magma of mass M_d + Rn-accumulating magma of mass M_a) should remain in radioactive equilibrium, which can be written using a mass-balance equation: $M_a (^{210}\text{Pb})_a + M_d (^{210}\text{Pb})_d = (M_d + M_a)(^{210}\text{Pb}) = (M_d + M_a)(^{226}\text{Ra})$.

By introducing $R = M_d/M_a$, this equation becomes:

$$(^{210}\text{Pb})_a + R (^{210}\text{Pb})_d = (R + 1) (^{226}\text{Ra}), \text{ and:}$$

$$(^{210}\text{Pb}/^{226}\text{Ra})_a = 1 + R [1 - (^{210}\text{Pb}/^{226}\text{Ra})_d].$$

$(^{210}\text{Pb}/^{226}\text{Ra})_d$ is given by equation (11) in the paper by Gauthier and Condomines (1999), where f is the fraction of ²²²Rn degassed. Thus,

$$(^{210}\text{Pb}/^{226}\text{Ra})_a = 1 + R f [1 - \exp(-\lambda t)].$$

Note that assuming $f = 1$ gives the minimum estimate of R , and that the steady state value of the $(^{210}\text{Pb}/^{226}\text{Ra})_a$ ratio is $1 + R$.

The ²¹⁰Pb-excess measured in a segregation vein in the 1966 lava flow on Surtsey island, can be explained by the model above and constrains the time for the formation of the segregation vein. Another example comes from mafic enclaves found in the 1939 and 1950 dacitic lava flows at Kameni island, Santorini, that have $(^{210}\text{Pb}/^{226}\text{Ra})_0$ as high as 6.9, implying a ratio R (mass of Rn-degassing magma over mass of Rn-accumulating magma) between 5 and 20 beneath the Santorini caldera in the first half of the 20th century.

Isotopic evidence for TCE co-metabolism stimulated by electron donor addition to groundwater

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For more than 10 years, electron donor has been injected into the Snake River aquifer beneath the Test Area North site of the Idaho National Laboratory of eastern Idaho for the purpose of stimulating microbial reductive dechlorination of the trichloroethene (TCE) in the groundwater. This has resulted in significant removal of TCE from the source area of the contaminant plume. It has also led to highly elevated concentrations of dissolved CH₄ in the groundwater extending for more than 200 m down gradient from the injection well. The $\delta^{13}\text{C}$ values of dissolved CH₄ in the groundwater increase from -55‰ in the source area to -18‰ with distance from the injection well whereas the $\delta^{13}\text{C}$ values of dissolved inorganic carbon decrease from 8‰ to -13‰, indicating a shift from methanogenesis to methane oxidation in the plume. This change in microbial activity is confirmed by PhyloChip microarray analyses of the 16S rRNA genes obtained from microbial communities within the groundwater. Accompanying this change in microbial populations is also a decrease in the abundance of dechlorinating microorganisms (e.g., *Dehalococcoides ethenogenes*) and an increase in organisms known to be capable of aerobic cometabolism of TCE (e.g., *Methylosinus trichosporium*). Incubation experiments with ¹³C-labeled TCE introduced into microcosms containing basalt and groundwater from the aquifer confirm that co-metabolism of TCE is occurring. The capacity of this system to degrade TCE determined from these experiments is estimated at approximately 7.5 µg of TCE per liter of water. The results of this study suggest that the change from anaerobic to aerobic microbial activity in the distal portions of groundwater TCE plumes undergoing electron donor addition to stimulate reductive dechlorination of TCE could lead to co-metabolism of TCE, further limiting the spread of the plume.

Atomistic simulation of the crystallisation and growth of calcium carbonate nano-particles

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Atomistic simulation of nano-particles is important because it allows the size and shape-dependence of their structure and thermodynamic properties to be studied directly. In this paper we report on four broad areas of work modelling the stability, aggregation and nucleation of CaCO₃ nano-particles.

We have simulated nano-particles of sizes ranging from 18 to 324 formula units, in vacuum and in water [1], from which it is clear that the breakdown of structural order in the smaller particles is caused by the rotation of CO₃²⁻ groups on the surface when there is little bulk mineral to stabilise the structure. When water is present, the surface ions bond to the water in the first hydration layer and thus are prevented from rotating to the same extent. The structure of the water close to the particle is strikingly similar to that previously seen when considering infinite planar surfaces.

In an attempt to extend this initial work we have begun to consider how such nano-particles aggregate to form macro-sized particles. Initially we have considered eight particles consisting of 75CaCO₃ units, both in vacuo and in solution, using a combination of potential of mean force and conventional molecular dynamics. Initial results suggest that if one face each particle is doped with Mg²⁺ the particles aggregate so as to maximise the amount of Mg²⁺ on the surface of the resulting combined particle.

At the other end of the scale it is also possible to use molecular dynamics to investigate the processes of cluster formation and growth of CaCO₃ from aqueous solution [2].

The influence of both temperature and concentration have been studied and, using a combination of order parameters we can relate the clusters that form to the structure of the larger nano particles, considered in our earlier work.

Finally we have begun to use meta-dynamic methods to study these systems over longer time-scales than can be accessed via standard simulation methodologies.

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[2] Hamad, Cristol & Catlo (2005) *J. Am. Chem. Soc.* **127**, 2580.

Time scales of magma reservoir processes from U-series dating of crystals

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Recent advances in analytical techniques, for example, measuring trace elements at small spatial scales, have resulted in advances in a wide variety of approaches to extracting information about magma dynamics from crystal records [e.g., 1]. U-series disequilibrium offers one of the only ways to obtain absolute ages of crystals over time scales relevant to dynamics of crustal magmatic systems (10's of yr to 100's of kyr) and therefore provides a key element to studies of crustal magma dynamics, particularly when combined with other types of crystal-scale information.

In the past decade, new techniques were developed to analyze U-Th *in situ* in accessory phases [2] and to account for the effects of Ra-Ba fractionation when calculating Th-Ra ages [3]. Application of these techniques has prompted new views of magmatic processes, for example: 1) zircon ages typically pre-date eruption by tens to hundreds of thousands of years, spurring discussion over what physical form (liquid vs. mush vs. solid) magmas typically have during storage; 2) recycling of crystals (antecrysts) within a magmatic system is common and dating can be one of the most effective ways to recognize these crystals; 3) timescales of crystal storage can vary widely between different systems [4 and references therein].

