

Burial diagenesis of siliciclastic reservoirs and control on formation water chemistry

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The general characteristics of the Jurassic clastic reservoirs offshore Norway have been reviewed Bjørlykke *et al.* [1], e.g. the Brent Group sandstones normally have a quartz content between 40-90%, up to 15-20% kaolinite, a variable albite content, and a K-feldspar content decreasing from about 10% at shallow burial to below detection limit at 3.5-4 km depth. Diagenetic phases include frequent carbonate cements, calcite, siderite, ankerite and ferroan calcite. The other burial diagenetic minerals are quartz, albite, illite and minor chlorite, reflecting the original clastic mineral assemblage. Major diagenetic reactions on a mass basis include recrystallization of carbonates, albitization of K-feldspar, later illitization of kaolinites and quartz precipitation. It has been argued by Bjørlykke *et al.* [1] for an overall closed system diagenesis during burial.

We have performed geochemical equilibrium modelling with PHREEQC along an average P, T and P_{CO_2} trend in these basins, and compared the results with formation water chemistry for the same formations [2-4]. The closed system hypothesis appears to be reasonable if also some of the kinetic constraints on mineral precipitation are included.

- [1] Bjørlykke *et al.* (1992) *Geol. Soc. Spec. Publ.* **61**, 263-287.
[2] Egeberg & Aagaard (1989) *Applied Geochemistry* **4**, 131-142. [3] Bjørlykke *et al.* (1995) *Geol. Soc. Spec. Publ.* **86**, 33-50. [4] Warren & Smalley (1994) *Geol. Soc. Memoir* **15**.

The impact of large scale contact metamorphism on global climate

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The formation of Large Igneous Provinces (LIPs) and sill intrusions in volcanic basins, like the Karoo Basin, South Africa, (~183 Ma), and offshore Norway, (~55 Ma) correlate with events of global warming and mass extinctions [1]. A negative shift in $\delta^{13}C$ recorded from these events suggests rapid release of large amounts of isotopically ^{13}C -depleted greenhouse gases to the atmosphere [2, 3]. Such gas releases might be triggered by contact metamorphism of organic-rich shales around magmatic sill intrusions associated with LIPs [4, 5]. In this study we use numerical models of the metamorphic devolatilization to constrain the amount, rate and duration of gas formation around sill intrusions as a function of rock type and sill thickness. The resultant isotopic gas composition is estimated from data on organic matter from natural aureoles in the Karoo Basin.

For a total organic carbon (TOC) content in an aureole of 5 wt% the amount of CH_4 generated is ~120 kg/m³, exceeding that of H_2O (40-120 kg/m³). The TOC loss is highest close to the sill. For 1 wt% TOC CH_4 generation is ~20 kg/m³. Basin scale extrapolation of our modeling suggests that at least 3500 to 9000 Gt CH_4 was generated through contact metamorphism in the Karoo Basin and conservative estimates for CH_4 generation offshore Norway are 500-2000 Gt. Geological evidence suggests that the gases vented to the atmosphere. We conclude that the amount and composition of methane that can be produced and vented from contact aureoles is of the same order of magnitude as required to explain global carbon isotope excursion and hence global warming.

- [1] Wignall (2001) *Earth-Science Reviews* **53**, 1-33.
[2] Hesselbo *et al.* (2007) *EPSL* **253**, 455-470. [3] Dickens *et al.* (1995) *Paleocean.* **10**, 965-971 [4] Svensen *et al.* (2004) *Nature* **429**, 542-545. [5] Svensen *et al.* (2007) *EPSL* **256**, 554-566.

A thermodynamic model for reaction rim growth in multicomponent systems

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If two phases, which have significantly different chemical composition and cannot coexist stably, are brought into contact, new phases may nucleate along their interface. Growth of the reaction zone on the expense of the old phases necessitates chemical mass transfer between the old phases. If chemical diffusion is rate limiting the newly nucleated phases will separate into distinct layers with different modal proportions of the new phases. For systems with only phases of fixed composition the component concentrations, diffusion fluxes and interface velocities at layer boundaries are related through mass jump conditions. The actual values of the interface velocities are obtained from application of the thermodynamic extremal principle [1]. The evolution equations can be integrated in time for known tracer diffusion coefficients of all components in the new phases and known molar Gibbs energies of all phases. If the model is complemented by appropriate experiments, the inverse problem can be solved so that tracer diffusion coefficients can be determined from rim growth experiments. We present applications to multilayer reaction rim growth in the SiO₂-MgO-CaO system.

[1] Svoboda, Turek & Fischer (2005) *Philos. Mag.* **85**, 3699 .

The role of elemental chemistry to discriminate diagenesis trend in sedimentary rocks study

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Carbon and oxygen isotopes are very helpful in getting to know sedimentary environment temperature, diagenetic temperature and diagenesis trends in diagenetic environments [1, 2].

This study has used trace elements (Sr, Mn, Na, Mg, Ca, Fe) and isotopic ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) analyses to determine diagenetic trend of Aptian limestones which are called Dariyan Formation located in Fars area that is placed at the south west of Iran.

Binary plots of trace elements and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values demonstrate that original carbonate mineralogy of Dariyan limestones was aragonite. Elemental and isotopic studies illustrate that these carbonates affected by non marine (burial) diagenesis in a closed to semi-closed system. Furthermore, paleotemperature calculation based on oxygen isotope indicates that very early shallow burial temperature was around 28.5°C.

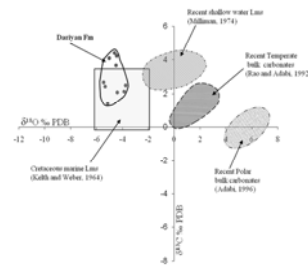


Figure 1: $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ cross-plot Samples are placed into Cretaceous marine Lms Field.

[1] Marshal (1992) *Geol. Magazine* **129**, 143-160. [2] Rao (1996) *Arts of Tasmania*, p.206.

Nitrate reduction and fermentation access different carbon sources in anaerobic degradation experiments

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Flow-through reactors were used to characterize anaerobic carbon degradation in sediments from the freshwater portion of a eutrophic estuary. Sediments were supplied for several months with or without the terminal electron acceptor nitrate and were periodically sampled for dissolved inorganic carbon (DIC) and a number of other analytes to compute carbon mineralization rates. Fermentation and nitrate reduction were responsible for the majority of carbon mineralization, with iron reduction and methanogenesis contributing minor amounts. Fermentation was largely independent of nitrate supply and was responsible for at least 50% of mineralization in both sets of reactors. Fermentation may thus be responsible for a large fraction of the DIC efflux from similar organic-rich, nearshore sediments. Nitrate reduction was driven by the simultaneous degradation of two carbon pools with different maximum oxidation rates and half-saturation constants. This mineralization was in part due to DOC release from fermentors, but primarily reflected degradation of a separate pool of organic matter. Together these data suggest that fermentation and nitrate reduction were relying on different pools of sedimentary organic carbon for their metabolism.

What was the role of the Iceland plume in triggering the Eocene-Oligocene cooling?

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The largest cooling event of Cenozoic at the Eocene-Oligocene transition (EOT) has occurred in two main steps of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ increase [1, 2]. In the first step, the *precursor*, the increase in the $\delta^{18}\text{O}$ is related to cooling and minor glaciation, attested by Mg/Ca ratio and the absence of sea level decline [2, 3]. The 2nd step in the $\delta^{18}\text{O}$ increase is related to domination of the Antarctica glaciation, attested by dramatic sea level fall [3].

Abelson *et al.* [4] have shown that the shut down of the Iceland plume at the EOT, and the plume renewal at the late Oligocene, strikingly correlate with the global signal of $\delta^{18}\text{O}$ and ϵ_{Nd} in the southern Atlantic. This suggests that the Iceland plume suppression enabled the overflow of deepwater from the Nordic seas, initiating one of the major engines of global thermohaline circulation for the first time in the Cenozoic. This notion is confirmed by several sedimentary records from the North Atlantic [4].

We suggest that this initiation of the proto-NADW due to the suppression of the Iceland plume has triggered a vigorous intensification of the thermohaline circulation [4], that in turn was the trigger for global cooling and CCD deepening during the *precursor* event; this event promoted the oceans stirring that increased the availability of nutrients [5] which has increased productivity of primary producers contributing to drawdown of Atmospheric CO_2 . The CO_2 decrease could initiate the Antarctic glaciation, hence forming the proto-AABW that has contributed to further invigoration of the thermohaline circulation, which initiated the 2nd event of the EOT cooling accompanied by dramatic sea level fall. This scenario of bipolar perturbation via 2-steps of cooling may be corroborated by the shift in occurrences between the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ increase, indicated in several sites: in the first step, the $\delta^{18}\text{O}$ increase slightly lags the $\delta^{13}\text{C}$ shift, whereas in the 2nd step, it shows the opposite relationship.

[1] Coxal *et al.* (2005) *Nature* **433**, 53-57 [2] Katz *et al.* (2008) *Nat. Geosci.* **1**, 329-334 [3] Miller *et al.* (2008) *GSA Bull.* **120**, 34-53 [4] Abelson *et al.* (2008) *EPSL* **265**, 33-48.

Metals in 'extreme' oils

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There are carried out analysis of 'extreme' oil set - oils from reservoirs in crystalline basement (White Tiger and etc.) and from Baikal lake and Black sea seeps, oils from oldest Proterozoik to 'young' Q reservoirs, oils from coal mine and oils from shale oil. All oils have outstanding peculiarity in biomarkers distribution. Oil samples have been analyzed to identify the presence of microelements using the substance composition analyzer - Energy dispersive X-Ray fluorescence spectrometer «ReSPEKT». The limit of detection for elements with nuclear number that is bigger than 17 is 0.5 ppm.

By the received results some conclusions have been made.

1. Vanadium and nickel had mainly negative correlation with other found out microelements –it can be explained by different genetic sources. V and Ni – may have organic source and other – inorganic. 2. V/Ni ratio exactly is reflected to type of source organic matter. 3. Among themselves ore elements, such as Cu, Zn, Fe, Pb, Mn correlate well 4. Very high positive correlation between the lead and arsenic content are found out. 5. The titanium has strongly pronounced correlation with ore elements. 6. It is not revealed any dependence of elements quantity on depth and age of the oil samples. 7. We see good correlation between high content of some elements in oils, such as Pb, As, Ti, and nearness to basement rocks (Fig. 1), at that just basalt rocks. 8. Oils direct from granite reservoirs have not characteristic property in elements distribution. 9. In some oils from strange group – Pz oil and Black sea seep there are very high concentration of strontium. 10. Ore elements could be extracted by oils from mineral matrix or solved in oils from hydrothermal fluids

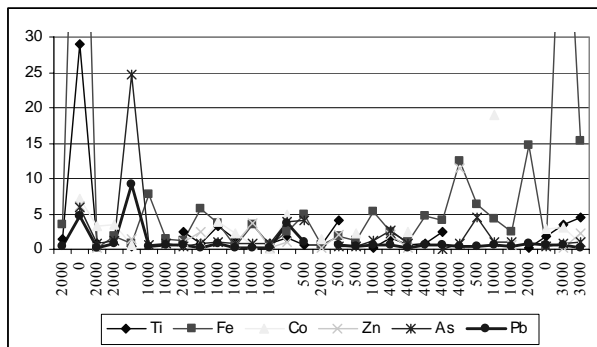


Figure 1: Elements in oils ranged by nearness to basement.

The origin of Palaeoarchaeon silicification inferred from coupled Si-O isotopes

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Silica alteration zones, a conspicuous feature of Palaeoarchaeon greenstone belts [1], demonstrate the ubiquity of extreme silica mobilisation in the early Earth's environment. To shed light on their origin, we investigated Si and O isotopic composition of two successions of variably silicified basalts and overlying bedded cherts from the Kromberg (K3c, 3.33 Ga) and Theespruit (3.54 Ga) formations of the Onverwacht Group in the Barberton Greenstone Belt, South Africa.

