Silicium isotopes as a proxy of weathering processes during the PETM

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The end of the Paleocene epoch (55.5 Ma) was marked by an abrupt episode of global warming ("Palaeocene/Eocene Thermal Maximum"; PETM) coincident with a large perturbation to the global carbon cycle. Because the PETM might represent an analogue in the past of the present anthropogenic accelerated emission of greenhouse gases, it has attracted a good deal of interest with both data collecting and modeling efforts. Most of the studies focused on ocean records through sediments, we propose here one of the first study on continental records during the PETM. We focus our study on silcretes sampled in north of France, rocks present on the Paleocene-Eocene boundary and on the silicification formed in the porosity during weathering processes.

Stable isotopes of Si have been used as proxies for understanding the Si cycle and its variations in the past. Here we analyzed silicon isotopes of in situ quartz using a new-generation secondary ion mass spectrometry apparatus. Secondary phases as overgrowths on primary detrital quartz and microcrystals of quartz have been measured. Our results are very unexpected : althought detrital quartz present same values than in other silcretes, secondary phases present very homogenuous signatures far from very negative values that can be reached (-8‰ in [1, 2]). It seems that the origin of silicium is not local as both primary and secondary phases are within the same range. The isotopic fractionnation link to the dissolution/precipitation phase during weathering processes is –1.5‰. The lack of a strongly ^{30}Si-depleted reservoir with negative isotopic values seem to show a low intenisity of alteration during the PETM in continental context.

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Dissolved iron isotopes in the Southern and Equatorial Pacific Oceans

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Iron is a fundamental element linking ocean biogeochemistry and climate. Iron isotopes are a very promising tool for the study of the iron oceanic cycle, notably for tracing its sources to the ocean and for studying its speciation.

Several studies reports iron isotopic data in the marine environment (plankton tows, pore waters, aerosols, seafloor or marginal seas [1-3]). To link these isotopic data together and to fully study the iron isotope marine cycle, we need to document the central reservoir in the marine environment : dissolved iron in seawater.

So far there are only very few available data of dissolved iron isotopic composition in the open ocean [4]. This work will present the first isotopic data of dissolved iron from full depth profiles in the Equatorial Pacific Ocean (EUCFe 2006) and in the Atlantic sector of the Southern Ocean (Bonus-GoodHope 2008), as well as from the Kerguelen Area (Southern Ocean, KEOPS 2005).

These results will be discussed in terms of iron sources to ocean. Potential applications of this new tracer for studying internal oceanic processes, such as biological uptake, will be discussed.

[1] Bergquist & Boyle (2006) *EPSL* **248**, 1-2 54-68. [2] Severmann *et al*. (2006) *GCA* **70**, 8 2006-2022. [3] De Jong *et al.* (2007) *Analytica Chimica Acta* **589**, 1 105-119. [4] Lacan *et al.* (2008) *Geophys. Res. Lett.* **35**, 24 L24610.

Effect of groundwater flow on dissolved As in a Bangladesh aquifer

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The hydrological and geochemical factors that regulate the partitioning of sediment and groundwater As in an aquifer with mobilizable As are not well understood. Recent work conducted in Bangladesh suggests that groundwater residence time may be an important factor controlling the spatial distribution of arsenic [1, 2].

To better characterize these factors and their potential relationship, a three dimensional array of monitoring wells was installed in a sandy, raised village and in adjacent agricultural fields covered with silt and silty clay bordered by a small stream. Dissolved As concentrations increase dramatically from <5 to 500 µg L^{-1} over the 300 m distance separating the village and the stream. A strong redox gradient, with increasingly reducing conditions towards the stream, is indicated by groundwater Fe and SO_4 concentrations and sediment FeII/Fe ratios.

Head measurements over the area show that the annually averaged groundwater flow is from the village towards the stream. Between the peak of the dry season and the onset of the monsoon, the hydraulic gradient reverses and groundwater flows from the stream towards the village. $^3H/^3He$ ages and vertical hydraulic head gradients indicate areas of rapid vertical recharge in the village and fields, with older water (10 to 30 yr) occuring near the stream. The role of groundwater flow dynamics in establishing the redox and As gradient is currently under investigation.

Field and batch adsorption experiments suggest the sediment-groundwater partitioning (Kd) decreases toward the stream. The observed decrease in Kd may be linked to the increasing reducing state of sediment along the transect, the input of sulfate with recharge within the village, or a combination of both.

[1] Stute *et al.* (2007) *Water Resour. Res.* **43**, W09417. [2] van Geen *et al.* (2008) *Environ. Sci. Technol,* **42**(7) 2283-2288.

Benthic boron isotopes and glacial CO_2

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The cause of glacial-interglacial CO_2 variations remains an unsolved problem. While changes in deep ocean carbon storage are invoked in all current models, the causal mechanisms are unclear. Robust proxies for the ocean carbonate system are therefore required to allow us to track the magnitude and timing of changes in deep ocean carbon storage, and how these relate to the ice core CO_2 record.

Boron isotopes in benthic foraminifera should record deep ocean pH. We have developed a technique for measuring boron istopes by MC-ICPMS [1]. This methodology overcomes several problems encountered with earlier NTIMS measurements, and has been further refined to allow accurate measurements of the small numbers of benthic foraminifera typically found in deep glacial-aged sediments. As few as 5 benthic tests (~5 ng boron) may now be measured with an external reproducibility of < 0.3 ‰ (95% confidence), equivalent to < 0.03 pH units.

We have tested our understanding of the $\delta^{11}B$-pH proxy with a thorough core-top study of a range of benthic species, spanning ambient living conditions from pH 7.4 - 8.2, and 1 - 20 °C. All $\delta^{11}B$ values for epifaunal species show a close match to predicted $\delta^{11}B$ of $B(OH)_4^-$ in seawater [2], and infaunal species show offsets to lower values indicative of calcification from more acidic pore-waters. Despite differences in B/Ca ratios between species, we find no evidence for a vital effect on boron isotopes, nor for any incorporation of $B(OH)_3$, nor a significant temperature effect on the isotopic fractionation factor. We also see no change in $\delta^{11}B$ with sample size or apparent dissolution.

These results provide strong evidence that our understanding of the $\delta^{11}B$-pH proxy is sound. Further, our ability to measure small numbers of foraminifera, and combine different sizes, preservation states, and even different epifaunal species highlights the enormous potential of boron isotope measurements for palaeoceanographic studies of the carbon cycle. We will further demonstrate this with a number of LGM to Holocene time series from several key locations.

[1] Foster (2008) *EPSL* **271**, 254-266. [2] Klochko *et al.* (2006) *EPSL* **248**, 261-270.

Challenges at the entry into the ecological age

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There can be no viable future for humanity without a healthy planet. Humanity now moves an order of magnitude more material per year than all of nature´s forces. In the past 30 years we have used up 1/3 of the Earth´s resoures, including 30% of of the world´s forest, 25% of the Earth´s soil and 50% of oil. Using the Earth´s atmpsphere for waste disposal for fossil fuel is significantly altering its composition and heating up the planet. Concordingly the globalising growth economic system is destabilising the planet´s life-supporting systems. The direct impacts on human development as well as rising food and resouce costs mean that current economic growth is rapidly becoming unsustainable and a global transition is needed to the ecological age of human civilisation. The transition to the this new age needs to occur before the middle of this century [1].

The way forward is for developing nations to contract their consumption to allow developing nations to increase their consumption and that we converge at an equitable amount of consumption of Earth´s resources as soon as possible. The world economic system needs to move from growth economics to balanced green economics [2] where we live withing the ecological boundaries of the Earth. By 2050 our western CO_2 emissions need to be decreased by at least 80%, the ecological fooprint reduced to 1.4 gha/capita (75% decudtion for EU) and the human development index to rise substantially. This includes raising overall wellbeing, life expectancy, and eduation. Development needs to move from growth to focusing on environmental protection and stabilising the human population as well as sustainable resource use (water, soil, materials), transport, energy, food, communication and urban design. Geochemists have a role to play at every stage of the process in making the ecological age a success.

[1] Head (2008) *Entering the Ecological Age.* The Institution of Civil Engineers Brunel Lecture Series. [2] Cato (2009) *Green Economics.* Earthscan.

Rhenium in Indian Estuaries and high Re in the Gulf of Cambay

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To understand the behaviour of Re in the tropical estuaries, water and sediment samples were collected from the Narmada Tapi, Mandovi and Mahi estuaries of the Arabian Sea. Samples collected during pre-monsoon and monsoon according to the salinity gradient from river water to open ocean were analysed for their Re contents by isotope dilution using ICP-MS. Re in river waters analysed in this study vary from 1 to 41 pM. In the Narmada, Tapi, and Mahi rivers, it is higher compared to the earlier estimates of the average global riverine Re concentration, 2.1 pM [1, 2]. An annual global flux of riverine Re is estimated to be ~350×10^3 moles with an average concentration of ~9.3 pM based on Re content of this study and those from literature. Re behaves conservatively in all the estuaries in the Arabian Sea. Its concentration in the water of the Arabian Sea, estimated based on the Mandovi estuaries, is ~40 pM, similar to the open ocean Re content of the Arabian Sea measured in this study and to its open ocean value in the other regions of the world. However, the seawater Re content in the Gulf of Cambay estimated based on Re data in the Narmada and the Tapi estuaries is 2 to 5 times higher compared to the open ocean. This is further confirmed by high Re concentration in the Mahi estuary and in coastal waters of the Gulf of Cambay. Higher concentration of dissolved Re in the Gulf of Cambay is probably of anthropogenic origin. Preliminary estimate indicates that polluted rivers and industrial waste waters supply ~2350 moles of Re annually directly to the Gulf of Cambay. Anthropogenic Re supply coupled with high residence time of water in the Gulf are the probable factors responsible for its high Re concentration. Petroleum, Chemical and pharmaceutical industries and coal, lignite and diesel burning in the power plants seems to be the major sources of anthropogenic Re to the rivers and to the Gulf of Cambay. Global riverine Re supply to the oceans, estimated in this study, is ~8 times higher compared to its sink in the reducing sediments [3], indicating non-steady state of ocean for Re. This study highlights the need for a detail study of Re in the various global rivers and in oceans particularly in coastal regions and semi enclosed basins of the world to understand its behaviour in various reservoirs and to constrain the residence time of Re in the oceans.

[1] Colodner *et al*. (1993) *Earth and Planetary Science Letters* **117**, 205-221. [2] Anbar *et al*. (1992) *Geochimica et Cosmochimica Acta* **56**, 4099-4103. [3] Ravizza *et al.* (1991) *Geochimica et Cosmochimica Acta* **55**, 3741-3752.

Climate-erosion coupling over the Himalaya during past ~100 ka

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In this study efforts are made to study the erosional history of the central Himalaya through the records preserved in the Gangetic plain. Sediments from a ~50-m long core, raised from the Ganga Plain at Kanpur and representing ~100 ka of flood-plain deposition [1], were anaysed for Sr and Nd isotope composition.

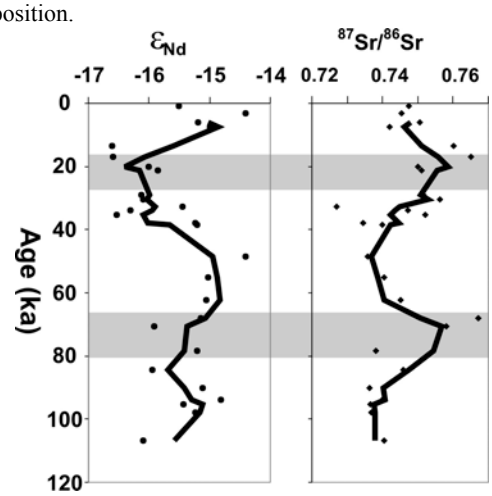

Figure 1: Nd and Sr isotope variation in the sediments

Both $^{87}Sr/^{86}Sr$ and ε_{Nd} vary significantly with depth in the core, 0.72701 to 0.76708 and -14.4 to -16.6 respectively, within the range for silicate rocks of the Higher and the Lesser Himalaya [2]. The variations in the isotope composition of these sediments reflect variations in the mixing proportion of sediments from the Higher and the Lesser Himalaya, the two major sediment sources to the Ganga. The isotope profiles exhibit two major excursions at ~ 20 ka and ~ 70 ka coinciding with periods of precipitation minima [3] and larger glacial extent [4] over the Himalaya. These excursions are result of decrease in the proportion of sediment from the Higher Himalaya due to decrease in monsoon precipitation and increase in glacial cover which in turn are caused by lower solar insolation. This study highlights the significant influence of climate on erosion in the Himalaya and indicates that there is almost no time lag between transfer of sediments from their generation site to deposition site.

[1]Sinha *et al*. (2007) *Sed. Geol.* **201**, 386–411. [2] Singh *et al.* (2008) *Jour. Geoph. Res.,* doi:10.1029/ 2007JF000909. [3] Prell & Kutzbach (1987) *Jour. Geoph. Res.* **92,** 8411-8425. [4] Owen *et al*. (2007) *Quat, Sci. Rev.* **21**, 147-157.

Understanding the fundamental mechanisms of $CaCO_3$ in water

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Calcium carbonate is one of the most widespread and studied minerals, especially within the field of biomineralization. Despite this, a complete understanding of the atomic mechanisms controlling its precipitation and dissolution in water is far from being achieved. Amongst the reasons why this material remains challenging are the long time scales and system sizes that are necessary to study this problem, which overwhelm even classical molecular dynamics simulations. The use of special techniques to accelerate the sampling of the configurational space is therefore an imperative. In this presentation, we report our recent results on the fundamental atomic mechanisms that control the diffusion of species on the flat and stepped ($10\bar{1}4$) calcite surface in water, which underpin the macroscopic growth and dissolution processes. The calculation of the ions solvation free energies as well as bulk properties provide an ultimate validation of the force field in describing the complex behaviour of the calcium carbonate/water interface. The use of metadynamics proves to be effective in accelerating the exploration of the potential energy surface and thereby determining the free energy barriers for relevant diffusion mechanisms.

Dangerous anthropogenic interference with climate change

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We have already loaded the atmosphere with a sufficient amount of greenhouse gases to warm the global climate by about 2.4°C (90% confidence interval of 1.4 C to 4.3°C). Not all of this warming has been realized because; about 50% of this warming is likely masked by the dimming effect of aerosols. Current air pollution laws have been remarkably successful in reducing sulphate aerosols, a major contributor to the masking effect. Even with a targeted reduction in emission of 50% by 2030, we would be adding more than 75 gigatons of CO_2 to the atmosphere. Thus addition of new CO_2 in conjunction with the unmasking effect of the aerosol cooling effect is likely to push the system beyond the tipping points for several elements of the climate system, such as the arctic sea ice and the Himalayan-Tibetan glaciers, to name a few. We face a formidable challenge to avoid such dangerous climate changes and I will discuss options we have to meet this challenge.

Geochemical features of a protracted magmatism in the Fitz Roy plutonic complex, Chaltén, Argentina

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It has been discussed whether the intrusion of the Fitz Roy plutonic complex (FRPC), like other Miocene intrusion in Patagonia, is related to ridge subduction. Yet, our new Ar-Ar data (16-19 Ma) show that the igneous cycles of this complex pre-date the collision of the Chile ridge. Here we present geochemical data to further discuss the relationship between magmatism and structural setting.

We distinguish four different magmatic units. From older to younger they correspond to: (i) an ultramafic unit (mainly pyroxenites); (ii) a mafic unit (diorites and various gabbros); (iii) a tonalite unit, and (iv) a granitic unit (granodiorite and two types of granites). Adakitic and some highly evolved subvolcanic dikes cut the entire igneous suite.

Harker diagrams illustrate a typical evolution from mafic to differentiated compositions. However, granodiorites do not entirely follow this trend. They show lower contents of TiO_2, MnO, MgO, FeOtotal, P_2O_5 and higher contents of Al_2O_3, Eu, Zr, Nb and Hf. Ultramafic rocks have low ∑REE-concentrations and diplay flat patterns in chondrite normalized diagrams. Mafic rocks present a large variation of REE-patterns with both positive and negative Eu anomalies. Consistently higher REE-concentrations are observed in tonalite and granodiorite. Granites show a decrease of the LREE and an increase of the HREE with an almost flat profile in the more differentiated granite. An adakitic dike (La/Lu=248) resembles the nearby Chaltén adakite body dated at 14.5 Ma [1].

The FRPC shows a protracted magmatic history (19-16 Ma) and sub-volcanic dikes suggest that magmatism was still ongoing in the late stages of exhumation. We will argue that the intrusives may have different source regions at depth as well as evolutionary – e.g. deformation – histories. However, there is no direct link between magmatism and ridge collision. We will further speculate about the structural control of the magmatism at Fitz Roy - does it reflect local kinematic conditions or is it related to the regional-scale architecture ?

[1] Ramos *et al*. (2004) *Revista de la Asociación Geológica Argentina* **59**, 693-706.

Subduction-related melts in the Alboran Mantle: The Tallante Xenoliths (B. Cordillera, SE Spain)

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The Alboran Sea region has been affected since the late Oligocene by a sequence of tholeiitic, calc-alkaline and alkaline magmatic events, related to lithospheric extension beneath the Alboran domain, as a consequence of slab roll-back. Mantle xenoliths from the Cabezo Tallante Late Neogene volcanic center (SE Spain) record a multi-stage history of melt-rock interaction and melt intrusion tracking an extension-related 30 km uplift, concomitant to the observed transition from subduction-related to alkaline magmatism. Diffuse tholeiitic melt percolation at spinel- and plagioclase-facies mantle depths was followed by rather shallow (0.7-1 GPa) intrusion of cm-sized gabbronoritic veins. The latters show a fine-grained orthopyroxene reaction rim against the host peridotite. Comparable gabbronorites were previously ascribed to slab-derived melts [1, 2]. A remarkable feature in these veins is the diffuse occurrence of Cl-apatite microcrystals in plagioclase. Clinopyroxene in the host peridotite, partly corroded by gabbronoritic apophyses, is significantly enriched in Th, U, L-M-REE, relative to cpx in both sp-and plag-peridotites, whereas they preserve low Nb and Ta contents. Plag and opx in the vein are also LREE-enriched. These features indicate that parental melts to the gabbronoritic veins were Si-saturated, enriched in LILE and volatile (Cl) components and depleted in Nb, Ta, consistent with subduction-related melts. The gabbronorite stage was followed by the intrusion of alkaline amphibole pyroxenites. According to recent models [3], we propose that lithosphere extension led to uplift and migration of lithospheric mantle sectors (as the mantle presently sampled at Tallante) from an inner part of the mantle wedge, where they experienced spinel-facies porous melt flow, towards a position above a slab edge or slab detachment zone. This allowed upwelling of hot asthenosphere, which generated the alkaline magmatism, and possibly induced melting of the subducting slab [4].

[1] Arai *et al*. (2003) *Proc. Jap. Acad.* **79**, 145-50. [2] Beccaluva *et al*. (2004) *Lithos* **75**, 67-87. [3] Duggen *et al*. (2005) *J.Petrol* **46** (6), 1155-1201. [4] Yogodzinski *et al*. (2001) *Nature* **409**, 500-502.

Soil and water analysis of selected areas in vicinity of brick kilns along the highway of Rawalpindi and Islamabad

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The research was conducted to determine the effect of 35-40 brick kilns in an area of 4-5 sq.m on the soil and water contamination in its vicinity and surrounding area. Sampling was done along the highway of Rawalpindi and Islamabad. Twenty (20) soil samples at the depth of 0-6 inches and 6-12 inches were collected. Fifty water samples (50) ranging in depth of 50-400m were collected. All soil and water samples were analyzed for different physiochemical parameters. Results of soil analysis shows high pH (max. 8.55) and high EC (max. 1890 uS/cm) values. Heavy metal analysis shows that all soil samples are high in Pb concentration than permissible limits of WHO (3 mg/l). Similarly Cu concentration of all soil samples exceeds permissible limits of WHO (0.5 mg/l). Water analysis showed high pH (max.8.9), EC (max. 4750 uS/cm), TDS (max. 3515 mg/l), turbidity (max. 196 NTU), alkalinity as bicarbonate (HCO_3^-) (max. 1293 mg/l), total hardness (max. 748 mg/l) and calcium (max. 652 mg/l). Piper plot shows that water of brick kiln areas is of Na^+-HCO_3^- -SO_4^{2-} type. During the survey of brick kiln areas, health effects were also noticed. People dwelling in the areas are suffering from various respiratory and dental diseases.

Stable oxygen isotopic variations in modern *Achatina* land snail shells from Southern India and their relation to rainwater isotopic composition

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High resolution reconstruction of terrestrial climatic record using proxies is a challenging task. Here we used the stable oxygen isotope ratios in the carbonate of land snail shells for environmental reconstruction. Studies concerning the controls of isotopic variations in modern land snail shells with observed regional climatic parameters provide a motivation for this study [1]. Here in this study, the land Snail *Lissachatina fulica* (Bowdich), a representative member of the family Achatinidae, one of the most invasive Mollusc species with a high growth rate were sampled from S. India (Bangalore). In the study we observed variability in the stable isotopic composition of aragonite sampled at intervals along the growth axis of 2 shell specimen and compared it with estimated $\delta^{18}O$ of aragonite precipitated in equilibrium with average monthly isotopic composition of rain water. Daily rainwater samples were collected during the period March to July, 2008. Live snail samples were collected on 16th July, 2008 and stable isotopic analyses were performed. Oxygen isotopic values of shell carbonate varies between 2‰ to -5‰ w.r.t. VPDB consistent with the estimated $\delta^{18}O$ of aragonite. The oxygen isotopic composition appears to be mainly a function of the rainwater isotopic composition, with direct influence of rainfall amount and evaporative effects. Our results indicate that the $\delta^{18}O$ values of shell carbonates are enriched by 3-4‰ relative to estimated aragonite precipitation in dependence with monsoonal wind patterns. Our observations also showed a low inter sample variability, clearly demonstrating the use of *Achatina* shell carbonate as a high resolution proxy for understanding the changes in the isotopic composition of rainwater over shorter timescales

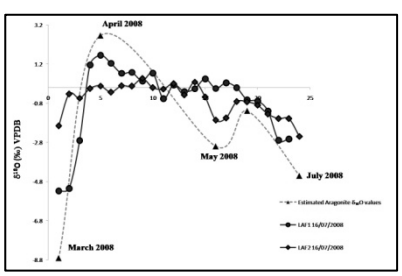

Figure 1:

Leng M. J., Heaton T. H. E., Lamb H. F., Naggs F. (1998), *Holocene*, Vol. **8**, 4, pp.407-412.

Advanced methods to characterize nanomaterials for environmental toxicity studies

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While nanotoxicology and econanotoxicology studies have made strides in the last few years, basic questions still surround the mechanisms of toxicity and best practices for testing nanomaterials and comparing the resulting datasets. A fundamental question is "what are we actually dosing the organisms with?" Addressing these basic questions begins with a thorough characterization of nanomaterials before, during, and at the completion of toxicity tests.

Flow field-flow-fractionation (Fl FFF) is a technique that separates nanoparticles (NPs) by hydrodynamic diameter. By coupling Fl FFF with inductively coupled plasma-mass spectrometry (ICP-MS), we have characterized the size, polydispersity, size-dependent metal content and element ratios of commercially available CdSe/ZnS quantum dots. Significant differences in NP characteristics, particularly elemental ratios, existed between manufacturers and between different types from the same manufacturer.

The characterized dots were shown to have different toxicity thresholds to *Daphnia magna* that may in part be more fully explicated by the results of the charaterization studies. Results of both characterization and toxicity studies will be presented and compared.

Experimental constraints on HFSE partitioning and Ti mobility in saline fluids

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High field strength elements are important geochemical indicators in many geological settings, and in particular in subduction zones. The HFSE signature of arc magmas is depleted relative to MORB, and there is much debate about the cause of this. Interaction between crustal and mantle rocks, and fluids liberated during metamorphism are critical for the transport of elements within the Earth, and the generation of diverse geochemical signatures, such as those at subduction zones. A fundamental premise of many mass-flux calculations in fluid transport is that Ti is essentially immobile in metamorphic fluids. Indeed, previous experimental data supports this 'constant Ti' frame of reference, demonstrating quite low rutile (TiO_2) solubility in aqueous fluids. However, we have performed novel experiments in saline fluids, which indicate that F (and Cl) greatly enhances the solubility of rutile, and hence increases the mobility of Ti. We will show that this has implications for the mobility of the other HFSE, which are strongly sequestered into Ti-phases such as rutile [1,2]. The experimental run products have been analysed using isotope dilution ICP-MS techniques [3,4] to estimate rutile/fluid partition coefficients which may be used to determine the relative mobility of HFSE in some potential metamorphic fluids. These new partition coefficients may aid us in unravelling the processes behind the observed HFSE depletion in subduction zone magmas, and may help to address the high field strength element budget of the Earth's crust and mantle.

[1] Klemme *et al*. (2005) *Geochim. Cosmochim. Acta* **69,** 2361-2371 [2] Klemme *et al.* (2006) *Chem. Geology* **234,** 251-263 [3] Münker *et al*. (2001). *G-cubed (G3)* **2,** 10.1029/2001GC000183 [4] Weyer *et al.* (2002) *Chem. Geology* **187** 295-313.

Secular trends in $\delta^{11}B$ and prospects for determining the direction of paleo-pCO_2 change

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The B isotopic composition of seawater is significantly heavier than average river input, which is the primary flux to the oceans. In fact today, a time of low pCO_2, the $\delta^{11}B$ of seawater is near a high end-member of measured isotopic values at 39.6 per mil. The 30 per mil offset between river water and seawater is controlled by sorption of $B(OH)_4^-$, which is at least 17 per mil lighter than $B(OH)_3$ and dominates B output flux out of the ocean. The speciation of B is controlled by pH, which has a quantifiable relationship to pCO_2, such that at lower pH less $B(OH)_4^-$ is available. Therefore, times of low pH and high pCO_2 should be times of significantly lighter seawater $\delta^{11}B$. Geologic intervals of high pCO_2 that approach the residence time of B, estimated to be between 8-20 Ma, should lead to $\delta^{11}B$ that approaches the river input value. Thus, we predict that to first order the secular variability in $\delta^{11}B$ through the Phanerozoic will give the direction of change in pCO_2. This hypothesis is supported by currently published $\delta^{11}B$ values of brachiopods, which report low values during greenhouse times and high values during icehouse times. Secular variability in B isotopes has been suggested to be the main problem for using the boron pH proxy for deep time. Our working hypothesis suggests that while it is true that obtaining absolute pH/ pCO_2 values may not be possible, we can obtain a high-resolution record of the change in direction. The use of B isotopes, especially when coupled with other indicators of ocean and atmosphere change, has tremendous potential for improved temporal resolution of climate change and its relationship to the processes that drive these changes.

Application of geo-microbial prospecting method for evaluation of hydrocarbon micro-seepage pattern in oil and gas fields of Mehasana, Cambay Basin, Gujarat, India

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Geo-microbial method for hydrocarbon exploration is the search for surface microseeps as clue to the presence of an active petroleum system and / or to the location of possible oil and gas accumulation. The paper presents the results of microbial prospecting survey carried out in existing Oil and Gas fields of Mehasana, Cambay basin, Gujarat, to define the geo-microbial signatures, to evaluate the hydrocarbon micro seepage pattern and to investigate whether the geo-microbial anomalies that can establish an upward migration of hydrocarbons from the deep subsurface over oil and gas proven areas. A set of 135 sub-soil samples collected, were analyzed for indicator hydrocarbon oxidizing bacteria. The microbial prospecting studies showed the presence of high bacterial population for methane (5.4 x 10^6 cfu/gm), ethane (5.5 x 10^6 cfu/ gm), propane oxidizing bacteria (4.6 x 10^6 cfu/gm) and butane oxidizing bacteria (4.6 x 10^6 cfu/gm) in soil samples. The high bacterial populations of hydrocarbon oxidizers were found between the producing wells and these high microbial concentrations were found to be either surrounded by radial withdrawal patterns. Mehasana is one of the larger Oil and Gas fields in India, and all of the predicted microbial patterns have been identified. Clusters of low microbial populations found over or adjacent to many of the producing wells, identify the reservoir drainage radius around the wells. Areas of high microbial activity of hydrocarbon oxidizers were found between the producing wells which indicate pockets of unproduced hydrocarbons within the field.

Integrating the microbial data with geologic and geophysical information can identify the drainage fabric within the reservoir to help define the most appropriate well spacing and well pattern and identify bypassed reserves for particular reservoirs. The study confirmed that seepage of light hydrocarbon from microbial studies and help in evaluation of hydrocarbon micro seepage pattern.

Climatic controls of regolith weathering and mass flux in granitic terrain – A synthesis of Critical Zone Exploration Network data

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What controls the depth and chemistry of the Earth's regolith? Answering this question is key to understanding landscape evolution, soil forming processes, and the feedback between mineral weathering and atmospheric carbon dioxide levels. We present a synthesis of regolith weathering data for granitic terrain associated with the Critical Zone Exploration Network. Data for regolith and rock geochemistry, climate and landscape age were compiled and a regolith geochemical mass balance calculated relative to bedrock using an immobile element approach [1]. A unitless mass transfer coefficient (τ, g g^{-1}) and mass flux (δ, g m^{-3}) were calculated for the entire regolith profile at each site [2]. The τ depletion profiles indicated greater depth of weathering and near complete loss of cations such as Na with increasing precipitation. Regolith integrated τ and δ values demonstrated threshold type functions relative to mean annual precipitation, with a dramatic increase of Si and cation loss above a mean annual precipitation (MAP) of 1,000 mm yr^{-1}. We fit a range of functions to depth profiles of bedrock normalized Na concentrations (mol m^{-3} regolith) to derive a lumped kinetic parameter (*K*), assuming albite weathering dominated the observed Na mass loss [3]. The regolith *K* values followed an exponential decay function relative to MAP, with the greatest *K* values at low precipitation, *i.e.*, less than 500 mm yr^{-1}, that decreased asymptotically with increasing MAP. The data suggest an interaction of climate, weathering rate and mass flux in that low MAP sites exhibited minimal mass loss but potentially rapid kinetics. This pattern reversed in a threshold-like fashion to large regolith mass flux and slow weathering kinetics with increasing precipitation.

[1] Brimhall *et al*. (1992) *Science* **255**, 695-702. [2] Anderson *et al*. (2002) *GSA Bulletin* **114**, 1143-1158. [3] Brantley *et al*. (2008) *Geoderam* **145**, 494-504.

Spontaneous D-H exchange between water ice and Complex Organic Molecules (COMs) in protostellar environments

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Multiply deuterated isotopologues of methanol have been detected in gas-phase in the protostar IRAS16293-2422 [1]. In this source, there is significantly more CH_2DOH than CH_3OD. The origin of this selective deuteration is not understood. Gas-phase chemistry modeling does not account for this multiplydeuteration [2], therefore cold atoms reactions onto the surface of the grains have been favoured thanks to experimental simulations [3, 4]. In this work, we test experimentally the hypothesis of spontaneous exchange between hydrogen and deuterium atoms in interstellar ice analogs composed of CD_3OD and H_2O. Thin films of intimate H_2O:CD_3OD ice mixtures, condensed at low temperature (<110 K), are monitored by Fourier transform infrared (FTIR) spectroscopy up to the complete evaporation of CD_3OD (~ 170 K). Rapid hydrogen/deuterium (H/D) exchange is observed, at 120 K and above, through the growth of the ν_{OD} stretching mode of HDO at ~ 2425 cm^{-1}. It is also shown that H/D exchange occurs i) on the hydroxyl functional group of methanol, i.e through hydrogen bonds, and ii) before the completion of crystallization. The present results suggest that the much lower abundance of CH_3OD compared to CH_2DOH in IRAS16293-2422 could reflect H/D exchanges in water ice prior or during the grain mantle evaporation. This solid-state depletion mechanism, so far neglected in the astronomical literature, is expected to affect other deuterated molecules with hydrogen bonds, i.e. containing –OH, -NH- or $–NH_2$ functionl groups [5]. This mechanism is expected to occur at any step of stellar evolution, as long as icy grains are expected to experience sublimation-condensation cycles. It is also suspected to occur in the solar nebula, and should be taken into account for interpreting the D/H ratio in organic compounds and water molecules, in comets and meteorites.