New frontiers in application of U-series crystal dating to understanding magma reservoir processes are focused around combining U-series ages with other crystal-scale information to provide direct links to chemical and thermal evolution of magma bodies. I will present examples of recent and ongoing work including comparison of zircon and major-phase ages in silicic systems (Tarawera, New Zealand, and South Sister, OR), comparison of oxygen-isotope and U-series data for plagioclase in Iceland, and comparison of diffusion ages, crystal size distributions, and U-series ages of crystals in andesite from Mt. Hood, OR as windows into the timescales of mixing and pre-eruptive storage. The combination of multiple techniques shows great potential for unlocking additional information about crustal magma dynamics.

[1] Putirka & Tepley III (eds) (2008) *Rev. Mineral. Geochem.* **69**. [2] Reid *et al.* (1997) *EPSL* **150**, 27-39. [3] Cooper *et al.* (2001) *EPSL* **184**, 703-718. [4] Cooper & Reid (2008) *Rev. Mineral. Geochem.* **69**, 479-544.

Ultrahigh resolution mass spectrometry of soil porewater DOM

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Mass Spectrometry of DOM

Ultrahigh resolution (UHR) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has revolutionized the characterization of dissolved organic matter, providing a level of molecular detail thought impossible just a decade ago [1]. We have reported on the use of this technique to identify the reactive and refractory components of DOM in porewaters from two distinctly different geoforms in the Glacial Lake Agassiz Peatlands in the northern US [2]. This work is a part of a larger study of geomorphic and hydrological controls on carbon sequestration in peats. Recent experiments have also attempted to identify specific molecular forms of black carbon that can be leached from biochars of different origins. This dissolved black carbon may well be responsible for the enhanced productivity associated with combusted soils

Conclusions from the Molecular Characterization of Soil Porewater DOM

The ¹⁴C content of respiration products in porewaters from Fen peatlands are similar to high molecular weight DOM, while respiration products in Bog peatlands are more similar to solid phase material. UHR MS confirms that DOM in sphagnum-woody plant dominated FEN peatlands is more reactive than aromatic-rich Bog DOM. We are currently exploring the *enzymatic latch model* as an explanation for this differential reactivity.

We have also been able to verify the presence of individual black carbon molecules in DOM leached from biochars. Black carbon DOM appears to have a molecular signature readily identifiable from UHR mass spectra.

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[2] Chanton *et al.* (2008) *Global Biogeochem. Cycles* **22**, GB4022.

Application of micro X-ray diffraction on lamellar, black shale related Mn ore, Urkut, Hungary

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Urkut (Hungary) hosts the largest Toarcian Mn ore deposit in Europe. It consists of both carbonate and oxide ore sequences. We studied a complete carbonate profile, consisting of a black shale sequence with two Mn-bearing horizons. This is the first time that this very fine-grained (μm - and nm -sized), lamellar sedimentary sequence was traced by systematic, real micrometer scale studies, including structural (micro X-ray diffraction), textural, and chemical (SEM+EDS, cathodoluminescence) observations. These data contribute substantially to the earlier genetic models.

The lamellar ore structure is a result of parallel or exclusive existence of phases recording redox conditions (and their changes). Mn occurs both in carbonate and (recently subordinated) oxide phases in the carbonate ore. Ore-forming carbonate minerals display a complex texture. Three different types of Mn-Ca carbonates were identified: 1) the main carbonate is a fine grained, sometimes nodular (pseudomorph after nodular manganite) Ca-rhodochrosite [$d_{104}=2.865(1) \text{ \AA}$], 2) Ca-rhodochrosite pseudomorph after Radiolarians, and 3) in smaller amounts in the ore, a post-diagenetic Ca [$d_{104}=2.876(2) \text{ \AA}$] Mn calcite [$d_{104}=2.99 \text{ \AA}$], showing red cathodoluminescence. The Mn-oxide phase of the carbonate sequence is manganite. No Mn^{4+} -oxide phase was found. Fe occurs both in reduced (euhedral and framboidal pyrite) and oxidized form (goethite and sheet silicates).

Manganite can be regarded as the primary ore accumulation form of Mn. It may be the result of oscillating suboxic/oxic conditions near the seafloor. In restored suboxic conditions microorganisms could utilize first Mn^{3+} , then Fe^{3+} when oxidizing organic material. With increasing concentration of $\text{Mn}^{2+}_{\text{aq}}$ and $\text{HCO}_3^-_{\text{aq}}$ (org), fine grained Ca-rhodochrosite ($d_{104}=2.865(1) \text{ \AA}$) precipitated, and allotigenic calcite, such as Radiolarian pseudomorphs, was also metasomatized by Mn^{2+} . This two-way Ca-rhodochrosite formation model explains the typical $\delta^{13}\text{C}$ values ($\sim 12\text{--}15$) and the poor correlation between Mn and $\delta^{13}\text{C}$ values published earlier [1].

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Siderophile elements and the single-stage core formation hypothesis

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The abundances of siderophile elements in the bulk silicate Earth (BSE) indicate that its iron-rich core most probably form at high pressure and high temperature in a magma ocean (e.g. Walker *et al.* 1993; Hillgren *et al.* 1994; Thibault & Walter 1995; Li & Agee, 1996). This is consistent with physical models of planetary accretion (Davies 1985; Benz & Cameron 1990; Tonks & Melosh 1993). Recent experimental works have proposed that the BSE concentrations of several siderophile elements are consistent with a scenario of single-stage equilibration at the base of a magma ocean $\sim 700 \text{ km}$ deep (Li & Agee 1996; Righter *et al.* 1997; Chabot & Agee 2003). More recent models using temperature sensitive partitioning data for V and Nb have casted doubt on this interpretation since the required basal temperature should greatly exceed that of the mantle liquidus (Wade & Wood 2005; Corgne *et al.* 2008; Wood *et al.* 2008). This temperature mismatch is meaningless in the framework of the magma ocean theory because the temperature at the base of the magma ocean should approximate that of the mantle liquidus. To resolve this anomaly, it has been suggested that the building materials of the Earth were initially reduced materials and then became progressively oxidized with time (Wade & Wood 2005; Corgne *et al.* 2008; Wood *et al.* 2008). Thus, rather than resulting from a single-stage event at relatively fixed conditions of high pressure and high temperature, the Earth's core may in fact have formed in a more complex event, imprinted by heterogeneous accretion and the progressive growth of the planet and its magma ocean.