The Kromberg Formation shows similar Si-O-isotope fractionation trends as a previously investigated section from the Hooggenoeg Formation (H5c, 3.45 Ga) [2]. $\delta^{30}\text{Si}$ increases by 1.1‰ as the degree of silicification increases from fresh basalt (-0.25‰) to the most silicified basalts (+0.81‰) with correlated changes in the $\delta^{18}\text{O}$ value (from +10.0‰ to +15.6‰, respectively). The correlation between Si and O isotope composition observed in both Hooggenoeg and Kromberg basalts agree well with the calculated difference in Si-O isotopic fractionation factors [3] for low temperature (<380°C) hydrothermal isotopic equilibria between quartz and kaolinite.

The older, more strongly metamorphosed basalts from the Theespruit Formation show similar changes for Si isotopes (-0.24‰ to +0.46‰), but a much more restricted range of O isotope composition ($\delta^{18}\text{O} = +8.9‰$ to +11.9‰). This Si-O decoupling suggests that Si isotopes are more resistant to metamorphic resetting than O isotopes.

[1] Hofmann & Harris (2008) *Chem. Geol.* **257**, 221-239.

[2] Abraham *et al.* (2007) *Geochim. Comochim. Acta* **71**, A3.

[3] Méheut *et al.* (2009) *Chem. Geol.* **258**, 28-37.

Thermal effects of impacts on the Hadean Earth

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To better understand the thermal effects to the Hadean Earth's crust by asteroid and cometary bombardments, and the timescales for cooling subsequent to very large impacts, we constructed two new numerical models: 1) A thermal conduction/radiation model of the lithosphere, which simulates the integrated thermal consequences of all impacts scaled to Earth as constrained by the lunar crater record, the size/frequency distribution of the asteroid belt, and dynamical models; and 2) A hydrothermal model for a detailed study of global layers of hot ejecta which are emplaced by giant impacts. Parameters tested in the study include the duration, mass flux, and average impact velocity, surface temperatures, and geothermal gradients. We also estimated the amount of water vapor released into the atmosphere by large impacts and its effect on surface temperature using the Eddington approximation to the radiative transfer equation. Results of this study indicate that the timescales of thermal equilibrium between global meltsheets and underlying crust are longer than the cooling time of the melts, that the top 4km of crust was not thermally metamorphosed to a significant degree, and that at least 2.8×10^{20} kg of water (corresponding to an average global depth of 560 m) was released into the atmosphere from the oceans and hydrothermal venting following the largest plausible impactor (500km in diameter).

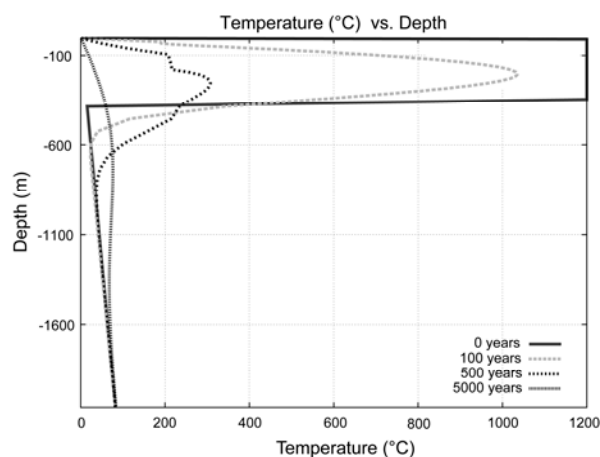


Figure 1: Cooling of a 350 m thick, 1200°C global ejecta blanket as modeled using HYDROTHERM.

New human activities in Africa affecting the ozone layer

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Since the beginning of the 1990's when the importation of fairly used Refrigerators, Air-conditioners and propellants that can easily go broken containing chlorofluorocarbon substances that is capable of destroying the Ozone layer started in commercial quantity in Africa, the African refuse mountains began metamorphosing into mountains of dumped broken Refrigerators, Air-conditioners and Propellants which are collectively becoming a threat to the Ozone layer, because of the continuous discharging of the Chlorofluorocarbon gases by the refuse in to the atmosphere in each passing second.

Nobody can actually quantify the numbers of Refrigerators, Air-conditioners and Propellants imported and disposed in Africa over the last fifteen years, but the facts still remains that the numbers of metamorphosing mountains keeps on increasing in both size and numbers in each passing day. They have even become sources of raw materials for the local blacksmiths, children and refrigerators repairers who use parts of the dumped refrigerators, Air-conditioners and Propellants for their constructions, toys and repairs respectively.

This explains the reason why despite the global efforts toward protecting the Ozone layer by the United Nations (UN), governments, International Organizations and climatologist among many others, but yet the hole in the Ozone layer keeps on expanding and the global temperature keeps on rising which resulted in the unusual phenomenon like the hurricanes "Katrina" and "Rita" the unusual floods in China, Thailand, Mozambique and to some extent even the Tsunami disaster that claims millions of lives in 2004. The Rapid rising in temperature of the Tropical world countries and increase in the cases of cancer patients among many other unusual happenings over the last eight years.

It was in review of the above situation that this research work was conducted and came up with the under listed suggestions/Recommendations:

1. The UN should use its capacity to discourage the importation of fairly used refrigerators, Air-conditioners and propellants to Africa and at the same time assist in the subsidy of the newer ones coming to Africa, so that the average African can afford buying them.

2. The UN through her specialized agencies on climate and meteorology in collaboration with sister related organizations should send their teams of researchers to come and investigate the trend of this ugly situation in order to proffer possible lasting solutions.

3. The African Union (AU), UN and other stakeholders on the World climate change should jointly encourage the companies manufacturing Refrigerator, Air-conditioners and propellants to open their factories in Africa, where their products are needed most, as this will help stop the importation of the fairly used refrigerators, Air conditioners and Propellants.

A crustal seismic profile across Sicily: Preliminary results

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In the frame of the Italian National Project Sicilia a Riflessione PROFonda (SIRIPRO), during the winter 2007-2008 a crustal seismic line was acquired in Sicily with the aim of identifying the deep structures of the crust. A crustal reflection seismic profile, more than 100 km long, has been recorded across central Sicily, from the Tyrrhenian shore to the Sicily Channel, to understand the deep structures and the collision mechanisms between Europe and Africa and the subsequent geodynamic evolution. The seismic profile was acquired using explosive sources and 240 active channels recorded by a Sercel 408-XL, 24 bits A/D converter, with a 12 km spread and a 24 fold coverage. The data has been processed following a non conventional procedure in order to preserve the relative amplitudes of the reflections and to better investigate the deep structures.

By using the ad hoc acquisition and processing, the dramatic flexure of the Iblean platform, the huge through of Caltanissetta filled by deep seated thrusts, olistostromes and nappes, the stack of thrusts characterizing the northern Maghreb chain have been highlighted in the stacked section.

Moreover, the deepest parts of the Caltanissetta through are imaged for the first time, and its bottom is now fixed at around 7 s TWT.

The seismic experiment allowed us to investigate for the first time the deep structures of the crust beneath Sicily. The results obtained and the further data elaboration and interpretation, utilizing well data and regional correlations, will help to better understand the geology of the area, giving more constraints to the structural and geological interpretation of Sicily and neighbouring areas.

In situ conditioning and stabilisation of dredging and mineral sludge

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Contaminated inorganic sludges are causing worldwide a large threat for humans and ecology. This is not only related to their often high contents of toxic compounds (heavy metals and organic pollutants), but also due to the huge amounts of sludges that need to be processed or disposed in landfills.

In the '*In situ* sludge consolidation' project, techniques are being studied and developed for the *in situ* consolidation and stabilization of inorganic sludges, both in landfills as directly in contaminated sediments.

This presentation will first explain the main objectives and research goals of the project. The research activities at VITO focus on *in situ* bioprecipitation (ISBP) of heavy metals and *in situ* chemical oxidation or reduction of organic pollutants. Batch experiments have been conducted with mineral sludge originating from the zinc industry, to study the effect of different types of additives on ISBP, by stimulating sulfate reducing bacteria, and on chemical precipitation of heavy metals. The stability of the metal precipitates formed during the batch tests was evaluated by sequential extraction. The technical and economic feasibility of chemical oxidation of organic pollutants (PAHs, mineral oil) in sediments has been evaluated by performing batch tests with different types of oxidants. The potential release of heavy metals by chemical oxidation of sediments has also been investigated.

The Alhama-Jaraba system as a natural analogue for CO₂-geological sequestration

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Geological disposal and storage of carbon dioxide is at present considered to be one of the main strategies to mitigate the impact of the emissions of this gas on global warming. Deep porous rock formations saturated with brackish or saline solutions are generally regarded as the most effective geological reservoirs for the long-term storage of carbon (Metz *et al.*, [1] and references therein).

Although valuable information on the hydrogeochemical processes expected throughout the interactions between the CO₂-enriched solutions and the hosting rocks can be obtained from modeling exercises and laboratory experiments, the only direct source of information about the long-term behavior of geological storages for CO₂ in deep aquifers are natural analogues.

In this work, a classical and simple geochemical methodology combining the results from ion-ion plots, speciation-solubility calculations, mass-balance and reaction-path calculations is successfully applied to the study of the features and hydrogeochemical processes determining the evolution of a Spanish thermal complex (the Alhama-Jaraba system) which can be considered as a natural analogue for a deep geological carbon storage placed in carbonate rocks. The geological structure and general hydrogeochemical behavior of this system provides with a good opportunity to explore the long-term water-rock interactions expected in carbon storage sites.

All the processes identified in the Alhama-Jaraba thermal system are to be very relevant for the long-term expected evolution of a carbon storage in deep carbonate aquifers. As shown in this study, the application of classical geochemical tools provide with an excellent startpoint for understanding the behavior of prospective storage systems and for optimizing the design of monitoring measures.

[1] Metz *et al.* (eds) (2005) Carbon Dioxide Capture and Storage. *Special Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, UK. 431 pp.

Dust inputs to the (sub-)tropical North Atlantic Ocean; Influence on ocean biogeochemistry

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The (sub)-tropical North Atlantic receives high dust inputs, originating in the Sahara. This presentation will discuss findings from the January-February 2008 UK-SOLAS cruise. The cruise was undertaken in winter, when dust inputs to the ocean are enhanced due to strong northeasterly tradewinds bringing dust from NW Africa and a more southerly position of the intertropical convergence zone (ca. 5-10°N). The nutrient concentrations in the study region were at nanomolar levels (nitrate 3-260 nM; phosphate 2-99 nM). Two major dust events were encountered during the cruise, resulting in an enhanced supply of Fe, Al, P and N to the surface waters.

Enhanced surface water dissolved Al (up to 50 nM) and Fe (up to 0.37 nM) concentrations were observed in regions subjected to enhanced dust inputs. The dust inputs did not yield immediate important changes in the bacterial community structure or their productivity. The dust inputs however had a strong influence on nitrogen fixation (diazotrophy), with the oligotrophic waters of the study regions showing enhanced levels of diazotrophy. The diazotrophs have high iron requirements which are met by the supply of atmospheric iron.

U-series recoil ages of ice cores samples from Dome C, Antarctica

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Determining the absolute ages of ice within ice cores, ice sheets and glaciers remains non-trivial especially for the oldest ice (>100ka). While both insolation and Be-10 records have proven invaluable in creating ice-core timescales, neither can be used to evaluate the length of hiatuses, the extent of ice folding in ice cores, or the age of ice at the bottom sections of ice cores. U-series recoil from mineral aerosols (dust) into the ice matrix is one possible technique for determining the absolute age of ice, independent of any other parameters. We report here our progress in measuring ages using U-series. Concentrations of parent (²³⁸U) and daughter (²³⁴U) isotopes in the ice and dust fractions of the ice cores were measured by MC-ICPMS (Nu Instruments). Blanks were minimized (< 10pg) and sensitivity optimized (>1% efficiency) to achieve the precision and accuracy required for small sample sizes (< 1mg of dust). Additionally, we measured the ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd isotopic compositions by TIMS (Triton) to assess the source of initial uranium within the ice (prior to accumulation of daughters ejected from the dust) as well as the geographical source of the dust. Ages of samples from Dome C were calculated using an age equation that includes an ejection factor, the fraction of daughter products implanted into the ice relative to the total number produced, based on the surface to volume ratio of the dust grains. This parameter was measured by specific surface area determination using a specially designed nano-scale for this purpose. Eight 500-800g samples of ice from Dome C were chosen to test the viability of this technique on ice core samples. Remarkably, U concentrations and ²³⁴U/²³⁸U measurements combined with BET measurements results in measured ages overlapping with the published ages from the EDC3 timescale [1] for samples in the upper 3000m of the ice core. Samples from the lower 40m yielded ²³⁴U/²³⁸U activity ratios that indicate ages older than 650 ka, possibly as old as 925 ka. This suggests that the oldest ice at Dome C may yet provide climate information prior to 800 ka.