[1] Parise *et al*. (2004) *A&A* **416**, 159. [2] Garrod *et al.* (2006) *Faraday Discuss.* **133** 51. [3] Nagaoka *et al.* (2005) *ApJ* **624**, L29. [4] Watanabe & Kouchi (2002) *ApJ* **571**, L173. [5] Ratajczak *et al*. (in press) *A&A*.

Carbonate veins as recorder of seawater-crust interaction

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Seawater circulation within mid-ocean ridge flanks plays a major role in global chemical budgets of crust-seawater interaction with particular importance of the ocean crust as a sink for CO_2. We have analysed carbonate veins in basement rocks of twenty-three drill cores from the North Atlantic and the Pacific. The average proportion of carbonate veins and vugs in the upper 600-700 m oceanic crust is on the order of 2-4 vol.% which is equivalent to a global CO_2 uptake of $1\text{-}2\cdot10^{12}$ mol/yr. Our data are intermediate between earlier estimates based mainly on investigations of drill cores from >110 Myrs old ocean crust [1, 2] and for < 7Ma sedimented ridge flanks [3, 4].

Analyses of trace elements across single veins reveal strong, often complex compositional zonations e.g. for Y and the rare earth elements (REE). In some veins, REE concentrations increase towards the contact to the host basalt and approach values similar to MORB, whereas the vein centres show distinctly lower values and seawater-like Y/Ho ratios. The Y/Ho ratios of the carbonate veins (~40-100) encompass the complete range between average MORB (~51) and seawater (~88), indicating highly variable extents of basement-seawater exchange, during carbonate vein formation. The REE spectra also define two distinct groups, one with a pronounced negative Ce anomaly and one without anomaly. Negative Ce anomalies are exclusively observed in carbonates from veins with excess $^{87}Sr/^{86}Sr$ (i.e., above that of contemporaneous seawater), consistent with open circulation by oxic seawater. In contrast, all sites where low $^{87}Sr/^{86}Sr$ ratios indicate exchange with basement show no Ce depletion, suggesting suboxic to anoxic conditions and hydrothermal uptake of Sr and REE from the basalt. We conclude that REE concentrations and Y/Ho ratios of carbonate veins are highly sensitive indicators for the extent of seawater-basement interaction during vein formation.

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Modeling deformation velocity in Himalayan urban centers from plate motion and elastic strain accumulation

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The instantaneous tectonic motions across the Himalayan region have been measured by the GPS. We processed GPS observation for the permanent stations established by GBPIHED Since GBPK-Almora (1997), GBNL-Nainital (2005) and GBSK-Sikkim (2003) using GAMIT/GLOBK. All these Himalayan urban centers, that are from the focus of our study, presents at least 2.5 years of data, the minimum time span for a reliable determination of the deformation velocity .

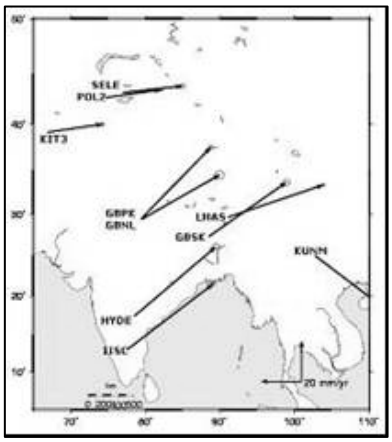

Figure 1: Velocities of GPS stations.

Results clearly shows the tectonic collision of Indian subcontinent towards Eurasia. Obtained distribution of sites velocities suggests the Indian plate which includes IGS sites IISC (53.12±0.57mm/yr) HYDE (52.68±0.91 mm/yr) [1] and our sites Almora (48.33±0.58 mm/yr), Nainital (45.09±1.16 mm/yr) are moving mostly as rigid.

Furthermore, baseline changes between the sites of study area indicates that Lahasa (southern Tibet) site is consistent with the east-west extension of Tibetan plateau with a extension of 18 mm/year relative to Indian plate. The baseline changes between GBPK-GBSK is 23 mm, as GBSK is moving towards east in comparison to GBPK.

[1] http://itrf.ensg.ign.fr

Tectonoic implications of dense GPS velocity fields at kumoun Himalayas

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A dense and wide semi-permanent GPS network has been studied in Gori-vally, Indian Central Himalaya by GBPIHED for 4 years since 2002 to 2007. Field campaigns for the GPS geodetic data are made every year for this network and is designed both for crystal deformation monitoring and to serve a highly précised GPS network in the Study area. Average distance between dense parts is about 10 to 20 km.

Velocity and precise position for the sites determined using GAMIT/GLOBK software.

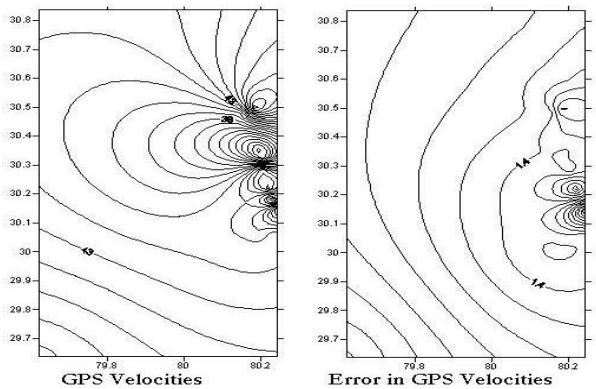

Figure 1: Contour map of GPS velocities and error.

The magnitude and direction of velocity vectors varies from south to north and from one thrust zone to other. The velocity has been found maximum in Dung (50.76±1.72 mm/yr), which falls in Tethys Himalaya zone. However the minimum velocity was estimated for martoli (28.85±1.34 mm/yr) in the fault zone of THF. The velocities indicate the tectonic movements are of similar magnitude and direction. Change in direction in Trans-Himalaya is observed towards east in case of Dung. The velocity of foot wall of MCT is also in the similar range (Munsiari 40.96±1.47 mm/yr) as compares to that of the velocity of hanging wall of MCT (Khalia = 42.73±1.34mm/yr).

Causes and impacts of tropical Pacific climate change during the early Pliocene warm period

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During the Pliocene warm period (ca. 5-3 Ma), global temperature was 2-3˚C warmer than present. Since solar forcing and atmospheric CO_2 were similar to today, the causes of Pliocene warmth must be related to oceanic and climatic factors. As such, the Pliocene can be used to study these factors and to validate climate models. The Ocean Drilling Program has recovered Pliocene sediments in critical regions allowing for an evaluation of the role of the tropics in Pliocene warmth. We present a synthesis of paleoceanographic data from the Indo-Pacific tropics including sea surface temperature (SST) and sub-surface temperature data, derived from analyses of alkenone saturation of organic matter in sediments, and of oxygen isotopic and elemental ratios of planktonic foraminifera. The SST data indicate a permanent El Niño-like state (referred to as 'El Padre') and an inferred reduction in Walker circulation. Eolian grain size data from these cores are used as a means to reconstruct past atmospheric circulation including the position of the Intertropical Convergence Zone. The sub-surface temperature data indicate a warmer and/or deeper thermocline, suggesting that the thermocline, whose conditions are determined at higher latitudes, plays a role in tropical climate change.

The possible explanations for, and extratropical impacts of, 'El Padre' conditions are explored by considering them in a global context. Theory and models of the processes that control the thermocline suggests that changes in the oceanic heat budget and enhanced ocean heat transport, relative to today, could explain observed Pliocene tropical temperature patterns. Observational and modeling studies indicate that these patterns could have impacted extratropical climate conditions in turn, via atmospheric teleconnections. Although much progress has been made studying the processes responsible for observed Pliocene conditions, coupled climate models cannot reproduce tropical oceanic conditions in the warm Pliocene. Solving this problem will take close interactions between modelers and the geologist that produce the paleoclimate data.

Andaman inner arc volcanoes: An evaluation of arc geochemistry and role of sediments in arc lavas

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The seismically active Andaman arc (~1100 km) is seismically very active, is one of the poorly explored double chain arc-trench systems worldwide. Along the Andaman-Nicobar subduction zone, the Indian Ocean crust and the overlying sediments are obliquely subducted beneath the Burmese plate, resulting in two inner arc volcanoes, Barren (currently active) and Narcondam (dormant). Preliminary published geochemical studies reveal that Barren island mostly erupts tholeiite to Andesitic lava while acidic and intermediate lavas are common for Narcondam island. The calculated $Si_{6.0}$ and $Ca_{6.0}$ [1] of Barren lavas are 2.98 and 10.5 respectively similar to Java volcanoes (3 and 10.1). High $Ba_{6.0}$ and $Th_{6.0}$ values (70 and 1) of arc basalts suggest substantial sediments input or source enrichment. The linear mixing as shown by Pb-Pb isotopic ratios suggest Barren lavas must have formed between two component mixing of depleted mantle (or N- MORB mantle) and oceanic sediments. Uniform ε_{Nd} and $^{87}Sr/^{86}Sr$ ratios further suggest homogeneity of subducting slab. The role of sediments in arc volcanism is also evident in incompatible trace element ratios. The Barren lavas show strongly increasing Ba/Th (i.e. indices of fluid addition) with decreasing Th/Nb (indices of sediment addition), and a maximum Ba/Th of about 100. Ba/Th and Nb/Ta co variations are comparatively weak and the lowest Ba/Th samples (~47) note the highest Nb/Ta value (14).

The tholeiitic basalts at Barren suggest its generation from subarc mantle at relatively high pressure and at low degrees of melting vis-à-vis Narcondam volcanics which display strong evidences of magma mixing.

[1] Plank & Langmuir (1988) *Earth Planet Sci Lett* **90**, 349-370.

Nb in basalts from Turrialba Volcano, Costa Rica revisited

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Basalts from Turrialba volcano have restricted REE concentrations (La/Yb=18-24) but La/Nb and Ba/La ratios that vary from those typical for an arc basalt (2.1, 20) to those typical for an ocean island basalt (1.0, 12). Reagan and Gill [1] attributed these observations to variations in the partition coefficients for Nb as the degrees of mantle melting changed with the extent of slab fluid fluxing. We have further investigated the origin of the Nb-Ta anomalies by applying modern microbeam techniques to analyze homogenized olivine-hosted glass inclusions for major-element, trace-element, and H_2O concentrations, as well as S^{6+}/S (fO_2). Like the whole rocks, the inclusions are enriched in LREE, and have variable La/Nb and Ba/La values. These incompatible trace element ratios, and the degrees of LREE enrichment however, are significantly more variable in the inclusions. The variations in most trace element concentratons in the glass inclusions including Ti can be explained by mixing between a small degree melt of OIB-like mantle source and large degree melt of a similar mantle in the presence of a LIL-element-bearing fluid from the slab. The exception is Nb, whose concentration varys by more than a factor of two above those of any other trace element, and thus cannot be successfully modeled without a siginficantly higher D_{Nb} during melting to generate the low-Nb mixing endmember. Because D_{Ti} does not need to simlarly increase, the changes in D_{Nb} do not appear to be the result of the presence or absence of a Ti-rich phase, but rather, results from changes in D_{Nb} for other residual mantle phases.

S^{6+}/S values appear to vary independently of La/Nb values for the data set as a whole, and taken at face value, these data indicate that fO_2 had little effect on D_{Nb}. However, H_2O contents of the inclusions range from 0-1.6 wt %, indicating that the host olivine crystals grew after varying levels of H_2O-CO_2 degassing. Thus, the S^{6+}/S values in these samples could have been affected by this degassing. Nevertheless, the glass inclusions with La/Nb < 1 all have near-zero S^{6+}/S values suggesting that their fO_2 values are generally below QFM. Glass inclusions with greater La/Nb values have wide ranging S^{6+}/S values and calculated fO_2 values as high as 1.1 log units above QFM, suggesting that magmas feeding into this system do indeed have variable fO_2, although the relationship of fO_2 to La/Nb remains uncertain.

[1] Reagan & Gill (1989) *JGR* **94**, 4619-4633.

Impact of the aerosols on the photolysis rates at regional scale

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Photolysis rates in the atmosphere are greatly affected by the presence of clouds and aerosols. In Chemistry Transport Model (CTM), and especially, in regional CTM, the aerosol feedbacks on photolysis rates are generally not taken into account. In this study we coupled a regional CTM (POLAIR3D) with a radiative transfer model (Fast-JX). We assessed the aerosol feedbacks on the photolysis rates and the subsequent impact on gas and aerosol species concentrations simulated over the European domain.

It was shown that some oxidant species as OH or NO are greatly affected through all the troposphere. Changes on ground O_3 concentrations and aerosols formation can also be locally important. Aerosols having the stronger impact are dust and carbonaceous aerosols. In the future climate, Biomass Burning (BB) are predicted to increase. The long-range transport of BB pollutants and their regional impact thousands of kilometres away from emissions may become a subject of importance.

For these reasons, a specific event was analysed: the long-range transport into Europe in July 2004 of Alaskan BB plumes. The indirect impact of these plumes on European air quality through the modification of photolysis rates was analysed together with their direct impact through the incorporation of BB pollutants in the boundary layer. Model results were compared with measurement taken during this period over Europe as part of the ICARTT (International Consortium for Atmospheric Research on Transport and Transformation) campaign.

Evaluation of geochemical characteristics of groundwater in Wailpally watershed, Nalgonda District, Andhra Pradesh, India

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Major ion chemistry in a hard rock fractured subsurface aquatic system indicates significant difference in mean content of many parameters. The ionic dominance pattern is in the order of $Na^+ > Ca^{2+} > .Mg^{2+} > K^-$ among cations and $HCO_3^- > Cl^- > SO_4^{-2} > NO_3^- > F^-$ among anions in pre monsoon. In post monsoon Mg replaces Ca^{2+} and NO_3^- takes the place of SO_4^{-2}. Soltan's classification categorizes the groundwater as Normal sulphate type with 66% of samples in pre monsoon and 92% in post monsoon having SO_4^{-2} content in <6 meq/l. The Base Exchange Indices of majority of the gound water samples are of Na^+-SO_4^{-2} type and rest belong to Na^+-HCO_3^- type. The groundwater based on meteoric genesis index show that almost all the samples belong to shallow meteoric percolation type. Weathering of silicate rocks in the region is one of the important processes responsible for the higher concentration of the Na^+ in groundwater. The Ca^{+2}/Mg^{+2} ratio of 1 to 2 in many (80% in pre and 74% in post monsoon) indicate dissolution of dolomite and calcite for Ca^{+2} and Mg^{+2} content in groundwater. Ca^{+2}+Mg^{+2} and Cl^- (m mol/l) plot confirm that ion exchange is the dominant process as Ca^{+2} and Mg^{+2} increase with increasing salinity, negative chloralkali indices in both the seasons further prove that ion exchange between Na^+ and K^+ in aquatic solution took place with Ca^{+2} and Mg^{+2} of host rock. The molar ratio of Ca^{+2}/Na^+ (0.60 to 0.90), Mg^{+2}/Na^+ (0.70 to 0.72) and Mg^{+2}/HCO_3^- (0.33 to 0.48) together with Na^++K^+/T_z^+ ratio (0.49 to 0.41) and (Ca^{+2}+Mg^{+2})/ T_z^+ ratio (0.51 to 0.60) suggest weathering of silicate rocks are responsible for major ion chemistry of groundwater in Wailpally watershed. The correlation coefficient and t test also prove that the groundwater has under gone substantial seasonal variations.

Methanethiol: A geochemical link between carbon and sulfur in hydrothermal systems?

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Current 'metabolism-first' models for a hydrothermal origin of life on Earth invoke abiotic formation of methanethiol (CH_3SH) as the crucial link between carbon and sulfur that may have led to primitive thioester-based (Acetyl-CoA) metabolism [1, 2]. However, the origin and distribution of CH_3SH in modern vent fluids has not been adequately constrained.

To evaluate this possibility, we conducted a survey of CH_3SH abundance in vent fluids from ultramafic (Rainbow, Lost City), basaltic (Lucky Strike, TAG, 9°N EPR) and sediment-hosted (Guaymas Basin) hydrothermal systems. These systems are characterized by a broad range of temperature, redox and sulfur fugacity. Highest levels of CH_3SH (15–16μM) were observed in Guaymas Basin fluids influenced by hydrothermal alteration of unconsolidated organic-rich sediment. Lowest levels (1.7nM) were observed in H_2-rich fluids at Lost City. A key finding is that CH_3SH concentrations in many high temperature (>300°C) fluids from H_2-poor basalt-hosted systems (3.98–20.1nM) were comparable to or greater than those in H_2-rich fluids at Rainbow (7.5–8.4nM). This observation strongly suggests that CH_3SH in vent fluids is not forming by CO_2 reduction as previously assumed [1,3], and is consistent with experimental evidence that CH_3SH formation from CO_2, H_2 and H_2S is kinetically inhibited under hydrothermal conditions.

Thermodynamic considerations suggest that the source of CH_3SH to many high-temperature fluids may instead be reaction of CH_4 with H_2S at reaction zone or upflow conditions. Unlike CO_2 reduction, CH_3SH formation by this mechanism is more favorable in higher temperature, more oxidizing fluids. Results of this study indicate that low temperature, high-pH reducing fluids emanating from serpentinite-hosted hydrothermal systems (such as Lost City) may not have been favorable for the production of critical 'prebiotic' carbon-sulfur compounds.

[1] Martin & Russell (2006) *Phil. Trans. R. Soc.* doi:10.1098/rstb.2006.1881 [2] Huber & Wächterhäuser (1997) *Science* **276**, 245-247. [3] Schulte & Rogers (2004) *Geochim. Cosmochim. Acta* **68**, 1087-1097.

Electrical conductivity associated with dissimilatory iron reduction: Do biofilms decrease resistivity?

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Dissimilatory iron reducing bacteria like *Shewanella* and *Geobacter* play an important role in the global iron cycle. However, the geochemical data necessary to calculate field scale rates of iron reduction are expensive and difficult to obtain. Recently, signals from electrical resistivity, induced polarization and self potential methods have been associated with zones of increased biogeochemical activity. We present data from batch experiments in the laboratory that suggest a geochemical reaction rate is obtainable by measuring changes in electrical conductivity. Geophysical and geochemical reaction rates were within 25% of each other. However, in some cases, the clear link between electrical conductivity and geochemical changes may be obscured by the presence of bacteria. Laboratory data from flow-through reactors reveal a 3 fold increase in electrical conductivity (0.02 S/m – 0.06 S/m) after 11 weeks that cannot be explained by changes in geochemistry. We model the electrical conductivity data using percolation theory to describe the presence and growth of an electrically conductive biofilm on mineral surfaces. Microbial biofilms must be between 5 and 75 times more conductive than the surrounding fluid to account for the measured increase in electrical conductivity. We also present preliminary data from electrochemical experiments that demonstrate a 3 order of magnitude increase in electrical conductance as biofilms form on graphite electrodes.

Mechanism and timing of Pb transport from subducted oceanic crust and sediment to the mantle source of arc lavas

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New high-precision (double-spike) Pb isotope analyses of lavas from the northern Tonga Arc are used to examine the source of Pb in these samples, and the relative timing of Pb addition from the subducting oceanic crust and subducting sediment. Lavas from the northern Tonga islands of Tafahi and Niuatoputapu have distinctive, radiogenic Pb isotope compositions, which are inherited from the basaltic crust of the subducting Louisville Seamount Chain on the Pacific Plate. The subducted oceanic plate and the overlying upper mantle beneath northern Tonga therefore have very different Pb isotope compositions, allowing the proportion of Pb derived from both of these sources, and from subducting sediment to be estimated for the first time. We show that between 42% and 90% of the Pb in northern Tonga lavas is derived from the subducting oceanic crust. The dominant process of transfer of mantle Pb to the crust at subduction zones is therefore dehydration of subducted oceanic crust. Oceanic crust is subducting at the northern end of the Tonga Trench at a rate of 0.24 m/y, and contains on average about 0.5 ppm Pb. Assuming that the magma production rate at the Tonga Arc is 0.13 x 10^6 kg/y/m, mass balance calculations show that the Pb flux from the subducting oceanic crust into the arc crust corresponds to complete Pb removal from the uppermost 114 to 244 m of the subducting oceanic crust, or up to 3.5% Pb removal from the entire 7 km thickness of oceanic crust. In the latter case, a 'subduction processing' signal would not easily be identified in the Pb/Nd ratio of the oceanic crust that is recycled into the deeper mantle.

The orientation of the Pb isotope arrays constrain the relative timing of Pb addition from these different sources, and show that sediment Pb must be mixed with the upper mantle before Pb from the subducted oceanic crust is added by fluids. Together with existing U-series and ^{10}Be data for Tonga-Kermadec lavas, this observation places strong constraints on the physical processes responsible for fluid-soluble element transfer from mantle to crust in subduction zones.

Corrosion and scaling in low-enthalphy geothermal systems in northern Germany

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Due to the increasing demand for sustainable, environmentally friendly energy the further development of geothermal techniques and the exploration of adequate reservoirs are essential. We aim to optimize the energy yield and evaluate the potential risks during well operation which requires a detailed process understanding of geochemical reactions. Especially, changes of the thermodynamic conditions in the course of fluid production and re-injection might result in potential corrosion or mineral precipitation (scaling) in the well-tubings or in the installations above ground, which would severely affect the planned long-term operation of the system.

Within the North German Basin, the GFZ maintains the geothermal research well doublet (*in situ* laboratory) Groß Schönebeck (Germany). Here, Lower Permian (Rotliegend) sandstones are encountered at a depth of approximately 4400 m that are saturated with a Ca-Na-Cl type formation fluid of high salinity (TDS = 265 g/l) at approximately 150°C and 500 MPa. The formation fluid of this low enthalpy geothermal system contains relevant concentrations of several compounds (Fe, Pb, Sr, Ba, SO_4, Si, Cu, Hg and As), which might be of importance for scaling and corrosion effects [1]. During well operation (start in 2009) changes in fluid pH-value, redox potential, and dissolved O_2 will be monitored *in situ* and the chemical composition of fluid samples will be analyzed in the lab. Due to the high temperature, pressure and salinity of the fluid the development of adequate techniques is one of the challenges within this study. Moreover, a simulation of the fluid-material interactions in dependence of the p-T path the fluid will take during extraction/re-injection will be devolped by geochemical and reactive transport simulation codes. Our overall goal is to transfer the results as obtained from Gross-Schönebeck to other locations considered for geothermal energy production. In this contribution, we will present an outline of the techniqus developed for geochemical in-situ monitoring campaigns as well as first data of formation fluid characterization.

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Methane efflux from marine sediments: Kinetic, microbial and bioenergetic controls

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Anaerobic oxidation of methane (AOM) is an efficient subsurface barrier for the methane produced globally in marine sediments. Its efficiency is a crucial control on global marine CH_4 fluxes to the ocean-atmosphere and, thus, on climate. This contribution reviews the different approaches that have been used to simulate the AOM reaction kinetics. The model types are organized according to their chemical and/or biological complexity, from the abiotic, encounter limited (or bimolecular) model, to the biomass-explicit thermodynamic-kinetic model. The role of intermediate energy substrates, the regulation of AOM rates by microbial growth and decay processes, and the possible thermodynamic limitation of AOM is then discussed. In addition to microbial and geochemical controls, the efficiency of the AOM barrier is also constrained by the magnitude of methane transport. Thus, using a similar reactive-transport framework but different AOM kinetics, predictions of AOM rates and methane release from the sea floor are compared for the typical environmental settings where AOM occurs. The performance of the kinetics models are also addressed under fully-transient conditions triggered by a variable fluid-flow regime.

Natural occurrences of liquid CO_2 emissions in the Okinawa Trough: Geological setting and variations of gas composition

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Three out of four sites known worldwide where liquid CO_2 is accumulated at – and/or emanating from - the seafloor, are located in the Okinawa Trough, South China Sea, west of Japan. All liquid CO_2 seep sites known so far are situated in Back-Arc hydrothermal systems in water depths between ~ 1200 and 1700 m. Recently, these occurrences have reached interest for applied marine environmental sciences as "natural laboratories" to evaluate the potential reactions of the marine system to deliberate storage of manmade liquefied CO_2 in the deep sea and deep-sea sediments, i.e., carbon capture and storage (CCS).

The expedition SO 196 of the German RV SONNE in March, 2008, visited two of these sites, the Hatoma Knoll and Yonaguni Knoll IV area, the latter being the working area of several of the presentations of this session.

We describe the geological setting of liquid CO_2 emissions in the Okinawa Trough. The condensed CO_2 is generated by complex phase separation processes of the hydrothermal fluids, with various additional components present, in particular CH_4 and H_2S. Data from Hatoma Knoll show distinct variations in gas composition at different vent sites on small spatial scale. We evaluate the phase transition and transport processes of the liquid CO_2-rich phase which may cause these variations, and emphasize the great potential as well as some caveats of the use of natural CO_2-emitting sites as analogues for future deliberate marine carbon storage scenarios.

Tl isotope constraints on the origin of the Earth's Pb paradox

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The Earth's Pb isotope systematics have been the subject of debate since Patterson's pioneering work provided the first accurate estimate of the age of the solar system [1]. A particularly contentious issue is the origin of the radiogenic $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ isotope ratios of the Earth's mantle. It is unlikely that this signature is solely due to the accretion of the Earth from volatile depleted matter. The radiogenic Pb isotope composition of the bulk silicate Earth (BSE) is thus thought to reflect U/Pb fractionations that occurred during the accretion, differentiation or chemical evolution of the Earth. Recent partitioning experiments that have investigated the behavior of Pb during metal/sulfide-silicate segregation at high pressures and temperatures have yielded conflicting results, however.

Lagos *et al*. [2] contend that Pb is not sufficiently siderophile and chalcophile to account for the high U/Pb ratio of the BSE. In this case, an alternative mechanism of Pb depletion is required and it has been suggested that this may involve degassing of Pb to a hot silicate atmosphere, which was subsequently lost during the giant impact. Such a scenario can be evaluated with the aid of the extinct ^{205}Pb-^{205}Tl decay system [3] in the context of current models of terrestrial accretion [4]. Studies of volcanic systems furthermore demonstrate that Tl is significantly more volatile during volcanic processes than Pb. Taken together, the data indicate that loss of Pb by degassing cannot have played a major role in establishing the U/Pb ratio of the BSE.

Other recent partitioning studies have shown that both Pb and Tl are moderately siderophile at high pressures and temperatures [5, 6]. Accretion models that apply such behavior can readily account for the Pb and Tl isotope systematics of the BSE, without requiring late volatile loss of Pb. At present, such as scenario thus provides the most reasonable solution to the terrestrial Pb paradox.

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Cristobalite nanofibers in volcanic ash from the ongoing explosive eruption at Chaitén Volcano, Chilean Patagonia

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The presence of cristobalite, one of the most toxic polymorphs of silica, has raised concern about adverse health effects of long-term exposure to volcanic ash [1, 2]. Although crystalline silica has been widely identified to cause silicosis and in some cases lung cancer, there is a lack of information on its mineralogical form and morphological variety at the nanoscale. In this study, we report nanoscale observations of the respirable fraction of ash from the ongoing explosive eruption of the Chaitén Volcano, Chilean Patagonia, showing that cristobalite occurs as nanofibers and nanowires.

Transmission electron microscopy (TEM) observations reveal that crystalline silica is abundant in the respirable fraction of ash, occurring as fibrous aggregates. Detailed TEM examination reveals that the aggregates are composed of (beta) cristobalite nanofibers, as confirmed by energy-dispersive spectrometry (EDS) and selected-area electron diffraction (SAED). The average lengths of the fibers are between ~5 µm and ~300 nm. The diameters of the nanofibers are uniform, on the order of tens of nanometers, with averages between ~20 and 50 nm. Nanofibers are usually associated with micrometer- to nanometer-scale fragments of amorphous silica glass.

The occurrence of beta cristobalite as nanofibers and nanowires raises new concerns about their toxicity because of the morphological resemblance to asbestos, known to induce progressive fibrotic disease of the lungs and potentially cancer. Therefore, more studies are needed for the better assessment of hazardous, mineralogical, and size-dependent effects associated with the short-term inhalation of nanofibrous silica during explosive eruptions and also long-term exposure in ash-covered areas.

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Surface complexation modeling of Pb(II) adsorption on mixtures of hydrous ferric oxide, kaolinite, and quartz

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Metal speciation is a primary control on metal mobility and bioavailability in the environment, and adsorption reactions can play a significant role in determining metal speciation. Pb is a common environmental contaminant due to its past and current industrial use, therefore, a better quantitative understanding of its interactions with common environmental sorbents should produce better predictions of Pb transport and mobility. Thermodynamic surface complexation models are commonly used to describe metal adsorption on single sorbents, but few tests of these models exist for mixed sorbents. In this study, Pb adsorption was measured as a function of pH, ionic strength (0.001 to 0.1 M $NaNO_3$) and sorbate/sorbent ratios (10^{-4} to 10^{-6} M Pb with 2 g/L solid) on hydrous ferric oxide, quartz and two varieties of kaolinite. Adsorption edges were measured by titrating 500 mL batch experiments from low to high pH, removing 10 mL aliquots at ~0.3 pH intervals. Aliquots were equilibrated for a further 24 hrs, centrifuged, and the pH of the supernatant remeasured. Pb sorbed was calculated by measuring supernatant concentrations by ICP OES with matrix-matched standards. A diffuse layer surface complexation model (DLM) was used with FITEQL to extract stability constants for the individual sorbent systems, testing a variety of reaction stoichiometries. Goodness-of-fit was assessed for best fit and median stability constants. For each sorbent, the stoichiometry yielding the statistically best fit for median stability constants was used in speciation calculations to predict Pb adsorption on binary and ternary mixtures of the three solids. Predictions are generally good, indicating that errors associated with DLM fits to individual sorbents are greater than uncertainties due to mineral-mineral interactions.

Sorption and diffusion of Np(V) in Opalinus clay

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Sorption and diffusion are the most important processes governing the migration behavior of ^{237}Np ($t_{1/2} = 2.1 \times 10^6$ a) and other long-lived radionuclides in the near and far fields of a high-level radioactive waste repository in an argillaceous host rock. Opalinus clay (OPA) from the Underground Research Laboratory in Mont Terri, Switzerland, was selected for studying the sorption and diffusion behavior of Np(V) in a natural clay.

The sorption of Np(V) on OPA was studied as a function of pH under ambient air ($p_{CO2} = 10^{-3.5}$ atm) and anaerobic ($p_{CO2} = 10^{-2.3}$ atm) conditions. The Np concentration was in the range of 9×10^{-12} to 8×10^{-6} M. The solid-to-liquid ratio was varied between 2-20 g/L. The sorption maximum for Np was at pH 8.5, i.e., 60% was sorbed under aerobic conditions and 90% under anaerobic conditions, respectively. The reduction of Np(V) to Np(IV) was found to be the reason for the stronger sorption of Np under anaerobic conditions. At pH > 8.5, the sorption of Np decreased with increasing pH due to complexation with carbonate in aqueous solution.