Here, we present an alternative to the dynamic model by showing that a single-stage core formation event could explain the mantle contents of the best-constrained siderophile elements (Ni, Co, V, Mn, Cr, Nb) provided that the core contains a few weight percents of oxygen. Our calculations based on partitioning and metallurgy data reveal that V and Nb become less siderophile with increasing the O content of core-forming materials, while the behaviour of Ni, Co, Cr and Mn is little affected. Since other light element candidates C, Si and S do not influence significantly the siderophile behaviour as does O, we conclude that a single-stage core formation scenario is a viable hypothesis only if O is a non-negligible contributor to the density deficit of the Earth's core relative to pure Fe or Fe-Ni alloy.

Petrophysic and geochemical study of Valpaços granite pluton (Northern Portugal)

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With this work, we intend to apply a multidisciplinary methodology to a pluton located in the Galiza Média Trás-os-Montes Zone, the granite pluton of Valpaços. The host rocks of this circumscribed pluton are composed by metasedimentary formations from Silurian age and by syn-tectonic granites. The Valpaços pluton consists of a coarse-grained porphyritic two-mica syenogranite, apparently not oriented. Primary minerals are quartz, potassium feldspar megacrysts (microcline and orthoclase), plagioclase, biotite and muscovite. Silimanite, andalusite, apatite, zircon and opaques occur as accessory mineral phases. As secondary minerals are present muscovite, chlorite, leucoxene and rutile. According to the classification of Frost [1], the geochemical data indicate that this granite is an alkali-lime magnesian potassic granite with highly peraluminous character with A/CNK average of 1.3. The REE patterns are characterized by high fractionation between LREE and HREE (La/Yb)_N with an average of 22.91 and a moderate negative Eu anomaly (Eu/Eu*_N=0.48). The mineralogical and geochemical data, including the peraluminous character and the REE fractionation values, and despite the lack of isotopic data, are compatible with the characteristics presented by S-type granites [2]. Preliminary studies of Anisotropy of Magnetic Susceptibility (AMS) were carried out in 51 samples in order to characterise the structure of this pluton. The susceptibility is comprised between 65.1 and 47.8 x 10⁻⁶ SI, typical of a paramagnetic behaviour and ilmenite type granites [3]. Magnetic anisotropy (3.0%) can be related to a magma emplacement late-tectonically driven. AMS fabric patterns show subhorizontal NE-SW trending magnetic foliations associated with subhorizontal N120°E trending magnetic lineations which point out the role of the last ductile Variscan deformation phase in the emplacement of this pluton. ASM ellipsoids are predominantly oblate which suggests that magnetic fabric is controlled by the muscovite and biotite.

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A new thermodynamic model for C-S-H solubility valid in the range of P-T conditions encountered around CO₂-injection wells

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Numerical simulation of the well-bore integrity in the context of CO₂ injection and storage requires dealing with the solubility of Portland cement constituents under pressure, temperature and high CO₂ activity. Along with portlandite, Ca(OH)₂, calcium silicate hydrates (C-S-H) are the main components of Portland cements. The solubility behaviour of C-S-H involves different solid-solution components. Kulik & Kersten [1] proposed a C-S-H solubility model based on two binary ideal solid-solutions depending on the Ca/Si ratio; for lower Ca/Si ratios amorphous silica and a tobermorite-like C-S-H are the end-members whereas for higher ratios, a jennite-like C-S-H and portlandite are the two end-members. Recently, Sugiyama & Fujita [2] modelled C-S-H as a single binary non-ideal solid-solution between amorphous silica and portlandite. These two models are based on abundant C-S-H solubility data at 25°C available in the literature.

Following [2], we designed a C-S-H solubility model, assuming a binary non-ideal solid-solution between amorphous silica and portlandite, but which applies to higher temperatures. The end-members activity fitting procedure exposed by [2] has been modified using simplified Boltzmann functions. The fits are based on the existing C-S-H solubility experimental datasets at 25°C and also at 90°C [3,4,5]. Furthermore, an interpolation of the modelled solubility at an intermediate temperature of 50°C is also proposed.

A comparison between this new model and the two existing ones will be discussed as well as its ability to predict the formation of C-S-H. This C-S-H dissolution model is now being implemented in a reaction-transport code and applied to the interaction between CO₂-rich fluids and Portland cement under pressure and temperature.

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Noble gases in the ureilites Kenna and RaS 247

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The high abundance of noble gases in ureilites in addition to their similar isotopic and elemental composition compared to primitive chondrites is one of the features that makes this type of differentiated meteorites interesting [1,2]. However, the exact origin of these gases, the nature of their host phase(s), and their relationship to phase 'Q' found in carbonaceous chondrites is still elusive. Here we present results of bulk measurements of Kenna and Ramlat as Sahmah 247 (RaS 247), a hot desert meteorite from Oman. Results of high precision measurements of acid residues from these meteorites will be available at the time of the meeting.

He and Ne noble gases in Kenna and RaS are dominantly cosmogenic (ca. 95% of the total Ne), whereas Ar is mostly primordial in composition. Despite weathering effects on Kenna and RaS 247, the air component in these samples is negligible. For RaS this is a rather unusual result since hot-desert meteorites tend to have high atmospheric ⁴⁰Ar abundances [3].

One-step pyrolysis and stepwise heating measured total gas concentrations in Kenna and RaS disagree beyond analytical uncertainty (~15%, up to a factor of 2, and ~50% for He, Ne, and Ar, respectively). Whether these variations are due to sample heterogeneity will be assessed by measuring different aliquots of Kenna sampled on a cm-scale. Stepwise heating experiments on both Kenna and RaS 247 reveal the presence of cosmogenic He and Ne at the lower temperature steps (600-800°C). If these gases are hosted in the same phase, then this phase cannot be carbonaceous, as suggested by [2] for the case of He, because the production of cosmogenic Ne requires a target in the mass range of Mg, Al, and/or Si (or heavier). However, a proper identification of the host(s) requires further tests.