[1] Parrenin *et al.* (2007) *Clim Past* **3**, 485-497.

Re-Os geochemistry of Fe-rich peridotites and pyroxenites from Horní Bory, Czech Republic

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Many recent studies have documented significant changes in the Re-Os systematics of mantle rocks caused by secondary processes including partial melting, melt percolation and weathering. It has been shown that melt percolation represents one of the most important process, during which Re and Os import or loss, and Os isotopic modification can occur depending on several parameters, including melt/rock ratios, sulfur saturation of the percolating melt, etc. In order to study such processes further, Re and Os concentrations, as well as Os isotopic compositions, were determined for a well-characterized suite of mantle peridotites and associated pyroxenites from Horní Bory, Bohemian Massif, Czech Republic. These mantle peridotites are of two types: Mg-Cr lherzolite and Fe-rich dunite/wehrlite associated with Fe-Ti pyroxenites. The Fe-rich suite formed by melt/rock reaction between lherzolite and a SiO₂-undersaturated basaltic melt characterized by a subduction-related signature. Associated pyroxenites likely represent crystallization products of these transient basaltic melts. The Mg-lherzolite samples have variable Re and Os concentrations of 130-510 ppt and 3.7-7.5 ppb, respectively, and ¹⁸⁷Os/¹⁸⁸Os ratios of 0.122-0.123. Therefore, the Re and Os contents are similar to ~2x higher than Primitive Upper Mantle (PUM) estimates. The Os isotopic compositions are all lower than PUM. In contrast, the Fe-rich suite and associated pyroxenites are highly enriched in Re (0.95-2.2 ppb), depleted in Os (0.1-1.8 ppb), and show very heterogeneous and highly radiogenic ¹⁸⁷Os/¹⁸⁸Os of 0.172-0.681 compared to PUM. The very high Re contents coupled with radiogenic Os isotopic compositions of Fe-rich dunite/wehrlites and pyroxenites imply significant Re and radiogenic Os import from basaltic melts during subduction-related mantle refertilization. For these rocks, such process evidently resulted in removal of primary Os from the source rock. On the other hand, the higher and coupled Re-Os concentrations in one sample of Mg-lherzolite suggest that this suite was also modified during melt infiltration, but with minimal effect on Os contents and ¹⁸⁷Os/¹⁸⁸Os, presumably as a result of lower melt/rock ratios.

Thermodynamic properties of kornelite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 7.75\text{H}_2\text{O}$) and paracoquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$)

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Hydrated ferric sulfates are abundant phases in many areas affected by acid mine drainage waters, in anoxic soils, and industrial waste. The precipitation of these phases exerts a control not only over Fe and sulfate ions in the waters but also over toxic metals and metalloids by coprecipitation or adsorption. Understanding the formation and stability of these phases plays an important role in estimating and modelling their solubility relationships and hence the scavenging effect of hazardous ions. In this work, we measured enthalpies of formation of kornelite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 7.75\text{H}_2\text{O}$) and paracoquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) by acid solution calorimetry at $T = 298.15$ K. The samples were characterized chemically, and structurally by single-crystal, in-house powder, and synchrotron powder X-ray diffraction. From the single-crystal diffraction data, we were also able to locate the H atoms and decipher the H-bonding system in kornelite. The measured enthalpies of formation from the elements (crystalline Fe, orthorhombic S, ideal gases O_2 and H_2) at $T = 298.15$ K are -4916.2 ± 4.2 kJ·mol⁻¹ for kornelite and -5292.7 ± 4.2 kJ·mol⁻¹ for paracoquimbite. We have used several algorithms to estimate the standard entropy of the two phases. Afterwards, we calculated their Gibbs free energy of formation and constructed a phase diagram for kornelite, paracoquimbite, $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, and $\text{Fe}_2(\text{SO}_4)_3$ as a function of temperature and relative humidity of air. Our calculations show that the topology of the phase diagram is very sensitive to the entropy estimates and a reliable construction of a phase diagram must await better constraints on entropy or Gibbs free energy of formation. A possible remedy of this problem is the measurement of entropy, even though it is difficult owing to the high H_2O concentration within the structures of these compounds.

Air quality in a changing climate

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Changes in the climate of our planet will be accompanied by changes in the major meteorological factors affecting air quality: temperature, vertical stability of the atmosphere, precipitation, humidity, cloudiness and wind patterns. To assess these climate change impacts, we have developed the Global-Regional Climate-Air Pollution modelling System (GRE-CAPS) by coupling global and regional models of air quality and meteorology. The GRE-CAPS system is capable of predicting ozone and particulate matter (PM) mass concentrations and is currently being extended to treat mercury and ultrafine particle number concentrations as well.

Climate change is expected to make the ozone pollution problems faced by developed and developing regions worse, causing more frequent and severe pollution episodes and a longer 'ozone season'. Major factors contributing to the degradation in ozone air quality include shifts in the PAN-NOx equilibrium at higher temperatures, increased emissions of biogenic VOCs, increased HOx abundance under more humid conditions, and increases in background ozone due to higher methane levels. In contrast, the situation for particulate matter (PM) is much more complex and the sign and magnitude of the climate effects will vary regionally and seasonally. Climate change will likely force additional emissions reductions to improve or maintain current air quality.

Carbon isotope fluctuations and Phosphorus accumulation during Late Devonian anoxic events in Erfoud Morocco

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The Late Devonian Frasnian-Famennian biotic crisis marks one of the most intriguing and largest mass extinctions in Earth history. The most severe biotic crises are the lower and upper Kellwasser events (LKWE-UKWE), which occurred at the end of the Frasnian and decimated the reef system, shallow benthos and some pelagic swimmers. These crises were associated with major sea-level rises, warm climate and widespread ocean anoxia.

Environmental and depositional changes across the Late Devonian Kellwassers events in the Anti-Atlas, near Erfoud, Morocco, are examined based on microfacies, mineralogy, $\delta^{13}\text{C}$ values and phosphorus (P_{tot}) analyses. Correlation based on $\delta^{13}\text{C}_{\text{org}}$ with other sections (e.g. Benner, Germany, Baisha, China) reveals the Erfoud section as stratigraphically complete across the Frasnian-Famennian transition. Microfacies analyses suggest outer shelf to hemipelagic conditions. Both LKWE and UKWE correspond to laminated black shales deposited during a sea-level rise under anoxic conditions and coincide with increased detrital inputs (quartz, feldspars) reflecting intense weathering on land. However, P_{tot} concentrations are quite different in the two Kellwasser horizons. The LKWE is almost completely depleted in P_{tot}, contrary to the UKWE, which is characterized by more variable contents, ranging from very high contents (3500 ppm) to background values (<200ppm). This may indicate that the two Kellwasser levels reflect different environmental conditions. The LKWE appears to be more anoxic preventing the effective retention of P into the sediments. In contrast, the UKWE reflects more variable conditions with episodic oxic intervals.

A multilayered ocean in the Ediacaran Yangtze platform? Insights from carbonate and organic matter paired $\delta^{13}\text{C}$

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The large carbon isotope fluctuations systematically reported for Ediacaran carbonate rocks are interpreted as evidence of strong environmental variations. New paired $\delta^{13}\text{C}$ data on carbonates and their associated organic matter are presented for the Yangjiaping section of the Doushantuo Formation (Hunan, South China), which, integrated with previously reported ones [1, 2], allow the reconstruction of lateral variations of $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{org}}$ and $\Delta^{13}\text{C}_{\text{carb-org}}$ for a shelf-to-basin cross section of the Yangtze platform. Strong lateral heterogeneities are revealed, with complex variations of $\delta^{13}\text{C}_{\text{carb}}$ and $\Delta^{13}\text{C}_{\text{dol-org}}$ ($\Delta^{13}\text{C}_{\text{dol-org}} = \delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$) in the inner shelf section, phased variations (positive $\delta^{13}\text{C}_{\text{carb}}$ and $\Delta^{13}\text{C}_{\text{dol-org}}$ close to 29‰) in the shelf margin section, and negative $\delta^{13}\text{C}_{\text{carb}}$ ($\Delta^{13}\text{C}_{\text{dol-org}}$ as low as 20‰) in the basin.

Assuming that carbonate $\delta^{13}\text{C}$ is acquired in bottom waters, we show that the spatial and temporal $\delta^{13}\text{C}_{\text{carb}}$ and $\Delta^{13}\text{C}_{\text{dol-org}}$ variations are compatible with a three-layered water column: (i) an oxic surface layer, which dissolved inorganic carbon (DIC) is probably in isotope equilibrium with the atmosphere; (ii) an intermediate euxinic layer with a DIC enriched in ^{12}C due to organic matter oxidation by sulphate reduction; (iii) a deepest euxinic layer that seems to be restricted to the inner shelf lagoonal facies, lacking sulphate, and with a DIC enriched in ^{13}C by methanogenesis. This model implies that some Ediacaran basins may have contained distinct DIC reservoirs, thus complicating our understanding of the global carbon cycle at the time.

[1] Guo *et al.* (2007) *Pal. Pal. Pal.* **254**, 140-157.

[2] McFadden *et al.* (2008) *PNAS* **105**, 3197-3202.

Structure, thermodynamics and transport properties of Mg_2SiO_4 liquid under high pressure from molecular dynamics

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Melting is an ubiquitous process in planetary interiors and one of the dominant mechanisms for thermal transport and chemical differentiation in planets. The properties of silicate liquids are thus essential for understanding a wide range of geophysical phenomena related to the Earth and its origin and evolution. Forsterite is a major component of the Earth's upper mantle and is thus of considerable importance in controlling its properties, rheological and thermal structure.

In the present study, we have used large-scale molecular dynamics simulations to compute structure, thermodynamics, and transport properties of Mg_2SiO_4 liquid up to 32 GPa and over a temperature range of 2600 to 3200 K. The interactions between the atoms are modeled by an aspherical ion model (AIM). The parameters of the potential are fitted to ab initio results. Simulations were performed using a cubic simulation box with 2016 ions (288 formula units), a time step of 1 fs, in the NVT ensemble. The equilibration is done using an isotropic barostat coupled to the thermostat for 50 ps before the production run of 150 ps length is started.

We find that the coordination of Mg and Si increase with pressure. There is also a large redistribution of bond angles. Under compression the Si-O-Si distribution is shifted to smaller angles, allowing for more dense packing of the SiO_4 tetrahedra. Contrary to solids under pressure we find thermal pressure and the Grüneisen parameter to increase with compression. We find that diffusivity decreases uniformly with pressure, and viscosity increases uniformly with pressure. Both transport properties can be readily fit with closed Arrhenius expression over the whole pressure and temperature range considered. The independent estimates on diffusivity and viscosity allow us to examine their relation through the Eyring equation: the proportionality factor between them, the translation distance for a diffusion event, is determined as 18 Å at 0 GPa, and decreasing with pressure. Combining thermodynamic results with the viscosity fit we compute a magma ocean adiabat and the associated viscosity profile. We find that viscosity in the magma ocean is $\sim 2 \cdot 10^{-2}$ Pas near the surface, and that it decreases by less than 0.1 log-unit up to 32 GPa.