The diffusion of 8×10^{-6} M Np(V) in an OPA bore core with synthetic pore water (pH = 7.6) as mobile phase was studied under ambient air conditions. The direction of diffusion was perpendicular to bedding. The diffusion properties of the intact OPA were characterized by through- and out-diffusion experiments using HTO and $^{22}Na^+$ as tracers [1]. The diffusion of Np(V) in OPA was studied by the in-diffusion method [2] due to the strong sorption of Np(V) on OPA. The diffusion parameters for Np(V) in OPA are $D_e = (6.9 \pm 1.1) \times 10^{-12}$ m^2/s and $\alpha = 243 \pm 4$. Using the diffusion accessible porosity $\varepsilon = 0.15 \pm 0.01$ of HTO, the distribution ratio of Np(V) in intact OPA was calculated as $K_d = (0.10 \pm 0.01) \times 10^{-2}$ m^3/kg. The K_d measured under identical conditions with OPA powder suspended in pore water was equal to $(1.5 \pm 0.9) \times 10^{-2}$ m^3/kg.

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Hf and Th isotope considerations for the origin of continental basalts

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Enriched mantle (EM1 and EM2) sources are responsible for many Cenozoic intraplate basalts associated with the intermountain region of the southwestern U.S. Melt generation may be largely or entirely within the spinel stability field [1] and tap sources enriched by admixing with sediment [2]. New Hf isotope data for young, mostly magnesian basalts from enriched mantle domains in the western Great Basin and southwestern Utah range in ^{176}Hf/^{177}Hf from 0.282505 to 0.282956 (ε_{Hf} = -9.5 to +6.5) and scatter to >10 epsilon units above the OIB array at a given ε_{Nd}. ^{230}Th excesses in these basalts (updated from [3]) are variable in size, ranging from 1.5% to 33%. Apparent Lu/Hf and Sm/Nd fractionations reveal that (1) a garnet signature is present, reflecting melting in either the garnet stability field or of a source recently infiltrated with melts generated in the presence of garnet and (2) spinel peridotite contributes more to higher-degree partial melts. The large ^{230}Th excesses show that residual garnet is present during melting and this can be reconciled with inferred depths of melting only if eclogite and/or garnet pyroxenite are present at shallow depths in the mantle lithosphere. Lithologically heterogeneous source regions may also account for the complex relationship between inferred degrees of partial melting and the magnitudes of ^{230}Th excesses.

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Carbon dioxide regulated nutrient demand in marine diatoms

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Marine phytoplankton fix carbon and grow in alkaline seawater with the aid of CO_2 concentrating mechanisms (CCM), but an understanding of how the nutrient costs of phytoplankton CCMs are regulated by ambient CO2 is still emerging. This study examines the effects of CO_2 on macronutrient demand in marine diatoms and its ecological and geochemical consequences. Nitrogen and phosphorus quotas in marine diatoms were inversely related to pCO_2 over the range of 150 ppm to 380 ppm CO_2, but were relatively invariant from 380 ppm to 1500 ppm CO_2. Carbon quotas showed small and inconsistent variation with pCO_2, but the strong declines in N and P with increasing pCO_2 resulted in increasing C:N and C:P ratios with increasing pCO_2. A steeper decrease in P than N quotas with rising pCO_2 resulted in increasing N:P ratios at higher pCO_2.

The decline in diatom nutrient quotas as CO_2 increases from 150 to 380 ppm will result in greater diatom biomass and a greater proportion of larger sized diatom cells. Lower diatom nutrient demands could have provided a negative feedback against past increases in atmospheric CO_2 from glacial to post-industrial levels by supporting a higher diatom-driven oceanic carbon sink, but little nutrient relief of diatom growth is expected as CO_2 levels rise above 380 ppm over the next 50 to 100 years since increasing diatom N:P ratios will drive surface oceans to more severe N limitation.

Oxidation and transformation of nanoscale zero-valent iron in geochemically relevant waters

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Nanoscale zero-valent iron (NZVI) used for in situ groundwater remediation is highly reactive and oxidizes rapidly. To reduce aggregation, enhance mobility through the subsurface, and potentially target pollution zones polymer coatings are being applied to the NZVI surface. Although particles with engineered surface modifications are more mobile, they are up to 20 times less reactive than simmilar uncoated particles in ideal conditions. The reactivity and toxicity of NZVI in the subsurface depends on the extent of oxidation and the type of surface oxide or mineral phase that has formed on the particle surface. The interaction between NZVI and environmentally ubiquitous anions can potentially affect the extent of oxidation and the types of oxidation products that form.

NZVI particles, both bare and coated, were allowed to age in the presence of common groundwater anions, and excess dissolved oxygen, for various periods of time up to 6 months. X-ray absorption spectroscopy (XAS) was performed on the particles at Stanford Synchrotron Radiation Laboratory, beamline 10-2, at the Fe K-edge (7112). The resulting X-ray near edge structure (XANES) region of the spectra revealed the degree to which the anions had hindered NZVI oxidation. The extended X-ray absorption fine structure (EXAFS) region was fit using a library of Fe model compounds. A linear combination fitting technique, in conjunction with a principal component analysis, identified and quantified the mineral species that had formed. These results have implications regarding the reactivity, eventual fate, and potential toxicity of engineered iron nanoparticles.

Dynamics of non-organic contaminants in meso-scale mountainous catchments

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Fine-grained sediments transported by rivers usually show increasing concentrations of contaminants and nutrients downstream, and there is thus an increasing awareness of the importance of non point-source pollution in fluvial systems. In mountainous basins, understanding the dynamics of the transport of sediment-related contaminants is necessary in order to select the optimum monitoring programme of the surface water quality.

This contribution reports some results of a case study located in a mountainous rural meso-scale catchment, with an area of 295 km^2, located in NE Portugal (the trans-boundary Douro river basin). The bedrock is composed of crystalline rocks; the land use is mainly forest and agriculture, with scattered urban settlements. The data discussed relate to the contents of selected metals in the fluvial sediments, which were sampled in two different periods of the hydrological year (high and low flow); the <63µm fraction was analysed to assess the potentially bioavailable elements. The established spatial trends are: a) Cu, Zn, Pb, Co and Mn are at anomalous levels in the samples from stations draining upstream agricultural areas; b) Cd occurs mainly in samples from stations draining areas with high urban pressure, where small agricultural fields intermix; c) Cu, Zn and Pb values reveal a general slight increase in these zones; d) As, Cr, Ni, and Fe present higher contents in the southern part of the basin, influenced by geological settings. A considerable proportion of these elements contents is found in the more labile fractions, which illustrate the important anthropogenic influence. Regarding bioavailability, the elements can be ordered by relative mobility: Cd>As>Co>Mn>Pb>Cu>Zn> Cr>Fe>Ni. The inter-site sampling variation of the relative contents of the metals is a response to the combination of geomorphology, rainfall events, use of river water for irrigation in summer time, and the consequent effect on streamflow regime at sampling site scale. The hydrodynamic regime controls the deposited sediment grain size, which in turns controls the distribution of mineral assemblages and metals associated with them.

Geochemistry of the Vila Nova granitic pluton (Central Portugal)

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The Vila Nova pluton is a small granitic pluton which occurs close to the contact between two major tectonoestratigraphic zones of the Iberian Massive, the Ossa-Morena Zone (OMZ) and the Central Iberian Zone (CIZ). The pluton intruded phyllites and metagraywackes of the Neoproterozoic-cambrian Beiras Group, which belong to the CIZ and originated a contact metamorphic aureole formed by micaschist with porphyroblasts in the outer zone and hornfelds in the inner zone. The pluton is affected by several minor shear zones and faults. The granitoid rock contains several small enclaves of surmicaceous composition which are enriched in andaluzite. It is a medium- to fine-grained rock and shows variable composition from tonalite to granite. The granitoid rock contains quartz, perthitic microcline, plagioclase, muscovite, biotite, apatite, zircon, monazite, rutile, pyrrhotite, ilmenite, pyrite and tourmaline. The alteration minerals are chlorite and muscovite. The textures are mainly magmatic except were the granite is affected by shear and the post-crystallization deformation originates kink-bands in the micas and in the plagioclase, mica-fish textures, very fine polygonal granoblastic texture in quartz, lamellas and deformation bands in quartz and K-feldspar.

The granitoid is enriched in muscovite (up to 12%), and its ACNK ranges from 1.31 to 1.69 so it can be classified as an S-type granite. It is also classified as a magnesian, calc-alkaline to alkaline-calcic granite. The ORG normalized pattern is crust-dominated with positive Rb, Th, Ce, Sm anomalies and its normalized primordial mantle pattern shows positive anomalies for K, U, Th and negative anomalies for Ba, Ta, Nb, Sr and Ti, characteristic of granites related to subduction.

The variation diagrams show regular trends with a decrease in TiO_2, Al_2O_3, FeO, MgO, Ba, Sc, V, Cr, Ni, Nb, Zr, Hf and □REE with the increase in SiO_2, while K_2O, Rb show segmented trends and CaO, Sr and Cs don't show any trend, which can be due to the hydrothermal alteration.

The REE patterns show a moderate negative Eu anomaly (0.47-0.77), a moderate fractionation of REE (La/Lu_N =7.04-9.65) and ΣREE varies from 126.84 to 179.61 ppm.

Does magma degassing affect rhenium contents of MORB?

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There is growing evidence that Re behaves as a moderately volatile element during subaerial and shallow marine eruptions, thus explaining the low Re contents of many OIB (e.g.[1]). However, the possibility that Re loss during magma degassing may also affect Re contents of MORB has received little consideration. Nearly all MORB magmas have experienced substantial volatile element loss (>80% for CO_2, the main volatile species in MORB [2]), suggesting that this process might be important. To investigate this possibility we determined the Re contents of 20 MORB glasses from the Southeast Indian Ridge (SEIR), previously investigated for major and trace element contents, isotopic compositions, and volatile element systematics [3, 4, 5]. A strong negative correlation exists between ln[^{40}Ar*] and ln(^{4}He/^{40}Ar*) among these samples [5], coherent with the expected results of variable degrees of solubility-controlled fractional degassing. (^{40}Ar* indicates ^{40}Ar corrected for atmospheric contamination).

Re contents of the SEIR samples (mean = 0.68 ±0.29 ppb, 2σ) are lower than those of most MORB. A negative correlation exists between [Re] and Mg# (R^2=0.49) indicating that fractionation is one of the main factors controlling Re concentrations. To minimize this effect, Re concentrations were normalized to those of Sm. A rough negative correlation (R^2=0.39) exists between ln(Re/Sm) and ln(^{4}He/^{40}Ar*), with the most degassed lavas (highest ^{4}He/^{40}Ar*) having the lowest Re/Sm ratios. Ln(Re/Sm) and ln(Ar*/CO_2) are positively correlated (R^2=0.37), which is also consistent with the expected consequences of degassing. These results must be interpreted with caution, given the weakness of the correlations and the possibility of source variations. Nevertheless, they suggest that degassing may have a significant effect on the Re contents of MORB magmas, and thus on estimates of Re partition coefficients during partial melting. They may also imply that magma degassing provides a non-negligible flux of Re to the oceans.

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The distribution of gold in biogenic and abiogenic carbonates

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Soil carbonates are important sampling media for geochemical Au exploration in the semi-arid and arid regions of Australia, because they are widespread, easy to sample and Ca shows a strong positive correlation with Au, but not with other metals in carbonates overlying buried Au mineralisation [1]. This suggests a unique mechanism of co-precipitation of Au with Ca during carbonatogenesis. Co-precipitation is biomediated through the activity of ureolytic bacteria and other microorganisms resident in these soils, and is not the result of purely abiotic processes [2]. However, at resolutions possible with LA-ICP-MS (>20 μm^2), Au was homogenously distributed in biogenic carbonates precipitated in the laboratory [2], in contrast to soil carbonates, in which Au displays a reduced nugget effect, but not a homogeneous distribution [1].

Synchrotron-based µXRF-mapping (at ~150 nm^2 resolution) was used to assess the fine distribution of Au, Ca and other metals in biogenically- and abiogenically precipitated carbonates containing ppm-levels of Au. In Ca-carbonates, precipitated by ureolytic bacteria enriched from calcareus Australian soils, the distribution Au was not uniform and differed from base metal distribution, thus mimicking the decoupling between these metals observed in field samples. In contrast, in abiogenically precipitated Ca-carbonates (produced by raising the pH or the concentration of CO_2^{3-} in solution) the Au distribution was homogenous and decoupling of Au and Ca from other base metals was not apparent. In conclusion, this study confirmes the importance of biomineralisation for the formation of Au anomalous carbonates in Australia.

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Multi-isotope investigation to identify general characteristics of different cold vent systems

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Pore waters from diverse cold vent systems of different geological regimes such as the Black Sea, the Nile Delta, the Gulf of Cadiz, and off Costa Rica were investigated with respect to their stable oxygen, hydrogen, chlorine, and radiogenic strontium isotopic as well as their chemical composition.

The fluids of cold vent systems may carry valuable information about the source strata and temperature, the diagenetic evolution, and the contribution of brine and gas hydrate. To unravel the mélange of information combined in the pore fluid it is essential to apply geochemical isotope and/or element correlations that indicate clear trends. Such a correlation is given by the $\delta^{18}O$ versus Na/Cl ratio, which combines information on mineral hydration and dehydration processes (light/heavy $\delta^{18}O$) and interaction with relictic brines or dissolution of evaporites. An important process of mineral dehydration is the smectite to illite transformation, which can be tracked by decreasing chlorine isotope and concentration values and a negative correlation of $\delta^{18}O$ versus $\delta^{2}H$ values. The most intense mineral dissolution and transformation processes are observed at the Nile Delta sites and some of the Black Sea and Gulf of Cadiz sites. In addition, $^{87}Sr/^{86}Sr$ ratios and Sr concentrations provide valuable information on the primary source of the fluid and its secondary diagenetic overprinting by alteration of crustal rocks and sediments in general.

Since the information from cold seep fluids is manifold, it is essential to evaluate different isotopic proxies to decipher the specific characteristics of a cold vent system. We will present systematic compilations of isotope data from locations covering a variety of different geological and tectonic settings and discuss the underlying trends and processes in detail.

Aerosol indirect effects from satellite: Skeptics vs. optimists

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The skeptics argue that satellite observations alone will not produce progress in understanding aerosol-cloud processes. Cloud condensation nuclei (CCN) are too small to be resolved from remote sensing. Chemical composition cannot be determined. Local updraft velocities in the cloud are not measured from space. Furthermore, aerosol retrievals in the vicinity of clouds are rife with problems. Finally, all those studies showing varying cloud properties as a function of aerosol optical depth are inherently limited – merely suggestive. From the most skeptical viewpoint, why bother?

On the other hand, the optimists show robust relationships between aerosol and cloud variables. These satellite studies have brought new understanding to aerosol-cloud interaction from the ship track images, through the relationships between cloud microphysics and aerosol optical depth, to opening our eyes to the broad implications of aerosol relationships with cloud fraction. Satellites offer a broad view of cloud and aerosol fields, and are exceedingly helpful in developing a conceptual understanding of how aerosols can affect clouds on regional to global scales. From the optimistic viewpoint, how can we ignore these data?

The key to using satellite data to answer scientific questions about cloud aerosol interaction requires a clear understanding of both the skeptical and optimistic viewpoints. Use the data. Know the limitations, and never forget the integral role of in situ data and models in interpreting the satellite observations, and establishing causality.

NanoSIMS imaging of insoluble organic matter in ordinary chondrites: Comparison with carbonaceous chondrites

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The insoluble organic matter (IOM) is known to be enriched in deuterium in carbonaceous chondrites (CC) and ordinary chondrites (OC) [1]. Moreover, the isotopic composition of the IOM in CI and CM chondrites is heterogeneous at the molecular scale [2] and the micron scale [3]. In Orgueil IOM, the occurrence of D-rich hot spots is related to the heterogeneous distribution of organic radicals caracterised by a D/H ratio of 1.5% [4]. The D-isotopic enrichment is related to ion-molecule like reactions - taking place in the outer areas of the protosolar nebula or the interestellar space - that have affected the IOM before accretion on the parent body. The isotopic variations of IOMs in various types of chondrites are complex and have been related to parent body processes [1], if we assume a comon precursor to the IOM in all the parent bodies. However, this hypothesis seems inconsistent with in situ imaging of organic matter in the matrices of carbonaceous chondrites, which reveals that it exists at least two kinds of organic matter [5].

We have performed NanoSIMS imaging of stable isotopes of C, N and H in the IOM of Murchison (CM), Semarkona (LL3) and Bishunpur (L3.1). Despites higher bulk D and ^{15}N contents, we do not observe any spatially resolved ^{15}N or D isotopic anomaly in the IOM of the two OC studied, in contrast to Murchison IOM. In addition, some ^{13}C anomalies are observed and are likely related to the occurrence of presolar silicon carbide. The lack of D-rich hot spots might be related to a lack in organic radicals. This could be the result of heating on the parent body (even if it is moderate for the two studied OC, less than 250ºC) or the lack of organic particles rich in radicals during the accretion of the parent bodies. As heating of Murchison IOM induces not only a destruction of D-rich hot spots but also a decrease of the bulk D/H, the later hypothesis appears more likely, ruling out the common precursor hypothesis.

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Olivine-rich troctolites from the Internal Liguride ophiolites (Northern Apennine, Italy)

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The Internal Liguride ophiolites represent an intra-oceanic domain of the Middle to Late Jurassic Ligure-Piemontese basin. The gabbroic plutons of these ophiolites consist mostly of coarse-grained gabbros to olivine-gabbros and contain, at different stratigraphic levels, sill-like lenses of olivine-rich troctolites.

The olivine-rich troctolites are mainly composed of rounded to polygonal olivine (70-90 vol%, Fo88-85), anhedral plagioclase, minor poikilitic clinopyroxene (Mg# 90-86) and accessory spinel (Cr# 54-46). Accessory Cr- and Ti-rich amphibole is locally present, as rim around spinel and as inclusion within spinel. Other silicate inclusions in spinel are Cr- and Ti-rich (Na-)phlogopite, and Al-poor orthopyroxene. The compositions of silicate inclusions in spinel document the involvement of melts rich in H_2O, alkalies and SiO_2.

Locally, the olivine-rich troctolites are associated with centimetre-scale layers that vary modally from troctolite to anorthosite and chromitite, and contain gabbroic dykelets with fuzzy contacts. In addition, one of the studied olivine-rich troctolite lenses shows a metre-scale layer displaying a "harrisite" pegmatoid texture, in which huge skeletal olivines (up to 30 cm) are intergrown with plagioclase [1].

The olivine-rich troctolites from the Internal Liguride ophiolites bear textural and compositional similarities to the olivine-rich troctolites from modern oceanic core complexes in slow and ultraslow spreading ridges. We show that the olivine-rich troctolites of the present study are not cumulates that developed under closed system conditions. Their formation most likely requires a complex interplay of petrogenetic processes.

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Argon isotope anomalies in lavas

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A common assumption in K-Ar and $^{40}Ar/^{39}Ar$ geochronology applied to volcanic rocks is that they equilibrate isotopically with atmospheric Ar. Several early studies [1, 2] suggested occasional violations of this assumption. Further work [3-5] on historic Japanese and Hawaiian lavas revealed common departures from atmospheric values, typically involving correlated subatmospheric $^{40}Ar/^{36}Ar$ and $^{38}Ar/^{36}Ar$ with some scatter towards supra-atmospheric $^{40}Ar/^{36}Ar$. This work, along with new data recently reported by us [6, 7], indicate that non-atmospheric initial Ar isotope ratios are common in volcanic rocks, and reflect two partially competing mechanisms: 1) retention of mantle and/or crustally derived ^{40}Ar-rich Ar; and 2) incomplete isotopic equilibration with atmospheric Ar inducing correlated $^{40}Ar/^{36}Ar$ and $^{38}Ar/^{36}Ar$ due to kinetic fractionation (KF) [8]. Samples dominated by KF tend to be isotopically light, suggesting a net flux of Ar from atmosphere into the melt or lava. Supra-atmospheric $^{40}Ar/^{36}Ar$ and $^{38}Ar/^{36}Ar$ values on the KF trend occur in some natural samples with high ^{36}Ar concentrations, and can be induced in some laboratory heating/quenching experiments. The most fractionated Ar isotopes observed are in obsidians, for which we measure $^{40}Ar/^{36}Ar$ and $^{38}Ar/^{36}Ar$ as low as –10% and –4% (respectively) relative to atmospheric Ar [9]. Field and laboratory experiments are underway to further clarify the scope and mechanisms of initial Ar isotope variations in volcanic rocks. Meanwhile, the assumption of initially isotopically atmospheric Ar in low-radiogenic samples should be evaluated e.g. by analyzing $^{38}Ar/^{36}Ar$ in unirradiated and unspiked (with ^{38}Ar) aliquots.

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Impact of urban stormwater on sediment quality in an enclosed bay of the Lule River, northern Sweden

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Sediment samples and porewater of an enclosed bay (*Skutviken*) affected by stormwater discharge near the centre of Luleå, northern Sweden, were analyzed for major and trace elements and 16 polycyclic aromatic hydrocarbons (PAHs), and compared to a reference site and local till. Among the studied metals, Cd, Cu, Pb and Zn were enriched at *Skutviken*. The use of trace metal ratios provided indications of pollutant sources for the sediment. Also, the PAH content was enriched, in particular for phenantrene, anthracene, fluoranthene and pyrene, which are regarded as common constituents in stormwater. Pb-210 dating was used to determine historical changes in metal and PAH fixation in the sediment. The bay *Skutviken* was enclosed by the construction of a road bank in 1962. The enclosure led to reduced water circulation in the bay, which promoted the occurrence of anoxic conditions with sulphate reduction within the bay. As a consequence of these conditions, metals are trapped in the sediments as sulphides.

This study suggests that enclosed bays with restricted water circulation may be efficient traps for urban pollutants. In areas with postglacial rebound, where such bays are common, enclosure may have an important impact on water and sediment qualities.

Due to the postglacial uplift, presently water covered sediments may rise above the groundwater level in the future. These sediments may then become a secondary pollution source if metal sulphides are oxidized.

U-Th-Pa-Ra constraints on mantle wedge metasomatism and melting beneath Volcán Llaima

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Volcán Llaima, Chile is one of the most active volcanoes in South America. Since 1640, six major effusive eruptions have produced basaltic to basaltic andesitic (~51-55 wt% SiO_2) lavas. Trace element signatures of these magmas show little evidence for crustal contamination and point toward a relatively homogenous and depleted mantle source. This provides an ideal case to constrain slab-derived mantle metasomatic and melting processes beneath arc volcanoes on the basis of U-series systematics.

Llaima magmas display ^{226}Ra and ^{238}U excesses that fall on the "slab fluid contribution" end of the regional ^{238}U/^{230}Th vs. ^{226}Ra /^{230}Th trend defined by Sigmarsson *et al*. [1]. Yet Llaima samples show no correlation between these two activity ratios, and only ^{238}U excesses correlate with Ba/Th. This suggests that although the overall extent of ^{226}Ra excesses may be imprinted by addition of slab-derived fluid, a second order process is likely to affect ^{226}Ra-^{230}Th disequilibrium. The samples display ubiquitous but variable ^{231}Pa excesses that are distinctly higher than the values predicted by the coupled ^{231}Pa-^{235}U vs. subduction rate model of Huang and Lundstrom [2]. The measured variability in (^{231}Pa/^{235}U) excess also indicates that the mechanism controlling ^{231}Pa excesses can produce significant variations beneath a single volcano on short time scales. A striking feature of our data is the positive correlation between (^{231}Pa/^{235}U), (^{238}U/^{230}Th), Ba/Th and Ce/Th. This suggests a link between mantle wedge enrichment and melting processes, however the positive correlation between ^{231}Pa-^{235}U and ^{238}U-^{230}Th systems precludes a direct relationship between the amount of slab fluid and degree (and rate) of partial melting and requires a more complex scenario.

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Multiple sulfur isotope measurements from the 2.4 Ga old Seidorechka Formation

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Mass independent fractionated (MIF) sulfur isotope data in Archean and earliest Paleoproterozoic rocks are considered to provide evidence for an anoxic atmosphere [1, 2]. The disappearence of large magnitude MIF is thought to occur between 2.32 and 2.47 [3, 4]. The ca. 2.4 Ga old Seidorechka Sedimentary Formation within the Imadra Varzuga Greenstone Belt may thus capture the oxygenation of Earth's surface environments. In this study 42 siliciclastic and carbonate samples were collected from outcrops or selected from the FAR DEEP drillcore. All were analyzed for δ^{34}S and half were selected for Δ^{33}S and Δ^{36}S measurement.

Both the drillcore and outcrop samples reveal comparable temporal variations in δ^{34}S, but the lower part of the drillcore appears condensed or partly eroded. δ^{34}S ranges between +3.3 and -15.1‰ with distinct temporal variations. These variations coincide with a change in lithology from siliciclastic to carbonate facies preserved in the drillcore. In the outcrop no stratigraphic trend is discernible.

Δ^{33}S measurements display variations between -0.47 to +0.06‰ with only two measurements yielding a positive Δ^{33}S value. A Δ^{36}S/Δ^{33}S crossplot for all samples displays a slope of -1.1, which is characteristic for Archean sediments. However, temporal variations in Δ^{33}S are discernible.

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Sr-poor Nyerereite and Gregoryite in ashes from Oldoinyo Lengai (Tanzania)

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Two distinct populations of both nyererite and gregoryite are found in mixed carbonatite-silicate ashes from the explosive September 2007 eruption. Na, K and Ca contents measured in both populations are in agreement with previously published data [1, 2], whereas the two populations differ significantly in their Sr content. The Sr-rich variety of both minerals is common to the lavas erupted in the period of 1992 to 2000 [2]. The Sr-poor one, however, is unique to the early ashes of the 2007 explosive event.

Gregoryite occurs as well-rounded crystals identical to that descibed by [1, 2]. Crystal shapes for nyererite varies from the typical lath shape to well-rounded crystals resembling gregoryite. The different crystal shapes are independent of the mineral compositions.

During effusive activity prior to the September 2007 eruption a significant volume of natrocarbonatitic magma was stored in small interconnected magma reservoirs at shallow depth below the crater floor [3]. As shown by crystallization experiments at atmospheric pressure elemental diffusion is very rapid in natrocarbonatitic magmas. Thus, the shallow storage provides sufficient time for reequilibration of phenocryst phases. This may explain the rather restricted variation of Sr in the main phenocryst phases of the lava flows [1, 2].

The origin of the Sr-poor mineral varieties is unclear. One possible explanation may be that it crystallized in a deeper-seated natrocarbonatitic magma which was rapidly pushed to the surface and erupted simultaneously with the shallow carbonatites and the nephelinitic magma.

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Monitoring $\delta^{13}C$ of TCE to evaluate microbial degradation in a fractured sedimentary rock aquifer, New Jersey, USA

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Chlorinated solvents, such as trichloroethene (TCE) are common contaminants of groundwater in industrial and urban settings. In order to investigate the fate and transport of these contaminants, it is important to evaluate the physical, chemical, and biological processes that effect changes in the concentration of these compounds. Microbial degradation can alter the isotopic ratio ($^{13}C/^{12}C$) of carbon in TCE, whereas, the isotopic ratio remains nearly constant for other processes, such as adsorption, dispersion and diffusion. Different microorganisms yield different kinetic isotopic fractionation factors (α); consequently, field evaluation of α is essential in evaluating the impact of microbial degradation. Monitoring of the concentration and isotopic ratio ($^{13}C/^{12}C$) of TCE in groundwater at a low-permeability borehole provided an in situ estimate of α =0.99345. The borehole acted as a batch reactor where there was little inflow or outflow because of the local low permeability in the rock. At other boreholes completed in more permeable sections of the same aquifer, deviations from the value of α estimated in the low-permeability zones indicates other hydrogeochemical processes are occurring. For example, estimates of α at other boreholes indicated the addition of un-degraded, free-phase TCE in the aquifer.

The original amount of TCE present in the aquifer, prior to microbial degradation, was estimated from the Raleigh equation using the established kinetic fractionation factor. Additionally, rates of natural bioremediation can be estimated. In areas of sparse sampling and complex subsurface geology, such as fractured-rock aquifers, this information is extremely useful in the characterization of TCE contamination.

How iron and arsenic reduction pathways in metal-reducing bacteria influence arsenic fate and transport

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A global health crisis has emerged due to the consumption of drinking water derived from arsenic contaminated aquifers. Iron(III) and arsenate reducing bacteria are implicated in processes that cause arsenic mobilization in aquifers sediments enriched in arsenic. Under oxic conditions arsenate predominates and is often adsorbed onto mineral surfaces such as amorphous iron oxide. However, under anoxic conditions metal-reducing bacteria can respire both iron(III) and arsenate, generating iron(II) and arsenite. It is unclear which pathway has the greater influence on the release of arsenic. To address the problem, genetic and geochemical approaches are being used to identify which metal reduction pathway has the greater influence over arsenic fate and transport. Using a model iron and arsenate-reducer, *Shewanella* sp. strain ANA-3, strains deficient in iron or arsenic reduction were generated and tested for their abilities to alter arsenic fate and transport within batch and hydrodynamic conditions. We inoculated various *Shewanella* iron and arsenate reduction deficient strains into anaerobic bottles with slurries of ferrihydrite. Iron(II) and dissolved and adsorbed arsenate and arsenite were monitored over time. Our results showed that the arsenate reduction mutant (ARM) did not reduce solid phase arsenate even though it could still reduce iron. The iron-reduction mutant (FERM) could reduced arsenate to arsenite similarly to the wildtype strain and did not reduce iron even after extended incubation (144 hours). We also investigated arsenic transport by quantifying arsenic mobilization using flow through columns containing arsenate and iron oxide coated sands inoculated with either FERM or ARM strains. These results showed that arsenate and iron(III) reduction occur independently, and that arsenate reduction is the dominant process controlling arsenic release. Currently we are using molecular techniques to determine whether the arsenate and iron genes are differentially expressed when cultures of ANA-3 are amended with iron and arsenate.

Calcium isotope fractionation in cave-analogue conditions

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Speleothems are proving to be fundamental archives for high resolution palaeoclimate studies, but quantitative understanding of their geochemistry in relationship to climate variables is still rather poor. Laboratory and marine studies of Ca isotopes suggest that speleothem $\delta^{44/42}$Ca may act as a proxy for past cave temperature and/or the amount of prior-calcite-precipitation (PCP), but no systematic study of speleothem Ca isotope fractionation has yet been performed.

We have measured the $\delta^{44/42}$Ca of laboratory-precipitated calcite, grown in an experimental setup designed to closely replicate speleothem precipitation. Calcium solutions with a constant saturation index of 0.34 were dripped onto calcite-seeded glass plates, at tightly-controlled temperatures. There is no significant difference in the $\delta^{44/42}$Ca offset between precipitates and initial solutions at four different temperatures (7–35ºC; ANOVA, p=0.94) and three drip rates (0.18–1.22 ml/min; ANOVA, p=0.49), with a mean precipitate-solution difference of $\delta^{44/42}$Ca = -0.82 ±0.11‰. Our results provide insight into the fractionation of Ca isotopes during carbonate growth. The absence of any temperature or growth-rate influence on $\delta^{44/42}$Ca suggests that, in the natural setting, $\delta^{44/42}$Ca will be controlled predominantly by PCP. This may provide a proxy specific to this one environmental factor, and serve as a powerful tool to correct other proxies for PCP. Continuing work will extend this study to carbonates grown on glass plates directly in the cave setting.