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Bioamplification of methylmercury in two trophically dissimilar marine ecosystems

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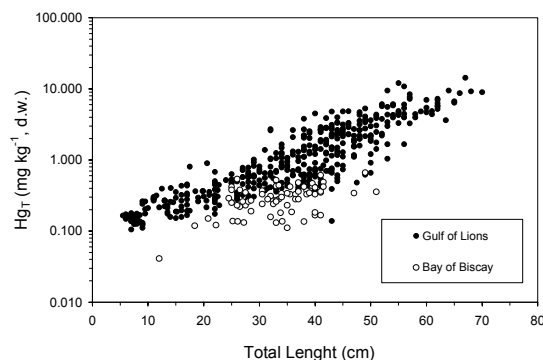
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Our recent data confirm that mercury concentrations in the muscle tissues of the European hake (*Merluccius merluccius*) caught in the North-Western Mediterranean Sea are significantly higher than those measured in the fish of the same species caught in the North-Eastern Atlantic (see figure). Trophic characteristics are commonly proposed to explain this type of bioamplification differences: oligotrophic ecosystems would favor the metal bioaccumulation, while the higher growth rates would favor the metal dilution in eutrophic ecosystems. While tagging experiments allow accessing to the true growth rates of fish, and the utilization of N and C isotopes to the structure of the food webs, most of the studies on mercury bioamplification suffer from the lack of data about the mercury bioavailability (i.e., methylmercury concentration) in the milieu, especially in marine waters, to confirm this interpretation. Here we address the question of the role of the mercury bioavailability in its bioconcentration at the base of the food chain in a meso-eutrophic environment (Bay of Biscay, N-E Atlantic) compared to an oligo-mesotrophic environment (Gulf of Lions, N-W Mediterranean). In both environments, methylmercury (MeHg) distribution profiles have been established in the water columns, and the MeHg concentrations determined in plankton and fish preys. The food web structures and growth rate of the hake were explored through $\delta^{15}\text{N}$ distributions and tagging.



Time scales of magmatic processes of mafic historical eruptions from Tenerife, Canary Islands

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The spatial and temporal distribution of recent volcanism on Tenerife shows that the island is a highly active volcanic zone and that future eruptions may occur from many different vent sites on the island. All historical activity corresponds to relatively mafic and small volume eruptions which have produced cinder cones, reduced lapilli and ash deposits and several kms long lava flows, causing a relatively low damage. However, the same type of eruptions would cause today a significantly higher loss, as the increase in population and infrastructure has made Tenerife much more vulnerable. We have started a study of the rates of magmatic processes involved in this type of eruptions to provide a temporal framework for the eventuality of such an event in the island.

We have concentrated on the NE rift basaltic eruptions of 1704 (V. Siete Fuentes) and 1705 (V. Arafo and Fasnía). These eruptions evolved from a fissure style activity to a small cinder cone and emitted magma volumes increase with time. New petrological and geochemical data show that the eruptions also became slightly more mafic with time. We found a large variety of olivine crystal populations, with core compositions ranging from forsterite (Fo) 88 to 79. Many crystals are homogeneous at Fo79-81, but others are normally or reversely zoned in Fo. Such variety of crystal compositions indicate that the magmas are the result of mixing/mingling involving at least three different mafic components (crystals and melts). Kinetic modelling of the Fe-Mg zoning in olivine (e.g., Costa *et al.*, [1]) gives times between the mixing and eruption that vary from a few months to a few years. The longer times are obtained from crystals that show reverse zoning and probably reflect an early event of mixing before the last one that brought the crystals to the surface. All times are longer than the ca. one week of earthquake activity that occurred prior to the 1704 eruption based on historical accounts. This shows that a hierarchy of times may be involved in the precursor activity of such types of volcanic events and it should be considered when making scenarios of future eruptions.

Genesis of syn-D3 two-mica granite from Aguiar da Beira (central Portugal)

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Medium-grained muscovite>biotite granite from the Aguiar da Beira area, central Portugal, crops out as an elongated NW-SE intrusion in the Central Iberian Zone of the Iberian Massif. It is syn-D3, heterogeneously deformed, showing in its western parts a gneissosity concordant with the D3 Variscan structures. The ID-TIMS U-Pb zircon age is 317 ± 2 Ma. This granite consists of quartz, plagioclase (An₀-An₁₉), microcline (Or₈₂-Or₉₇), primary muscovite, biotite Fe²⁺/(Fe²⁺+Mg) of 0.64 to 0.83, zircon, apatite, monazite and ilmenite. It exhibits a compositional variation (SiO₂ = 70-74 wt %), is strongly peraluminous (A/CNK = 1.2-1.4), has low Ca, Mg, Ti and ΣREE contents, high Rb/Sr values (2.6-17.4), (⁸⁷Sr/⁸⁶Sr)₃₁₇ of 0.7104-0.7146, εNd₃₁₇ of -7 to -8.7, suggesting a crustal origin. Its REE pattern is enriched in LREE with respect to HREE (La_N/Lu_N = 16-69) and has a negative Eu anomaly (Eu/Eu* = 0.20-0.48). There is a good agreement between the εNd₃₁₇ values for this granite (-7.7 to -8.7) and the Cambrian and Early Paleozoic metasediments (εNd₃₁₇ = -6.6 to -11.9). However, the (⁸⁷Sr/⁸⁶Sr)₃₁₇ ratios for the granite (0.7104-0.7146) are lower than those of the probable crustal sources [(⁸⁷Sr/⁸⁶Sr)₃₁₇ = 0.7134-0.7180]. As the Sr isotopic ratios of the granite and potential protoliths could have been disturbed by disequilibrium partial melting and/or post-magmatic alteration, the geochemical and isotopic characteristics of the granite are well accounted for by moderate degrees of partial melting of the basement metasediments under vapour absent conditions.

$\delta^{66}\text{Zn}$ as a tracer of the zinc biogeochemical cycle

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Zinc is an essential element for plants but excessive uptake can lead to (phyto)toxicity and contamination of the foodweb. Mobility and bioavailability depend on zinc speciation in solid and liquid phases, and exchange processes. Zinc isotopic ratios are a new and sensitive tool as biogeochemical cycle tracers.

The substrates were two soils contaminated by aerial fallouts - a clayey calcareous soil (CaS) and a loamy shale-derived soil (ShS) - and a gravelly slag dump (SD) from metallurgical industry. Fine earth fractions (f_{ef}, <2mm) were obtained by dry sieving. The soil solutions were collected *in situ* through zero-tension lysimeters inserted under organic horizon (O) and organo-mineral horizon (Ah). Shoots of plants growing on substrates were also sampled. After zinc purification by a novel chromatographic method performed on micro-columns (Zn blanks ≤ 2ng), the values of the Zn isotopic ratio ($\delta^{66}\text{Zn}$) were measured on a Nu Plasma MC-ICP-MS.