Colder NADW leads to salty deep water formation in the South

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Today the deep ocean is filled with a mixture of warm/salty North Atlantic Deep Water (NADW) and cold/fresh Antarctic Bottom Water (AABW). While NADW is more dense at the surface of the ocean, its relative warmth means that it is less dense than AABW at 3,000 meters deep, and as a result there is substantial mixing of the two water masses. However, there is growing evidence that at the Last Glacial Maximum (LGM) this arrangement was very different. Cold-salty waters from the south filled much of the deep Atlantic at the expense of cold-fresh waters from the north. In this configuration temperature and salinity do not oppose each other in the two water masses, and LGM AABW can be isolated from LGM Northern Source waters. I will show how this LGM water mass architecture can be a natural result of cooling NADW.

The densest component of AABW forms in winter time on continental shelves where sea ice formation and export leaves the remaining water enriched in salt. However, continental ice shelves impinge in these regions and provide a degree of 'pre-freshening' due to contact with the relatively warm ocean waters and subsequent melting. As the source of this ocean heat is largely NADW itself, I will explore a feedback mechanism where cooling NADW leads to less 'pre-freshening' of proto-AABW and eventually salty-cold waters forming in the south that are denser than all other open ocean water masses. Contrary to popular belief, cooling of NADW could sow the seeds of its own demise and lead to the LGM arrangement of very dense, isolated waters forming around Antarctica.

Methanogenesis and methanotrophy in Lake Kinneret (Israel)

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In this research we quantified the rate profiles of methane production (methanogenesis) and consumption (methanotrophy) in Lake Kinneret (Israel). This is by performing seasonal high resolution chemical and isotopic profiles in the lake water column and sediments' porewater and by modeling the data.

Water samples and sediments cores were collected from the lake every two months for 14 months and being analyzed for methane and its possible coupled species - sulfide, sulfate, oxygen, iron (II and III), alkalinity and dissolved inorganic carbon (DIC), as well as the stable isotopic composition of carbon in the DIC and methane. Sulfate reduction, methanogenesis and methanotrophy rate profiles were conducted based on the chemical and the isotope profiles.

The results show that anaerobic sulfate reduction dominates the upper 7 cm of the sediments, and dissolved iron (almost entirely Fe(II)) starts increasing as sulfide is depleted. Methane starts to accumulate when sulfate is almost depleted, where there might be an overlap between methanogenesis and sulfate reduction. Methane and the stable isotopic composition of carbon in the DIC porewater profiles imply that methanogenesis is restricted to a certain layer (5-12 cm depth). The obvious methanotrophy occurs at the thermocline, however our data and incubation experiments suggest the possibility for anaerobic methane oxidation in Lake Kinneret.

Genomics as a tool to analyze bioremediation potentials and functional diversification in subsurface environments

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Anaerobic subsurface environments such as anaerobic aquifers, terrestrial deep subsurface materials and marine sediments are inhabited by massive amounts of bacteria. Population analyses using molecular techniques have demonstrated diverse communities including many bacteria for which no physiological characterization and no ecological role is known. While population analyses mostly rely on sequencing of 16S rRNA genes, genome analyses of either single (isolated) strains or of full communities can contribute to the understanding of physiological characteristics because functional genes are identified.

As an example, a specific group of the bacterial phylum *Chloroflexi* was detected in many contaminated and non-contaminated subsurface environments but cultivation yet failed. The closest relatives of this group are bacteria of the genus *Dehalococcoides* that are physiologically characterized and the genome of three *Dehalococcoides* species is fully sequenced. *Dehalococcoides* species are strictly anaerobic bacteria that rely in their metabolism on halogenated compounds which are used for a respiratory process. Genome sequencing shows evolution of a wide range of respiratory proteins that enable growth with unusual substrates. Judged from the genomes, the bacteria rely on symbiotic partners in regard to buffering of redox conditions, cofactor production, hydrogen production, acetate production and nitrogen fixation. The presented genomes not only give a reference point to genomes of respiratory dehalogenating bacteria, they also allow comparative analysis and possibly comparative annotation of yet unknown genes identified by metagenomic approaches from other subsurface environments.

[1] Kube *et al.* (2005) *Nature Biotechnology* **23**,1269-1273.

Low-temperature melt-fluid miscibility: Experimental evidence for enhanced mass transport in the upper crust by cooling fluids

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Half a century after Tuttle and Bowen's hypothesis [1], we present experimental evidence for extensive fluid-melt miscibility in residual granitic solutions at upper-crustal pressures (P) and temperatures (T) as low as 350° C. We demonstrate that late-stage magmatic-hydrothermal fluids separating from hydrous granitic magmas by boiling can largely increase their solute contents upon cooling, resulting in a fully miscible solution at very low temperatures.

We have characterized the composition of aqueous fluid in equilibrium with quartz, muscovite and K-feldspar at 1.0 GPa and 650 to 700°C and found that high- P granitic fluids are very siliceous and peralkaline, with non-negligible but low aluminum content. Quartz-hosted fluid and melt inclusions were synthesized to investigate the low- T fluid phase relations of such solutions in the quartz-saturated $K_2Si_4O_9$ - SiO_2 - H_2O system. In this system, strongly retrograde solubility behaviour leads to the down- T evolution of low-density aqueous vapors towards high-density melt-like phases.

Lower critical solution phenomena can be explained by a negative excess enthalpy of mixing in K_2O - SiO_2 - H_2O melts at low P and T . Also at low- T , the increasing strength and directional nature of hydrogen bonds and associated silicate polymerization play a vital role in solvent-solute ordering and thus ultimately lead to the onset of supercriticality in peralkaline aqueous-silicate solutions at low- P upon cooling.

Such alkali-silicate aqueous solutions and their phase relations have been underestimated in Earth science literature. Their high solvent power is likely to play an important role in the evolution of many low- PT geological processes, such as the origin of coagulated colloidal silica in geothermal waters and potassic metasomatism associated with granites. Supercriticality is not restricted to the deep Earth, as often thought.

[1] Tuttle & Bowen (1958) *Geol Soc Am Mem* 74.

Effect of humic acid redox status on the sorption of organic pollutants

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Natural organic matter (NOM) is the primary environmental sorbent for many organic pollutants. While their sorption to oxidized NOM has been extensively studied, it is unknown whether NOM-redox status (i.e., quinone/hydroquinone ratio) affects NOM-pollutant interactions. Yet, many contaminated soils, sediments and aquifers contain (partially) reduced NOM. The aim of this work was to test whether NOM-redox status affects organic pollutant sorption. To this end, we studied the sorption of the following test chemicals to oxidized (o-) and reduced (r-) Leonardite Humic Acid (LHA): apolar naphthalene, monopolar acetophenone and quinoline, bipolar β -naphthol, and cationic methyl viologen.

We generated r-LHA from o-LHA by bulk electrolysis with an average of 1040 (± 80) $\mu\text{equiv g}^{-1}$ transferred. None of the tested chemicals showed significant differences in sorption to o-LHA and r-LHA (tested at pH 7 for all non-ionic chemicals and at pH 7, 9, and 11 for methyl viologen). This implied that the organic probe molecules did not experience any differences in the cohesive energies (apolar probe), the H-donor and acceptor properties (mono- and bipolar probes) and numbers of anionic sorption sites (cationic probe) between o-LHA and r-LHA. Yet, when comparing the sorption of all non-ionic compounds relative to a hexadecane reference state in which only van-der-Waals interactions occur, the mono- and bipolar chemicals sorbed more strongly to LHA than apolar naphthalene. This showed that the polar molecules indeed probed for H-donor-acceptor properties of LHA and that these properties were not significantly changed by reduction. Re-oxidation of r-LHA to o-LHA over the course of the experiment could be ruled out as an explanation for the lack of differences as r-LHA reduced the redox-dye dichlorophenol indophenol to the same extent before and after the sorption experiment.

These results indicate that model parameters that describe the sorption of organic pollutants to oxidized NOM may also be applied to reduced NOM.

Electrochemical characterization of humic substance redox properties

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Humic substances act as electron donors/acceptors and as electron shuttles. As such, humics are of key importance in many biogeochemical cycles and in pollutant dynamics. The objective of this work was to characterize the major redox-properties of humics using an electrochemical approach.

First, we developed a new chronoamperometric method using a carbon working electrode (negligible background current from H^+ reduction) to transfer known amounts of redox equivalents (RE) to model humic acids (HA). Reduction for 20h at $E=-0.6V$ (SHE) and pH 7 resulted in RE transfer that increased in the order Suwannee River HA ($510 \mu\text{equiv g}^{-1}$), Pahokee Peat HA ($930 \mu\text{equiv g}^{-1}$), Leonardite HA (LHA) ($1030 \mu\text{equiv g}^{-1}$) and Elliot Soil HA ($1190 \mu\text{equiv g}^{-1}$), and correlated with values reported in [1]. Second, we employed mediated cathodic and anodic chrono-amperometric detection to quantify the RE in a set of LHA samples pre-reduced to different redox states. Detection of the RE in LHA was quantitative (95% of transferred RE were detected), irrespective of the degree of LHA pre-reduction. This method quantifies RE directly by current measurement at very low detection limits. Third, we studied the re-oxidation kinetics of reduced LHA ($1050 \mu\text{equiv g}^{-1}$) by excess O_2 at pH 7. The re-oxidation kinetics were strongly biphasic: fast initial transfer of 40% of the RE to O_2 in less than 1 min was followed by slow LHA re-oxidation over 5d, at which 12% of RE still remained in LHA. Biphasic kinetics are taken to reflect the variability in the reactivity of the redox-active moieties in HA. Fourth, we coupled the reduction of LHA to H^+ titration (Fig. 1). The ratio e^-/H^+ transferred during reduction decreased from 1.00 at pH 7 to 0.86 at pH 9, 0.75 at pH 10 (not shown), and 0.38 at pH 11. This strongly supports that quinone-type moieties dominated the redox-properties of LHA, as hydroquinones deprotonate successively at $pH > 8-9$.

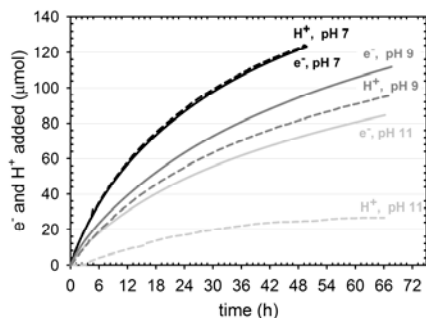


Figure 1: Electrochemical reduction of 0.15g Leonardite humic acid coupled to H^+ -titration at pH 7, 9, and 11.

[1] Ratasuk & Nanny (2007) *ES&T* **41**, 7844.

Noble gas temperatures from speleothems

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Speleothems have proven to be excellent paleoclimate archives, providing accurately dated high-resolution stable isotope and trace element records. However, the interpretation of such data in terms of past temperatures is difficult. Noble gases dissolved in microscopic water inclusions in speleothems have the potential to provide direct paleotemperature information, in analogy to noble gas paleothermometry in groundwater. While the extraction and precise measurement of noble gas concentrations from speleothem samples of about 1 g are feasible, the main difficulty of the method arises from the often large amounts of air included in the samples. Apparently only few speleothems provide naturally low air to water ratios suitable for noble gas temperature (NGT) determination. However, stepwise extraction procedures can reduce this ratio and thereby increase the number of speleothems accessible by the method. In addition to temperature, the water content of speleothems appears to provide useful information on paleohumidity.

Several speleothems from Bunker Cave in Northwest-Germany provided the first reasonably precise NGTs. Combined data from two stalagmites yield a temperature record encompassing several relatively warm phases during the past ~130 kyr. A large temperature increase of about 9°C is found at the transition into the Eemian Interglacial, which appears to have been significantly warmer than the Holocene. The early Eemian warming correlates well with high resolution stable isotope data, highlighting the potential of the method to calibrate the stable isotope paleothermometer. NGTs during the Holocene show no significant variation within the uncertainties of about ± 1 to 2°C. Variations of the water content in this cave as well as a cave from southern Chile are correlated to established humidity indicators such as stable isotopes and Mg/Ca ratios, suggesting that wet phases and high drip rates lead to comparatively high water contents in the stalagmites.