Understanding the global marine δ^{30}Si distribution

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The silicon isotopic composition of opal sediments can be used as a proxy for past Si utilization, and hence paleo-productivity given constant upwelling rates. Interpretation of this Si utilization proxy is limited by our understanding of the present marine Si isotope distribution (which is being addressed within the GEOTRACES program), and the effect of hydrographic changes on this distribution. Observations show significant Si isotopic variations (expressed as δ^{30}Si) of silicic acid between deep-water masses (>0.3‰). However, no variations (<0.1‰) should be expected following a GCM model of the marine Si cycle [1], or by comparison to the observed δ^{15}N distribution [2].

Although the quality and reproducibility of the δ^{30}Si values have been questioned, intercalibration exercises have confirmed the precision and accuracy between laboratories and measurement techniques [3]. We thus have to question current estimates of Si fluxes and the modeling of the Si cycle.

The apparent conflict between observations and model results have been investigated using simplifed multi-box models of the global oceans (e.g. Pandora). These simple box models for the Si cycle can predict the observed 0.3‰ difference between Atlantic and Pacific deepwater δ^{30}Si values, using published estimates of regional opal export fluxes. Thus, the δ^{30}Si distribution is in agreement with existing estimates of the marine Si fluxes. Futhermore, the sensitivity of the δ^{30}Si distribution to changes in the Si cycles has be explored to estimate likely changes that may occur over glacial-interglacial cycles.

The δ^{30}Si difference between deepwaters results from (1) a high δ^{30}Si of dissolved Si subducted in the North Atlantic and (2) the dissolution of opal with low δ^{30}Si values in the deep-waters around the Southern Ocean which feeds into the Pacific. Contrasting deep-water δ^{30}Si values are not strongly affected by increasing meridional overturning circulation, unlike δ^{13}C. The marine δ^{30}Si distribution is distinct from δ^{13}C and δ^{15}N because Si behaves differently between the high latitudes of the North and Southern Hemispheres.

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The relationship between quartz diorite and granite: An example from the Uromieh-dokhtar magmatic belt

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Uromieh-dokhtar magmatic belt is one of the major granitic provinces in the Iran and has long attracted the interest of Iranian geologists. It lies along the tectonic boundary between the Sanandaj-Sirjan (metamorphic belt) and the micro-continental of Central Iran. The NW Saveh intrusions are a part of this belt and consist of three main intrusive rock types including hornblende- and pyroxene-bearing quartz diorite, hornblende- and pyroxene-bearing granodiorite and hornblende granite. They are vary in silica contents between 46 and 72%, and are metaluminous. Excepting Na_2O the major element oxides vs. SiO_2 diagrams display linear trends. SiO_2 vs K_2O [1] and SiO_2 vs Na_2O+K_2O [2] diagrams suggest that the bulk of the samples plot in the calc-alkaline field. The ASI (Aluminium Saturation Index, molar Al_2O_3/ Na_2O+K_2O+CaO) for all samples is <1, and molar Al_2O_3/Na_2O+K_2O is higher than one, indicating that they are metaluminous I-type granitoids. The low normative corundum values (<1.6%) are consistent with I-type granitoids. On Harker variation diagrams, Sr and Ga show linear descending trends versus SiO_2, whereas Zr, La and Ce increase with the SiO_2 increasment. However, Sr and Ba show a good correlation in the granites whereas an opposite trend occurs in the quartz diorite. In most of the variation diagrams, the granite lie along or close to the trends defined by quartz diorite rocks and commensurate with fractional crystallization. The NW Saveh intrusions plot in the volcanic arc granite field in both the Rb vs Y+Nb and Nb vs Y discrimination diagrams of Pearce *et al.,* [4]. They behave homogeneously on the chondrite normalized REE plots, with La_N/Yb_N = 5, fairly flat HREE from Dy to Lu, and negative Eu anomalies. Base on major and trace element signatures, they are typical of calc-alkaline series developed at active continental margins by partial melting from metasomatised mantle wedge.

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Gypsum precipitation kinetics in Dead Sea brine - seawater mixtures

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Experimental work and thermodynamic calculations show that mixing sulfate-rich seawater (SW) with calcium-rich Dead-Sea brine (DSB) results in supersaturation with respect to gypsum. In order to determine the relevant kinetic parameters for nucleation and crystal-growth, batch experiments were conducted with and without crystallization seeds, respectively, using various ratios of DSB-SW.

In the nucleation experiments, the induction time (the time elapsed before the detection of a new phase) varied dramatically from merely several days to more than 100 days. A U-shaped dependency curve of the induction time on Dead-Sea fraction (DSF) was observed, with a minimum at DSF of 85-88% (fastest nucleation kinetics). In the crystal growth experiments, the rate was found to be controlled by two concurrent mechanisms. The first, which dominates the overall rate under far-from-equilibrium conditions, shows a 15th order dependency with respect to ($DSG^{1/2}$-1), where DSG is the degree of saturation with respect to gypsum. The second mechanism, which dominates the growth rate under close-to-equilibrium conditions, has a 2nd order dependency on ($DSG^{1/2}$-1). Accordingly, the overall growth rate (mol s^{-1}) is described by the following equation:

$$Rate=[k_1(DSG^{1/2}-1)^2 + k_2(DSG^{1/2}-1)^{15}]m$$

where k_1 and k_2 are kinetic constants (mol s^{-1} g^{-1}) and m is the mass of crystallization seeds (g).

A U-shaped dependency curve of k_1 and k_2 on DSF was found, with a minimum (i.e. slowest growth rate) at DSF of 85%, exactly oppositely to nucleation rates. Previous studies suggested that adsorption of cations onto gypsum retards the precipitation kinetics. Since the concentrations of all cations change monotonically with DSF, this inhibitory mechanism cannot solely explain a U-shaped behavior. However, electrical conductivity measurements (EC) indicate that when DSB is slightly diluted by the addition of SW, EC increases, suggesting that the increase in the concentration of free ions, due to the break-down of ion pairs/complexes, is greater than the decrease in concentration due to dilution. Upon further dilution, the EC decreases, resulting in an overall U-shaped behavior of EC vs. DSF. Therefore, we suggest that k_1 and k_2 are controlled by an adsorption inhibitory mechanism which depends on the concentration of free ions.

Restoration of *in situ* leached uranium mines with iron nanoparticles

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In situ leaching (ISL) provides a method of extracting uranium from the subsurface without direct excavation or perturbation. Following ore removal at an ISL site, environmental responsibility lies with subsequent restoration of the groundwater system. The experiments outlined in the current study were driven by the possibility of injecting metallic iron nanoparticles into the ore zone with the purpose of (i) immobilising residual soluble uranium (VI) as insoluble uranium (IV) oxide and (ii) restoration of anoxic conditions within the subsurface. The study also explores the possibility of persistent inflow of oxygen into the ore zone or change in the redox conditions of the geological zone,

Solutions highly concentrated in uranium (1000 ppm) with an initial pH ranging from 3 to 7 were studied in presence of zero valent iron nanoparticles under mildly oxic conditions (1.2 % O_2 and 0.0017 % CO_2) to simulate the oxidizing conditions of a exhausted uranium mine.

Characterisation of both solid and solution phases indicated that at 4 hours period of reaction the Eh stabilized at values ranging from -0.1 to -0.4 V. The addition of iron nanoparticles triggered the reductive precipitation of UO_2, which was demonstrated to be the main process responsible for the removal of uranium from solution at reaction times between 1 to 4 hours [1,2] .

The reoxidation of uranite precipitated on the nanoparticle surface was studied at mildly acidic and at neutral-basic conditions to account for the possible disruption of the reducing conditions in the geological zone. Despite thermodynamic modelling calculations of the studied system using NEA-TDB [3] indicate $UO_3.2H_2O$ as the only uranium solid phase for $4 < pH < 9$, the experimental results indicated that a Fe-uranyl phase with becquerelite-like crystalline structure stabilized at neutral basic pH [4].

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Lithogeochemistry and stable isotopic geology (C,S,O) of the Cristalino Cu(Au) Deposit, an archean IOCG-type, Carajás Province, Pará, Brazil

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Lithogeochemistry and stable isotopic data from country rocks and sulfide ores of the Cristalino Cu(Au) deposit (*CD*) were studied. The *CD* occurs in the Carajás Province, Brazil. It is a world class IOCG-type (estimated resources >500Mt @1.0%Cu and 0.3 g/t Au), Archean in age (ca. 2.7Ga), located in a low-grade volcano-sedimentary sequence (Itacaiúnas Supergroup) that was hydrothermalized: alkalinization; chloritization; carbonatization; Fe-metassomatism; and, sulfidation. Ores occur in breccias, stockworks, disseminations, and stringer to massive types in the host (mafic and felsic volcanic) rocks. Diorites and quartz diorites crosscut these supracrustals and could relate to Cu(Au)-mineralization. Lithogeochemistry (mass balance and Harker diagrams) of these rocks determined enrichment or depletion for several elements. Na, K, Ca, Fe, Mg, Mn, P, Sr, Ba, Ni, Co, Cu were severely hydrothermally mobilized whereas Al, V, Ti, Y and Zr were more immobile. Discrimination diagrams (mainly using Y, Zr and Ti) for metamafics associated them to an intraplate (rift) environment with magmatic affiliation of MORB-type. Stable isotope data come from calcite (whole rock samples) and from chalcopyrite and pyrite (separated grains) from mafic and felsic volcanics, and "hydrothermal breccias". They all show $\delta^{34}S_{(CDT)}$ (0.6 to 1.5‰) values closer to mantle sulfides and to MORB values. $\delta^{13}C_{(PDB)}$ (-7.2/-4.4‰) and $\delta^{18}O_{(SMOW)}$ (+8.1/+9.3‰) values plot on primary carbonatite field. *CD* data set corroborate former proposals of other researches [1] which suggested a bimodal tholeiitic magmatic afilliation for these IOCG-type deposits in Carajás Province and an Archean intracontinental rift environment for the Carajás Basin (Pará, Brazil).

Stable isotope signature of the Middle Holocene climatic change in the SW Iberia

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Between 7.5 kyr and 4 kyr a fluvial limestone tuffs system developed in the south-western corner of Iberia. This system is characterised by a segmented up to 60 meters thick limestone sequence dated by radiocarbon.

The system is calcite dominated, and the other coeval mineral constituents comprise iron oxides and hydroxides and clay minerals. Other mineralogical components such as quartz and feldspar are seldom and detrital, from the surrounding Upper Carboniferous and Upper Triassic formations.

Most of the tuffs are well banded, with a layering which ranges in thickness from the micrometric scale to the centimetric scale.

The different centimetric layers were sampled and bulk $\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ were determined. The oxygen and carbon isotopes were used as recognized proxies for paleoenvironmental conditions and the Sr isotopes with the purpose of understanding the residence time of the meteoric waters in the surrounding carbonate formations.

The main results point to: (i) the hydrologic conditions of the system were not suitable for the waters from which the limestone tuffs precipitated to equilibrate with the Mesozoic carbonate formations; (ii) the probability of having 'old carbon' in those waters is very low increasing the reliability of the ^{14}C age determinations; (iii) the composition in stable isotopes of the waters were probably close to the meteoric water composition for the period under consideration; (iv) between 7.5 kyr and 4 kyr the oxygen isotopic composition of the limestone tuffs show a gradual depletion in ^{16}O with the values of $\delta^{18}O$ increasing from -5‰ to -3.5‰ probably related to an increase in the importance of the evaporation in the hydrological system; (v) during the same time interval the ^{13}C composition of the limestone tuffs remains crudely constant reflecting the stability of the vegetation cover.

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Direct determination of uranium, thorium and lead isotopes ratios in crude oils by fs-LA-ICP-MS.

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Estimation of crude oil expulsion timing from the rock source has important implications for the modeling of petroleum systems. Moreover, trace metal quantification in organic matrices (oil-to-oil correlation, oil-to-source correlation, biodegradation, migration,…) represents a challenge for organic geochemistry.

A new analytical approach using a high repetition rate IR-femtosecond laser coupled to an ICP-MS detection was developed. This technique allows the direct determination of trace elements in crude oil without sample preparation. Limits of detection are obtained at the ppb level in pure petroleum matrices.

The study of Uranium, Thorium and Lead isotopes in petroleum matrices by fs-LA-ICP-MS gave two important informations:

(1) Crude oils are very poor in Uranium and Thorium (concentration < 1 ppb) compare to Lead (10 ppb – 10 ppm) i.e. very low U/Pb and Th/Pb ratios. So the determination of crude oil expulsion time is hardly realizable with classical U/Th/Pb isochrones, but needs the comparison between lead isotopes ratios obtained from source rocks and crude oils. Indeed, the crude oil fixes the lead isotope signature of the expulsion time.

(2) Lead isotopic ratios trace clearly a mantle contribution. Therefore, they can discriminate 3 end-members: mantle lead, crustal lead, and anthropic contamination.

Hourly-size segregated sampling of trace elements and subsequent source apportionment

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Measurements of trace element concentrations in ambient aerosol were conducted at different sites (urban and rural) with the objective to apply source apportionment analysis.

Sampling was performed in three size ranges (0.1-1, 1-2.5 and 2.5-10 μm) with a rotating drum impactor (RDI). Samples were subsequently analyzed with synchrotron radiation X-ray fluorescence spectroscopy (SR-XRF) which allows for the detection of low mass concentrations (a few ng/m^3). For SR-XRF the sampling time can be significantly reduced compared to wet-chemical and conventional filter analysis and the investigation of diurnal variations becomes feasible. XRF-analysis at different incident energies lead to a range of detected elements from Al – Zn, resp. Ba.

Although trace elements do not appear in high concentrations they can provide indications about the origin of different kinds of air pollution (e.g. traffic, wood burning, mineral dust etc). Without a-priori knowledge about the sources positive matrix factorisation (PMF) was employed to mimic their contribution as well as their time evolution. For 0.1-1 μm particles one typical factor is wood burning showing contributions of sulphur, potassium, calcium and zinc. Furthermore there is a fraction related to soil and terrestrial elements, and a single peak of sulphur presumably representing secondary sulphate. Another factor leads to the assumption of a vehicle/traffic related exhaust/abrasion source. The final goal is to combine for the first time the RDI-SR-XRF data set with aerosol mass spectrometer (AMS) data, providing information on the composition of the particles over an extended range of elements and chemical compounds, including organics.

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Origin of U-mineralizing brines in the Athabasca Basin, Canada

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High salinity brines are commonly sampled as fluid inclusions in close paragenetic relationship with unconformity-related U mineralizations in the Proterozoic Athabasca Basin. The large range of brine composition results from the mixing of two end-members (NaCl-rich and $CaCl_2$-rich) during or after maximum burial (T from 120 to 180°C) [1]. Here, we address the question of the origin of these brines and their possible interactions with basin and basement lithologies.

Chorinities of 5-7 molal, coupled with Cl/Br ratios of 100-400 and negative $\delta^{37}Cl$ values, are unambiguously in favour of a common dominant evaporated seawater origin for both brines, typical of primary brines having past the point of halite precipitation. Such brines either have immediately percolated through the sedimentary pile, or alternatively have been trapped in the evaporitic formation and were expelled afterwards during compaction events. $\delta^{18}O$ values of inclusions-hosting quartz and dolomites are compatible with evolved deep basinal brines.

The $CaCl_2$-rich brines are thought to result from strong interactions with basement lithologies where they have up-taken uranium, as shown by the very high content detected by LA-ICP-MS. The range of $^{87}Sr/^{86}Sr$ ratios of inclusions-hosting dolomite veins suggests a mixed origin, between a marine origin and a more radiogenic component typical of basement lithologies. D/H values of brines, coupled with $\delta^{13}C$ values of dissolved CO_2 argue for interactions with organic matter and D-depleted materials. The isotopic trends may indicate the involvement of C-rich components in the water-rock processes in relation with the U mineralization.

[1] Derome *et al.* (2005) *Econ. Geol.* **100**(8), 1529-1545.

Post-subduction porphyry and epithermal Au deposits

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An increasing number of porphyry and epithermal deposits, commonly rich in Au (and in some cases also PGE), are being recognized in post-subduction tectonic settings ranging from collisional to arc-rifting, as well as arc migration or reversal. Examples include deposits such as Porgera, Ok Tedi, and Lihir in Papua New Guinea, Grasberg in Indonesia, Emperor in Fiji, Sari Gunay in Iran, Çöpler in Turkey, and porphyry Cu-Au deposits in Tibet. The magmas associated with these deposits are commonly weakly alkaline in character (shoshonitic or hawaiitic, and their derivatives), and are emplaced in relatively small volumes distal to any contemporaneous volcanic arc.

Studies of paleo-arc sections suggest that during arc magmatism, large volumes of mafic cumulates, including hydrous minerals such as amphibole, are left at the base of the crust from fractionating primitive arc magmas. These magmas are S-rich but oxidized, meaning that the bulk of the S is present as SO_2. Under such conditions, trace amounts of magmatic sulfides left as residual phases in these cumulate sequences will be enriched in highly siderophile elements such as Au and PGE, having strongly partitioned these elements from a much larger volume of mafic silicate melt.

If these amphibolites are subjected to later dehydration melting, they will yield a felsic melt and garnet residue, and any sulfides will likely be resorbed into the relatively S-poor melt. Such melting may be triggered, after subduction-related magmatism has ceased, by crustal thickening during arc collision, delamination of sub-continental mantle lithosphere, or arc rifting, the latter two processes permitting invasion of hot, mafic asthenospheric partial melts that may also carry a subduction-modified geochemical signature. Common elements of these processes will be a relatively small volume and degree of partial melting (leading to mildly alkaline magmas), and a range of magma compositions from mafic to intermediate with trace element signatures reflecting the presence of amphibole and garnet in the deep crustal source. Such rocks have been identified as adakites by some authors, but no link to slab melting is here suggested.

Key to the potential Au-(PGE)-rich metallogeny of these magmas (vs. the Cu-rich nature of normal arc magmas) is the opportunity to remelt small amounts of siderophile element-rich residual sulfide left behind in the deep lithosphere by the prior passage of oxidized, S-rich arc magmas.

Novel application of organic and inorganic geochemical proxies for exploring ocean-continent linkages over the last 1400 years from Gulf of Mexico sediment

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We use a multi-proxy approach to explore the linkages between moisture balance in the Gulf of Mexico (GOM) and North American (NA) continental hydrology during the Late Holocene. The Pigmy Basin in the northern GOM is ideally situated to capture decadal-scale variability of both terrigenous inputs via the Mississippi River (MR), and sea surface variability in the GOM. This study focuses on the sedimentary record spanning the Little Ice Age (LIA) and Medieval Warm Period (MWP) (i.e. the last 1400 years) and utilizes both organic and inorganic geochemical analyses to define intervals of varying continental inputs and to assess changes in the moisture balance (E-P) in the GOM. Results indicate multi-decadal episodes of increased terrestrial inputs interpreted as increased MR discharge (wet intervals) that coincide with intervals of increased $\delta^{18}O$ seawater, interpreted as increased salinity. Episodes of decreased continental inputs (i.e. dry intervals) are associated with lower salinity in the GOM. Variations in atmospheric circulation, position and intensity of the Bermuda high, can provide a coherent mechanism that can control evaporative processes over the GOM and the amount of moisture transport to and precipitation over the NA continent. Through the development of a molecular ^{14}C chronology and dD record of terrestrial biomarkers, fundamental questions regarding the role of climate change on: 1) the age and export rate of continentally derived organic carbon to oceans and 2) the time-dependent regional patterns of precipitations in the MR basin on the NA continent will be discussed.

Carbonate burial, circulation and CO_2 release at terminations

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Whether the concentration of carbon dioxide (pCO_2) acts as a passenger or driver of glacial terminations remains unclear. Despite nearly three decades of research, an unchallenged explanation for the rise of 90 ppmv in atmospheric carbon dioxide (pCO_2) associated with each termination of the late Pleistocene remains elusive. Here we investigate changes in ocean ventilation (via benthic $\delta^{13}C$ in a high latitude North Atlantic core) and ocean alkalinity (via trace metals in benthic foraminifera from the Weddell Sea) to outline the evolving ocean carbon cycle during the deglacial release of CO_2.

We document three deglacial $\delta^{13}C$ minima in the intermediate depth North Atlantic, which builds the picture of a near-ubiquitous deglacial intermediate depth $\delta^{13}C$ minima, synchronous with the deglacial minimum in $\delta^{13}C$ of atmospheric CO_2, and pulses of CO_2 output to the atmosphere. Globally, intermediate depth $\delta^{13}C$ signatures converge to the same value at the start of the deglaciation. These observations appear characteristic of ventilation and flushing of a CO_2-laden isolated reservoir at depth. In addition to this flushing, alkalinity changes may contribute a major fraction of the deglacial pCO_2 rise. Our trace metal records from the Weddell Sea indicate a lower CO_3^{2-} during the deglacial terminations and peak interglacial warmth, relative to the coldest glacial periods. An increase in whole ocean alkalinity during the glacial period, is almost inevitable due to the near elimination of available shelf area for the burial of alkalinity by coral reefs. This increase can be reconciled with reconstructions of the depth of the glacial lysocline, if carbonate burial rates also increased *above* the lysocline as a result of enhanced pelagic calcification by foraminifera and coccolithophores. Should the pelagic burial rate of alkalinity in the more alkaline deepwaters of the glacial ocean outstrip the rate of weathering supply of alkalinity to the ocean towards the end of glacial maxima, the consequent whole ocean decrease in CO_3^{2-} could provide an orbital-independent mechanism to trigger the deglacial rise in pCO_2. The extreme interglacial periods with elevated pCO_2 may be exceptional events resulting from the rebounding deglacial imbalance in the carbonate system.

Carbonates, riverine chemistry and incongruent weathering of hafnium

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The variability of dissolved hafnium (Hf) and neodymium (Nd) isotopic compositions and concentrations in four Swiss rivers are reported and compared to the concomitant changes in riverine chemistry. The rivers were sampled ten times between March 2004 and July 2005. The dissolved Hf and Nd isotopic compositions are compared to those in the suspended load to determine incongruent weathering effects for both elements.

The average dissolved Hf isotopic compositions of the four analyzed rivers (εHf = -1.7, +5.4, -1 and +2.3) are markedly more radiogenic than the isotopic compositions in the river suspended matter (εHf = -9.3, -6, -5.4 and -4.2), documenting strong incongruent weathering effects on Hf. Furthermore, the seasonal variability in the dissolved Hf isotopic composition of the individual rivers is large and spans a range from 2.7 to 9.2 εHf. In contrast, the isotopic composition of the dissolved Nd is virtually identical to that of the suspended load and varies by only 1 εNd throughout the seasons.

The abundance of Hf in the weathered lithologies does not seem to exert the primary control on the riverine dissolved Hf concentrations. Hafnium concentrations are approximately one order of magnitude higher in rivers dominated by carbonate weathering than in those draining gneissic catchments. The Hf/Ca ratios in the dissolved load of the Hf–rich rivers, are about two orders of magnitude lower than in carbonates. It seems likely that Hf concentrations are controlled by the availability of appropriate ligands to keep Hf in solution, although there are no firm constraints on the speciation of Hf in these rivers.

The data suggest that the offset between terrestrial rocks and seawater in εHf vs. εNd includes recycling of radiogenic Hf stored in carbonates. The large isotopic contrast in Hf between the presumably nearly zircon free riverine suspended particles and the dissolved load indicates that other factors apart from the incomplete weathering of zircon contribute to the isotopic compositon of dissolved Hf, consistent with preferential weathering of minerals containing radiogenic Hf, as previously proposed by others.

Evolution of MORB at fast-spreading ridges

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The composition of magmas erupted at fast spreading ridges, such as the East Pacific Rise, integrate a variety of processes that modify the compositions of melts sourced within the underlying asthenosphere. It is generally accepted that the majority of MORB erupt from one or more shallow melt lenses located below, but proximal to, layer 2 of the oceanic crust. These reservoirs act as catchments for melts that percolate through several kilometers of crystal mush that form the nascent layer 3 crust. Within these reservoirs melts are homogenized and cooled allowing them to traverse specific liquid lines of descent (LLD). Consequently, the compositions of erupted magmas, which normally include N_MORB, ferrobasalts and Fe-Ti basalts, principally reflect the processes of shallow level mixing and crystal and *in situ* fractionation. In some specific tectonic settings, such as segment terminations and overlapping spreading centers, andesites and dacites are erupted in significant volumes. Commonly, their major and trace element compositions are decoupled and cannot be modeled as extensions of the LLD from N-MORB to FeTi basalt. Specifically, their concentrations of Cl and the most incompatible trace elements are too high and appear to require the input of an external chemical component. Modeling of magmatic fractionation coupled with partial melting of surrounding country rock (probably the base of layer 2b) and assimilation of anatectic melt provide a close, although not perfect, fit to the major and trace element chemistry. Rare gabbroic xenoliths enclosed in neovolcanic lavas provide further details about the complex melt-mineral reactions, mixing of melts, and precipitation of crystals that take place as melts percolate upward through the crystal mushes of the developing crust. Thus, lavas and xenoliths provide complementary information with which to decipher the evolution of MORB.

Surface speciation of yttrium at the rutile-water interface: Incorporation of structural information and charge distribution within the MUSIC model

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Ion adsorption at metal (hydr)oxide surfaces is dependent on the surface structure and the coordination geometry of adsorption complexes. At the microscopic scale, surface structure and ion sorption have been examined extensively using various X-ray techniques. Additionally, theoretical simulations also provide molecular-scale details of mineral-solution interfaces. The binding configuration of adsorbed ions may change as a function of solution conditions; for example, surface complexes may protonate or deprotonate. Such changes are best investigated at the macroscopic scale as function of pH. Therefore, to develop an unambiguous understanding of the reactivity of mineral-solution interfaces it is necessary to scale from the molecular to the macroscopic scale. Surface Complexation Models (SCM), specifically the MUSIC model, provides a powerful framework in which microscopic information can be utilized to rationalize bulk experimental adsorption data.

This contribution will concentrate on the adsorption of Y^{3+} on rutile. The sorption of Y^{3+} was studied as a function of pH and loading, in NaCl media at 25 and 50°C. The potentiometric titration data were rationalized successfully using the MUSIC model in combination with the charge distribution (CD) model. The CD values for the surface species were evaluated in relation to available structural information from X-ray techniques and MD simulations. Moreover, changes in surface speciation as a function of pH and surface loading, were also evaluated. X-ray studies have shown that on the predominant (110) rutile surface Y^{3+} adsorbs mainly as an inner-sphere tetradentate complex, comprising two bridged and two terminal rutile surface oxygens. In addition to this tetradentate complex, SCM revealed a bidentate inner-sphere complex (one bridged and one terminal group) with increased surface loading Furthermore, both inner-sphere Y^{3+} complexes hydrolyze with increasing pH.

Dehydration processes in the subducting slab: Seismological observations from the Andean subduction zone

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Subduction zones, the expression of convergent plate boundaries, generate the world's largest and most destructive earthquakes. The Chilean subduction zone is an ideal natural laboratory to study the processes involved in generating these devastating earthquakes. While the upper limit of the seismogenic zone will be soon in reach of scientific drilling projects the lower limit of the seismogenic zones will only be accessible by remote techniques like passive seismological observations. In the last decade several high resolution passive seismic imaging experiments have been carried out to shed light into subduction zone processes, focussing on the lower limit of the seismogenic zone and its transition into intermediate depth seismicity (300 km).

While in the upper depth range (depth < 20 km) seismicity is predominantly related directly to the subduction thrust a more complicated seismicity feature is found at greater depth. At greater depth (~100km) a double seismic zone with a separation distance of about 8 km could be identified at intermediate depth. Additionally, the analysis of guided wave arrivals suggests, that a thin low velocity layer (thickness < 3 km) is present down to a depth of 200 km, preferably located between the upper and lower band of the double seismic zone. At shallower depth (<50 km) a low velocity layer associated with the subducting oceanic crust can be identified in the nucleation are of the 1960 Chile earthquake. Dehydration processes in the subducting slab can explain most of the seismological observations made.

Marine organic aerosol: Characterization by proton nuclear magnetic resonance spectroscopy (^{1}H NMR)

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The water soluble and insoluble organic fraction of marine aerosols, collected under strict clean marine sector conditions, in the framework of the EU Project MAP, has been analyzed by proton nuclear magnetic resonance spectroscopy (^{1}H NMR). Samples have been collected during a one-year-long sampling campaign at Mace Head (Ireand), covering the year 2006, and during a cruise in the East North Atlantic Ocean, that took place between June and July 2006.

The composition of water soluble organic carbon (WSOC) was characterized by ^{1}H NMR analysis in D_2O solution, while the water insoluble fraction (WIOC), mainly of primary origin [1], by a novel 1H NMR method in deuterated trifluoroacetic acid solution.

The ^{1}H NMR analysis of WSOC samples showed that during the spring-summer period the organic composition was characterized by a large contribution from methanesulphonate (MSA), associated with two additional components: a) one from nitrogen-containing species (mainly alkylammonium ions), and b) another from oxygenated compounds (mainly short chain carboxylic acids and polyols, possibly including carbohydrates). The ^{1}H NMR analysis highlighted also the different distribution of S-containing, N-containing and oxygenated compounds between different seasons and between fine and coarse aerosol particles. The main features of marine aerosol WSOC resulted compatible with a secondary origin.

The NMR spectrum of WIOC showed, instead, long chain aliphatic compounds as major components, similar to the insoluble organic compounds of biological origin found in laboratory-produced sea spray particles and described in Facchini *et al.* [1].

[1] Facchini *et al.* (2008) *Environ. Sci. & Technol.* **42**, 9116-9121.

Are glacials (interglacial) in the easternmost Pacific Ocean drier (wetter) during the last 300 000 years?

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How precipitation patterns on the western area of South America and Central America behaved according to high latitude glaciations and deglaciations is still not well known. Eastern equatorial Pacific (EEP) sedimentary records of past sea surface temperatures (SSTs), productivity and water column stratification have been interpreted as El Nino-like, La Nina-like, or as simply a oceanographic response linked to high latitude climate during the ice ages. In this study we analyze organic and inorganic sediment composition of marine sediments from ODP Site 1239, located 120 km off Ecuadorian coast, in order to reconstruct climatic changes in western tropical South America and EEP during the western tropical South America and EEP during the glacial/interglacial climate variability of the last 300 000 years.

Alkenones derived-SST showed a difference of ~3°C between the last glacial maximum and the Holocene and ~2°C between termination II and the Eemian. The patterns of siliciclastic elements (Fe, Ti, Al) input, measured by X-Ray fluorescence (XRF) scanning, and SST in the eastern tropical and subtropical Pacific reveal a generally good correlation with the 100-kyr-cycles. During this time-span, maxima in siliciclastic elements deposition correspond to inter-glacials, suggesting higher terrigenous input and thus increased tropical precipitation during warm-phases. Higher input of terrigenous material is also supported by terrestrial plant biomarker abundances (i.e. long-chain [C_{25} to C_{33}] *n*-alkanes). Modern rainfall changes over the coast of Ecuador are closely coupled to offshore SSTs and intertropical convergence zone (ITCZ) seasonal migration. We suggest a strong link between EEP atmosphere and high latitude climate, expressed as latitudinal migrations of the ITCZ. Then during ice-ages, hydrological deficit in the coastal area of Ecuador might respond to shifts on the the mean annual position of the ITCZ; while during interglacial times, the ITCZ had a similar spatial distribution to the one it has today.