In agreement with the known effect of industrial Zn extraction process, f_{ef} determinations showed that SD was richer in heavy isotopes than soils contaminated by aerial fallout. Throughout the soil profiles, systematic enrichment in light Zn isotopes was recorded from Ah horizons (0.18-0.34‰) to O horizons (0.09-0.18‰). In addition, soil solutions showed stronger light Zn isotope enrichment, especially solutions leached from O horizons, with a fractionation magnitude up to 0.41‰. Plant uptake involved mainly heavy Zn isotopes in plants and, therefore, was associated with decrease of heavy Zn isotopes in soil solutions. Finally, isotopic ratio of bedrocks influenced $\delta^{66}\text{Zn}$ in f_{ef} of deep soil horizon. In CaS, there was a transfer of heavy Zn isotopes from bedrock to deepest soil horizon; whereas in ShS, there was transfer of light Zn isotopes.

In summary, Zn isotopic fractionation is highly sensitive and helpful to study the mobility of zinc in the soil-plant cycle.

Geomicrobiology of microbialites from the Alchichica alkaline lake

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Microbialites are organosedimentary structures resulting from the activity of microbes. Although they dominate the Precambrian geological record, the abiotic and biological processes leading to their formation and thus the exact information that can be retrieved from them are still poorly understood. In this study, we used a combination of molecular biology and mineralogy analyses to study modern microbialites from the Alchichica lake at different spatial scales. Alchichica is an alkaline (pH ~8.9) crater lake located at high altitude (2,300 m above sea level) in the Puebla State, Mexico, that harbours an extensive collection of living microbialites. XRD analyses on bulk samples showed that they are formed of hydromagnesite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$ and aragonite consistently with precipitation in a Mg-rich, alkaline solution. The textures of these mineral phases, and their relationships with the distribution of the microbes were assessed down to the nm-scale using SEM, FIB milling, TEM and synchrotron-based X-ray microscopy (STXM). In parallel, we explored the microbial diversity of a subset of samples by amplifying, cloning and sequencing 16S rDNA genes from microbialite DNA, revealing a large diversity of cyanobacteria but also various other groups of Bacteria. Finally, some samples were incubated in laboratory aquaria. The growth of cultured microbial mats was monitored using the same analytical approaches. Moreover, we used confocal laser scanning microscopy to better link the results provided by the molecular biology and the mineralogy approaches. This ongoing but comprehensive analysis of the Alchichica microbialites will provide a better picture of the microbial-mineral interplay in modern microbialites from an alkaline lake. The implications for the decryption of ancient microbialites will be discussed.

Life in subglacial lavas as an analogue for life on Mars

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Basaltic subglacial volcanism is a process that is widespread on Earth that is also believed to have occurred on Mars. The interaction between erupting lava and overlying ice produces a number of environments that are available to microbial colonisation. These include active environments such as subglacial caldera lakes, and post-eruptive environments, notably subglacial lava flows (pillow basalts and hyaloclastites). Active subglacial volcanic systems commonly exist entirely within the subsurface several hundreds of meters below the ice. As a result, these environments on Mars would have been protected from UV radiation, surface desiccation and low temperatures. Additionally, post-eruptive subglacial lava environments that exist within dry Arctic climates can serve as an analogue to such environments on Mars when the surface environment was perhaps less limiting. We use Iceland and its examples of basaltic subglacial volcanic activity as an analogue for these proposed Martian environments. 16S rDNA metagenomic analysis was carried out on pillow basalt glass, interpillow material, and hyaloclastite lava from Askja central volcano, Iceland. Additionally, these lavas were used to test the viability of subglacial volcanic environments on Mars. Two components of the subglacial volcanic system that are beneficial to habitability are the overlying ice and the underlying geothermal heat source. An experiment was devised whereby Icelandic pillow basalt (and its residing microbial community) was placed inside a simulated subglacial volcanic system that incorporated an underlying heat source and overlying water-ice layer. This was incubated inside a Mars chamber with ~8mbar pressure Martian atmosphere and UV radiation for 1 week at -30°C. Viability was based on the ability to culture the *in situ* community after incubation. We found subglacial volcanism to be a highly suitable environment for life on Mars, with 76% survivability compared to the original microbial community.

Arsenic reactions and mobility along redox gradients in lake sediments

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Arsenic (As) and a suite of geochemical parameters were measured in sediment cores, as well as in porewater from four lakes spanning a range of redox and geochemical conditions. Inverse modeling of the porewater As profiles, using a one-dimensional transport-reaction equation, coupled to thermodynamic calculations and comparisons among the various porewater and solid phase profiles were used to identify reactions involving As and to estimate their kinetics.

In two of the lakes, whose bottom waters were oxygenated at the time of sampling, solid-phase and porewater profiles of As and Fe indicate that dissolved As was released to and scavenged from the porewater as a consequence of the reductive dissolution of Fe oxyhydroxides and the adsorption of As onto authigenic Fe oxyhydroxides, respectively. Kinetic modeling of the arsenic profiles indicates that the rate of As adsorption onto Fe oxyhydroxides in these two lakes is relatively slow and is consistent with the rates determined in laboratory experiments studying As adsorption onto synthetic Fe oxyhydroxides suspended in solutions containing dissolved organic matter [1].

In the two other lakes, whose bottom waters were sulfidic at the time of sampling, As removal from porewater occurred at depths where FeS_(s) was being formed and where peaks in dissolved zero-valent sulfur (ΣS(0)) were observed. Thermodynamics predicts that porewaters were undersaturated with respect to all known solid As phases; it also predicts that some of the As^{III} in anoxic environments was oxidized by zero-valent sulfur to As^V, as suggested in a recent study where As equilibria in anoxic laboratory systems were reinterpreted [2]. All these results are consistent with As removal from porewater by the adsorption of As^V onto FeS_(s).

[1] Redman *et al.* (2002) *Environ. Sci. Technol.* **36**, 2889–2896. [2] Helz & Tossell (2008) *Geochim. Cosmochim. Acta* **72**, 4457–4468.