Mass spectrometric effects on 'clumped isotopes' calibration

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Carbonate 'clumped isotopes' thermometry is based on a Δ_{47} -temperature relationship that was obtained using calcite formed at known temperatures and verified using biogenic carbonates, all analysed on one mass spectrometer. Wider spread of 'clumped isotopes' measurements requires strict examination of its applicability to other analysis conditions.

Decomposition-recombination reactions of CO_2 within the ion source promote random distribution of isotopes among all isotopologues, thus modifying Δ_{47} without affecting $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. We observed persistent deviations from the nominal Δ_{47} values of NBS-19 and cylinder CO_2 , indicating randomization of 5% of the CO_2 molecules. A scaling factor of 0.95 was thus applied, resulting in an offset of up to 0.005‰ from previously determined Δ_{47} in speleothem samples.

CaCO_3 precipitated inorganically at a temperature range of 26–40°C resulted in $\Delta_{47}=0.617\text{--}0.545\text{‰}$, and a correlation of $\Delta_{47}=56808/T^2-0.026$. Scaling the data by 0.95 resulted in Δ_{47} values that were within 0.004‰ of the original 'clumped isotopes' thermometer, thus providing a confirmation of the original calibration using a different set of carbonate materials and independent sample preparation and analysis.

The observed offsets are small and easily overlooked, as they are within the analytical errors of one analysis. However, they are significant compared to the desired precision (obtained through replicates) and are likely to vary among mass spectrometers. Thorough standardization is required to account for these effects, highlighting the need to develop standard materials before a wide spread application of 'clumped isotope' thermometry.

Mobility of lithophile trace elements during the late magmatic stage in the felsic Gawler Range Volcanics, South Australia

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The Mesoproterozoic (ca. 1.6 Ga) Gawler Range Volcanics (GRV) and the coeval Hiltaba Suite Granite form a silicic large igneous province (10^5 km^3) emplaced in an intracontinental setting in the Gawler Craton, South Australia [1, 2]. The world-class Cu-Au-U Olympic Dam deposit is both spatially and temporally associated with the province. The hydrothermally altered rocks hosting the Olympic Dam deposit are associated with high REE contents ($\text{La}+\text{Ce} = 0.5 \text{ wt\%}$) and fluorine-bearing phases are ubiquitous [3].

The transition between magmatic and hydrothermal stages is considered to be crucial for the formation of ore deposits and the exsolution of an aqueous fluid has been proven to be an effective way of sequestering metals from the magma [e.g. 4]. However, lithophile elements are considered to be immobile in aqueous solutions and need to be complexed to be transported. The GRV-Hiltaba Suite province offers the opportunity to study a F- and lithophile element-rich system and establish possible relations with the mentioned deposit.

We report the occurrence of lithophile trace element (REE+Y, HFSE)-bearing accessory minerals (zircon, fluorite, Nb-bearing Ti oxide, REE-fluoro-carbonate) inside cavities (amygdales, micromiaroles, lithophysal vugs, $\leq 2 \text{ mm}$ in size) in the GRV. These minerals can account for most of the content of lithophile trace elements in these rocks. Textures and the association with non-magmatic phases (e.g. epidote) suggest that these minerals crystallised from a fluid. Melt inclusion analysis suggests the magma as a possible source of F ($F \leq 1.3 \text{ wt\%}$).

We hypothesise that, due to a high solubility of accessory minerals, trace elements and F were concentrated in the melt by fractional crystallisation. Upon saturation, they could have been extracted by an exsolving F-bearing fluid. Trace element-bearing accessory phases could have then crystallised from such a fluid.

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A simplified approach to estimate aerosol water content under near ambient humidity conditions using two SMPS systems in parallel

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Introduction

The aerosol direct effect, atmospheric heterogeneous chemistry and visibility are largely controlled by the water content of aerosol particles. Several reports on aerosol water-uptake ability can be seen recently [1-2], however, as of our best knowledge, there is no study in which percentage aerosol water content (AWC) is determined under the ambient humidity conditions (i.e., amount of aerosol water relative to atmospheric water-vapor).

Here, we operated two scanning mobility particle sizer (SMPS) systems in parallel, one under dry and the other under ambient humidity (wet) conditions to simultaneously measure the size distributions of ambient aerosols (PM_{1.0}) (Figure 1). Based on two types of particle size distributions and densities assumed, we calculated aerosol mass for dry and wet particles ($\mu\text{g m}^{-3}$), respectively, in order to estimate aerosol water content ($\mu\text{g m}^{-3}$). Using exponential empirical relation between atmospheric water-vapor concentrations ($M_{\text{water-vapor}}$, g m^{-3}) and temperature ($^{\circ}\text{C}$), the $M_{\text{water-vapor}}$ in the atmosphere at given temperature and RH can be calculated.

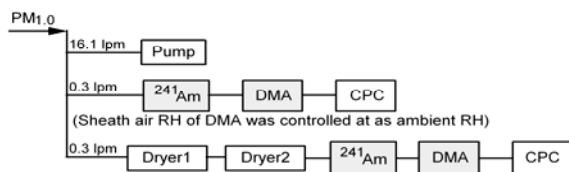


Figure 1: Experimental setup.

Results and Discussion

We performed SMPS measurements of atmospheric aerosols at Hokkaido University campus, Sapporo, Japan from July 23-25, 2008. For an unimodal distribution on July 24 (02:35 LT), AWC was calculated to be $10.6 \mu\text{g m}^{-3}$ at 71.1% ambient RH and 23.6°C , which is 17% of total aerosol mass (M_{aerosol}) and 0.00007% relative to $M_{\text{water-vapor}}$. Similarly, for a bimodal distribution on July 24 (09:05 LT), AWC was $41.4 \mu\text{g m}^{-3}$ at 65.2% RH and 24.8°C , which is 54% of M_{aerosol} , and 0.00028% relative to $M_{\text{water-vapor}}$. Aerosol water-uptake characteristic (hygroscopicity) is also measured based on the shift of particle mode peak obtained under dry and wet conditions, and verified to be consistent with the data predicted using AIM model (based on the chemical compositions determined from PM_{1.0} filter samples) [2].

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Fluorescence emissions and infrared-spectroscopies of uranyl sorption on organic colloids and clay minerals

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Reactions occurring at mineral surfaces and organic matter significantly affect the mobility of radionuclides in the environment. Sorption and complexation equilibrium constants between uranyl ions on organic colloids and clay minerals, were determined by measuring the system response to clays suspensions (pre-equilibrated with or without uranyl) and to perturbations of the solution chemistry.

The interaction of kaolinite, smectite and Fe-smectite and three fractions of dissolved organic matter (DOM) (colloidal, hydrophobic and transphilic) solutions saturated with uranyl ions were studied by molecular fluorescence, FT-IR and ATR-IR spectroscopies. The fluorescence emission analysis of uranyl ions aqueous solutions (concentration of 5.0×10^{-6} M and at pH=6.0) shows a decrease on the fluorescence intensity when DOM fraction are present. The IR spectra of sorbed uranyl on clay minerals are shown in. Symmetric stretching vibrations were observed in KBr pellets. The stretching vibrations at 936 cm^{-1} and 805 cm^{-1} are assigned to $\nu_3 \text{UO}_2^{2+}$ and $\nu_1 \text{UO}_2^{2+}$. Kaolinite sorbed uranyl show a large shoulder at 936 cm^{-1} , which would also corresponds to inner surface OH bending in kaolinite. Also, two strong vibrations were identified at 803 and 760 cm^{-1} in the same sample. The ν_1 stretching band of UO_2^{2+} is superimposed on Si-O bending vibration in kaolinite. Sample smectite sorbed uranyl show evidences of the UO_2^{2+} stretching band at 800 cm^{-1} superimposed on the band at 810 cm^{-1} corresponding to Al-O-Si out-of-planes. Both 810 and 770 cm^{-1} bands are typical for beidellite. Organic colloids, beidellite and kaolinite evidence good sorbents for uranyl ions.

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Geochemistry and petrogenesis of igneous rocks in the Saveh region, NW Iran

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Saveh region is located in Central Iran (CI) and Urumieh-Dokhtar Magmatic Assemblage (UDMA) and is consist of major varieties of Paleogene igneous rocks. Granitoid, diorite and gabbro (intrusive) and rhyolite, andesite and basalt (volcanic) are exist in the region. Pyroclastic rocks and tuff are observed as well. Their west-northwest trend is perpendicular to the subduction zone and is parallel to major faults trend. Approximately all igneous rocks have calc-alkaline metaluminous affinity and Harker's variation diagrams of major and trace elements show a continuous range that indicate they are cognate. The enrichment of LILE and depletion HFSE which are consistant with continental volcanic arc magmatism. Some basic rocks are enriched in both LILE and HFSE, which is consistent with the undepleted, asthenospheric mantle. On the other hand, the enrichment of Ti, Fe, Mg and Ca in the igneous rocks in the region can be considered as decompressin melting of oceanic lithosphere or mantle wedge derived parent magma. Whole rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Silijerd intrusion range from 0.704759 to 0.705166 reflect their lower crust nature and low contamination of their magmas with upper crust [1].

Geochemistry of igneous rocks in the Saveh reveals an extentional backarc basin with high-angle slab or rapid subduction (slab roll-back) tectonic setting in the region during the paleogene. This may be preceded by a flat-slab subduction of Neotethyan oceanic lithosphere beneath Central Iran in the Mesozoic [2].

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Using chromespinel for petrogenetic implications of South-eastern Iranian mantle peridotites

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In Iranian mantle peridotites (Kuhshah, Soghan and Abdasht complexes), there are various types of spinels with distinct chemical and textural features. The unique speciality of spinel for indication of its environmental conditions during crystallization leads us to use it for understanding the origin of these Iranian mantle complexes. In these peridotites, each of lithologies contains special types of Spinel. In dunites, chemical composition and texture of disseminated spinels indicate a replacive origin for dunites that leftover after passage of ascending melts. In harzburgites, spinels are refractory and show nearly 20 percent partial melting of host rocks. In chromitites, spinels are magmatic in origin and their composition is similar to those crystallized from boninitic melts. In some lithologies, there are two types of spinels including refractory ones and interstitials that have been formed from perculating melts. These features indicate south-east Iranian upper mantle has been affected by partial melting and impregnation events and it is highly heterogenous.

The orthoenstatite/clinoenstatite phase transition under the upper mantle conditions determined by *in situ* X-ray diffraction: Implications for nature of the X-discontinuity

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In-situ X-ray diffraction experiments were performed and the orthoenstatite(Oen)/high-pressure clinoenstatite (C2/c, HP-Cen) phase boundary in the MgSiO₃ system was determined. All the experiments were carried out using a Kawai-type multi-anvil apparatus installed at BL04B1 in SPring-8, Japan. Two types of experiments were carried out, (1) 'phase observation experiments' at varying pressures and temperatures, and (2) 'quench experiments' at fixed pressure and temperature. The phase boundary, determined precisely by integrating the results of both sets of experiments, was found to be P (GPa) = $0.0035T$ (°C) + 3.7, using a MgO pressure scale [1]. The Oen/HP-Cen phase boundary at 1400°C determined here is 0.7–1.0 GPa lower than previous reports based on quench experiments. The phase transformation of orthopyroxene is expected to occur at 260 km depth along a typical mantle geotherm, and the shallower part of the observed X-discontinuity can be explained by this phase transformation in Opx-rich mantle.

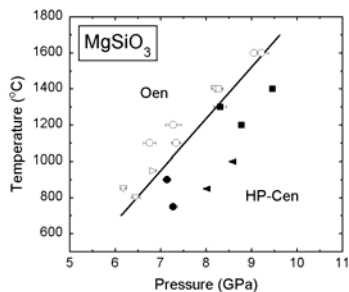


Figure 1: Phase boundary determined in this study (modified after Akashi *et al.* [2]).