Multi proxy approach for the formation of calcium carbonates in alkaline man-made environments

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The formation of calcium carbonates, e.g. in drainage systems of tunnels, may be induced by degassing of CO_2-rich groundwater. However, the dissolution of portlandite ($Ca(OH)_2$) from cements or the shotcrete of the tunnel wall bears an additional and immense potential for the formation of carbonates from alkaline solutions.

The main tasks of this study are the reconstruction of the environmental conditions during $CaCO_3$ formation and monitoring of ongoing precipitation of calcium carbonates and cement-water interaction in alkaline man-made environments. Variations in trace element incorporation and distribution of the stable isotopes of carbon and oxygen in the precipitated calcium carbonates may represent powerful tools to identify individual mechanisms for carbonate formation.

As portlandite dissolves, highly alkaline solutions are obtained. In this case, precipitation of calcium carbonate can be related to the absorption of CO_2 from the atmosphere. Isotopic analyses of the calcite show that fixation of CO_2 from the Earth's atmosphere leads to significantly lighter $^{13}C_{calcite}$ values (down to -25 ‰, VPDB) as would be expected for the fixation of groundwater carbonate (typical $^{13}C_{calcite}$ values between -10 and -16 ‰, VPDB).

The evolution of Sr/Ca ratios in the alkaline drainage solutions and in the corresponding calcium carbonate precipitate provides insight into the dissolution process at the concrete with respect to the amount of primarily dissolved portlandite from the cement. Moreover, an inverse relationship between Mg/Ca and Sr/Ca ratios is observed due to the liberation of aqueous strontium by the dissolution of portlandite and the formation of brucite ($Mg(OH)_2$) under alkaline conditions. Low magnesium incorporation into the calcite structure is a strong indicator for carbonate precipitation from highly alkaline environments.

Several case studies demonstrate the potential applications of such multi proxy approaches for the understanding of the carbonate dynamics.

Influence of vegetation on chemical fluxes in a tropical watershed: Mule Hole, South India

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The experimental watershed of Mule Hole (4.3 km^2) is located in the sub-humid zone of a steep climatic gradient induced by the Western Ghâts in South India. It is covered by a dry deciduous forest whose evapo-transpiration accounts for almost 90% of the 1100mm annual rainfall [1]. The forest induces low groundwater recharge and maintains the groundwater disconnected from the stream: for this reason, Mule Hole constitutes an ideal site for estimating the influence of vegetation (throughfalls, forest fire ashes) on the chemical fluxes exported by a stream.

The chemical composition of rainfall, throughfalls, stream water and soil solutions are monitored since 2004. The composition of ash dissolution was characterized with batch experiments on ashes of the main tree leaves and grass species [2]. The contribution of vegetation components were calculated using End-Member Mixing Analysis (EMMA).

The signature of the ash end-member varies during the experiment according to (1) the vegetal species, i.e. high Ca, Mg, carbonate, K in leaves and high Si, K, Cl, OH in grass, (2) the dissolution kinetics of minerals present in ashes, in decreasing order salts (KCl, KOH), carbonates and amorphous silica. This latter factor influences the nutrient cycles: for instance, K mobility is enhanced by the instantaneous dissolution of salts whereas the slow dissolution of silica may allow efficient recycling within the soil profile.

The application of EMMA on the stream composition indicates that when forest fire occurs (in 2004) the chemical composition of the first storms of the humid season is >90% controlled by the vegetation component (mostly ashes) for K, Ca, Mg, Si, alkalinity and Cl. The relative contribution of the vegetation component decreases through the season as a result of (1) increase of soil solution contribution and (2) drop of ash contribution. The vegetation component still dominates during the first storms of 2005.

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[2] Akerman *et al*. (2008) *Geochim. Cosmochim. Acta* **72**, A1-A40.

Multi-step dissolution of baddeleyite for ID-TIMS U-Pb dating

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Numerous studies have highlighted both the power and potential complexities of U-Pb baddeleyite geochronology. We present results from multi-step digestion experiments designed to understand and reduce the effects of Pb loss and secondary zircon growth in complex baddeleyites. The research was motivated by the recently developed chemical abrasion (CA) method for zircon U-Pb dating [1]. The experiments were carried out on both complex Neoproterozoic baddeleyites with zircon inter- and overgrowths and fragments of a large gem-quality Paleoproterozoic baddeleyite.

The first group of experiments focused on isolating the baddeleyite and zircon ages from complex grains. To discretely dissolve the two phases, we used a two step HCl-HF digestion procedure on annealed grains. Initial 48hr-220ºC HCl digestions completely dissolved baddeleyite, leaving behind intact zircon rims. The remaining zircon was dissolved in either a 48hr-220ºC HF digestion or in a multi-step chemical abrasion digestion. The data define two distinct populations. Baddeleyite (HCl) data plot along a statistically significant linear array with a zero age lower intercept. In contrast, the zircon rim analyses scatter to the left of the discordia, suggesting they may represent multi-component mixing between the baddeleyite crystallization age and younger non-zero age Pb loss or zircon growth. Single step digestion data from this sample produced significant scatter, reflecting mixing of the baddeleyite and zircon ages. The results demonstrate the potential for resolving both the igneous and metamorphic history of complex baddeleyites.

Multi-step chemical abrasion experiments on the two samples had more complex results. Annealed grains were subjected to a series of HCl digestion steps (120–220ºC) followed by a final HF digestion. The HCl digestion steps define discordia lines with upper intercept dates equal to the sample ages. However, individual digestion steps were both normally and reversely discordant suggesting that U and Pb were fractionated in the multi-step digestions. The data indicate that the CA method is not an effective way to reduce the impact of Pb loss in U-Pb baddeleyite geochronology.

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U/Pb-dating of calcite slickenfibres

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A new method for determining the age of brittle deformation is presented, which utilises U/Pb-dating of tectonic carbonates, i.e. synkinematically grown fibrous calcite such as slickenfibres and tension gashes. Brittle deformation typically occurs at relatively low temperatures, where only few *datable* minerals grow synkinematically. Tectonic carbonates form abundantly during brittle deformation, but have so far proven to be difficult to date.

Under favourable conditions, calcite can have high uranium and low lead concentrations resulting in elevated U/Pb-ratios, and calcite has been shown to be sufficiently resilient against secondary influences to make it suitable for dating [1, 2, 3].

To gain an overview of the range of naturally occurring U- and Pb-concentrations in tectonic carbonates, samples from a wide range of different host rock lithologies, tectonic settings and deformation ages were taken from several areas along the Alps.

Initial trace element profiling by LA-ICPMS reveals element distributions and concentrations, allowing for a quick overview of each individual sample. U concentrations of 0.4 – 3 ppm and approximate $^{238}U/^{204}Pb$-ratios of up to ~2000 – 10000 (with variations spanning 3 orders of magnitude) are comparable to published data of successfully dated calcites.

An attempt of in-situ U-Pb isotope ratio measurements by LA-ICPMS reveals the highly radiogenic character of some samples, but lower precision of in-situ analysis by a quadrupole ICPMS compared to more sensitive MC-ICPMS and an inherently high ^{204}Hg background prohibiting direct measurement of ^{204}Pb limits precision of such age information, even though those preliminary ages appear to fit into the respective geological framework.

Thus, selected samples are being microsampled, dissolved, followed by low-blank U-Pb ion exchange chromatography and isotope dilution MC-ICPMS; these results will be presented.

The new method not only yields insight in regional tectonic evolution, e.g. by providing 'absolute' age control for relative ages of fault sets obtained from paleo-stress analysis, but may also be applied to gain information on dynamics of single faults, like deformation rates and (minimum) durations.

[1] Woodhead *et al*. (2006) *Quaternary Geochronology* **1**, 22.
[2] Cole *et al*. (2005) *Geol. Soc. Am. Bull.* **117**, 276-287.
[3] Kelly *et al*. (2006) *Environ. Sci. Technol*. **40**, 2262-2268.

Evidence for ultra-depleted Pb isotopic component in the backarc Patagonian mantle wedge

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Inferences on melt and fluid migration trough the Patagonian mantle wedge are provided by the ultramafic xenoliths occurrence of Tres Lagos (TL; lat. 49.13°S, long. 71.18°W). It is placed at the eastern border of the Meseta de la Muerte backarc basaltic plateau, where a post-plateau volcanic diatreme contains mantle xenoliths in both pyroclastites and lavas. Its latitude corresponds with the Northern limit of the Austral Volcanic Arc (AVZ), which is separated from the Southern Volcanic Zone (SVZ) by a gap in the arc magmatism between 49° and 46°30′ latitude S. The selected xenoliths have been distinguished into two groups (Group 1 & 2). Group 1 consists of lherzolites and harzburgites, whereas Group 2 is constituted only by harzburgites. The Sr, Nd and Pb isotopic compositions of the Group I clinopyroxenes (Cpx) form arrays from DM to the TL basaltic lavas, according to the presence of EM1 component. Group 2 Cpx have much more radiogenic Sr and less radiogenic Nd values, approaching those of EM1 and EM2 end-members: these features are associated to very unradiogenic lead isotopic compositions ($^{206}Pb/^{204}Pb$ = 17.4-18.1; $^{207}Pb/^{204}Pb$ = 15.55-15.60; $^{208}Pb/^{204}Pb$ = 37.3-38.5). The combination of petrographic, trace element and isotopic fetures indicate that TL harzburgites are residua after melt-assisted partial melting triggered by melt/fluid migration in the hottest, and perhaps deeper, parts of the pristine DM lithosphere. The interpretation of the Pb isotope composition of Group 2 Cpx is not trivial. In analogy with the interpretation proposed for SWIR, it could unravel the occurrence of mantle sources which incorporated ancient crust and failed to homogenise with the DM mantle. Alternatively, it could be the evidence for ancient continental crust of the South America plate dragged down into the mantle by slab motion.

Black carbon as a climate agent: Least cost strategies for abatement

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Research has identified the significant radiative forcing (RF) effects of black carbon (BC) emissions. Yet controlling BC emissions is beyond the remit of the Kyoto Protocol, and instead falls under the umbrella of particulate matter (PM) control, driven largely by human health impacts. National PM legislation would offer climate effects as a co-benefit, but the question remains whether BC reduction is itself an optimal approach to climate change mitigation.

We develop cost-effective scenarios for global BC abatement in 2030. We assess the cost of abating the radiative forcing effect of BC, and the cost-effective distribution of these efforts across regions and sectors. The scenarios account for the concomitant warming effect of organic carbon (OC) reduction.

The scenarios are built upon marginal abatement cost (MAC) curves of BC abatement in each region, and the region-specific global warming potentials (GWPs) of BC and OC. The MAC curves represent the least-cost deployment schedule of BC/OC abatement technology, while the GWPs represent the climate impact of BC and OC emitted in each region relative to CO_2.

Our results suggest that the total GWP-100 (including both direct and indirect effects) of BC is highest in the Middle East, Africa, and South Asia. The annual cost of reducing global total BC RF from the 2030 baseline by 10, 20, and 30% is estimated at 2000€ 3bn, 23bn, and 97bn respectively. The industrial process and transport sectors are the largest contributors to this abatement, with China, South Asia, and Africa the dominant regions. From a global cost-saving perspective, Asia is an ideal candidate for prioritisation, owing to high baseline emissions levels and numerous low-cost abatement options – factors which outweigh its low BC GWP.

Finally, we assess the optimal level of BC abatement under alternative CO_2 permit prices. Assuming GWP-100 (direct and indirect), permit prices of €20, 40, and 60 per tCO_2 would warrant global least-cost BC reductions of 8, 10, and 12% from the baseline level.

Calibration of carbonate composition using micro-Raman analysis: Application to planetary surface exploration

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Laminated accretionary carbonate deposits, containing various amounts of kerogenous organic matter, are a prominent feature of thes sedimentary record over the past 3,500Myr. The macroscopic similarity to modern microbially-produced structures, has led to the inference that these structures may represent evidence of ancient life. Recently, Mg-Carbonates preserved in Martian dust were found by orbital-probe boarded IR spectrometry [1], but the analytical scale was too large to detect macroscopic carbonate structures of possible biologic origin. Raman micro-spectroscopy may offer an important innovation in planetary research, since it offers fast, high spatial resolution (µm) and in-situ identification of carbonates. Raman portability is also well-suited for planetary surface exploration.

Raman micro-spectrometry analysis was performed on a set of carbonate standards (calcite, ankerite, dolomite, siderite, magnesite) of known composition. Each carbonate Raman spectrum is characterized by six bands of different intensities and wave number. We show that Raman band shifts of siderite-magnesite and ankerite-dolomite solid solutions display a well defined positive correlation ($r^2 > 0.9$) with the Mg number (Mg/Mg+Fe+Mn+Ca) of the carbonate analyzed. Raman shifts calibrated as a function of Mg number were used in turn to evaluate the chemical composition of carbonates. Raman analysis of a suite of carbonates (siderite, sidero-magnesite and ankerite) of hydrothermal and sedimentary origin from the 3.5 Gyr old Dresser Formation, Australia, show good compositional agreement with electron microprobe analysis. These results indicate that Raman spectrometry can provide crucial information on the composition and origin of carbonates on planetary surfaces.

[1] Banfield *et al*. (2003) *Science* **301**.

Arsenic remobilization from paddy soil during monsoon flooding in Bangladesh

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Groundwater containing high concentrations of arsenic (As) is extensively used for the irrigation of dry season rice in Bangladesh [1]. Though this enables Bangladesh to be self-sufficient in food, As accumulation in paddy soils may jeopardize rice production in the long term. Monsoon flooding strongly attenuates As accumulation in the topsoil of rice fields [2, 3], but the pathways of As release remain unclear. We present data from paddy fields near Sreenagar (Munshiganj, Bangladesh) which show that As was reductively mobilized and released into the overlying floodwater throughout the duration of monsoon flooding. As concentrations in topsoil porewater increased over time, reaching values of up to 1160 µg L^{-1} at 3-7 cm depth after 16 weeks of flooding. The floodwater column was either vertically well mixed exhibiting As concentrations between 5 and 20 µg L^{-1} over a height of 1-2.7 m, or characterized by distinct gradients of increasing As concentrations towards the soil surface. On days of limited vertical mixing, As concentrations ranged between 40-120 µg L^{-1} in floodwater 2.5 cm above the soil. Using different methods we estimate that between 53 and 250 mg m^{-2} of As, corresponding to 13-63% of the As annually added via irrigation, were mobilized into floodwater over the course of one monsoon season. A large portion of this arsenic is likely to be exported through the river system draining Bangladesh to the Bay of Bengal.

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Interpreting Nd isotope and $^{231}Pa/^{230}Th$ records in the deep Western North Atlantic

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Advances in the our knowledge of past changes in ocean circulation have been made using Nd isotopes, as a proxy for changes in water mass structure [1], and $^{231}Pa/^{230}Th$ ratios as a proxy for the rate of ocean circulation [2]. Despite the potential power of these proxies when applied together, no records have yet been published of both proxies measured at the same location.

Based on previous records of ocean circulation [2, 3], we know the central deep Western North Atlantic is sensitive to changes in water mass structure and advection rates on a glacial-interglacial timescale, making the Bermuda Rise hydrographically one of the best places to test the application of both proxies together.

Here we will present Nd isotopes measured on multiple sediment phases from the core OCE326-GGC6 (33º41.443'N; 57º34.559'W, 4541m), which is a sister core to OCE326-GGC5 on which the McManus *et al.* $^{231}Pa/^{230}Th$ record was measured. Both cores were taken at the same depth and location, allowing accurate comparison of the two proxy records.

[1] Piotrowski *et al.* (2004) *EPSL* **225**, 205-220. [2] McManus *et al.* (2004) *Nature* **428**, 834-837. [3] Curry & Oppo (2005) *Paleoceanography* **20**.

Proterozoic crustal growth in SW Fennoscandia

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Vast belts of juvenile continental crust are preserved on many continents that often include evidence for older crust at depth, i.e. inherited zircons and evolved Hf-in-zircon signatures. An example of this is SW Fennoscandia. In this study it is hypothesised that tectonic-switching, i.e. relative movement of a subduction hinge towards or away from a continental mass, in an extensional accretionary orogen [1] was responsible for crust formation in this region. The proposed model can be applied to other regions such as Yapavai-Mazatzal (SW America), and the Arabian-Nubian Shield.

The 1.8-0.9 Ga crust of SW Fennoscandia is scrutinized with new and published Hf-in-zircon data. Magmatism occurred throughout most of the period, but the largest concentration of juvenile crust formed at 1.7-1.5 Ga. Post-1.5 Ga juvenile magmatism is more sporadic, and in the literature is often related to back-arc settings. The Grenvillian orogeny (1.15-0.9 Ga) comprises few juvenile signatures, and is largely represented by recycling of 1.6-1.2 Ga crust.

The proposed model comprises a 1.8 to 1.1 Ga subduction zone system that was located on the western/southwestern edge of Fennoscandia. The subduction hinge migrated away from the craton over time, but featured tectonic switching episodically. Crust was produced in volcanic arc settings, and was successively accreted onto the craton. Some arc terranes feature older inherited zircons and evolved isotopic signatures, this is attributed to arc formation on stretched continental crust.

Nd model ages from Fennoscandia reveal episodic extraction of crust from the mantle, with major peaks at 2.7, 2.1 and 1.5 Ga. However, during the 1.8-1.1 Ga period crust was continually being produced in a relatively 'steady-state'. The setting of which was a long-lived subduction zone similar to that seen in the western Pacific today, with the rate of growth varying with relative movement of the subduction hinge. From the 1.4 to 1.1 Ga period, preserved magmatism is generally ascribed to back-arc settings.

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300 m.y. of komatiite evolution in the Barberton Greenstone Belt

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Ultramafic magmas erupted through the 300 m.y. history of the Barberton greenstone belt in South Africa, the type locality of komatiite. Despite 30 years of investigation, there are very few complete geochemical analyses of these rocks. We analyzed major and trace elements of samples from four stratigraphic formations that span the complete history of the belt. The oldest well preserved komatiites are in 3.5 Ga Komati Fm. Most of these have sub-chondritic Al/Ti and depleted HREE; they are thought to have formed during deep (>300km) partial melting in a hot mantle plume. Less abundant are komatiites with chondritic Al/Ti and undepleted HREE, which formed during shallower melting. Most komatiites in the Komati Formation are non-vesicular and show no evidence of having erupted as hydrous lavas, but some uncommon examples, which contain large amygdales and are coarse-grained, may have contained some water. 3.48 Ga Hooggenoeg Fm komatiites have chondritic Al/Ti and undepleted HREE. 3.3 Ga Weltevreden komatiites have slightly super-chondritic Al/Ti and positively sloping REE profiles, characteristics consistent with shallower melting of a source that either was enriched in garnet or had previously undergone extensive partial melting. Some Weltevreden komatiites contain olivine with the composition Fo96. The liquid composition inferred using this composition and whole-rock compositions contains 33% MgO. If anhydrous this magma erupted at about 1660° C making it the hottest magma on earth. Two types of komatiites occur in the 3.3 Ga Mendon Fm. The first has Al/Ti and HREE similar to most komatiites from the Komati Formation; the second has very high Al/Ti which may indicate a garnet enriched source.

The diversity of komatiite compositions implies that there were major variations in the temperature and perhaps composition of the source and the melting mechanism through the 300 m.y. history of the Barberton belt.

Measurement of ^{232}Th, ^{230}Th and ^{231}Pa in modern and fossil deep-sea corals

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Deep-sea corals are abundant in the ocean and their aragonite skeletons have the potential to form dateable, high-resolution records of past ocean processes. In this study we make precise analyses of U, Th and Pa isotopes in the skeletons of both modern and fossil deep-sea corals using multiple-ion-counting ICP-MS. Neither Th nor Pa are expected to reside in the crystal lattice of aragonite, nevertheless the concentrations in cleaned modern corals are measurable, with typical values of ^{232}Th 100-2000pg/g, ^{230}Th 40-100 fg/g and ^{231}Pa 1-3 fg/g. Cleaning experiments on fossil deep-sea corals show that ^{232}Th contamination from ferromanganese crusts can be reduced to the levels seen in modern corals. Such incorporation of Th and Pa at formation is potentially problematic for accurate dating, but coupling U-Th and U-Pa analyses offers the potential to improve the chronology, and to reconstruct the initial ^{231}Pa/^{230}Th ratio.

We analyzed four species of modern deep-sea corals (*D. dianthus, F. alabastrum, C. ambrosia, and L. pertusa*) in a global distribution including samples from the North Atlantic, Southern Ocean and Pacific. ^{232}Th/^{230}Th ratios ranged from 210 in the central Pacific where detrital inputs (and hence ^{232}Th inputs) are expected to be low and up to 36,000 in samples from the detrital-rich continental shelf in the Atlantic. In the west Atlantic basin comparison of typical seawater ^{231}Pa/^{230}Th ratios to our seven-point modern-coral depth transect shows that the corals have a ratio that is approximately 40 times lower than seawater. This result is consistent with the observation that falling marine particles (with the marked exception of opal) scavenge Th more efficiently than Pa. The fractionation caused by this difference in scavenging is recorded in marine sediments, and has been used as a proxy for ocean circulation and productivity. Yet sediment composition generally varies through time, complicating the interpretation of the signal. Deep-sea corals may form a new, high-resolution, pure carbonate archive of marine ^{231}Pa/^{230}Th ratios in the past.

Mantle end-members (DM, EMI, EMII, HIMU and PM) – Geochronological interpretation

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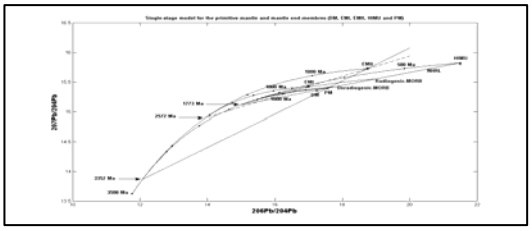
The mantle components (DM, EMI, EMII and HIMU) are treated in diagram ($^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$) in ordre to predict their relationships with the primitive mantle (PM). Calculations assuming isotopic ratio U/Pb as time-dependent according to the fundamental equation of radioactivity have shown that the age provided by the northern hemisphere reference line (NHRL), including radiogenic- and unradiogenic-MORB (R-MORB, U-MORB), is similar to the age provided by a geochron, including primitive lead in Canyon Diablo Troilite (CDT) and common lead in R-MORB and U-MORB corrected from in-situ decay. Moreover, concordance between these two slope-ages suggestes that the primitive lead in CDT and the common lead in R-MORB and U-MORB are conformable with the growth curve of the PM evolved in a single-stage model. On the other hand, the components DM and HIMU that plot on the NHRL are expected to be related to the PM by a mantle isochron, indicating an age of 1778 Ma. The available isotopic data on xenoliths exhibits trends between EMII with the PM for mantle xenoliths and between EMI with EMII for crustal xenoliths. Accepted as true isochrons, these trends imply that the EMII is related to the PM by a mantle isochron, indicating an age of 3352 Ma. Whereas, the EMI is related to the EMII by a mantle isochron, provinding an age of 2572 Ma. Corresponding radiogenic systems of components PM, EMI and EMII are found compatible with isotopic lead in volcanic lavas or intrusive granites from old cratons testifying of their involvement in crustal growth. Overall of EMII with continentally derived sediments support these points of view. We suggest that the recycling models of crustal and altered oceanic materials in mantle sources for generating EMI- and EMII-like melts have to be revised.



Mica as a recorder of pegmatite evolution: The Fregeneda-Almendra pegmatite field (Spain and Portugal)

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In the Fregeneda-Almendra area (FA), (Central-Iberian-Zone, Spain and Portugal), many pegmatite bodies occur. They mainly intruded pre-Ordovician metasediments of the schist-metagraywacke complex, showing a zonal distribution from barren to enrichment in Li, F, Sn, Rb, Nb>Ta, B, P and Be, with an increase in the evolution degree as the distance to the Lumbrales leucogranite increases, northwards. Five types of evolved pegmatites have been characterized: petalite-rich, spodumene-rich, lepidolite-spodumene-rich, lepidolite-rich and cassiterite-rich pegmatites, plus six types of barren and intermediate pegmatitic bodies.

Representative micas from the different pegmatite types, as well as from the close leucogranite were analysed for major and trace elements by EMPA, ICP-MS and AA techniques. All these micas belong to the muscovite-lepidolite series. Micas from the different pegmatite types show well defined evolutionary trends. In the lepidolite-rich dykes the incorporation of Li is mainly controlled by the combination of the $Li_3Al_{-1}[Y]_{-2}$ and the Si_2LiAl_{-3} exchange vectors, where [Y] represents vacancies in octahedral positions. In the lepidolite-free pegmatites, mica compositional variations can be described by the combination of the $Al_4Si_{-3}[Y]_{-1}$ and $(Fe{\pm}Mg{\pm}Mn)_3Al_{-2}[Y]_{-1}$ substitutions.

Micas from the lepidolite-bearing pegmatites are the richest in Li, Rb, Cs, Be, Ta and Nb, and the poorest in Ba; followed by the spodumene-bearing and the petalite-bearing dikes. Micas from the intermediate pegmatites show intermediate values for these elements but the highest for Sn and Zn. Micas from the leucogranites and barren pegmatites are the richest in Ba and the poorest in the other elements.

Compositional variations in micas from the FA field are controlled by petrological factors and bulk-rock compositon rather than crystal-chemical constraints. Therefore, micas may be a helpful tool to understand the petrogenesis of pegmatitic rocks.

The use of magnetic susceptibility and colour on dune samples for forensic purposes

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Soils and sediments can provide trace evidence in forensic investigations since they display unique physical and chemical signatures. A technique used to determine the nature of the magnetic carriers in sediments is magnetic susceptibility measurement, which is directly proportional to the quantity and grain size of ferromagnetic materials. Another important characteristic used to distinguish soils and sediments is colour measurement. Therefore, both techniques can be applyied for forensic proposes.

In order to investigate the variability of these properties in three different coastal dune sites from different geological contexts (limestones, granites and metasediments), three samples were collected at each site and prepared for magnetic susceptibility and colour analysis. Magnetic susceptibility (MS) was measured on 15g of dry bulk samples using a Kappabridge KLY4S equipment. Colour measurements were performed on bulk, sieved (<150µm or <63µm), and ashed (850ºC) samples, using a Konica Minolta CM-2600d spectrophotometer. The MS values range between $0.59x10^{-8}m^3/kg$ and $34.33x10^{-8}m^3/kg$, with higher values obtained on samples from dunes in metamorphic area (mean value of $27.34x10^{-8}$ m^3/kg), and lowest values (mean value of $1.05x10^{-8}$ m^3/kg) on dune in sedimentary areas. Intermediate values were obtained on samples from dunes surrounded by granites (mean value of $19.67x10^{-8}$ m^3/kg). Concerning the L*a*b* system colour sphere: the L* values measured varied between 48.50 (measured on <150µm size fraction) and 66.81 (measured on ashed samples); a* varied between 1.44 (measured on <150µm size fraction) and 9.03 (measured on ashed samples); b* between 4.84 (measured on <150µm size fraction) and 14.76 (measured measured on ashed samples). L*a*b* lowest values were always observed on samples from dune with limestone on its surroundings and the highest values on samples from dunes surrounded by metasediments. As a conclusion we have found that each technique discriminates the dune samples of the three selected sites.

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Bioavailability and potential human health impacts of Hg, As and other potentially toxic elements soil contamination near mining sites: Current knowledge and future priorities

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Summary

This study provides evidence of severe contamination of agricultural soils surrounding 3 mining areas in the South-West of Portugal. It also showed that soil contamination by Hg, As and other elements affects crop quality leading to potential human health risks. Since no National contaminated land management strategy has been implemented so far in Portugal [1] these findings raise important questions on how to develop a suitable risk management approach that includes bioavailability aspects and focus on links between soil contamination and human exposure to be used as a basis for future interventions and remedial actions.

Case-studies

In 2008, a total of 97 soil and 100 plant samples (*Lolium perenne, Brassica oleracea, Secale cereale*) were collected from agricultural fields surrounding three mining areas in South-West, Portugal (sulphides, pyrites, and Cu extraction). Soils are characterized by pH values of 3-7, a low organic carbon content (<5%) and clay content from 2 to 33%. Total soil Hg ranged from 0.01 to 98 mg/kg, crop Hg levels ranged from 0.01 to 42 mg/kg. Soil As varied from 0.2 to 1325 mg/kg; plant As ranged from 0.1 to 56 mg/kg. Maximum Cu, Pb and Zn contents in soils were 7635, 11546 and 1139 mg/kg and 543, 572 and 432 mg/kg, respectively in crops.

[1] Rodrigues *et al.*(2009) *Environ Int* **35** 214-225.

The realtime kinetics and mechanisms of nucleation and growth of dolomite from solution

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Dolomite ($CaMg(CO_3)_2$) is a common sedimentary rock-forming mineral [1], yet virtually no quantitative information about its formation mechanism is available. Here we demostrate how *in situ* and time-resolved synchrotron-based diffraction, combined with conventional imaging and spectroscopy were successfully applied to quantify the kinetics and mechanisms of crystallization of dolomite from solution.

Experiments were carried out by mixing equimolar aqueous Ca/Mg and CO_3^{2-} solutions (CO_3^{2-}:Ca^{2+}:Mg^{2+}=2:1:1) at 60° to 220°C and the crystallization was followed via synchrotron-based *in situ* and time-resolved Energy Dispersive X-ray Diffraction (ED-XRD).

Upon mixing of the two solutions a poorly ordered precursor (amorphous calcium-magnesium carbonate, ACMC) precipitated instantaneously. After a temperature dependent induction period (t_0=45 min and 10 min respectively at 60 and 220°C) dolomite nucleated and crystallized rapidly (2-3 min) forming nanocrystalline aggregates (Fig. 1A). The changes in Bragg peak areas over time for the dolomite (104) peak were fitted using the Johnson–Mehl-Avrami-Kolmogorov model [2]. The results suggest that dolomite crystallized following first order kinetics. The activation energies of nucleation (EA_{nucl}) and crystallization (EA_{cryst}) were derived from the Arrhenius equation (Fig. 1B and 1C).

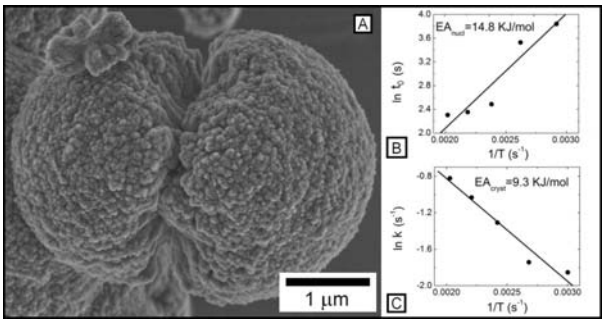

Figure 1: Photomicrograph of nanocrystalline (<100nm) dolomite aggregates formed at 60°C (A); Arrhenius plots for the dolomite induction time, t_0 (B) and growth rate, k (C).

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Nanoelectrophoresis studies of magnetite and silica in hydrothermal environments

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Iron oxides and silica minerals are ubiquitous in aqueous geochemical environments, including hydrothermal solutions. These minerals are often present in nano-colloidal form and play important roles in biogeochemical and environmental cycles. The study of the surface properties of these oxides provides important information about their interaction and behavior, especially in hydrothermal regimes, where experimental data are scarce.