The biogeochemistry and ecology of deep sediment-buried basement biosphere: Juan de Fuca Ridge Flanks

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Our Deep Biosphere project is designed to exploit the unprecedented opportunities provided by new generation long-term borehole-CORK observatories installed on the flanks of the Juan de Fuca Ridge (JdFR) by the IODP, to study the microbial geochemistry and ecology of the sediment-buried ocean basement. We describe the new CORK's attributes with respect to deep biosphere studies, and supporting instrumentation sleds and associated equipment. Our GeoMICROBE sled allows for 'in situ' (i.e., seafloor) geochemical analyses (e.g., electrochemistry: O₂, H₂O₂, HS⁻, S(0), S²⁻, S₂O₃²⁻, S₄O₆²⁻, Fe(II), Fe(III), FeS_{aq}, Mn(II), and Zn(II)) of the 30-65°C fluids circulating within the basement, as well as the *in situ* filtration of fluids for molecular biology, culture, biomass and geochemical procedures. Preliminary results of our August '08 cruise to the JdFR flank CORKs indicate that basement fluids there have elevated NH₄⁺, CH₄ and H₂, reduced SO₄ and DOC relative to deep ocean water. Basement fluids from nearby (<1 km) boreholes showed distinct geochemical differences (e.g., Borehole 1301A: ~40 uM free sulfide, ~100 uM Fe²⁺, trace of FeS_{aq} clusters; Borehole 1026B: <1 uM free sulfide, detectable Fe²⁺ but no detectable FeS_{aq} clusters). Differences between *in situ* e⁻chem and subsequent ship-board analyses illustrate changes in speciation and oxidation states that occur between sample collection and delayed (few hours) analyses. Future access to multiple depth horizons within basement should help to elucidate relative contributions of *in situ* microbial activity vs diffusion across sediment-basement interface. Analysis of community structure is underway using environmental genomic DNA successfully extracted from 1301A basement fluids. Cell counts in 1301A basement fluids were ~10⁵ cells/ml. Results of volatile dissolved organics (e.g., amino acids and LMW organic acids) will also be reported.

Spatial distribution of soil erosion in southwestern France watersheds—Modelling sediment transport by interpretation of rating curves

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Suspended Particulate Matter (SPM) transport in rivers reflects soil erosion processes and controls fluxes of many contaminants. This study is based on water discharges (Q) and SPM concentrations of 15 contrasting watersheds of the Adour-Garonne River systems obtained by our high temporal resolution observation network (> 1 sample per day during 3-18 years covering different hydrological situations). Spatial analyses of soil erosion risk were performed with an expert system based on the RUSLE equation and from land cover, soil and climatology databases, DEM managed by a GIS (ArcView®, IDRISI®). The range of sediment yields (5-180 t.km⁻².yr⁻¹) reveals high spatial variability of erosion, mainly attributed to key factors such as lithology, runoff and human disturbance (e.g. agriculture, dam trapping). We propose alternative approaches using statistical relations in order to develop models for SPM flux estimates as final recourse in case of an inappropriate sampling frequency. The latter may induce unacceptable errors in flux estimates as demonstrated by numerical simulation for different watershed typologies [1]. Rating curves relate SPM concentration to Q, with Q measurement data as the independent variable. Comparisons of actual and rating curve-predicted SPM concentrations show that the use of common rating-curves partially suffers from data scattering around the regression line and often underestimates annual flux. Therefore, we have developed truncated regressions based on log-transformed-SPM and -Q values for each watershed for data representing Q values superior to 1.5 times the mean annual Q (Q_m), where SPM_# data represent y-intercept:

$$[SPM] = [SPM_{\#}] \times \left(\frac{Q}{1.5Q_m} \right)^{\alpha}$$

The regression coefficients, SPM_# and α, are respectively attributed to lithology and soil erosion sensitivity index. The use of watershed properties allows estimating annual SPM flux and the deviation from modelling values can be used to evaluate human disturbances (e.g dam trapping).

[1] Coynel *et al.* (2004) *Sci. Tot. Envir.* **330**, 233-247.

First results from the C1XS X-ray spectrometer on board Chandrayaan-1

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⁶See: <http://www.sstf.rl.ac.uk/c1xs/CO-I.htm>

The Chandrayaan-1 X-Ray Spectrometer (C1XS) is a UK-built instrument that was successfully launched on 22 October 2008 on India's first mission to the Moon [1,2]. By performing high spectral (~110 eV) and spatial (50 km) resolution measurements of the abundances of major rock-forming elements in the lunar surface, including the presently poorly constrained Mg abundance, C1XS will address important unresolved questions in lunar science [3]. An example of the capabilities of C1XS during an A-class solar flare is shown in Fig. 1. The spectrum shows that the Mg, Al and Si lines are detected and well-resolved. A compositional analysis of this spectrum, and comparison with the ground-truth from the Apollo 14 samples, will be presented.

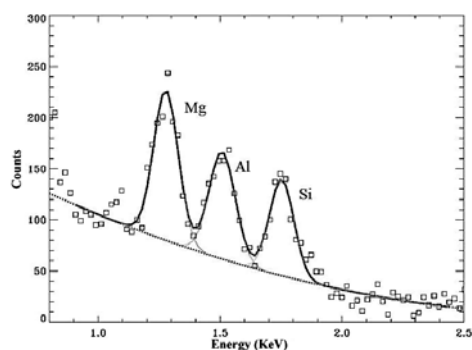


Figure 1: A spectrum obtained on 10 Jan 2009 (15:55 - 16:04 UT); corresponding to a ground track of ~50 × 750 km (including the Apollo 14 landing site at 17.5° W, 3.7° S).

[1] Grande *et al.* (in press) *Planet. Space Sci.* [2] Howe *et al.* (in press) *Planet. Space Sci.* [3] Crawford *et al.* (2008) *Planet. Space Sci.* DOI: 10.1016/j.pss.2008.12.006.

Mg/Ca ocean paleo-temperatures from New Zealand foraminifera in the Eocene greenhouse world

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We have used laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) techniques to measure *in situ* element/Ca ratios of planktonic and benthic foraminifera of Early Eocene age, in order to reconstruct sea surface (SST) and bottom water (BWT) temperatures for the high-latitude South Pacific during the period 51 – 46.5 Ma, which includes the Early Eocene Climatic Optimum (EECO). The same suite of samples have been analysed for $\delta^{18}\text{O}$ and TEX_{86} , allowing comparison between independent geochemical temperature proxies and the Mg/Ca paleothermometer [1].

Thirteen species of planktonic and benthic foraminifera have been analysed from four samples from the mid-Waipara and Hampden sections, New Zealand (paleo-latitude ca. 55°S; paleo-depth ca. 1000 m). Electron microscopy shows that the preservation of these specimens is variable. However, the laser ablation technique permits multiple analyses per specimen, and yields a trace element/Ca profile through the test that makes it possible to identify and avoid zones of surficial and internal contamination resulting from diagenetic coatings, mineralisation and detrital sediment.