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VFAs concentrations in the hydrothermal fluids venting from the sediment-hosted hydrothermal system in the Wakamiko submarine crater, Japan

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Marine shallow-water hydrothermal activity was discovered at the Wakamiko submarine crater of 200 meters water depth in Kagoshima Bay. The Wakamiko crater is filled with recent thick (up to 80 m) unconsolidated clayey ~ silty fine sediments, therefore the hydrothermal fluids interact with the sediment during penetration the sedimentary layer. As a result hydrothermal petroleum generation has been occurred at the center area in the crater [1]. We successfully collected the venting hydrothermal fluids ($T_{max} = 200^{\circ}\text{C}$) from the different three vents and also recovered seven piston core samples in and around the crater. Some pore water samples obtained from the cores contained hydrothermal components, which has the same source with the venting fluids [2], however detail of the concentrations of minor components, such as VFAs (volatile fatty acids), were different among the vents and the pore waters. In this study we discuss the cause of the variation in VFA concentrations.

'White Cone' vent was characterized by significantly low VFAs (formic and acetic acids) and hydrogen sulfide concentrations relative to the fluids venting from the other vents ('Hairly Cone' and 'Daifuku-yama'). The relationship between acetic acid and magnesium concentrations in the pore water, which was obtained from the venting site and contained hydrothermal components, was similar to the relationship of the Hairly Cone and Daifuku-yama fluids. Those VFAs may be considered to derive from pyrolysis of the sedimentary organic matter, however, the variation in the concentrations among the vents may suggest subvent microbial activity. $\delta^{34}\text{S}$ values of hydrogen sulfide were slightly higher at the White Cone vent than the other vents, such isotopic difference may also suggest microbial contribution.

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[2] Yamanaka *et al.* (2007) AGU, Fall Meet., Abstract V41B-1375.

¹⁰Be production rate from 1717 AD rock avalanche in Val Ferret (Mont Blanc Massif, Italy)

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On September 12th 1717 AD, one of the largest rock avalanches of the Alps destroyed two small settlements with 7 casualties and loss of their cattle in the upper Ferret valley (Mont Blanc Massif, Italy). A rock volume larger than 10 million m³ and a huge volume of ice from Triolet glacier were mobilized by this avalanche [1]. Composed of ice and sediment, this mass moved more than 7.5 km downvalley and reached the lower part of the valley. Can this historically recorded natural hazard be a well suited site for the ¹⁰Be production rate calibration?

With the aim of answering this question, seven samples from the granite boulders within the rock avalanche deposit were collected in June 2008 and prepared for AMS analysis. In order to compute sea level – high latitude ($\geq 60^\circ$) ¹⁰Be production rates from the measured concentrations of these seven boulders, local scaling factors were first calculated after Stone [2]. The production rates are corrected for shielding of the surrounding topography, dip of rock surface and sample thickness, but not for snow cover and vegetation. Temporal changes in palaeomagnetic intensity and polar wander were taken into account [3]. Our results from Val Ferret reveal a sea level – high latitude ($\geq 60^\circ$) ¹⁰Be production rate of 5.82 ± 0.69 atoms per year per gram SiO₂ for an exposure time of 291 years (from 2008 back to 1717 AD). This production rate scales to 5.61 ± 0.66 for a integrated exposure age range comparable to the calibration samples used by Stone [2]. This is then in agreement with the sea level – high latitude production rate of Stone [2] although somewhat high. A pre-exposure of about 30 years only would bring it into perfect agreement. Such a small amount of pre-exposure most probably induced by deep muon production can never be ruled out completely.

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Identification of active microbial communities linked to bioremediation and natural attenuation of radionuclides and heavy metals in contaminated aquifers

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Groundwater contamination with radionuclides and heavy metals is a global problem resulting from nuclear weapons production during the Cold War Era. Microbial activity may limit the mobility of radionuclides and heavy metals through natural attenuation or bioremediation. The aim of this study was to identify the active microbial communities controlling metal mobility at two different subsurface locations heavily contaminated with uranium and heavy metals. Stable isotope probing (SIP) was applied to microcosms of subsurface sediments from the Oak Ridge Field Research Center (ORFRC), USA and surficial soils of the Gessenbach Creek within a former uranium-mining district in Germany. ORFRC sediments are characterized by pH 3.7-6.7, >20 mM NO₃⁻, and 70 µg g⁻¹ U, whereas Gessenbach soils are pH 4.9-5.9, 12 mM SO₄²⁻, 1000 µg g⁻¹ U, and contain high concentrations of heavy metals. Reduction of NO₃⁻, Fe(III), SO₄²⁻, and U(VI) was stimulated in ORFRC microcosms with ¹³C-ethanol addition. Addition of ¹³C-substrates stimulated activity in Gessenbach soils under Fe(III)- and SO₄²⁻-reducing conditions. Fe(III)-reduction was associated with immobilization of Cu and mobilization of Co, Ni, Zn, As, and U, whereas, SO₄²⁻-reduction was associated with immobilization of Ni and Co and mobilization of U. Members of the *Firmicutes*, δ - and β -*Proteobacteria* (*Geobacter* and *Dechloromonas*), and *Actinobacteria* (*Arthrobacter*) were the predominant active microbial populations in ORFRC and Gessenbach microcosms. Although some overlap was observed in the metabolically active microbial communities, subsurface microorganisms at the two metal contaminated sites greatly differed in their ability to mediate U bioimmobilization. Thus, the mechanism of uranium bioremediation is likely to be site-specific and dependent upon geochemical conditions.

Petrogenesis of Pan African Dokkan Volcanics of the Northeastern desert, Egypt: Mineralogy and geochemistry considerations

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The volcanic activities in the Eastern Desert of Egypt were formed by two major magmatic episodes at two different periods of time. Dokkan Volcanics is the main component of the younger episode started about 600Ma and continued for several decades. Lithologically, these volcanics have been found to vary from basalt to andesite to dacite. Field, mineralogy and geochemical data were used to test these variations and envisage their tectonic genesis, particularly at Esh El Mellaha area.

Dokkan volcanics form a consistent compositional spectrum with a wide range of SiO₂ (43.62-63.91 wt.%), CaO (2.34-10.56 wt.%), Sr (494-906 ppm), Zr (124-304 ppm) and are moderately enriched in incompatible elements. The fractionation index (FeO_{total}/MgO) increases gradually from basalts through andesites to dacites (2.71, 2.88 and 3.80 respectively). These chemical variations support the idea that a fractional crystallization process has played a major role during the evolution of the Dokhan volcanic magma series. The enrichment of LILE (Sr, K, Rb and Ba) and the relative depletion of HFSE (Zr, P, Y, Ti) seem to be inherited from a mantle source. Manipulating these data with field relations and mineral phases verified three magmatic assemblages comprising tholeiitic basalts, calc-alkaline andesites and dacites. Tectonically, these assemblages postulate a transitional development between island arc and active continental margin volcanics in a subduction related tectonic environment.

Structural analyses of Bentonite under high pressure and high temperature

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The thermal stability of bentonite is of particular interest for containment barrier in nuclear waste storage facilities. However, very little is known about the stability of bentonite under high-pressure (HP) and high-temperature (HT) conditions. The goal of this work is to investigate the stability of the bentonite structure under HP and HT conditions using Fourier transformed infra-red (FTIR) *in situ* measurements on diamond anvil cell (DAC), and X-ray diffraction (XRD) measurements after the HP and HT processing on thoroidal chambers. The HP-HT experiments were performed in thoroidal chambers (Process A, B and E) and HP experiments were also performed using the DAC (Process C and D). The sample, calcium bentonite, was characterized by FTIR, XRD and X-ray fluorescence. Table 1 shows the HP/HT processing conditions. For experiments A and B the results of FTIR and XRD analyses showed no differences in the bentonite structure from the original sample. In the experiment C, FTIR analyses show that the bentonite structure is stable with a reversible deformation in the Si–O bond and experiment D show that bentonite did not lose water. For experiment E the result of FTIR analyses show changes in the chemical bonds and the XRD analyses for this experiment are in process.

Process	Pressure (GPa)	Temperature (°C)	Time (min)
A	7.7	25	30
B	7.7	200	90
C	7.7	25	-
D	12.66	25	-
E	7.7	1000	210

Table 1.

Significance and robustness of the highly siderophile elements and $^{187}\text{Os}/^{188}\text{Os}$ primitive mantle estimates

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A recurrent question in planetary sciences is: what is the nature of the 'late veneer' Indeed this late extra-terrestrial addition to the Earth is seen as the carrier of water and possibly the life seeds on earth. However as recently summarized [1] the nature of this late component remains elusive and constraints from various geochemical systems seem at first glance contradictory. Especially, the primitive upper mantle (PUM) highly siderophile elements (HSE) abundance and $^{187}\text{Os}/^{188}\text{Os}$ rules out carbonaceous chondrites – the only wet chondrites - as the source of the 'late veneer' However, one may wonder about the robustness and significance of the PUM estimate.

Indeed we will present several examples (i.e. Lherz peridotite massif [2], Oman ophiolite [3], Montferrier and Kilbourne Hole xenoliths), in which despite multiple and obvious evidence of considerable modifications by partial melting and by percolation-reaction of sulfide bearing-melt or by metasomatism with S-bearing volatile rich fluid(s), still display HSE and $^{187}\text{Os}/^{188}\text{Os}$ composition very akin to recently refined estimates for the Earth's PUM [4, 5].

These suggest that HSE-Os 'resetting' mechanism [6, 7] via sulfide enrichment promoted by melt/fluid-rock reaction occur worldwide [8], casting thus strong doubt on the relevance and significance of the PUM at least for the absolute and relative HSE abundances and $^{187}\text{Os}/^{188}\text{Os}$ composition of the Earth's primitive mantle. Therefore the $^{187}\text{Os}/^{188}\text{Os}$ and HSE composition of the PUM as defined today cannot be used to ruled out any type of chondrite.

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The accretion of volatiles in terrestrial planets

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Planetary accretion left the terrestrial planets depleted in volatile components. As shown by the isotope compositions of K and Zn in planetary objects, such depletion does not result from volatilization but from early removal of the nebular gas by T-Tauri winds before accretion was complete. Accretion was largely a stepwise process which, for the material that eventually formed the Earth, stopped when the temperature reached ~1000 K. The narrow temperature ranges of condensation (30-150 K) of the elements suggest a stepwise accretion with temperature gaps: for terrestrial planets, accretion failed before water could condense. At the time of the lunar giant impact and core segregation (~30 Ma after CAIs), both the Moon and the proto-Earth were essentially dry and only later gained volatile elements through accretion of material from the asteroid belt and beyond (the late veneer). The U/Pb ratios of both planetary bodies were very high. As indicated by U-Pb and I-Xe chronologies, late veneer accretion took place 100 ± 50 Ma after isolation of the Solar System. Late delivery not only affected water, but also elements such as Zn, Pb, and S, which were replenished by the late veneer. The 'young Pb-Pb age of the Earth' is in fact the age at which asteroidal Pb was reset by impacts. The proto-Earth must, therefore, have been quickly covered with a water ocean, and interaction with the underlying magma ocean during asteroidal showers must have released a steady flow of hydrogen into the atmosphere. Over geological history, enough water entered the mantle for plate tectonics to function and our planet is about half way to losing its water by subduction. The ocean is not outgassed from the mantle but entrained into it, carried by hydrous minerals such as phase D. On Mars, in contrast, the stagnant lid regime resulting from a dry mantle choked the dynamo and the resulting loss of a magnetosphere caused the quick erosion of the atmosphere by the solar wind. I suggest that Venus may have lost all water to its mantle, thereby promoting the vigorous convection of wet mantle material, which explains the recent resurfacing of the planet.

Spectroscopic study of the local chemical environment during biotransformation of uranium

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Previous studies [1] have identified changes in uranium solubility in sediments as a result of processes such as uranium reduction, microbial activity or ion exchange. In that study, radionuclide and microbiological analyses have demonstrated changes in uranium solubility and shifts in biological profiles in response to nitrate reduction. However, there was no direct information on local structure and oxidation states of uranium so this has been studied using X-ray absorption spectroscopy (XAS) to define speciation changes.

Microcosms (50 mL; 20 g sediment) containing 100 ppm and 2000 ppm of uranyl ion in solution were set up with nitrate as TEA. EXAFS spectral data were collected before and after reduction of nitrate. The data obtained showed the presence of uranyl ion both before and after nitrate reduction and in both solution and solid phases, showing that this process was not associated with uranium reduction [2,3]. The uranium speciation changes can be related to formation of either dihydroxy-bridge oligomeric species or uranium-carbonato complexes [4].