We have recently developed a nanoelectrophoresis apparatus for determining the electrophoretic mobility and zeta potential of nanoparticulate materials (particle size down to 80 nm) at temperatures up to 260 °C and pressures up to 70 bar [1,2]. In the past, we were successful in obtaining the zeta potential data for micron-size particles of ZrO_2 and TiO_2 at hydrothermal conditions [2,3], which helped to understand the effect of temperature on the interface reactions in the elecrical double layer (EDL) on the oxide surface [4].

In this study, we obtained new zeta potential data for magnetite (Fe_3O_4) and silica (SiO_2) in hydrothermal solutions of KNO_3 and NaCl, respectively. The electrophoretic mobilities and zeta potentials of the studied materials were determined as a function of pH and temperature for different particle sizes. The isoelectric point (IEP) values – pH at which the zeta potential is zero – were determined by fitting the zeta potential data. Consideration of the particle size as well as kinetics of the aggregation processes in the system was found critical for correct calculation of the zeta potentials from the high temperature electrophoresis data.

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Assessment of the heavy metal contamination in surficial sediments from Kalimanci Lake (Macedonia)

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Major disaster happened on the 30.08.2003 in the eastern Macedonia (Europe), when one part of the Sasa Mine tailings dam collapsed and caused intensive flow of the tailings material. 70 000-100 000 m^3 of the tailings material was discharged and dispersed through the Kamenica River valley, to the city of Kamenica and into the Kalimanci Lake. The damaging tailings flow comprised an elevated amounts of the heavy metals (Ag, As, Cd, Cu, Mo, Pb, Sb and Zn) that seriously affected the surrounding environments, especially Kalimanci Lake. This artificial lake is supplied by two rivers: the main, Bregalnica River and Kamenica River, flowing directly from the Sasa ore district. The Sasa mine is situated 10 km N from the Kalimanci Lake and has been in production for over 45 years yielding 90 000 t of the high quality Pb-Zn concentrate annually.

The sampling of the surficial sediment from the Kalimanci Lake occurred before the accident in August 2001 and was revised in September 2007, three years after the accident. The geochemical analysis of the heavy metals (Ag, As, Cd, Cu, Mo, Pb, Sb and Zn) were performed in Acme Analytical Laboratories, Ltd. by ICP-MS.

The results showed that the concentrations of the heavy metals in the study area are extremely high compared with the background concentrations and world average values. The calculated enrichment factor (EF) for the samples collected in the year 2001 was much higher than 1 for all heavy metals: Ag, 38; As, 36; Cd, 279; Cu, 6; Mo, 1.5; Pb, 140; Sb, 1.3 and Zn, 50. The EF values suggest anthropogenic impact on heavy metals input in sediments due to the acid mine drainage, waste and tailings effluents from the Sasa mine area which are including high concentrations of heavy metals and are flowing out into the Kamenica River and then to the Kalimanci Lake. The EF values for the investigated heavy metals in the sediment samples from the year 2007 are following: Ag, 146; As, 48; Cd, 735; Cu, 21; Mo, 2; Pb, 387; Sb, 10 and Zn, 151. They are strongly indicating the effects of the tailings dam accident.

For a further discussion more detailed studies on the heavy metal concentration in the sediments from the Kalimanci Lake and the remediation process of the sediment are essential.

Fe/Mn and $^{187}Os/^{188}Os$ ratios in mafic lavas from the Ethiopian flood basalts

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The Fe/Mn ratio in mafic lavas has become the subject of interest following its association with radiogenic Os isotope ratios in Hawaiian picrites[1]. Such characteristics have been attributed to the entrainment of core material in mantle plumes. Ti-rich mafic lavas from the 30ma Ethiopian flood basalts were derived from a primary magma with 16 wt% MgO and 8 wt% Al_2O_3, consistent with an origin at 5 GPa and a potential temperature of ~1600°C. Precise ICPMS analysis of the Fe/Mn ratio reveals a range of values between 65.4 to 78.5 in MgO rich samples, comparable with and greater than those observed for Hawaiian lavas. Os contents in the same samples vary from 46 to 3916 ppt although the majority have Os>1000 ppt. Age-corrected $^{187}Os/^{188}Os$ ratios are generally sub-chondritic, although samples with <1000 ppt Os have more radiogenic $^{187}Os/^{188}Os$ ratios. The latter are broadly correlated with the Re/Os ratio and lie close to a 1Ga reference line, implying contamination by the underlying late proterozoic crust. The more Os- and MgO-rich samples, however, also show possible evidence of contamination, indicating that the uncontaminated $^{187}Os/^{188}Os$ ratio of the primary magma may have been as low as 0.12608 to 0.12477 (γ_{Os} = -0.73 to - 1.76). These low values imply a depleted source with a sub-chondritic Re/Os ratio, consistent with the positive ε_{Nd} values of +6 [2]. The results demonstrate that radiogenic Os isotope ratios and high Fe/Mn ratios are not correlated and their status as indicators of core entrainment is challenged. Comparison with experimental results indicates that high Fe/Mn ratios are not generated during melt extraction but are a feature of some plume source regions. Moreover, in the case of the Afar plume, which bears many of the characteristics of a deep mantle origin, these results indicate a plume composition that is depleted in Mn rather than one enriched in iron and the siderophile elements.

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Carbonate stability in the Earth's lower mantle and redox melting across the 660 km discontinuity

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The formation of the deepest melts in Earth's mantle is likely to be related to small degree carbonatitic melting [1]. The critical variables are (a) the solidus temperature of carbonate bearing peridotite and, (b) the oxygen fugacity (fO_2) conditions in the mantle. fO_2 determines whether or which volatile phase or species is present in the mantle (i.e. C vs. CO_2, in presence of H_2O also CH_4) and therefore strongly influences the peridotite solidus temperature.

Here we determined the solidus temperature of carbonate bearing fertile mantle and the fO_2 position of redox equilibria controlling carbonate stability in the mantle relative to solid state oxygen buffers. Experiments were performed in Walker type multianvil presses at ETH Zürich using 14/8 and 10/3.5 assemblies.

The solidus temperature of a CO_2 enriched mantle composition at 13.6 and 23 GPa is considerably lower than extrapolation of lower pressure data [1] would predict. The solidus temperatures at the investigated pressures are in the range of a normal mantle geotherm implying that small degree carbonatitic melting would be feasible at transition zone and lower mantle P–T conditions. To investigate the stability of carbonate with regard to oxygen fugacity, we have equilibrated a fertile peridotite composition containing 5 wt.% CO_2 with Fe–FeO, Ni–NiO, and Re–ReO_2 solid state buffer assemblages at 13.6 GPa, 1450°C and 23 GPa, 1600°C. The result is that at fO_2 conditions lower than NNO-3 all CO_2 is reduced to diamond and magnesite is unstable. In view of increasingly reducing conditions in the Earth's mantle with increasing depth [2–5], carbonate induced melting is unlikely as long as the capacity of ferric/ferrous redox buffers exeed the capacity of the carbon/carbonate buffer. However, in upwelling mantle containing fragments of previously subducted carbonate-enriched oceanic lithosphere, redox melting across the lower/upper mantle boundary or within the transition zone is likely to occur.

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Comparison of iodine and selenate retention mechanisms onto cementitious materials

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Cementitious materials are commonly used to stabilise radioactive wastes prior to their deposition in different types of repositories. The degradation of these materials produces highly alkaline leachates, whose interaction with the surrounding host-rock can produce a chemically disturbed zone. Iodine and selenate exhibit high solubility and poor sorption onto these materials, and its retention mechanism is still poorly understood. This work presents experimental and modelling results on the uptake of I^- and SeO_4^{2-} by mortar and concrete in contact with artificial cement pore water.

Batch and dynamic experiments results suggest that, under similar conditions, selenate is more retained than iodine. In batch experiments at S/L ratios = 100 g/L, Rd values obtained for selenate are between $9\cdot10^{-3}$ and $3\cdot10^{-2}$ m^3/kg for all the initial selenate concentrations studied ($1\cdot10^{-7}$M to $1\cdot10^{-4}$ M). Iodine Rd values are lower and decrease as the initial I^- concentration increases. In dynamic (column) experiments, higher selenate retardation is observed.

Several authors have previously suggested the possibility of incorporation of these anions into AFt- (ettringite) or AFm- (monosulfate) cement phases instead of SO_4^{2-} [1], [2], [3]. Results obtained in the present work indicate that the incorporation of SeO_4^{2-} into secondary AFt- phases can be a suitable retention mechanism for selenate. Iodine/sulfate substitution seems to be lower.

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Regulation of biogeochemical fluxes through microbial networks

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Microbiological research on biogeochemical processes, such as hydrocarbon degradation, is greatly stimulated by the application of the new meta-omics techniques (metagenomics, metatranscriptomics, metaproteomics). The integration of the resulting data and their interpretation in relation to biogeochemical processes requires new modelling tools. We recently developed ecological regulation analysis (ERA) [1]. ERA quantifies how changes in biogeochemical fluxes are actually regulated by the microorganisms performing the process. ERA was applied to data sets obtained from scientific literature. In general, changes in flux were found to be related to changes in cellular activity and not to changes in cell numbers. ERA has now been extended to enable dissecting how these changes in cellular activity are achieved, by metabolic regulation (changes in the interaction of enzymes with their substrates, products and co-factors) or hierarchical regulation (changes in enzyme concentrations due changes in translation, transcription, post-translational modification and degradation of mRNA and protein). The extended ERA allows for the integration of data on fluxes through specific functional groups, their cell numbers, and mRNA and protein levels of specific genes.

Mathematical modelling approaches can also provide insight into how the trophic structure of microbial networks, in relation to environmental conditions, affects biogeochemical processes. The combined influence of predation of bacteria by protozoa and nutrient limitation on biogeochemical fluxes was assessed and subsequently followed up by experiments. Paradoxically, the presence of protozoa can stimulate bacteria-catalyzed processes under nitrogen or phosphorous limitation, via protozoa-mediated nutrient recycling. The effect of predation on biogeochemical flux depends on the type of nutrient limitation, predation had a slight negative effect under carbon limitation.

Systems biology approaches integrating microbial ecology and biogeochemistry, like the two examples presented here, will enhance understanding on ecosystem functioning.

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Impact of environmental conditions and skeletal ultrastructure on the Li isotopic composition of scleractinian corals

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An important challenge towards reaching a better understanding of the global CO_2 cycle is to better quantify the weathering rate of continental silicates. The isotopic composition of Li that gets incorporated into marine carbonates has the potential to be a proxy for the seawater composition and the amount of Li weathered out of continental rocks and transported into the oceans.

The lithium isotope compositions ($^7Li/^6Li$) of shallow-water (*Porites lutea* and *Cladocora caespitosa)* and deep-sea corals (*Lophelia pertusa* and *Desmophyllum cristagalli*) were measured using a Caméca ims 1270 ion microprobe. The two *C. caespitosa* samples were grown in laboratory under controlled conditions at CO_2 partial pressures (pCO_2) of 416 ± 29 µatm and 729 ± 30 µatm, respectively. *In situ* analyses show that all samples are isotopically homogeneous and display significantly lower δ^7Li values relative to seawater, indicating a significant isotope fractionation during aragonite formation. In contrast to essentially all other elements analysed so far, there is no relationship between the Li isotopic compositions and the skeletal ultrastructure. This implies that the biomineralization mechanisms, which are supposed to be different for the different skeletal components COC and fibers), do not influence the Li isotopic composition in corals. We also show that changes in pCO_2 (pH) did not significantly affect the Li isotope signature. Nevertheless, a small but significant and systematic difference between deep-sea azooxanthellate and shallow-water zooxanthellate species is highlighted. The lack of dependence on pH on skeletal ultrastructure indicates that Li isotopic signature of corals could be used as a proxy for reconstructing the paleo-δ^7Li of seawater and, potentially, for deconvolving past continental weathering rates.

Geochemistry in space

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At present time geochemistry solves the problems of the existing natural scientific disciplines. However this approach isn't the only one of its kind. If we consider that all the chemical elements exist in nature not as a mixture of atoms and compounds but in the form of spatially organized geochemical fields, then it is possible to treat the environment as a result of the interaction of a combination of geochemical fields of chemical elements and their compounds. Different abundances, chemical and physical properties define a variety of fields of elements. The difference in mass, spatial structure, dynamics makes the field of iron different from the field of carbon, the field of gold – from that of helium, and so on.

The proposed approach has important corollaries in terms of theoretical geochemistry. In particular it allows to overcome the important paradigm, according to which the concentration of chemical elements at every point of space is estimated on the statistical basis, and to replace it by a new paradigm in which the content of any element at the particular point of space is a function of the coordinates of this point.

As a result of our efforts in this area we have come to two important conclusions: 1) geochemical fields are regular organized and exhibit themselves in space as the hierarchical fractal structures; 2) the fields can be identified, typified and studied by means of mathematical modeling using the concept of field theory.

The proposed approach does not contradict with the basic scientific concepts and opens broad prospects for purely geochemical studies in both theoretical and practical aspects.

Extremophile bacteria: Ultimate sink for U(VI) from contaminated mine water?

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In order to better develop remediation technologies for cleaning mine water and sediment originated from mining activities further understanding of the key biogeochemical processes that control transport and fate is needed. The distinction and quantification between biological and physical chemical processes is an area that needs attention if microbes are to be used as potential remediation technology. We present the findings of a study of bacterial interaction with uranium in aqueous environment.

To this aim, the behaviour of 2 strains of the chemolithotrophic acidophile, *Acidithiobacillus ferrooxidans* (Type strain NCIMB 8455 from acid bituminous coal mine effluent, and NCIMB 13538 isolated from an abandoned uranium mine in Dera Ghazi Khan, Pakistan) towards the presence of U(VI) were studied under various environmental conditions. In order to understand the biotic and abiotic contributions to the removal of U(VI) from mine water, the constructed systems were analysed by ICP-MS, FT-IR, potentiometric titrations and XPS and EXAFS. Changes in O_2 consumption and bacterial biomass were also studied. The presence of Fe(III) was also carefully monitored.

Results showed that both the presence of bacterial biomass and Fe(III) have an effect on the removal and speciation of U(VI) from solution at acidic pH. It also demonstrated that although the bacteria is capable to accumulate U (VI) there is a significant amount of U (VI) immobilised by Fe(III) precipitates. The study allowed also to establish the adequate parameters for the potential use of this bacteria on the clean-up of mine water and sediments at very acidic conditions.

Which trivalent phosphate controls acidic surface water P availability?

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Phosphate concentrations in natural waters have been of increasing concern because if they are too low they may hinder forest and agricultural growth, but if they are too high they may lead to eutrophication [1]. Thermodynamic calculations suggest that the Al and Fe phosphates, variscite and strengite, control aqueous phosphate concentrations in acidic (pH<7) environments [2]. This study is aimed at assessing experimentally the role of these minerals in controlling phosphate availability in natural waters.

The formation and dissolution of Al and Fe-phosphate phases were investigated experimentally at 25°C to 200°C and 1.5<pH<9. Solids were characterized by XRD, FTIR, FEG-SEM and HR-TEM, and Al, Fe, and P in solution were analysed by ICP-AES, IC and UV-Vis. Batch reactor experiments show that Al and Fe phosphate phases readily precipitate from supersaturated solutions. Precipitation is iniated by the nucleation and growth of amorphous Al or Fe phosphates (AAP and AFP, respectively). At T=100°C the amorphous phosphates recrystalize into either variscite (V) and metavariscite (MV), or strengite, respectively. At lower T, amorphous phosphates persist for at least several months. Dissolution experiments demonstrate these phases rapidly dissolve in undersaturated solutions. These results suggest that amorphous Al and Fe phosphates limit P availability in many natural environments.

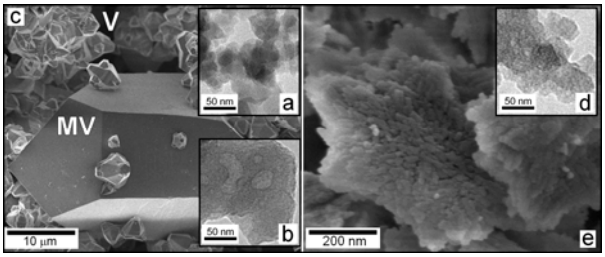

Figure 1: Photomicrographs of (a) AAP at t=0, (b) AAP at t=12 days; (c) MV and V at t=21 days at 100°C; (d) AFP at t=0 and (e) strengite crystals at t= 5days at 100°C.

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REEs in authigenic carbonates: A new proxy for tracing fluid sources at cold seeps

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At cold seeps, authigenic carbonates form as a result of the microbial oxidation of methane and, hence, represent suitable archives of fluid seepage on continental margins. Here, we have investigated the potential of using REEs in authigenic carbonates for tracing fluid sources at cold seeps, and providing additional constraints on associated biogeochemical processes. A series of carbonate samples was analysed, collected from various active sites of fluid venting, and characterised by distinct mineralogical compositions. These samples were recovered from the Niger Delta area over the past few years [1], during several expeditions funded by IFREMER and TOTAL (NERIS and ERIG-3D projects).

The samples were leached with 5% acetic acid, and analysed by SF-ICP-MS (ELEMENT II) after Tm addition [2]. They exhibit a wide range of shale-normalised REE patterns. Most aragonite concretions recovered from hydrate-rich pockmarks display very similar patterns (e.g. distinct MREE bulge), but their total sum of REEs (ΣREE_N) vary significantly from one sample to another. In contrast, high-Mg-rich samples are characterised by similar ΣREE_N contents, but display a wide range of REE patterns. A few siderite concretions recovered from a mud volcano exhibit much higher REE concentrations. Taken together with additional data for stable isotope ratios and REEs in selected pore water samples, these results will be discussed to provide contraints on the factors controlling REE distribution in cold seep carbonates.

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Modelling plant-soil interaction: From the soil particle and fungal scale to root scale

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In this talk I will present models that deal with plant nutrient uptake and the role plant exuded organic acids and mycorrhizae can have on this process. I will begin by describing our recent work on modelling exudation of 2'-deoxymugineic acid (DMA) and the effect this has on plant acquired zinc. We assume that DMA and zinc are both present in two forms in the soil, in the soil solution phase and bound to the soil particles. We will develop a model that describes this competetive binding reaction and then link it up to a model for plant exudation and zink uptake. In particular we will investigate the effect of the diurnial DMA exudation pattern on the zinc uptake. The second model I will describe deals with the uptake of nutrients, such as phosphate, that in addition to binding to the soil particle surfaces can also diffuse into the soil particle micropores and bind to their internal surfaces. This leads to a so called dual porosity models for the soil and we will show how the results for nutrient uptake by plants differ when one considers simple particle surface binding in comparison to dual porosity nutrient binding. We find that the results are qualitatively and quantitatively very different. This highlights the need for the simultaneous measurement of soil properties and root nutrient uptake properties. A third model I will discuss deals with modelling the effect mycorrhizae have on phosphate uptake by plants. We consider the phosphate movement within the soil, uptake by roots and fungus, and transport of phosphate within the fungus to the root surface. We find that the model predictions for phosphate depletion profiles in the soil differ significantly for two plausable and experimentally reported fungal phosphate uptake rates. Whilst both depletion profiles have support within the literature clearly, only one of them has to be correct. I will suggest a controlled experiment which has not yet been performed that can decide between the two scenarios.

Binding of uranium to organic-rich soils in an alpine region in Switzerland

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Naturally occuring uranium was found at extremely high concentrations (up to 7,000 ppm) in a soil of the alpine region (Dischma valley), in Grisons, Switzerland. The goal of this study was to characterize the binding of uranium to the soil matrix and to determine its redox state in order to assess the potential for uranium mobilization. Pore water profiles collected from Dischma soil revealed the establishment of anaerobic conditions with increasing soil depth. A combination of chemical extraction methods and spectroscopy was applied to characterize the redox state and binding environment of uranium in the soil. Bicarbonate extraction under anaerobic conditions released most of the uranium (> 63 %) indicating that uranium occurs predominantly in the hexavalent form. Surprisingly, the uranium speciation did not vary greatly as a function of depth. This was confirmed by X-ray absorption near edge spectroscopy (XANES), which indicated that U was present as a mixture of U(VI) and U(IV) with U(VI) dominating. A soil sequential extraction method revealed that the majority of uranium was released concomitantly with soil organic matter. Extended X-ray absorption fine structure (EXAFS) spectroscopy revealed that uranium in the soil matrix is octahedrally coordinated with two axial (at 1.77 Å) and six equatorial oxygen atoms (at 2.36 Å) indicating a short-range uranyl-like (UO_2^{2+}) structure. An additional EXAFS signal (at about 3.2 Å), as identified in some spectra, showed that uranium was also bound to a light element such as carbon, phosphorus or silicon.

High-resolution chemo- and biostratigraphic records of the Early Aptian Oceanic Anoxic Event in Cantabria (northern Spain)

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The Early Aptian Oceanic Anoxic Event (OAE1a) is one of the most widespread and best-defined OAE of the Cretaceous. This event was associated to abrupt perturbations of the carbon cycle as indicated by both negative and positive $\delta^{13}C$ excursions in organic mater and carbonate records. The $\delta^{13}C_{car}$ record of the OAE1a has been subdivided in a series of segments, labelled C3–C7 [1], that can be regionally reproducible. Most of the studies come from hemipelagic and pelagic sections but only few studies exist on the reproducibility of these C-isotope shifts in shallow water settings.

New detailed litho- bio- and chemostratigraphic (TOC, $\delta^{13}C_{car}$, $\delta^{13}C_{org}$, $\delta^{18}O$) investigation of the Lower Aptian succession of northwestern Cantabria, allowed to recognize the local expression of the OAE1a in shallow platform carbonates of northern Spain. The event is characterized by a ~ 40 m thick marly interval (Patrocinio Fm) that records an abrupt negative $\delta^{13}C$ excursion in both bulk organic matter (up to 5‰) and carbonates (up to 6‰, mean 3‰). The negative shift is attributed to the $\delta^{13}C_{car}$ curve segment C3 [1]. It is followed by a positive shift recorded in carbonates, attributable to the curve segment C7 [1]. These records can be accurately calibrated against new ammonite and nannofossil biostratigraphy, which allow a confident attribution of the OAE1a to the middle part of the *Hayesites irregularis* calcareous nannofossil Zone, and to the *Deshayesites weissi* ammonites Zone. Our data help to refine the age of the OAE1a [2, 3] and reveal the existence of a stratigraphic gap in these carbonate series that could cover the record of the C4–C6 segments of the $\delta^{13}C_{car}$ curve.

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CO_2 sequestration by basalt: Experimental studies and geochemical modeling

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Basaltic rocks are potential repositories for sequestering carbon dioxide (CO_2) because of their capacity for trapping CO_2 in carbonate minerals. We carried out series of geochemical models and experiments, reacting basalt with CO_2-charged fluids over a range of conditions from 50°C to 150°C and from 100 to 300 bars. Experiments were carried out in flexible gold-cell apparatus with a serial online sampling capability of the fluids to permit monitoring reaction progress. Results indicate basalt has a high reactivity to supercritical CO_2 and carbonic acid. Initial reactions caused a rapid drop in pH and an increase in cations including Ca, Mg, Fe, and Mn followed by a decrease to steady-state values. CO_2 decreased asymptotically to steady-state concentrations in experiments that were under-saturated with CO_2, a repeatable pattern following re-injection of CO_2 into the experiment. These results showed that the basalt continued to have a capacity to react with CO_2. In experiments that were supersaturated with CO_2 containing a separate supercritical CO_2 phase, the rock took up over 10% of its weight in carbonate.

Reaction path simulations predicted calcite would initially precipitate then later dissolve in the sequential addition of P_{CO_2} to be replaced by dolomite and siderite at equilibrium. SEM analyses of the solid reaction products found only Fe and Mg bearing phases consistent with the kinetic barriers to forming dolomite. Experiments are currently underway to find the optimal conditions for CO_2 sequestration in basalt.

Radium co-precipitation in evaporitic systems

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High concentrations of naturally occuring radium pose environmental and health concerns in natural and industrial systems. Compared to fresh water, adsorption of Ra^{2+} is limited in saline conditions while co-precipitation may become an effective process in decreasing Ra concentration. Despite its importance, co-precipitation was hardly studied in high ionic strength environments such as evaporitic systems.

The fate of Ra in the concentrate of a desalinization plant was studied by evaporation batch experiments at ionic strength ranges (I) of 0.7-7.8 m. Precipitation sequences revealed that Ra co-precipitates in barite with an apparent partition coefficient of $K'_D=(Ra/Ba)_{solid}/([Ra]/[Ba])_{solution}= 0.8\pm0.2$. Although co-precipitation of Ra in barite is a well documented phenomenon, this value of K'_D is significantly lower than the accepted value for relatively diluted solutions (1.8±0.1 [1]). We examined the effects of both kinetic and ionic strength on Ra co-precipitation and K'_D value.

Ra activity coefficients were calculated with the Pitzer formalism using PHREEQC geochemical software. Pitzer parameters for Ra^{2+}-Cl^- interaction where evaluated primarily through linear regression of published parameters for Ca, Mg, Sr and Ba to their 8-fold hydrated ionic radii.The $RaSO_{4,aq}$ ion pair was explicity recognized as suggested by Paige *et al*. [2]. Using these parameters we were able to describe the results with a numerical model. Distribution of Ra and Ba between the solid and aqueous phases was determined by their activity ratio in the solution. The partition coefficient that best fit the results, $K''_D=(Ra/Ba)_{surface}/(a_{Ra+2}/a_{Ba+2})_{solution}= 1.7$, is in good agreement with the accepted value (1.8), suggesting that the reaction is near equilibrium and kinetic effects are insignificant.

It is often assumed that activity coefficient ratios of similar alkaline earth elements is close to unity and therefore may be neglected when deriving K''_D. Our calculations show that above I=1m the ratio $\gamma_{Ra+2}/\gamma_{Ba+2}$ decreases significantly, therefore reducing Ra removal. Understanding such effects is crucial for risk assessment in systems where both high Ra concentrations and high ionic strength conditions are met.

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Can aerosol-induced slowing of rain formation weaken hurricanes?

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It has been recently recognized that aerosols, by slowing the conversion of cloud water into precipitation, can invigorate deep tropical convective clouds. Simulations of the impact of the same aerosol-induced microphysical changes to tropical cyclones suggest the weakening of the storm intensities. We hypothesize that the fundamental cause for these opposite effects is their organization. In unorganized or linear storms such as squall lines, the low level exhauset cool air is left behind. In contrast, the surface convergence in closed circulating tropical storms forces this cool air to be eventually lifted on expense of the kinetic energy of the storm.

More specifically, the small CCN make a larger number of smaller cloud drops, which then are slower to coalesce into rain drops. The unprecipitated cloud water can either evaporate or ascend to the heights above the freezing level. The cloud water that evaporates cools the low level air. The cloud water that is carried to the cold regions freeze onto ice precipitation, and release there the latent heat of freezing. This invigoration at the periphery decreases the convergence of mass and moisture to the center, because some fraction ascends at larger radii, and so weakens the winds around the center. In addition, the ice precipitation melts at the low levels and cools the air there further.

The added evaporation and melting cool the low level air, which converge towards the center of the storm. Some of the kinetic energy of the storm has to be invested in lifting the cooler and heavier air when it reaches towards the eye wall. This takes away from the wind speed of the storm, and reduces its intensity.

A major challenge in this hypothesis is the extent to which ultrafine aerosols can slow the conversion of cloud drops into precipitation in the presence of sea spray giant CCN. This question is addressed initially by observations of polluted convective clouds over ocean. The recent eruptions of Kilauea volcano in Hawaii emitted plumes of SO_2 and fine aerosols that were ingested in convective clouds downwind. Analyses of the clouds with combined satellite and radar observations of cloud microstructure and precipitation are exploited to look into this question. Initial results show that precipitation is suppressed, but to a lesser extent than previously reported due to air pollution and smoke over land areas.

Linking small scale soil chemical variability to fungal niche preference

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Ectomycorrhizal fungi are root symbionts of woody plants. Their host plants, for which this symbiosis is obligate, cover the majority of forested land on earth. Estimates of diversity vary greatly, but generally 30 or more (in some cases hundreds) ectomycorrhizal fungal species can be found in a 1ha area of forest even when those forests may have just one or two ectomycorrhizal hosts. Soil heterogeneity is often proposed to be a factor driving this diversity. Significant evidence exists to suggest that, at least on the scale of horizon to horizon variation, consistent shifts in fungal (including just ectomycorrhizal) community can be found to correlate with soil chemical variables. However, significant diversity is still found in a given soil horizon, suggesting that if soil chemical factors and niche heterogeneity are driving fungal diversity then a smaller scale of sampling is necessary. We looked at a large number (150) of small (<5g) soil samples taken from a bishop pine forest at Point Reyes National Seashore in northern California. A 70 cm vertical transect was drawn across a soil profile and 10 samples were taken per vertical transect. Each pit had three vertical transects X 3 pits X 2 sites (one on granitic, one on sandstone parent material). Climate, stand age, stand history were all constant between pits. For each sample %C, %N, pH, and $BaCl_2$ exchangeable Na, Ca, K, and Mg were measured. Also for each sample, the fungal community was characterized using terminal restriction fragment length polymorphism in conjunction with cloning and sequencing. Spatial correlation (within and between pits) was tested for. The most significant factor shaping fungal communities was parent material, followed by pH, exchangeable Ca and exchangeable Mg. While there was a significant amount of co-correlation between these factors, soil chemistry is still significantly correlated with fungal community when the effect of parent material is removed. The overall variability of soil chemical variables is discussed, as are individual fungal species habitat preferences. To our knowledge this is the first study which links soil chemical variability in the field to fungal species presence on a scale relevant to individual hyphae.

Gene regulation of iron acquisition in *Serpula lacrymans*

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The dry rot fungus, *Serpula lacrymans*, is a major decomposer of constructional wood. In houses, its extensive mycelia connect sources of minerals (gypsum or concrete), carbon (wood) and water (leaking pipes). Long distance translocation of recourses within the mycelia makes *S. lacrymans* well adapted to growth in buildings. In nature, where *S. lacrymans* is rare, it colonizes stumps and dead wood in contact with soil.

Calcium oxalate crystals are commonly observed in association with hyphae of *S. lacrymans*. Based on these observations it has been suggested that calcium is dissolved from mineral sources and translocated to the wood during decomposition. However, a pilot study demonstrated no correlation between calcium content and wood decay. Instead, increased decay was correlated with increased iron content in the decomposed wood. Supporting the idea that the Fenton reaction, involving Fe^{2+} and H_2O_2, may drive cellulose decomposition. Thus making dissolution, uptake and translocation of iron central in the wood decomposition process of *S. lacrymans*.

We here examine growth, exudation and gene expression of *S. lacrymans* in pure liquid cultures with iron supplied as iron chloride or as Goethite. Carbon was supplied as glucose or cellulose and samples were taken at 10, 20 and 30 days after inoculation. Over the experimental time, pH of the growth media decreased and the capacity to complex iron increased, as determined by the CAS assay. In a parallel experiment, *S. lacrymans* was grown in microcosms with wood and soil. In this wood decomposition, fungal biomass and gene expression was analysed over the same experimental time.

The genome of *S. lacrymans* is currently being sequenced at JGI. We used the sequenced isolate in our experiments. When the genome sequence becomes available, obtained results on expressed genes can be analysed in a whole genome context. Results obtained from systems of different complexity, ranging from liquid media with glucose, to cellulose, to wood chips on soil, will be combined to determine how genes involved in iron acquisition of *S. lacrymans* are regulated in response to form of iron as well as the form of carbon.