The species *Morozovella crater*, *Acarinina primitiva*, *Cibicides* spp. A, *Vaginulinopsis marshalli* and *Bulimina subbortonica* were identified as being best suited for temperature reconstructions, and used to develop inter-species Mg/Ca-temperature calibrations. Subsequently, these species were used to produce a temperature record for the EECO at ca. 200 kyr resolution. The Mg/Ca temperatures are broadly consistent with those derived from $\delta^{18}\text{O}$ and TEX_{86} , with near tropical SSTs of ca. 25-30°C and BWTs of ca. 15-19°C. A cooling event of ca. 4°C occurred ca. 48.5 – 47.5 Ma, which may coincide with the *Azolla* interval of [2].

These results demonstrate the ability of LA-ICP-MS to recover reliable past ocean temperatures from less than ideally preserved foraminifera, and provide important constraints on climatic conditions in the Early Eocene.

[1] Hollis *et al.* (2009) *Geology* **37**(2) 99-102. [2] Brinkhuis *et al.* (2006) *Nature* **441**, 606-609.

$\delta^{15}\text{N}$ chemostratigraphy of Ediacaran-Cambrian sections of South China

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Marine productivity and biogeochemical processes may be inferred from the isotopic compositions of sedimentary rocks. Isotopic trends of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ can also be useful for stratigraphic correlation. The use of $\delta^{15}\text{N}$ data for such purposes has been debated for a long time in the literature, resulting in its still ambiguous utility as a geochemical tracer and stratigraphic tool. Here, we compare nitrogen isotope trends for five sections in South China that straddle the Ediacaran-Cambrian boundary. Nitrogen isotope values for bulk samples range from +8‰ to -3‰, showing highly systematic variability during the period of interest and testifying to changes in the biogeochemical cycle of the ancient ocean. Negative values might reasonably be ascribed to the action of purple bacteria in the euphotic zone. Many sections show the same general trend, with positive values in upper Ediacaran strata and a strong negative shift in Cambrian strata (more pronounced in black-shales). If these isotopic trends are confirmed, at least two conclusions may be drawn. On the one hand, this evidence is a clear demonstration of nitrogen isotopic signal conservation, thus excluding diagenetic alteration or isotopic contamination during the time elapsed since marine sedimentation. On the other hand, the use of $\delta^{15}\text{N}$ profiles could then be considered a genuinely useful chemostratigraphic correlation tool, especially where biostratigraphy is of limited usefulness.

Alkaline earth metal adsorption to gibbsite as a function of temperature

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Surface potential of mean force (PMF) calculations between the alkaline earth metal cations and the gibbsite basal surface suggest that the alkaline earth metals do not form inner-sphere surface complexes at 298K because of the activation energy barriers associated with the removal of the hydration water around the cations as they near the surface. The activation energy barriers between outer- and inner-sphere complexes increase in height with decreasing cation radii. Consistent with the PMF calculations, molecular dynamics simulations at higher temperatures resulted in the formation of inner-sphere complexes. The temperature at which inner-sphere complexation occurs in the simulations decreases with increasing ionic radii. Barium forms both inner- and outer-sphere surface complexes at 298K; however, Mg only forms inner-sphere complexes at temperatures over 500K.

To investigate these results further, macroscopic experiments were performed to examine alkaline earth metal cation adsorption in different electrolyte solutions as a function of temperature and ionic strength. The trends in alkaline earth metal ion adsorption follows that predicted for a low dielectric constant surface such as gibbsite ($\text{Mg} > \text{Sr} > \text{Ba}$) over the range of temperature studied. The experimental findings are consistent with the modeling results; the ionic strength dependence of alkaline earth adsorption decreases with increasing temperature suggesting an increase in inner-sphere complexation, and the temperature at which the ionic strength dependence on adsorption is no longer evident decreases with increasing ionic radius. Indeed, no ionic strength dependency was observed for Ba adsorption onto gibbsite at ambient temperature.

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Deep water production in the GIN Seas: The Nd record from Feni Drift

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The Greenland, Iceland, Norwegian (GIN) Seas are a key area of modern deep water production. Recent evidence suggests deep and intermediate water was generated continuously in the GIN Seas during the last glaciation and contributed to Glacial North Atlantic Intermediate Water (GNAIW) [1]. However, various attempts to reconstruct GIN Seas surface conditions have resulted in contradictory interpretations [2], thus impeding efforts to determine the role and response of deep water production to specific climate events of the glaciation and deglaciation. To gauge variations in the intensity of GIN Seas deep water production over the last 45 ka, the Nd isotope composition (ϵ_{Nd}) from hydrous/ authigenic FeMn oxyhydroxides in marine sediments was used as an inorganic water mass tracer. The ϵ_{Nd} record, from ODP Site 980 (Feni Drift), is well placed to capture exchanges between the overflow of GIN Seas water and incursion of southern sourced waters (SSW), both of which are identifiable by their distinct range of ϵ_{Nd} .

The ϵ_{Nd} record indicates rapid radiogenic excursions of up to +2.8 ϵ_{Nd} units toward a more radiogenic end member coeval with Heinrich events and the 19 ka meltwater pulse. These shifts most likely reflect incursion of radiogenic SSW in the Rockall Trough when deep water production in the GIN Seas ceased or was dramatically reduced, implying a concomitant reduction of GNAIW in the North Atlantic. The return to less radiogenic ϵ_{Nd} between excursions suggests intermittent deep water production was present in the GIN Seas during the LGM. The ϵ_{Nd} record correlates with the timing of slowdown in meridional overturning circulation (MOC) inferred by $^{231}\text{Pa}/^{230}\text{Th}$ proxy records [3, 4], and testifies to variable deep water production rates and climate cooling in the GIN Seas in response to the rapid advance and retreat of NW European ice sheets.

[1] Yu *et al.* (2008) *EPSL* **271**, 209-220. [2] de Vernal *et al.* (2006) *QSR* **25**, 2820-2834. [3] Hall *et al.* (2006) *GRL* **33**, GL026239. [4] McManus *et al.* (2004) *Nature* **428**, 834-837.

On the growth of calcium carbonate in the presence of Cr(VI)

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Due to its high mobility and toxicity hexavalent chromium Cr(VI) is an environmental pollutant that may pose a serious threat to human health. Sources of Cr(VI) contamination are diverse, ranging from weathering of basalts and amphibolites to industrial activities. The coprecipitation of Cr(VI) may be an effective mean of reducing the mobility of the toxic soluble anion (CrO_4^{2-}), its bioavailability and, consequently, its toxicity. There are strong evidences supporting that Cr(VI) incorporates into the structures of different CaCO_3 polymorphs.