[1] Al-Bokari *et al.* (2007) *Environmental Radiochemical Analysis III* **312**, 95-100. [2] Kelly *et al.* (2003) *Advance Photon Source*, Activity Report. [3] Moyes *et al.* (2000) *Environmental Science & Technology* **34**, 1062-1068. [4] Walter *et al.* (2003) *Environmental Science & Technology* **37**, 2898-2904.

Silicate weathering in anoxic marine sediments: Detailed mineralogical investigation

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The continental weathering of silicates is known to be the largest sink of atmospheric CO₂ on geological timescales. Recent studies have shown that silicate weathering processes also take place naturally in the marine environment (Wallmann *et al.* 2008 [1]).

In order to study these processes anoxic sediments from the northern slope of Sakhalin Island, Sea of Okhotsk, were analyzed for their mineralogical and geochemical composition. The resulting down-core trends in mineral abundance suggest a transformation of reactive silicate phases (e.g. plagioclase, pyroxene) into cation-depleted silicates due to reactions with CO₂ produced during methanogenesis.

Further detailed mineralogical analyses were conducted in this study by means of smear-slide counting, electron microprobe analysis, and XRF of the clay fraction. The results show a variety of reactive and refractory minerals in the silicate phase, whereas mineral trends imply down-core decreasing abundances. The main component, being reactive plagioclase, decreases down-core from 7 to 4.5 %.

The data will now be used to extend an existing transport-reaction model for silicate weathering by incorporating the individual mineral phases, and will thus help to quantify individual rates of singular phases. This will improve our understanding of the naturally occurring neutralization of CO₂ and constrain the timescales of mineral trapping during CO₂ sequestration.

[1] Wallmann *et al.* (2008) *Geochim. Cosmochim. Acta* **72**, 3067-3090.

Seven years record of ^{127}I and ^{129}I in precipitation

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Despite the significant role of iodine (^{127}I) in human nutrition, cloud condensation and global climate forcing together with the overwhelming anthropogenic supply of the radioactive ^{129}I , there is scarcity of long time series data of the isotopes in precipitation. Here we report a 7 year time series on iodine isotopes atmospheric distribution in precipitation from sites situated between latitudes 55°N- 68°N and longitudes 12°E-19°E, namely in Sweden and Denmark. Precipitation (rain and snow) samples were mainly collected during single events and thus would reflect contemporary atmospheric iodine fallout. ^{127}I was measured using ICP-MS with a detection limit, as 3 SD of blanks, of 0.03 ppb and ^{129}I was measured with AMS using NISTSRM 4949C standard and samples $^{129}\text{I}/^{127}\text{I}$ at two orders of magnitude above blanks background of 10^{-13} . The range of ^{127}I concentration is 0.05-10.8 μgL^{-1} with the highest values occurring in rain and the lowest in snow. The range of variation in the ^{129}I concentrations is wider between sites with respect to individual precipitation ($0.4\text{-}298 \times 10^8 \text{ atoms L}^{-1}$) and averages ($7.4\text{-}42 \times 10^8 \text{ atoms L}^{-1}$). As is the case with ^{127}I , there are clear differences in the ^{129}I between the southern and northern sites and higher concentrations are also more frequent in the rain compared to snow. The annual ^{127}I wet fallout represents minor amount of the estimated global oceanic iodine flux. Similarly, the annual wet flux of ^{129}I comprises minor amount when compared to the total annual gaseous and liquid discharges from the Sellafiled and La Hague Facilities. Calculated air mass back trajectories indicate that a major source for enhanced ^{129}I in precipitation is related to southwesterly weather fronts.

Effect of CO_2 interaction with Svalbard shale: Implications to caprock integrity for subsurface sequestration of CO_2

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Reactive behavior of CO_2 with caprock material is one of the main factors that determine the sealing capability for long-term sequestration of CO_2 . A shale seal rock from Adventdalen Group, a proposed CO_2 storage site in Svalbard near Longyearbyen, was used for this experiment. The lithology of the caprock varied from homogenous shale to silty-sandy shale over a thickness of 155m, present burial depth of 654.77- 810.13m below surface. Crushed rock samples from different layers of the caprock were reacted with CO_2 -brine mixtures for a period of six weeks in closed reactors at 250°C. Experimental pressure conditions were close to site conditions, while temperature has been raised in order to speed up reaction rates. Chemical alteration in the rock was studied with XRD and SEM and compared with unreacted material. Solutions sampled from the experiment, were analyzed for major ions, and showed a fair relation with changes in mineral grains in the shale rock. Results from the experiment were also used in PHREEQC simulation in order to predict the effect of reactions for long-term exposure conditions.

Cadmium adsorption to mixtures of geosorbents: Testing the component additivity approach

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The component additivity (CA) approach accounts for solute adsorption onto mixtures of sorbents with the assumption that the solute distribution is controlled only by the adsorption affinity of the solute for each sorbent and by the relative concentrations of sorption sites on each sorbent. Success of the CA approach requires that sorbents do not interact with each other, and that all solutes in the system have access to all surfaces. Previous applications of the CA approach have met with varying degrees of success. For example, Davis *et al.* [1] showed that the approach does not adequately predict the adsorption behavior of Zn(II) onto assemblages of minerals. However, Pagnanelli *et al.* [2] and Fowle *et al.* [3] demonstrated that the CA approach can be successful in predicting metal adsorption to mixtures of pure minerals and bacteria, respectively.

The objective of this study was to determine if the CA approach accurately predicts adsorption behavior for systems containing mixtures of mineral phases, bacteria, and dissolved organic acid anions. Specifically, we test if the CA approach can account for the distribution of Cd(II) in mixtures of kaolinite, *Bacillus subtilis* bacterial cells, iron oxyhydroxide, and dissolved acetate. Potentiometric titrations and Cd(II) adsorption experiments were conducted for each sorbent separately in order to obtain stability constants for proton- and Cd-surface complexes for each sorbent. This suite of stability constants was used to independently predict the distribution of Cd(II) in both binary and ternary mixtures of the sorbents at different component ratios as a function of pH. We compare these predictions to results from Cd adsorption measurements in these same systems to test the validity of the CA approach. Our results indicate conditions for which the CA approach may be appropriate in predicting Cd(II) distribution, and those for which more complex models that include interactions between the sorbents are necessary.

[1] Davis *et al.* (1998) *Environ. Sci. Technol.* **33**, 2820-2828.

[2] Pagnanelli *et al.* (2006) *Chemosphere* **63**, 1063-1073.

[3] Fowle & Fein (1999) *GCA* **63**, 3059-3067.

Palaeohydrogeology in coastal site characterisation: A case study at Horonobe, Japan

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Designs for radioactive waste repositories consist of multiple safety barriers which include the waste form, the canister, the engineered barriers and the geosphere. The three most important safety features provided by the geosphere are mechanical stability, favourable geochemical conditions and low groundwater flux. Consequently, any repository site characterisation has to not only define if these features are currently appropriate, but also assess if they will remain adequate up to several hundred thousand years into the future. To this end, palaeohydrogeology has been used as a powerful tool in site characterisation. Here, the temporal changes of various characteristics of a site are studied to build up a conceptual model for the overall site evolution over geological time, up to the present. These characteristics and processes may include tectonics, geology, groundwater flow characteristics, groundwater chemistry and topography including uplift and erosion processes. Multidisciplinary expertise is employed to describe these key aspects.

Traditionally, the data produced are then synthesised into a conceptual model of the site evolution over the last several hundred thousand to a million years and this is used to define the likely future evolution of the site and to assess if the main safety features will continue to function adequately. Here, the concept and approach of this programme are presented, which is focussed on the palaeohydrogeology of the coastal site at Horonobe in northern Hokkaido, Japan, with the integration of input from the ongoing Horonobe Underground Research Laboratory Project. In the first phase, a conceptual model of the site will be developed, which takes into account the geological evolution of the Horonobe area, with focus very much on the impact of glacial/post-glacial related changes in the Japan Sea on the site. This will be tested against data currently being produced at new deep boreholes in the area and amended as necessary. This new conceptual model will then be expanded to cover other sites on Japan's western seaboard, with the final aim of producing a regional understanding of the palaeohydrogeological evolution of all coastal sites on the Japan Sea since the last glacial termination.

Reaction of U(VI) with iron sulfides

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In sulfidic environments, iron oxides undergo reductive dissolution by S(-II) leading to the formation of FeS. Iron oxides are important sorbents for U(VI) and their reductive dissolution may lead to the mobilization of adsorbed U(VI). However, mobilization of uranium might be counteracted by reduction of U(VI) by FeS [1]. In previous experiments, reduction of U(VI) to U(IV) was observed when S(-II) solution was added to iron oxide suspensions with adsorbed U(VI). Uranium reduction coincided with FeS formation and in this study we aimed at establishing the role of FeS as reductant for U(VI) in these systems.

For this purpose, U(VI) was added to FeS suspensions, which were either produced by combining Fe(II) and S(-II) containing solutions, or by complete reduction of the iron oxide lepidocrocite by S(-II). The solids from these experiments were collected and analyzed by X-ray absorption spectroscopy.

Sorption of U(VI) to the solids and the extent of U(VI) reduction varied considerably between the different FeS substrates and depended on experimental conditions. When U(VI) was added to FeS suspensions, which were formed by reducing lepidocrocite and aged for several weeks, very little U(VI) adsorption and no reduction of U(VI) was observed during two weeks incubation at pH 8. On the contrary, U(VI) was completely reduced within a time scale of hours when added to freshly precipitated FeS suspensions and reacted at pH 6.

The data indicate that pronounced U(VI) reduction occurs in experiments in which the FeS phases are only metastable. That is, U(VI) reduction might predominately take place during FeS precipitation or FeS dissolution. This implies that not FeS, the endproduct of iron oxide reduction by S(-II), but an intermediate, which forms during the reductive dissolution of iron oxides, may be the most effective reductant for U(VI).

[1] Wersin *et al.* (1994) *GCA* **58(13)**, 2829-43.

The systematics of ^{36}Cl production rate calculations in limestone and dolomite

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One of the major radionuclides that are measured by Accelerator Mass Spectrometry (AMS) is chlorine-36 ($T_{1/2} = 301\text{kyr}$). It is produced in very low concentrations ($^{36}\text{Cl}/\text{Cl} \sim 1\text{E}-12 - 1\text{E}-15$) by the cosmic rays in atmosphere and upper meters of lithosphere, mainly in limestone and dolomite.

There are several production pathways of ^{36}Cl in limestone and dolomite: spallation of Ca by fast neutrons, capture of slow negative muons on ^{40}Ca , fast-muon induced reactions on Ca, capture of thermal and epithermal neutrons on ^{35}Cl , where these neutrons are also produced by several pathways. The complexity of ^{36}Cl production makes it difficult to calibrate each separate pathway and ultimately to use this radionuclide in the exposure dating. Here we summarize our investigation in the ^{36}Cl production systematics and draw an outline for the recommended calibration constants and calculation procedure.

Modeling of possible limits for Sr values in Early Proterozoic waters of continental flow (the Baltic shield)

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Continental chemical weathering, as a reason for changing the Sr isotope ratio in seawater was examined only qualitatively. The composition of drainage waters and river waters is fully caused by the interaction of climate and rocks, which form a drainage basin, thus the changing of the composition of the upper continental crust and atmosphere through time should affect the composition of the drainage waters and continental flow in general.

The profiles of continental weathering are widely found in all stratigraphic levels in Karelia. Some of these profiles were examined and by means of mathematical modeling the amount of main elements and isotopic values of Sr were reconstructed in drainage waters of these profiles. Mathematical models are based on the Rb-Sr isotope data for the most ancient weathering profile at the Baltic shield – 2.8 Ga [1], and geochemical data for a number of Proterozoic weathering profiles. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at the granite source was calculated relative to their age, according to the measured contemporary value 0.70391, with the $^{87}\text{Rb}/^{86}\text{Sr}$ contemporary ratio 0.0736. The results of the models are shown in picture 1.