Boron isotope composition of crop plants

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Boron (B) and its isotopes have been used for a long time in geo- and environmental sciences to study mixing and fractionation processes as well as sources of anthropogenic contamination. The authentication of food using isotope compositions of specific reservoir- and process-sensitive elements is a relatively new and growing application in isotope chemistry. Unlike some well-established stable and radiogenic isotope systems (C-N-O-S-Sr-Pb) the use of B isotopes to trace the origin of food is almost unexplored. However, due to the essential role of B for embryonic development and organogenesis in plants and animals and the enormous range of isotope compositions found in nature B is a very interesting tracer to verify the origin and possible cultivation methods of various types of crop plants.

Our first B isotope data of vegetables, corn and fruits cover most of the natural variation of about 100‰ in δ^{11}B. These highly variable B isotope compositions reflect regionally varying contributions of the natural background (geology, hydrology, soil) as well as anthropogenic processes during cultivation (fertilization/irrigation).

Most of the crop plants investigated show δ^{11}B values between -5 and +20 ‰. Those values likely reflect the geogenic background of the rocks and soils where the crops were cultivated. Corn samples from Europe (EU TRACE project) show a total range in δ^{11}B from -2 to +22 ‰. However, within specific growing areas the range of δ^{11}B values for corn samples is much smaller (~10 ‰). To date the isotopically most extreme samples are a pepper sample from Israel (+35 ‰ δ^{11}B) and a cabbage reference material from NIST (-24 ‰ δ^{11}B). The high, seawater-like, δ^{11}B value of the Israeli pepper may reflect irrigation with waters derived from the Dead Sea (~50-60 ‰ δ^{11}B) or salinar aquifers. The low δ^{11}B value of the NIST cabbage may reflect fertilization of a boron-loving crop with fertilizers coming from non-marine evaporate deposits.

In addition to the direct tracing of reservoirs and processes using the δ^{11}B of crop plants, B isotope fractionation during incorporation, transport and integration of B in the plants is an unexplored field to study the function and transport mechanisms of B in biological systems.

An empirical comparison of expected versus observed REE distribution in mantle pyroxene

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The stability of clinopyroxene (Cpx) over a wide range of P – T conditions makes this rock-forming mineral an important constituent of the sub-arc environment, both in the subducting slab and the overlying mantle wedge. Because of its relatively high partition coefficients for many lithophile elements, Cpx exerts considerable control over arc magma chemistry.

However, because Cpx chemistry is variable, partitioning of elements depends on the exact type of pyroxene present. Subduction related Cpx constantly undergo thermo-dynamically induced crystallo-chemical transformations in response to increasing P-T conditions, commonly resulting in elevated Al, particularly Al in tetrahedral coordination (Al_{IV}), or the Ca-Tschermak component (CaTs). Experimental results pertaining to the distribution coefficient (D) of REE in these high Al Cpx phases [1] show that for heavy (H)REE in high Al Cpx the distribution coefficient is greater than unity. In the depleted mantle wedge, Cpx can become very Cr-rich and Ca-poor, chemical changes that also affect the M2-site dimensions.

Here we endeavoured to test empirically the correlation between crystallographic parameters (which ultimately reflect composition) and the REE distribution in a suite of mantle and eclogitic Cpx. For the first time we present unit cell dimensions and fractional atomic coordinates derived from structural XRD data for the very same grains on which trace element compositional data were acquired by LA-ICP-MS.

The data show (within experimental error) remarkable agreement between the average metal – oxygen (M2-O) bond-length obtained from XRD data minus the ionic radius of O and the optimal ionic radius inferred from REE distribution in an Onuma diagram [2]. This suggests that, indeed, the recorded REE distribution in the Cpx is a direct consequence of the atomic crystallographic arrangement that permits a trace cation into the lattice site [3], which in turn is a physical manifestation of the major element chemistry. This results in Onuma diagram apices ranging from Pr to Er.

Consequently, as shown experimentally for high Al Cpx [1] the major element chemistry has an influence on which trace cations are preferentially retained in the solid phase both in direct slab melting and fluid-induced sub-arc mantle melting.

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Indoor radon concentrations: The influence of geological factors in Italian study case

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The indoor radon exposition is internationally known as a health hazard. For this reason, many countries have introduced specific laws and regulations and radon-risk maps have been consequently produced. In Italy the radon exposure legislation regards only general workplaces (D. Lgs. n. 241/00) and only one national survey in the 90's has been currently conducted by APAT, ISS and ARPA regional agencies. This survey assessed the exposure to indoor radon concentration in national dwellings on large scale. In absence of guidelines, only few Italian Regions have prepared a surveying protocol using independent standards in order to identify "radon prone areas", inducing a bigger uncertainty on the definition of a national risk map. In the present work a standardized methodology for indoor radon measurements has been set up, with attention to the development of a passive measurement technique, validated through a comparison with other international laboratories. Data from a wide sampling (Lombardia, with the case studies of Milano Province and Milano city, Emilia Romagna, Toscana, Puglia) of radon indoor monitoring has been elaborated and georeferenced, using geo-statistical technique, to produced a map of annual average radon concentration and to verify the relapse of seasonal fluctuations on radon concentrations. Applying the recently introduced international approach, the elaborated maps has been integrated with geological knowledge of highest concentration macro-areas identified in order to better determine them. This study allowed to point out not negligible radon concentrations also in traditionally no–risk zone; moreover the application of the developed methodology will be useful to give advices to fill legislation gaps or to draft urban development plans.

Seismic constraints on the fine scale structure of Earth's mantle

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Seismic tomography is very successful in imaging the large scale structure of the deep Earth on wavelengths of a few hundred kilometers. On the other hand geochemical studies indicate heterogeneities on all scale lengths. Much of what we know about the small scale structure of the Earth's deep interior comes from studying high frequency reflections and conversions of seismic waves at boundaries. Besides this information the seismic recordings also contain extensive energy that is attributed to scattering of the high-frequency components of the seismic wavefield. This information can be used to probe the fine-scale (approximately 10 km and smaller) heterogeneities of the Earth's interior, and can help to solve questions such as the existence of melt, the location of geochemical reservoirs and the fate of subducted crustal and slab material Here we use observations of scattered energy related to seismic mantle waves to image the likely introduction of geochemical heterogeneities into the lower mantle in the vicinity of subduction zones. These data indicate that crustal material enters the lower mantle at least beneath some subduction zones. Using scattered energy sensitive to small-scale structure at the core-mantle boundary we are able to detect regions of increased scattering at this important boundary of the Earth. The region of the large low shear velocity province beneath Africa seems to contain strong heterogeneities leading to increased scattering form this region. Using geodynamical models in conjunction with these seismic results it might be possible to explain the location and origin of some of the Earth's small scale structure.

Molybdenum isotopes record past instabilities of the Arabian Sea oxygen minimum zone (OMZ)

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Molybdenum is a redox-sensitive trace metal and Mo enrichments and isotopic compositions in marine sediments can be used to reconstruct paleo-redox conditions. Fractionation values reflect the partial or complete scavenging of pore water Mo and the precipitation of different Mo-bearing species including sulfur. The Arabian Sea OMZ is maintained by high oxygen consumption due to organic matter oxidation and low oxygenated intermediate water inflow. During the last 50 kyr, the stability of the OMZ is related to millennial climate variability. During massive ice-sheets collapse in the North Atlantic (Heinrich events HE), the inflow of oxygen-rich Antarctic Intermediate Water (AAIW) was stronger causing a transient weakening or disappearance of the Arabian Sea OMZ. We present Mo isotopes ($\delta^{98/95}$Mo) and authigenic Mo concentrations [Mo] measured by MC-ICP-MS in a sediment core collected within the OMZ offshore Pakistan. The transition from HE5 to warm interstadial Dansgaard/Oeschger event 12 (DO12; 48 to 46 kyr) is characterized by an important increase of total organic matter (TOC). [Mo] and $\delta^{98/95}$Mo mirror this pattern, with low [Mo] and low $\delta^{98/95}$Mo pointing to oxic to suboxic conditions during HE5. By contrast, during DO12, TOC and [Mo] increase and the $\delta^{98/95}$Mo isotopic composition is higher. This points to an anoxic water column due to a well-developed OMZ (but without free H_2S in the water column). During DO interstadials 12, 11 & 10 and stadials 12-11 & 11-10, $\delta^{98/95}$Mo values stay relatively high indicating that anoxia persisted throughout this period. Interestingly, the $\delta^{98/95}$Mo signature allows distinguishing between ventilation conditions during 'cold' DO stadials and HEs. This is probably linked to isotopic fractionation thresholds, highlighting the advantage of Mo isotopes in comparison with other redox-sensitive geochemical proxies (TOC, $^{15}N/^{14}N$, lycopane…).

Anthropogenic aerosols and Southern Hemisphere climate change: A modelling perspective

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Climate modelling suggests that because the distribution of aerosols is highly variable in space and time, anthropogenic aerosol forcing can actively drive changes in atmospheric circulation. Possible impacts of anthropogenic aerosols in the Northern Hemisphere (NH) include summertime floods and droughts in China [1], droughts in the Sahel [2], and a weakening of the South Asian Monsoon [3].

Anthropogenic aerosol concentrations are much lower in the Southern Hemisphere (SH) than in the NH. However, several climate modelling studies show a southward shift of tropical rainfall in response to an aerosol-induced cooling of the Northern Hemisphere [2,4,5], which also implies the possibility of effects on circulation and rainfall in the SH.

We performed 20th Century transient simulations with a low-resolution version of the CSIRO global climate model (GCM), designed to isolate the effects of anthropogenic aerosols on recent climate change [6]. The results suggest that anthropogenic aerosols (principally from the NH) are important for understanding late 20th-Century trends in the climate of the SH, including rainfall changes over Australia [6], the structure of temperature changes in the Indian Ocean [7] and changes in the Southern Annular Mode [8]. Changes in oceanic heat transport are important in modulating these responses in our GCM; this emphasises the importance of using coupled ocean-atmosphere GCMs in future studies of aerosol effects on climate.

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Soil erosion rates at field plot studies in Bulgaria

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Soil erosion is recognized as the most serious soil degradation process on the territory of Bulgaria. This report aims at presenting results from the field plots for soil erosion studies in Bulgaria.

Field plots have been set up in 9 experimental sites, belonging to 6 research institutes, to study soil erosion at diverse soil, climate, topography, cover and management conditions in agricultural and forest lands since 1958. The slope of the plots ranged from 9.5 to 26.6%, the lengths were from 4 to 70 m and the area was from 12 to 350 m^2. Reported average annual data respond to measurement periods from 4 to 21 years.

The average annual number of erosive rains varied between the sites from 1 to 7 and the respective amount of a single event – from 15 to 24 mm. The annual kinetic energies varied between study sites from 7.7 to 29.3 MJ ha^{-1} and the rainfall erosivity indices from 204 to 796 MJ mm ha^{-1} h^{-1}. In addition to the spatial variability, the studied rainfall parameters varied also temporally from year to year.

The mean average annual soil loss from the 21 different soils found at the 9 experimental sites was 15.3 t/ha/y. The average annual soil losses from 3 Haplic Kastanozems ranged from 15.6 to 42.5 t/ha/y and those from 14 Chromic Luvisols – from 0.8 to 75.4 t/ha/y. The mean standard error of the soil losse, characterizing their temporal variability was 4 t/ha/y, varying from soil to soil from 0.2 to 13.3 t/ha/y. The average annual soil loss from Dystic Cambisol measured from 1960 to 1970 was 17.8 t/ha/y with standard error 5.4 t/ha/y but 42.8 t/ha/y and standard error 10.5 t/ha/y when measured between 1985 and 1988.

The mean soil loss rate found for cover crops (wheat, triticale, rye, medick, perco, grass mixture and brassica) is 0.8 t/ha/y and that for row crops (maize, sunflower and oriental tobacco) is 2.5 t/ha/y. The mean standard error of the soil erosion rates in the discussed data set is 0.6 t/ha/y, varying from 0.03 t/ha/y to 1.7. Average annual amount of soil eroded from grass varied from 0.03 t/ha/y with standard error 0.01 t/ha/y to 6 t/ha/y with standard error 2 t/ha/y. Observed average annual soil loss from Scots pine plantations was 0.03 t/ha/y with standard error 0.01 t/ha/y and that from thin Oak forest was 0.47 t/ha/y with standard error 0.16 t/ha/y.

Magnesium isotope compositions of CAIs from Rumuruti chondrites

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Introduction

Recently, Rout and Bischoff [1] analysed 101 Ca,Al-rich inclusions (CAIs) from 20 R chondrites. From three hibonite-bearing CAIs (H030/L (from Hughes 030), 2446D/2L (NWA 2446), and 1476/124 (NWA 1476)) and one spinel-plagioclase-rich CAI (753C/51 from NWA 753) Mg isotope compositions were obtained.

Results and Discussion

None of the inclusions show ^{26}Mg excess corresponding to a canonical ^{26}Al/^{27}Al ratio [2]. Only the hibonite-rich CAI (H030/L) studied earlier [3] shows a resolvable excess of ^{26}Mg, which corresponds to an initial ^{26}Al/^{27}Al ratio of ~7 x 10^{-7}. Surprisingly, this CAI was found within a type 4 lithology of the Hughes 030 chondrite [3], whereas the two other hibonite-bearing CAIs having no ^{26}Mg excess were found in type 3 lithologies. The upper limits for the $(^{26}Al/^{27}Al)_0$ in the CAIs 2446D/2L, 1476/124, and 753C/51 are $<3x10^{-6}$, $<5x10^{-6}$, and $<5x10^{-7}$, respectively. Hibonites in 2446D/2L are characterised by having isotopically light magnesium: F_{Mg} up to -4.7‰. For hibonites in H030/L a high ^{27}Al/^{24}Mg ratio of up to ~57000 was obtained.

Absence of resolvable ^{26}Mg excess in the CAIs 2446D/2L and 1476/124 is not related to post-accretion metamorphism. Most probably, they formed from percursors with lower than canonical ^{26}Al/^{27}Al ratio. On the other hand CAI 753C/51 is from a metamorphosed lithology and its magnesium isotope composition has been disturbed. Inclusion H030/L is similar to the HAL-type CAIs [4,5] as inferred from its high ^{27}Al/^{24}Mg ratio and low $(^{26}Al/^{27}Al)_0$ values and formed by distillation of the precursors. Some O-isotope data on R-chondrite CAIs will also be presented at the meeting.

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Photosensitized aging of succinic acid aerosol

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Ultraviolet or visible light absorbing organic constituents of atmospheric aerosols may act as photosensitizers for a number of processes. Photosensitizers may be primary organics from combustion sources or be formed in situ during oxidation in the atmosphere. The significance of photosensitized processes has been demonstrated by showing enhanced uptake of atmospheric oxidants to organic films or aerosol particles.

A solution containing ammonium sulfate, succinic acid and benzophenone or Benzoyl Benzoic Acid (BBA) was nebulized. The aerosol flow passed through a photoreactor with about 9 min. residence time, which was coupled to a High Resolution Time of Flight Aerosol Mass Spectrometer (AMS) and two Scanning Mobility Particle Sizer (SMPS).

The AMS signal at mass to charge ratio (*m/z*) 44 typically comes from organic acids. During the photooxidation experiments we observed changes to the ratio of m/z 44 to 43 and a loss of organic aerosol mass, while the flow tube was irradiated. We also performed laser photolysis experiments of benzophenone triplet quenching kinetics in solution, confirming that succinic acid reacts with the excited benzophenone triplet.

Sulfur isotope evidence for microbial sulfate reduction in altered oceanic basalts

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The subsurface biosphere in the basaltic oceanic crust is potentially of major importance in affecting chemical exchange between the ocean and lithosphere. Alteration of the oceanic crust commonly yields secondary pyrite that are depleted in ^{34}S relative to igneous sulfides. Although these ^{34}S depleted sulfur isotope ratios may point to signatures of biological fractionation, previous interpretations of sulfur isotope fractionation in altered volcanic rocks have relied on abiotic fractionation processes between intermediate sulfur species formed during basalt alteration. In a recent study, we reported multiple-S isotope (^{32}S,^{33}S,^{34}S) compositions of 165 Ma-old altered basalts at ODP Site 801 in the western Pacific and provided evidence for microbial sulfate reduction within the volcanic oceanic crust. The average $\delta^{34}S$ value of -6.8 ‰ for the bulk altered oceanic crust samples further demonstrated that S-based metabolic activity of subsurface life in oceanic basalt is widespread, and can affect the global S budget at the crust-seawater interface.

Here, we report $\delta^{34}S$ analysis of secondary pyrite in younger altered oceanic basalt (<3.5Ma) using ion-microprobe (*Cameca 1280*) and LA-MC-ICPMS (*New Wave UP213* laser coupled to *ThermoElectron Neptune*). In-situ $\delta^{34}S$ analysis of secondary pyrite in basement rocks from ODP Hole U1301B, located east of the Juan de Fuca Ridge, show a very large range of $\delta^{34}S$ values, from 1‰ down to –70‰, although most values are restricted between 0 to -10‰. Similar range has also been found in altered basalts from several DSDP Holes near the Galapagos Rift, with pyrite $\delta^{34}S$ values ranging from 10‰ down to -58‰. Such ^{34}S depletion in pyrite is consistent with previous S-isotope studies of deep-sea sediments showing extreme S-isotope fractionation (α~1.077) during single-step microbial sulfate reduction. These new results further support the importance of microbial sulfate reduction during oceanic crust alteration in hydrothermally-active ridge flank settings, but also prompt further work to identify and culture these widespread deep-endolithic sulfate reducing microorganisms.

Kīlauea 2008: Primitive components and degassing recorded by olivine-hosted melt inclusions and matrix glasses

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Simultaneous summit and rift zone eruptions in 2008 reflect a shallow eruptive plumbing system inundated by a bourgeoning supply of new magma from depth. Comparisons of olivine-hosted melt inclusions, host glass, and bulk lava compositions of magma erupted at both the summit and East Rift Zone demonstrate chemical continuity at both ends of a well-worn summit-to-rift pipeline. Our analysis of high-temperature summit pyroclasts shows the predominant and most primitive component erupted to be a homogenous, trace-element depleted melt, relative to prior summit eruptive products. This component is a genetic match for all post-1998 rift lava and distinct from enriched signatures of recent and historic summit lava.

These results suggest that both eruption sites share a common magma source. East Rift Zone melt inclusions (50.8 wt% SiO_2, 7.7 wt% MgO), however, are slightly more fractionated relative to summit material (50.6 wt% SiO_2, 8.4 wt% MgO). In addition, melt inclusions from summit material are sulfur enriched relative to East Rift Zone inclusions, with S concentrations typically ranging from 1200 to 1000 ppm at the summit. Melt inclusions from East Rift Zone spatter record a range of S concentrations from ~1200 to 300 ppm, only slightly elevated relative to matrix glass (~200 ppm S). Average Fluorine and Chlorine concentrations in East Rift Zone and summit melt inclusions are equivalent, indicating little to no halogen degassing concurent with sulfur degassing. Olivine core and rim compositions are also more evolved in East Rift Zone lavas, although a small population of melt inclusions and olivine hosts match compositions erupted at the summit. Olivine-hosted melt inclusions and matrix glass confirm prior models indicating that both the Kīlauea summit and East Rift Zone share a magma source and portray a history of magma degassing and minor olivine crystallization with cooling during transport over 16 km from the summit to the East Rift Zone.

Controls on groundwater geochemistry and arsenic mobilisation processes in aquifers of Eastern Europe (Pannonian Basin)

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The Pannonian Basin, found in Eastern Europe, spans Hungary, Romania, Serbia and Croatia. Groundwaters in Quaternary and Neogene sediments from this region are known to contain elevated levels of naturally occuring arsenic (see also [1]). These aquifers are utilised by the local population for drinking water with published estimates predicting ~ 750,000 people, the largest group so affected in Europe, are impacted by these high levels of As.

A range of artesian (70–800 m), thermal (400–3000 m) and pump (70–200 m) wells in Hungary and Romania were sampled to identify the general groundwater chemistry and arsenic mobilisation processes. As was predominantly in the reduced form (AsIII), and over half of all wells contained >10 µg/L As (WHO and EU limits for drinking water) [1].

Due to the complex nature of the water chemistry, cluster analysis was used to identify groups of similar groundwaters. Two dominant water groups were revealed, (A) end member waters with geochemistry controlled by thermal and marine influences, both containing low As (<10 µg/L), and (B) waters showing a mixing trend between end member waters and meteoric waters with variable As (<0.5 µg/L to 220 µg/L). Differing As concentrations between these groups imply that it is not sourced from external inputs, i.e. As rich geothermal waters, but from in-aquifer processes.

Waters in group B contained high DOC, PO_4, NH_4 and CH_4, and variable SO_4 and H_2S. Geochemical reasoning implies that As is released by reductive dissolution of As bearing Fe-oxides. Subsequent controls on the concentration of As are thought to be due to the variability of SO_4 and H_2S in the waters. Low As waters in group B have higher concentations of SO_4 and under the naturally reducing conditions within the aquifers, sulphate reduction could lower As concentrations in groundwater by the formation of As-bearing sulphides. In contrast, waters containing higher As in the same group have minimal levels of SO_4 and so As released by reductive dissolution remains in solution.

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The PGE geochemistry of the on-craton kimberlites from Eastern Dharwar Craton, Southern India

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Although some platinum-group minerals (PGMs) have been found in kimberlites, studies on the geochemistry of gold and PGE in kimberlites are limited. The restricted nature of the database has prevented detailed modelling of the geochemical behaviour of PGE in Kimberlites. A detailed study on PGE geochemistry of 19 kimberlitic bodies from various regions within and around Anantapur area, which intruded in Eastern Dharwar Craton, has been taken up to understand their behaviour, abundances, fractionation trends as well as their genesis as they are derived from the deepest part of the earth. The PGE ratios of the kimberlites compared with other upper-mantle-derived rocks using a Pd/Ir vs. Ni/Cu plot are shown in Fig.1. HTPGE concentrations in kimberlites significantly exceeded those concentrations found in oceanic and continental basalts and overlap the range of concentrations found in komatiites and also mantle peridotites. Kimberlite PGE signature in Dharwar craton reflects a combination of process related to PGE retention in the source, possible loss of PGE during ascent, possible addition of some LTPGE during ascent, and incorporation of a primitive, HTPGE rich component. The likelihood of incorporation may be influenced by the thickness of the craton and lithosphere intruded by the kimberlite which had resulted in incorporation of more HTPGE component as a possibility of upwelling of asthenosphere bringing primitive as well as HTPGE signature in the source region of kimberlite magma.

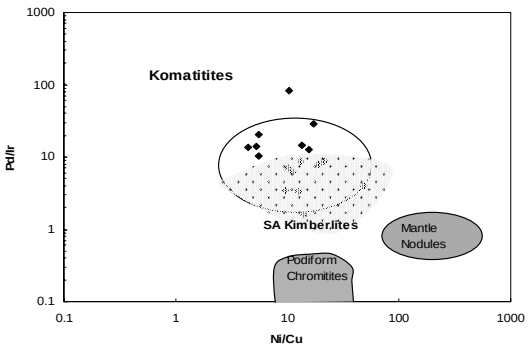

Figure 1: Metal ratio diagram of Pd/Ir vs. Ni/Cu for kimberlites and other mantle-derived melts.

Cobalt uptake and resistance to trace metals in *Comamonas testosteroni* isolated from heavy-metal contaminated sites in the Zambian Copperbelt

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A biogeochemical study of a polluted wetland site in Kitwe, Zambia shows high concentration of trace metals, including cobalt, with many of them sequestered with the sediment organic phase. Depth profile in surface sediments suggest trace metal cycling between porewater and solid phases. Organic carbon degradation mediated by bacteria is a possible mechanism for the mobilization of trace metals. Although little is known of microbially mediated Co cycling, this study documents a bacterium that may be involved in the uptake, accumulation and possible cycling of Co in aquatic sediments. The dominant isolate was enriched from the microbial community and identified using 16S rRNA gene sequence analysis as a strain of *Comamonas testosteroni* (designated C. testosterone TDKW). Improved growth of *C. testosteroni* TDKW was seen with the addition of up to 200 μM of cobalt (optimal growth ca. 100 μM), whilst concentrations above 4 mM completely inhibited growth. *C. testosteroni* TDKW also exhibited resistance to high concentrations of iron and manganese, but showed limited resistance to copper or nickel. Further analysis revealed cellular cobalt accumulation and the presence of heavy-metal resistance genes, suggesting this organism could be contributing to in vivo biological cycling of cobalt in mineral contaminated aquatic systems.

Solubility measurements of hydrotalcite-like solid solutions

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Hydrotalcite-pyroaurite $Mg_3(Al,Fe)(OH)_8(CO_3)_{0.5}\cdot nH_2O$ LDH phases are of interest as potential sorbents for anionic radionuclides. Synthesis and analysis of end-members and individual phases in this solid solution series were described in [1]. PXRD measurements confirm the presence of a single phase LDH. Cell parameters as a function of x_{Fe} follow Vegard's law and corroborat the existence of a continuous solid solution series. Measured solute concentrations from coprecipitation and dissolution experiments were modelled using [2]. Results are presented as Lippmann total solubility products $\Sigma\Pi=\{Mg^{2+}\}^3(\{Fe(OH)_4^-\}+\{Al(OH)_4^-\})\{OH^-\}^4\{CO_3^{2-}\}^{0.5}$ in Figure 1, together with the theoretical solidus and solutus curves for the ideal solid solution using $\log_{10}K_{sp}(Ht) = -35.5$ and $\log_{10}K_{sp}(Py) = -34.5$.

Solutus points generally show too low $Fe(OH)_4^-$ aqueous activity fractions, indicating the following complications: (i) too low Fe or high Al concentrations, (ii) not attained equilibrium, (iii) presence of minory secondary phases like *brucite*, *gibbsite*, *ferrihydrite* not detectable by PXRD. Available data within its uncertanty do not contradict the ideal solid solution model Ht–Py. Aging (on-going experiments) results in decreasing total solubility products.

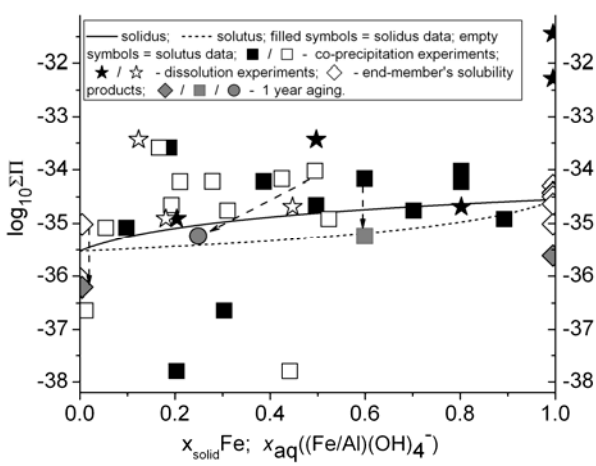

Figure 1: Data for hydrotalcite-pyroaurite solid solutions.

[1] Rozov *et al*. (submitted) *Cem. Conc. Res.* [2] GEMS-PSI code package, http://gems.web.psi.ch.

Timing of melting in collisional orogenies

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Partial melting of the continetal crust commonly occurs in orogenic settings at the root of mountain belts. The timing of melting has significant implications for the modeling of orogenic processes, heat transfer and rheology of the crust. We present here a detailed geochronological study of melting in anatectic terranes in the Alps and the Himalayas using U-Pb ion microprobe dating of zircon and monazite.

In the migmatite belt of the Central Alps, fluid-assisted melting occurred repeatedly, and at roughly constant temperatures of 650-700°C over the period 32-22 Ma. This repeated melting is timed by multiple zircon overgrowths within the same leucosome or even within the same zircon crystal. The melting and remelting events were controlled by the local rock composition and the influx of external fluids. This period of protracted melting was followed by fast cooling of the region from middle to upper crustal levels.

The Sikkim sequence of the Himalayas reached high-grade metamorphic conditions (800°C) followed by rapid isothermal decompression [1]. Geochronology of several samples indicates that high-grade metamorphism and melting occurred over several million years. The growth of zircon and monazite records different snapshots within this period. Melting resulted in the formation of multiple generations of leucosomes but also reworking of previous melt products.

In both localities, melting conditions were protracted over time, but allowed for the crystalization of accessory minerals, and likely of leucosomes, in episodic fashion. The timing of repeated accessory mineral crystallization was diachronous and not systematic within an area.

Despite the extended melting period, the episodic nature of melt production prevented large melt volumes from accumulating in such terranes. This has bearings for tectonic models that predict fast exhumation driven by the buoyancy of mountain roots with a high percentage of melt produced over a short time.

[1] Ganguly *et al*. (2000) *Earth and Planetary Science Letters* **183**, 471-486.

Imprecisions and errors in ^{226}Ra-^{230}Th volcanic mineral ages from Ra-Ba partitioning difference estimates

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Mineral isochron dating using ^{226}Ra-^{230}Th ($t_{½}$=1.6 ka) differs somewhat from more common isotope systems (e.g., ^{87}Rb-^{87}Sr) because there is no stable Ra isotope to normalize parent and daughter abundances (e.g., ^{86}Sr in the ^{87}Rb-^{87}Sr system). Many papers have thus advocated using the geochemically highly similar element Ba as an imperfect, yet plausible stable analogue for ^{226}Ra-^{230}Th isochron dating. Various other authors have taken a modified approach, whereby a non-unity solid-melt partition coefficient ratio, D_{Ra}/D_{Ba}, is used to estimate a mineral ^{226}Ra/^{230}Th intial ratio, the result generally portrayed as being always both more accurate and more precise (e.g., [1,2]) than age estimates made with the assumption that $D_{Ra}=D_{Ba}$. Such studies mostly apply a mineral-specific strain parameterization estimate of D_{Ra}/D_{Ba} [3], although recently a small experimental data set has also become available [2]. While we do not question the theoretical framework of D_{Ra}/D_{Ba} variations or the plausibility that some predictied or experimentally determined values can be usefully applied in some circumstances, we caution that in geochronologic applications, where the prediction of initial abundances is paramount for determining an accurate age, the $D_{Ra}\neq D_{Ba}$ model has significant limitations arising from, among other things, (1) the vagaries of natural minerals growing under magmatic conditions; (2) the small number of experiments; (3) incomplete strain parameterizations; (4) mineral impurity or inclusion estimates; and (5) age errors from D_{Ra}/D_{Ba} approximations, which tend to be grossly under-estimated in the literature. Age estimates of minerals with $D_{Ra}/D_{Th} > 1$ (e.g., plagioclase) using $D_{Ra}\neq D_{Ba}$, must be viewed and used with extreme caution. However, D_{Ra}/D_{Ba} estimates have generally minor age effects on minerals where $D_{Ra}/D_{Th} << 1$ (such as magnetite and clinopyroxene [4,5]). Nevertheless, adhoc application of poorly constrained D_{Ra}/D_{Ba} in a mineral can lead to variably erroneous ages.

[1] Cooper *et al.* (2001) *EPSL* **184**, 703-718. [2] Fabbrizio *et al.* (2009) *EPSL*, **280**, 137-148. [3] Blundy & Wood (2003) *Rev. Min. Geoch.* **52,** 59-123. [4] Zellmer *et al.* (2008) *EPSL* **269**, 387-397. [5] Rubin & Zellmer (2009) *EPSL*., **281**, 115-123.