Here, we present data on the crystallization of CaCO_3 in a silica hydrogel medium in the presence of different concentrations of Cr(VI) at 25°C. The crystals obtained have been characterized by using XRD, microprobe and SEM. Our observations indicate that the presence of Cr(VI) in the growth medium (i) has an inhibitory effect on nucleation, and (ii) strongly affects the morphology of calcite crystals (Fig. 1). Furthermore, our results confirm that CrO_4^{2-} incorporates into the calcite structure, most probably substituting carbonate anions.

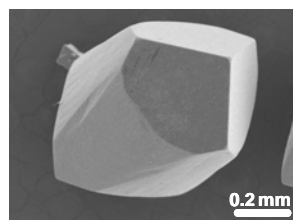


Figure 1: Calcite crystal grown by the silica gel method in the presence of Cr(VI). The initial $\text{CrO}_4^{2-}/\text{CO}_3^{2-}$ ratio in the reactant solution was 0.2.

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Trace element distribution in pelitic garnet: Implications for petrogenesis, PT modeling, and geochronology

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Trace element zonation patterns were determined for garnet from the schist of Mahogany Peaks in the Raft River and Albion Ranges of Utah and Idaho, USA. Variations in HREE and Y that cannot be explained by Rayleigh fractionation can be linked to previously interpreted garnet growth reactions determined from major element analyses used for pressure-temperature (PT) path modeling. Near-rim spikes in HREE and Y occur in garnet analysed from two samples from the Albion Range and one sample from the Raft River Range and are up to an order of magnitude higher in concentration than surrounding concentrations. The near-rim spike present in one garnet from the Albion Range corresponds to a previously interpreted hiatus in garnet growth, after which garnet grew by the reaction $pg + st + qtz = gt + ms + ky + ilm + H_2O$. The subtle major element and petrographic evidence of the growth hiatus is supported by the much more obvious spikes in the HREE and Y profiles; in addition, the presence of a sharp decrease in Ti at the hiatus supports the proposed garnet- and ilmenite-producing reaction. A second garnet from a nearby outcrop in the Albion Range exhibits a near-identical rim increase in HREE and Y and a sharp decrease in Ti, suggesting the presence of a growth hiatus at this point; this interpretation provides an explanation for the lack of fit to a portion of the simulated major element profile produced from PT-path modeling, which assumed no hiatus [1]. The near-rim spike in HREE and Y in one garnet from the Raft River Range corresponds to an interpreted hiatus followed by a garnet-producing reaction that consumed paragonite. This interpretation is supported by a spike in Na concentration at the hiatus.

HREE zoning in metamorphic garnet also has implications for geochronology, in particular for the Lu-Hf system. Lu zoning in garnet provides insight into the tectonic interpretation of garnet Lu-Hf ages determined for the rocks studied here [2]. Near-rim spikes in Lu suggest that garnet ages are biased toward garnet rims, and thus represent the later stages of garnet growth and modeled PT paths.

[1] Harris *et al.* (2007) *J. Metamorphic Geol.* **25**, 915-934.

[2] Cruz-Uribe *et al.* (2008) *Eos Trans. AGU* **89**, (53).

Raman spectroscopic detection of urea, a possible biomarker, in calcite and gypsum mineral matrices

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Urea ($(NH_2)_2CO$) is created in the biochemical urea cycle (also called the ornithine cycle). This metabolic pathway serves to dispose of ammonia, a waste product of metabolism of chemical substances containing nitrogen. Nitrogen containing organic materials can form minerals in the geological environment (urea) or can transform into newly created secondary minerals (struvite, phosphammite, boussingaultite). The urea cycle, to a certain extent, is present in all animals and even in fungi and a few bacteria. Since urea is a biomarker on Earth, it is important to search for it on other Earth-like planets.

Raman spectroscopy has often proven to be a very suitable detection method for studies in geology, organic geochemistry and exobiology. This concerns above all the possibility of nondestructive detection of both organic and inorganic parts of rocks, including minerals, biomolecules as well as micrometric inclusions. Raman spectroscopy is also one of the instruments to be employed during the ESA Exomars mission to Mars.

Raman spectroscopic detection (514 nm laser) of urea has been tested in experimentally prepared powdered mineral matrices to ascertain the detection limit of this method. Other biomarkers such as β -carotene [1] and usnic acid [2] have been previously tested for detection in similar experimental conditions. The detection limits of urea in both calcite and gypsum mineral matrices have been determined as 1wt% using Raman spectroscopy. These results are important because of the planned Exomars mission and consequent evaluation of the collected data.

[1] Vitek *et al.* (2009, in press) *PSS*, doi:10.1016/j.pss.2008.06.001. [2] Osterrothova *et al.* (2009, in press) *SAA*, doi:10.1016/j.saa.2008.09.005.

Deuterium isotopic fractionation through the cell membrane of plants

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Water inside the cells is believed to exhibit no fractionation when it passes through the cell membrane [1]. The experimental results show a non-evaporative fractionation between intracellular and extracellular water, both in embryonic and non-embryonic carrot cells.

Materials and Methods

The carrot (*Daucus carota*) was grown *in vitro* and has been exposed to a water solution with uniform isotopic content. The water from aqueous solution and the cell water were analysed for H/D by isotope ratios mass spectrometry.

Results and Discussion

The isotopic data revealed a deuterium isotopic fractionation between the extracellular and cellular water in addition to the evaporative fractionation. The deuterium content was found to be higher within the cells by ~10 % for the non-embryonic cells and by ~13% for the embryonic cells. This is a non-evaporative fractionation between the intracellular and extracellular water and represents a new step in the overall fractionation of the deuterium water in plants.

[1] DeNiro & Cooper (1989) *GCA* **53**, 2573-2580.

Contribution of natural/biogenic sources to particulate matter levels over Europe: A multi-scale modelling study

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A long-term assessment of biogenic/natural contribution to PM levels over Europe is still missing. We report on a multi-year modelling study including emissions for all relevant biogenic/natural sources calculated in the frame of the EU/FP6 NatAir project: vegetation, soils, sea, fires and volcanoes. Emissions were integrated into the regional scale chemistry transport model CHIMERE. Boundary conditions are updated with daily frequency using output from the global model GEOS-Chem, that includes an explicit calculation of desert dust emissions. Natural/biogenic sources are calculated to contribute ~40% to PM10 and ~25% to PM2.5 over Europe on a yearly basis, with more important contributions in Southern Europe (e.g. Iberian Peninsula) and during hot summers (e.g. 2003).

The work is part of the Pilot Project QUITSAT, funded by the Italian Space Agency (ASI), contract I/035/06/0 – <http://www.quitsat.it>.