The double spike toolbox

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The double spike technique is a well established method for correcting for instrumental mass fractionation in mass spectrometry [1]. The precision of the technique is controlled by the choices of double spike composition and the proportions in which the double spike and sample are mixed. To make these choices easier, we present a collection of MATLAB codes ("the double spike toolbox") for calculating optimal double spikes for any isotope system. Optimal double spikes are chosen purely on the basis of minimising error propagation on the isotope ratios of the samples, rather than by geometrical methods [2]. In addition, we have produced "cocktail lists" of optimal double spikes for all 33 elements that have 4 or more naturally occurring isotopes, using some sensible default parameters. As examples, we discuss the application of the software to Fe, Pb, and Ca isotopes. The software is freely available at www.johnrudge.com/ doublespike.

[1] Dodson (1963) *J. Sci. Instrum.* **40**, 289-295. [2] Galer (2007) *GCA* **71**, A303.

Optical properties of aerosols with organic components using cavity ring down spectrometry

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Atmospheric aerosols affect Earth's climate in direct and indirect manners. The direct effect of aerosols on climate is by scattering and/or absorbing incoming solar and outgoing terrestrial radiation, which strongly modify Earth's radiation budget. These climatic effects depend on the chemical composition, size and morphology.

We will present laboratory studies aiming at understanding how the organic components of atmospheric aerosols affect scattering and absorption. We will present the use of cavity ring down (CRD) spectrometer to derive the extinction and complex refractive index of aerosols containing a significant organic component. We will present results on aerosol particles containing humic like substances (HULIS). HULIS are a common component of aerosols in the atmosphere. They contribute to the CCN activity, hygroscopic properties and the density of aerosols. In addition, HULIS absorb throughout the visible range, and hence contribute to the direct climatic effect of aerosols. The absorption by organic aerosols is largely unaccounted for in models. Specifically, we will present how the absorption of aerosols containing HULIS and inorganic salts varies with wavelength, test various optical mixing rules and will present results on the extinction of core-shell model and soot aerosols. Finally, a new continuous wave CRD system will be presented.

Environmental geochemistry of volcanic ashes from the Southern Puna, NW Argentina

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Twenty-one rhyolitic volcanic ash deposits were sampled in the Southern Puna plateau (NW Argentina). The goal of this study is contribute to define a specific analytical methodology for environmental characterization of volcanic ash, as well as recognize the geochemical impact of such materials on the environment mainly on natural water. The SEM examination allows recognize the ash by the presence of glass shards. In addition, the coupling with EDX spectrometry provides a complementary way to identify compositionally glass and crystalline phases and to compare ashes of different eruptions. Whole rock geochemistry and two types types of leachates (deionised water and nitric acid) were performed on these samples allowing to follow the environmental behaviour of about 50 major and trace elements. The analyses were carried out by ICP-OES and ICP-MS.

Significant differences have been reported in the two types of leachates with, generally, higher concentrations in the acid leachate, whereas Si and B were enriched in water leachate. Both leaching results have demonstrated high levels of Ca, Na, and Si as the most abundant cations, while SO_4 and Cl are the most abundant anions. High concentrations of B, Co, Cu, Ni, Rb, V, and Zn were also reported in both leachates, while only high levels of As, Br, Cs, Mo, Pb, and Se were observed in acid leachate. The comparison of the leachates and the bulk compositions of the ash (expressed as Relative Mass Leached, RML, %) shows in acid leachates a high mobility (40-90%) for P and Zn, and a moderate mobility (20-40%) was presented by Ca, Ni, Cu, and As. In water leachate, the behaviour is more complex with a large variability between ash samples. In general, the RMLs are lower than 20% for water leachates. However, in some ashes some elements risen 40-90% RML (P, Sb, and Zn).

This work is a contribution of Project ASH (CGL2008-00099) in the framework of the PEGEFA Research Group (SGR2005-00795).

Global carbon cycle turnover at the Triassic-Jurassic boundary

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The late Triassic is recognized as one of the five major mass extinction events of the Phanerozoic. Similar to the other extinction events, this interval is associated with a distinct perturbation in marine C-isotope records, likely related to turnovers in the global carbon cycle. The nature and causes of such isotopic events however, are not always similar and often poorly understood. The Triassic-Jurassic (T-J) boundary interval is marked by two negative excursions in bulk C_{org} and C_{carb} isotope records, of 7 and 3‰ respectively. The rapid and short-lived *initial* Carbon Isotope Excursion (CIE) concurs with the onset of Central Atlantic Magmatic Province (CAMP) volcanism. Deposition of this largest igneous province on earth is thought to be related to the break-up of Pangaea. The onset of the prolonged *main* CIE concurs with the base of the Jurassic and postdates the extinction event by ~100kyr. Volcanic CO_2 outgassing and the possible release of methane clathrates are likely causes for a whole set of environmental changes (e.g. global warming, biocalcification crises, ocean anoxic events) that ultimately led to the final end-Triassic extinction event. To constrain changes in the global exchangeable carbon reservoirs at the T-J boundary, it is necessary to understand the nature and size of the negative CIEs. Several high resolution C-isotope records were established for the western Tethys realm. We show that large changes in kerogen type with increased hydrogen index values of over 600mg HC/ g TOC, demonstrated by Rock-Eval VI measurements on sediments from the proposed T-J boundary GSSP, concur with the *initial* CIE and increased TOC values of 9%. Palynological study show that increased terrestrial organic matter supply to the basin is followed by the mass occurrence of green algae in this interval. Changes in origin of the sedimentary organic matter is potentially responsible for the observed extreme amplitude of the *initial* CIE in the western Tethys realm. However, high resolution records of compound specific carbon isotopes, measured on long chain *n*-alkanes originating from higher plant leaf waxes, provide an independent tool for estimating the actual amplitude of the carbon isotope excursion at the T-J boundary.

X-ray absorption fine structure investigation of uranyl-phosphate biomineralization

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The storage and disposal of radioactive waste has resulted in extensive uranium contamination of groundwater resources. The application of dissolved polyphosphate offers an inexpensive and efficient method to precipitate soluble U(VI) from contaminated aquifers as uranyl-phosphate phases. Bacteria can affect the extent of precipitation that occurs and the morphology of the resulting precipitate. In the first part of this study, we documented the effect of non-metabolizing bacteria in the precipitation process. The presence of bacteria in systems at higher saturation states leads to the nucleation of nanoparticulate uranyl-phosphates within the bacterial cell walls. The objective was to use XAFS spectroscopy to characterize the uranyl-phosphate precipitate that forms in both biotic systems and abiotic controls.

X-ray Absorption Near Edge Structure (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS) at U L_3-edge were collected at Beamline 10-ID, Advanced Photon Source, Argonne National Laboratory. Samples had initial U concentrations ranging from 2 to 31 ppm, and initial P concentrations from 0 to 10 ppm. Two sets of experiments were conducted, all at pH 4.5: 1) those containing non-metabolizing *Bacillus subtilis* cells, and 2) parallel experiments without bacteria. For each sample, 10 XANES measurements were taken at first, each less than a minute, in order to monitor the radiation damage. EXAFS were collected afterwards at 10 spots, with 2 measurements at each spot. No radiation damage was observed. The valence state for all the samples is U(VI), so no reduction to U(IV) occurred. The EXAFS spectra suggest the presence of two possible uranyl-phosphate phases in the abiotic samples, but only one dominant phase in the biotic ones. Further analysis of EXAFS spectra for the biotic samples also indicates that the structure of the precipitate is close to that of the autunite group of minerals. This study provides molecular level details of how bacteria influence the uranyl-phosphate formation, and hence the effectiveness of the remediation approach.

Cassiterite and wolframite Nb-Ta content in leucogranites, Central-Iberian Zone

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Sn–W quartz veins in the Central-Iberian Zone are associated to Variscan granites [1].The Jálama batholith has three units: inhomogeneous granitoids, porphyrytic granites and leucogranites [2, 3]. Ore minerals are mainly cassiterite and wolframite. Electron microprobe analyses from both ore minerals show that cassiterite has a higher Nb and Ta content than wolframite, and that the observed range in Nb and Ta concentrations is higher in cassiterite than in wolframite.

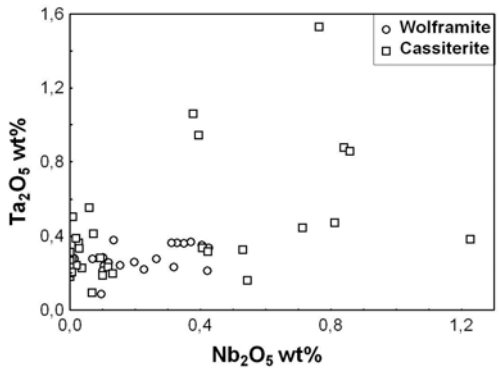

Figure 1: Nb_2O_5 vs Ta_2O_5 in wolframite and cassiterite.

Nb-Ta from granitic melt would deposite Nb-Ta rich cassiterite in a first magmatic mineralizing event. Therefore Nb-Ta are depleted and the magmatic evolution process would deposite Nb-Ta poor wolframite in a second magmatic-hydrothermal event.

[1] Neiva (2008) *Ore Geol. Rev.* **33**, 221–238. [2] Ruiz *et al.* (2008) *Chem. Erde* **68**-4, 337-450**.** [3] Fernández-Leyva *et al.* (2007) *SGA* Vol.**1,** 431-435**.**

Growth and phase transformations in Mg hydrated sulfates: Effect of organic additives

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Crystal growth in the presence of organic molecules commonly occurs in nature and it is a strategy successfully employed in industry to control or avoid the growth of crystalline solids. Little is known about the effects of organic additives on the formation and transformations of highly soluble salts, such as Mg-sulfates. This may have important implications in agriculture, medical or chemical applications, where Mg-sulfates are commonly used, and also may be of interest in planetology, as deposits of sulfates (present in Mars and Jupiter satellites [1]) have been claimed as optimal places to look for evidence of extra-terrestrial life. [2].

$MgSO_4{\cdot}7H_2O$ (epsomite) crystals were precipitated in the absence and in the presence of additives (polycarboxylic and polyphosphonic acids) following free evaporation of saline solutions. Subsequently, they were subjected to TG, DSC, and FTIR analyses, and their dehydration was studied *in situ* by means of XRTD and hot stage-ESEM. Several of the tested additives act as inhibitors of epsomite crystallization and growth. AFM observations point to H-bonding between the organic molecules and epsomite water molecules on {110} as the main mechanism of additive-crystal interaction. The large number of water molecules on such faces reduces the selectivity of such interaction. Stepwise loss of water is observed both during the dehydration of pure and doped epsomite crystals. This reaction can be classified as a 3D, interface advancement reaction. The dehydration rate is substantially reduced in the presence of additives. These results are consistent with the establishment of H-bonds between the additives and structural water in epsomite and the lower hydrates resulting from the progress of the dehydration reaction. The combination of techniques used here is a novel approach which may give insights into the organic-inorganic interactions that are relevant in many fields, from planetary science to biomineralization or industrial crystallization.

[1] Chipera & Vaniman (2007) *Geochim. Cosmochim. Acta* **71**, 241–250. [2] Bishop *et al.* (2004) *International Journal of Astrobiology* **3**, 275–285.

Heavy metals and sediment fluxes in Coatzacoalcos River estuary: A history of land use changes

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[2]IAEA. P.O. Box 100, A-1400 Vienna, Austria (J.A.Sanchez@iaea.org, J.Gerardo-Abaya@iaea.org)
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This work describes the historical changes in sedimentation rates and trace metals supply from Coatzacoalcos River into the continental shelf of the Gulf of Mexico. The Coatzacoalcos River estuary is considered the most polluted coastal area of Mexico, mostly due to the oil industry established in its watershed. Magnetic susceptibility data and ^{210}Pb-derived sedimentation rates suggested that a substantial sediment remobilization occurred during the last 30 years, attributed to watershed erosion due to land use changes, promoted by the petrochemical activities in the area. Despite the pollution potential, low metal enrichment was observed in this study. This work was supported by the IAEA-Regional Project RLA7012.

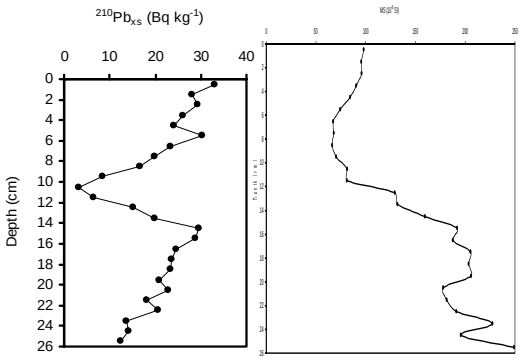

Figure 1: ^{210}Pb and magnetic susceptibility depth profiles from Coatzacoalcos River Estuary.

In situ surface Raman analysis of organics: Applications in planetary exploration

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Introduction

ExoMars is the first ESA flagship mission of the Aurora program that will send a rover to the surface of Mars in 2016. The main aim of this mission is the search for past and present life on Mars. The Raman Laser Spectrometer (RLS) is part of the rover's payload (Pasteur). This instrument will perform experiments outside and inside the rover with two dedicated optical Raman heads. Outside the rover analysing surface samples and inside the rover analysing cores obytained by a drill.

Results and Discussion

In the present work results obtained in relation with the objectives of identify organic compounds and search for life and identify mineral products and indicators of biological activity are presented and discussed. These results were obtained using a portable prototype for field surface analysis at AMASE 2007 and 2008 campaigns in the Artic [1]. In Figure 1 the Raman probe head working on surface samples at Palander Bay and the spectra obtained in-situ are depicted. The mineralogy of the samples was established in detail. Also beta-carotene was detected in several cases allowing to show the potential of Raman spectroscopy for detection of indicators of biological activity.

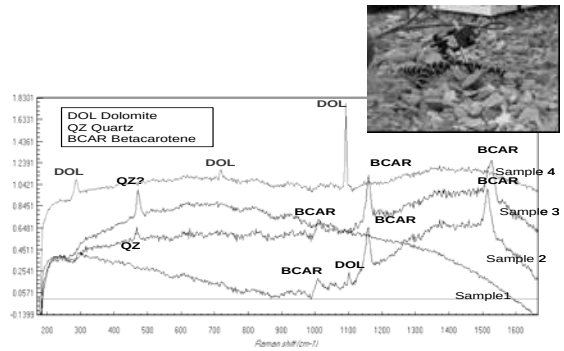

Figure 1: The Raman probe working at the surface in Palander Bay and some of the Raman spectra obtained.

[1] AMASE- Artic Mars Analog Svalbard Expedition, 2007 and 2008.

Hadean-Archean oxygen isotope fractionation

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The Terrestrial Fractionation Line (TFL) for oxygen isotopes is defined by $^{17}O/^{16}O$ and $^{18}O/^{16}O$ analyses of meteoric waters, seawater, sedimentary, metamorphic, and igneous rocks and constituent minerals. Steeper slopes of mass fractionation lines on $\delta^{17}O$ vs. $\delta^{18}O$ diagrams indicate an approach towards isotope exchange equilibrium. Lower slopes are expected when isotope equilibration is inhibited and fractionation is kinetically controlled [1]. Interlaboratory measurements of the slope of the TFL on a plot of $\delta^{18}O$ vs. $\delta^{17}O$ show eclogitic garnets with a slope of 0.526 and hydrothermal quartz whose slope was 0.524 [2] from rocks younger than 0.8 Ga. New measurements show Archean metamorphic rocks and minerals from Barberton, (3.2 Ga, S. Africa), Isua (3.8 Ga, Greenland), and Acasta (4.0 Ga, Canada) have a slope of 0.524 ± 0.002 (95% confidence, MSWD = 0.66 [3]). Continuing analyses of samples from Porpoise Cove (4.3 Ga, Canada) give a slope of 0.528 ± 0.004 (MSWD = 0.47).

Analysis of Ag_3PO_4 prepared from apatite mineral separates from Isua meta-sediments gives a slope of 0.509 ± 0.022 (MSWD = 0.59). Ongoing analyses seek to improve the precision of this slope. The lower slope of 0.509 for Isua apatite suggests the formation of orthophosphate was kinetically controlled.

Conclusions: (1) Mixing accompanying the violent birth of the Earth-Moon system had already succeeded in establishing Earth's current oxygen isotope composition by 4.3 Ga; and (2) No trace of an episode of meteorite bombardment remains in the oxygen isotope compositions of Earth's oldest rocks.

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Volatiles and melt inclusions in high-Mg Andesite from Mt. Shasta, CA

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High-Mg andesites (HMA), though relatively uncommon in volcanic arcs, are potentially important in the formation of continental crust. Their primitive chemical characteristics suggest equilibration with mantle wedge peridotite, and they may form through either shallow, wet partial melting of the mantle or re-equilibration of slab melts migrating through the wedge. A well studied example of HMA from near Mt. Shasta, CA has been a topic of recent debate as petrographic evidence for magma mixing calls into question whether HMA melts exist (as opposed to hybrid bulk rocks containing harzburgite debris) or have a mantle origin [1]. We have re-examined naturally-quenched, glassy, olivine-hosted (Fo_{87-94}) melt inclusions from this locality (*cf.* [2]). Inclusions were analyzed by FTIR and electron probe. Compositions (uncorrected for post-entrapment modification) are quite variable (54-63 wt% SiO_2; 2-8 wt% MgO) and can be divided into high-CaO (>10 wt%) melts in Fo>90 olivines and low-CaO (<10 wt%) melts in Fo<90 olivine hosts. There is evidence of extensive post-entrapment modification in many inclusions, and we evaluated the effects using three methods. High-CaO inclusions experienced 2-3 wt% FeO^T loss by diffusion and 20-40 wt% olivine crystallization. In contrast, low-CaO inclusions experienced lesser amounts of both FeO^T loss and olivine crystallization (≤12 wt%). After correction for these effects, we find that melt inclusions in Fo_{87-88} olivine have HMA compositions (55-58 wt% SiO_2; 8-8.5 wt% MgO) whereas those in Fo_{93-94} olivine are primitive basalt to basaltic andesite (50-54 wt% SiO_2; 14.2-16.2 wt% MgO). Importantly, both types of inclusions are volatile rich, with maximum values in HMA and basaltic melt inclusions, respectively, of 3.1 and 3.2 wt% H_2O, 800 and 1800 ppm S, 1500 and 2200 ppm Cl, and 460 and 590 ppm CO_2. Measured S Kα peak positions suggest oxidizing conditions (≥NNO+1), similar to other arc magmas. Our results demonstrate that H_2O-rich, HMA melts exist within the magmatic system in the Mt. Shasta region and have similar major element compositions as bulk rock samples (*e.g.* [3]) despite clear petrographic evidence for mixing and entrainment of crystal debris. In addition, the presence of basaltic to basaltic andesite melts trapped in the Fo_{93-94} olivine provides evidence that these are magmatic phenocrysts that crystallized from unusually primitive, subduction-related magmas.

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Petrogenesis of TTG magmatism: Generating chemical diversity in different tectonic settings

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Although the detailed geochemical studies on Jack Hills zircons tell us that felsic crust was formed soon after accretion and provide important insight into potential compositions, they cannot tell us *how* this crust was formed. This point was emphasized in a recent paper on early Earth and orgin of the earliest crust by Blichert-Toft & Albarede [1] and whether or not TTG's represent this earliest crust and with it, subduction zone processes? Their potenital presence in the earliest Earth can help determine whether or not subduction was active during the Hadean. There is debate within the TTG community on their petrogenesis and whether or not subduction is required. Lowermost crustal melting of mafic material may be as viable an option as partial melting of subducting crust The Hadean link places the processes that can produce TTGs in an important new light.

Experiments on mafic material have been conducted in order to assess the generation of TTG suites in a lowemost crustal setting and include melt segregation processes. The expeirmental testing of the genesis of TTGs by a combined partial melting and segregation process uses the results of the numerical model developed by Jackson *et al*. [2] which explores the production of volumetrically significant TTG magmas in the lowermost crust. This work is based on the hypothesis that arc crust is generated by a combination of physical and chemical migration steps allowing re-equilibration of melt as it segregates upwards through a thermal gradient. Experimental results have demonstrated that it is possible to change the Mg-numbers in a tectonic setting that involves only a mafic underplate. TTGs form from partial melting of a hydrous mafic protolith, but their associated tectonic setting may vary. This research does not support either the hypothesis that TTG petrogenesis is required through slab melting alone nor a model requiring subsequent melt interaction with the mantle wedge to increase Mg-numbers. These results will be applied to new experiments on the most ancient mafic crust [3].

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Linking particulate matter sources to health

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There are an estimated 2.8 million premature deaths annually from exposure to particulate matter (PM). Most of those are in the home from smoke due to solid fuel use, but over 800,000 come from exposure to ambient PM in urban areas. However, it is not currently apparent which sources of ambient PM have the greatest health concerns. Two links are currently uncertain. First, we do not know which constituents of urban PM are responsible for the health impacts. Historically, epidemiologic studies have developed associations between PM and its components with health endpoints. These studies suggest that there are differences between PM components and health endpoints, and this is substantiated by toxicological studies. However, the source contributions of those components are uncertain. The various methods used for source apportionment can lead to significantly different results. More recently, investigators are trying to directly associate sources with health endpoints by using source apportionment analyses.

Analysis of approaches for conducting source apportionments shows that the typical techniques have significant weaknesses. Here, examination of the weaknesses of using different source apportionment techniques in health studies are presented, along with weaknesses of individual methods, as well as how methods can be combined to alleviate limitations. Two new approaches, using ensembles and multi-method optimization, are found to improve performance.

Mid–late Pleistocene deep-water circulation in the Southwestern Subtropical Pacific

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The modern $\delta^{13}C_{DIC}$ distribution in the deep-waters of the southwestern subtropical Pacific is consistent with a regional mixing regime between deep-waters of open-Pacific and Tasman Sea origin (Fig 1). Comparison of a down-core record of benthic foraminiferal (*C. wuellerstorfi*) $\delta^{13}C$ from site MD06-3018, New Caledonia Trough (2500m water depth), with a similar record from the Pacific deep western boundary current region shows that the relative influence of open-Pacific deep-waters on the mixing regime is reduced during glacial in comparison to interglacial stages over the past 1100ka. This offset arises from the continued presence of mid-depth deep-waters of southern Atlantic origin in the glacial Tasman Sea whereas the glacial southern Pacific is dominated at the same depths by waters from the Southern Ocean.

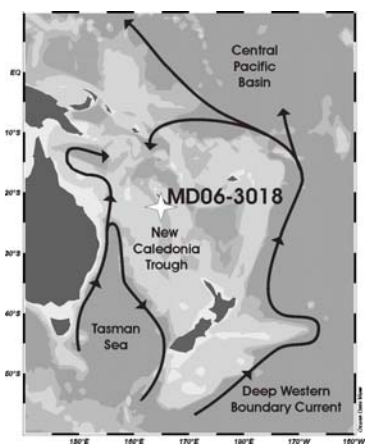

Figure 1: Schematic diagram of regional deep-water flow.

Molecular paleoclimatology

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The geological investigation of global change phenomena is becoming increasingly dependent on a better molecular level understanding of key geochemical processes that record the characteristics of ancient atmospheric and oceanic reservoirs. Many of these processes involve the uptake of stable isotopes of elements such as carbon, boron, and iron into minerals that form over geological timescales in soils and ocean floors in contact with these reservoirs. Effective use of these tools of climate reconstruction depends critically on input at the molecular level.

The isotopic composition of boron trapped in calcite is used to estimate the pH of seawater in the geologic past. Recent work [1] has clearly shown that the low value of 1.019 (25°C) for the equilibrium constant (K_{34}) for the reaction $^{11}B(OH)_3+^{10}B(OH)_4^-=^{10}B(OH)_3+^{11}B(OH)_4^-$ results from misassignment of the vibrational spectrum of $B(OH)_4^-$(aq) [2]. Our interpretation of 20 million years of earth history thus depended on a simple missasignment of the asymmetric stretching vibration of $B(OH)_4^-$(aq). Despite definitive experimental determination of the equilibrium constant at 1.028 [3], controversy surround K_{34} with many groups claiming that the erroneous value for K_{34} is in better agreement with geological observations.

The $Fe(CO_3)OH$ proxy uses the isotopic composition of CO_2 dissolved in goethite [CO_2(m)] to estimate the PCO_2 of the atmosphere. Here, computational studies [4] indicate the possibility of heterogeneous isotopic signatures for CO_2(m), ranging from -20 to +7 per mil, with respect to CO_2(g), most of which appear to be inconsistent with geological evidence pointing to a value of ~ +2.5 [5]. Paleoclimate science is becoming increasingly dependent on precise knowledge of the structure and isotopic fractionation associated with the chemical species that record climate. These problems have immense importance in setting environmental policy, and deserve our best molecular-level tools. It is already clear that computational methods will play an important role in the molecular transformation of paleoclimatology.

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Noble gas in volcanic thermal springs: A window on hydrothermal system

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Magma-derived gas studies have been used for volcano monitoring and especially for detecting degassing of shallow magma intrusion. However, interactions between those gases and hydrothermal system lead to strong modifications of the magma initial gas composition. To better understand this effect we propose to study noble gases in hot spring water from active volcano.

Noble gases are of particular interest since they are chemically inert and show a wide range of solubilities in water. Their study in hot spring water may then provide insights on interactions between magmatic gases and hydrothermal water.

We focused our study on the Lesser Antilles Arc and more precisely on the Guadeloupe and Dominica islands. Those two volcanic islands show well-developed hydrothermal systems which played a key role in the last phreatic eruptions (1976-1977 in Guadeloupe and 1997 in Dominica).

Samples were collected from thermal spring water and sealed in copper tubes. A new method has been developped to extract He and Ne from the samples. He and Ne analysis (concentration and isotopic ratio) were performed with a QMS200 spectrometer and a Noblesse (Nu Instrument) mass-spectrometer.

Preliminary results show that, on the first hand, most of the hot springs have a mantellic signature with a $^3He/^4He$ similar to the MORB mean value (R/Ra=8). However some springs are slightly more radiogenic and then show a dilution of the magmatic signal in water in equilibrium with air. On the other hand, for neon, the results fall on the mass fractionation line.

Further He and Ne measurements, and other noble gas measurements (Ar, Kr, Xe) will allow to provide informations such as kinetic processes, equilibrium temperature or residence time.

Volatiles in plume-related magmas (Siberian traps)

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Magmatism in the Siberian CFB province is mainly represented by the voluminous lava flows of tholeiitic plateau basalts and subordinate amounts of highly magnesian volcanics and dyke rocks. These highly magnesian rocks are strongly enriched in incompatible trace elements and are characterized by high LREE/HREE ratios. It suggests that their primary magmas were near solidus melts formed at high pressures. P-T conditions of the generation of these hi-Mg melts must be nearly identical with the P-T parameters characterizing magma-generating mantle plume.

To assess the formation conditions of hi-Mg Siberian magmas we investigated melt and fluid inclusions in the phenocrysts of these rocks, which were analyzed for major and trace elements (EMPA and SIMS methods). High Ti/Na ratios and high normative olivine contents in the melt compositions recalculated to the condition of equilibrium with mantle peridotites imply, that initial pressure of magma-generation is in the range of 7–9 GPa.

Ion microprobe data for reheated melt inclusions in phenocrysts from Siberian rocks show relatively low concentrations of volatile and fluid-mobile components. The assessment of the contents of volatiles in the mantle source of these magmas is based on the ratio of volatiles to nonvolatile elements with similar bulk partition coefficients. F/Sr ratios for meimechites (1.18) are close to MORB (0.84) and BSE (1.23). Cl/Ba (1.50) values are similar to MORB (1.09), whereas B/Ce ratios are lower than MORB and they are similar to OIB. Estimate average H_2O content in melt inclusions is 1.2 wt%, whereas for modeled primary magmas after correction for olivine fractionation it is below 1%. Concentrations of volatiles in the mantle source of Siberian magmas are similar to estimates for the sources of OIB magmas.

Low levels of volatile contents imply that the estimates of near-solidus temperature based on comparison with volatile-free systems would not be changed significantly. Comparison of the estimated from melt inclusion data pressures with experimental data shows that the temperature of rising plume material was ca 400°C higher by comparison with convecting upper mantle at the same depth. This proves that plume material arrived from deep levels in the mantle below certain thermal boundary layer.

Recognizing the forearc (serpentinite) component in volcanic arc magmas

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A growing body of geochemical data for lavas erupted at convergent plate boundaries indicate inputs to arc source regions from a chemical reservoir very similar in its elemental and isotopic signatures to that of serpentinites and associated fluids erupting today in the Mariana forearc. This "forearc" component is distinguished by anomalous enrichments in the fluid-mobile elements (FME) B, As, Cs and (to a lesser extent) Rb, Sb, and Li; extremely elevated B isotopic ratios; moderately elevated $^{87/86}$Sr; and low abundances of Ba, K, and other large-ion lithophile elements. These selective elemental enrichments relate to the limited menu of species which can be mobilized in the H_2O-rich, silica-poor fluids generated in the shallow forearc, and they match to a great degree the elemental menu depleted from sediments and basalts during low metamorphic grade devolatilization in the Catalina Schist and other forearc metamorphic complexes [1].

Models for the involvement of serpentinite in arc magmatism include its transport to depths in subduction melanges [2], and the decomposition of slab-hosted serpentine at depth beneath arcs [3]. A problem with slab-hosted serpentine inputs is generating the variable FME enrichments seen in arcs, which best approximate the outfluxes from devolatilizing shallow slab materials, and not the species likely to be hosted in marine serpentinite. Models for forearc serpentine inputs may be tested to a first order by examining subduction settings where slab thermal structure, crustal thicknesses, and/or geometric constraints preclude shallow fluid releases into the forearc mantle. In both the Cascades and the western Trans-Mexican volcanic belt (TMVB), two "hot" subduction systems, FME abundances and B isotopic ratios are low, consistent with minimal inputs of a forearc-derived component. B enrichments in the TMVB increase eastward as cooler slab temperatures and longer slab travel times increase the likelihood of shallow fluid releases reaching the shallow mantle wedge.

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Single-particle characterization of summertime Arctic aerosols collected at Ny-Ålesund, Svalbard

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There have been many studies on wintertime Arctic aerosols, but just a few studies on summertime Arctic aerosols. In addition, the composition of aerosol particles has been studied mostly with bulk chemical methods. In this work, a quantitative single particle analytical technique, named low-*Z* particle electron probe X-ray microanalysis [1, 2], was applied to characterize aerosol samples collected at a Korean scientific base located at Ny-Ålesund, Svalbard (78°55′N, 11°66′E). Major chemical species frequently encountered in the summertime Arctic samples are of marine, soil, and anthropogenic origins. Marine aerosols are observed as either genuine sea-salts or aged secondary aerosols such as $NaNO_3$ or Na_2SO_4. Some aluminosilicate particles contain nitrate and/or sulfate, suggesting that anthropogenic nitrogen and/or sulfur species were entrained in the soil-derived particles. Secondary organic particles are also significantly encountered.

According to backward trajectory analysis, in the first part of the sampling period (25-28 July), air-masses came from the Arctic Ocean and in the second part (28-31 July), they either had stayed near Spitsbergen island or came from the Greenland Sea. For samples collected when the air-mass arrived from the Arctic Ocean, marine aerosols predominated, where genuine sea-salts are the most abundant, followed by aged sea-salts. When the air-mass stayed near Spitsbergen island, soil-derived aluminosilicate particles are the most abundant, followed by anthropogenic secondary organic aerosols. This result indicates that the summertime Arctic aerosols are mostly influenced by regional sources.

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