The majority of published data concerning the isotopic value of Sr, including data for the Tulomozerskaya formation of the Baltic Shield [2], are shown at picture 1 and most of them are inside calculated levels of $^{87}\text{Sr}/^{86}\text{Sr}$. Thus, the calculated values of the isotope composition of Sr can indicate possible limits for the continental flow in Early Precambrian time.

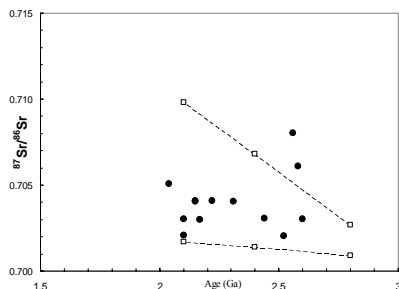


Figure 1: Limits of possible variation of Sr isotope ratios in continental flow. Lines – limits of $^{87}\text{Sr}/^{86}\text{Sr}$, black spheres – the analyses of carbonates [2].

[1] Matrenichev *et al.* (2005) *Reports of Russian Academy of Science* **400** (1), 83-87 (in Russian). [2] Bekker *et al.* (2003) *American Journal of Science* **303**, 865-904.

CarbFix - CO₂ sequestration in basaltic rock: Chemistry of the rocks and waters at the injection site, Hellsheidi, SW-Iceland

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Storage of CO₂ as solid Ca, Mg, and Fe carbonates in basaltic rocks may provide a long-lasting solution for reduction of industrial CO₂ emissions. Here, we report on the chemical composition, crystallinity of the rocks, their alteration and water chemistry at the targeted field site for injection of CO₂-charged waters, the Þrengsli, Hellsheidi area SW-Iceland.

The stratigraphy of the injection rocks consists of basaltic glass formations (hyaloclastite formations) and crystalline lava flows. Whole rock chemical analysis from drill cuttings of the boreholes, show that the overall chemical composition spans the picrite to tholeiite rock types, with relatively low Si content. The dissolution rate of natural glasses increases with decreasing silica content [1]. Thus the rocks below 400 m are reactive due to the low silica content and will readily react with the proposed CO₂-charged injection waters.

The water chemistry of the injection site show two different groundwater systems. The upper groundwater system spans from 0 – 400 m depth. The pH is around 8 and temperatures range from 8 – 12°C. It has more dissolved Ca, Mg, Cl and O₂, but lower Si, Fe, B and Al compared to the deeper ground water system. The deeper system spans from 400 – 800 m depth and is the targeted injection system. The pH range from 8,5 – 9,6 and temperatures from 20 – 30°C. The concentration of toxic metals, like Al, As, Cr, Hg and Pb are all below limits for EU drinking water standards.

PhreeqC was used for modelling the results. The percent error for charge balance was on average 2%. The calculated saturation index for secondary minerals show that the deeper system is saturated with respect to calcite, but undersaturated with respect to Fe-Mg carbonates. It is oversaturated with respect to calcium rich zeolites and clays, such as heulandite, stilbite, mesolite, chabazite and smectite. The upper system shows similar results, but is undersaturated with respect to calcite and Fe-Mg carbonates. This is in concert with the observed spatial distribution of the secondary minerals found in the drill cuttings of the boreholes.

[1] Wolff-Boenisch *et al.* (2004) *GCA* **68**, 4843-4858.

Distribution of Rare Earth Elements between cave-drip water and speleothem calcite

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Speleothems are among the most robust paleoclimatic archives because of the conditions in which they are formed. The use of minor and trace elements in the calcite, such as Mg, Sr, Ba, has been used to trace hydrogeochemical processes in the karst, associated with the climatic conditions. However, these proxies are not sensitive to changes in redox conditions in the karst, or to the changes in the percolation route, or water-rock interactions.

In this work, we present the results from the ongoing long-term calibration taking place in 'Grutas Las Karmidas', a cave developed in volcanic tuff, located in Zapotitlan de Mendez, Puebla, Mexico (N 20° 00' 01.19" and W 97° 42' 58"). The current climatic conditions of the cave are been monitored (temperature, humidity, PpCO₂), percolating and stagnant water, as well as calcite precipitated from them have been collected every three months for the last 26 months, and analyzed for their trace element composition, including REE.

Discrepancy between measured and modelled behaviour of aerosol as cloud condensation nuclei

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The hypothesis that aerosol water content can be represented by a single hygroscopicity parameter has been evaluated against measured cloud activation potential and sub-saturated hygroscopicity of aerosol in a number of environments. A comparison between model-measurement reconciliation in the marine, tropical forest, temperate clean continental and polluted continental environments has been made. It was found in certain environments that the simple hygroscopicity parameterisation consistently and systematically led to over-prediction of the threshold supersaturation for cloud activation.

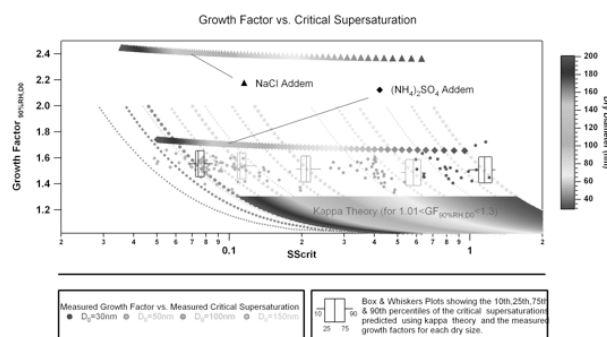


Figure 1: Measured & predicted marine CCN behaviour

In other environments, the degree of measurement / prediction discrepancy was size dependent. However, the discrepancies, where they exist, are always such that the particles are easier to activate into CCN than would be expected from the measured sub-saturated hygroscopicity. The differences in measured and predicted threshold dry diameter for cloud activation will be presented, along with the corresponding difference in cloud condensation nuclei number across the range of supersaturations for the average measured aerosol distribution.

Silicate dissolution kinetics under acid conditions: Applications to CO₂ sequestration

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We have studied the rates of interactions of mineral separates and reservoir rock samples with saline solutions acidified with HCl, using unstirred mineral suspensions with a dialysis membrane technique to maximize the proportion of mineral in the system. Starting materials were mineral separates of albite, labradorite, kaolinite, illite, and smectite, and disaggregated reservoir sandstones from the Huldra and Beryl fields, North Sea.

The rate of dissolution was tracked through analysis of both Al and Si and yielded mineral dissolution rates comparable to literature values.

Sandstone dissolution rates are faster by a factor of c.2 than the rates predicted from their modal mineralogy. For Huldra sandstone, dominated by quartz with albite, kaolinite and minor illite, Si and Al levels peak and decline, which is attributed to growth of secondary kaolinite. The Beryl sandstone has significant illite-smectite and both K-feldspar and albite, but only minor kaolinite, but again rates are reasonably close to those predicted. In particular, feldspar dissolution has not been inhibited by clay coatings.

We conclude that silicate minerals are effective at neutralising acidity introduced to pore waters, albeit more slowly than carbonates. Dissolution is enhanced by increased ionic strength. To a first approximation, dissolution rates of natural rocks can be modelled from the dissolution rates of their constituent phases, with little evidence of blanketing effects due to clay coatings.

Tracing weathering/erosion processes using colloidal iron from the rio Negro basin (Brazil)

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The suspended solids from representative toposequences and rivers of the rio Negro basin (Brazil) are studied using electron paramagnetic resonance spectroscopy and geochemistry to specify processes of weathering and erosion. Consistently with a previous study [1], two organic-rich size fractions are separated by tangential-flow ultrafiltration : particulate supernatant and colloidal fractions. Analyses of FeII and FeIII in solution are consistent with several endmembers including waterlogged podzols and drained laterites. Besides, all solid samples contain FeIII complexed to organic matter (FeOM) as well as iron oxides in the broad sense. [FeOM] is low in the toposequences whereas it is several times higher in the rivers. This is thought to originate from oxidation of FeII that is relatively abundant in porewaters and creeks from waterlogged podzol areas. Data mainly reveal the signature of podzolization, coupled to subsequent evolution of suspended matter. Effects of rain events, hydrological season as well as distance in the course of rio negro will also be discussed.

[1] Allard *et al.* (2004) *GCA* **68** (14), 3079-3094.

Using atomistic simulation to study the interaction of water and carbonate with oxide surfaces

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With recent environmental concerns, understanding the interactions of carbon with mineral surfaces is essential for the effective use of carbon sequestration. The adsorption of carbon dioxide can be considered through surface carbonation on the model surfaces of magnesium and calcium oxide. In addition, understanding the role water has on this process is also essential.

Potential based atomistic simulation techniques can be utilised for this purpose, due to their speed and efficiency compared with other techniques. The screening of a large number of different surface configurations allow for the evaluation of free energies as well as the identification of important surfaces.

The calculation of vibrational frequencies can give information regarding the mode of carbonate adsorption. Results suggest that whilst the adsorption of a single carbonate leads to incorporation *into* the surface, higher concentrations will give rise to the formation of a mineral carbonate layer.

We have also modelled the mixed adsorption of carbonate and water on the low index surfaces of these simple oxides. Water adsorption has also been considered as both associative (hydration) and dissociative (hydroxylation). Through the modelling of varying surface coverage, the generation of surface phase diagrams is possible, showing the variation of surface composition with changing chemical potential of water and carbon dioxide.

The key results indicate the feasibility of these materials for a role in carbon sequestration. In particular, calcium oxide surfaces are more susceptible to surface carbonation at standard conditions than their magnesium equivalents. Also, the stepped {310} surface shows that it can take up more carbonate than a flat surface. However, the preference of the polar {111} surface to hydroxylate makes it unsuitable for carbon uptake.

Finally, we examine the effect surface carbonation has on the mineral – water interface using molecular dynamics. The results indicate that the water layering, which is evident in the uncarbonated surface, is severely disrupted upon carbonation.

Tracing terrestrial organic matter by $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ signatures in an Arctic and a subarctic estuary

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Arctic regions holds a third of the world's soil carbon [1]. A major concern is that thawing permafrost would lead to a release of this stored organic carbon and an increased discharge to the Arctic Ocean. However, the fate of terrestrially derived organic carbon in the marine environment is poorly understood [2]. One significant problem has been to precisely estimate the fraction of terrestrially derived carbon in marine dissolved organic matter (DOM). We have developed a method using $\delta^{34}\text{S}$ signatures, in addition to $\delta^{13}\text{C}$ signatures, to trace DOM in coastal environments. The values for dissolved organic S ($\delta^{34}\text{S}_{\text{DOS}}$) have twice the range between terrestrial and marine endmembers compared to those for dissolved organic C ($\delta^{13}\text{C}_{\text{DOC}}$); hence, the share of terrestrial DOM in the total estuarine DOM can be calculated more precisely. Also, $\delta^{34}\text{S}_{\text{DOS}}$ from estuarine primary production has a typical marine $\delta^{34}\text{S}$ signature, so terrestrial organic matter can be distinguished from both marine- and estuarine-produced organic matter. In contrast, a significant fraction of the C in estuarine primary production can be assimilated terrestrial dissolved inorganic C (DIC), which cannot be readily distinguished from terrestrially derived organic matter.

We have measured $\delta^{34}\text{S}_{\text{DOS}}$, first in DOM of the Gulf of Bothnia [3], and now also of the Laptev Sea in a transect from the Lena River. While the Northern Baltic Sea is a constrained system with known hydrological fluxes, the Laptev Sea is an open system, where it is harder to estimate fluxes of DOC, but by precise and accurate estimates of the fraction terrestrial, marine-produced and estuarine-produced DOC the fate of terrestrial organic carbon could better be described.

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Experimental constraints on rhyolite magma genesis, Yellowstone hotspot

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An experimental study was carried out to constrain the phase relations in Cougar Point Tuff (CPT) rhyolite, from the Bruneau-Jarbridge eruptive center [1], representative of the silicic magmatism of the Snake River Plain – Yellowstone (SRPY) volcanic province. Crystallization experiments were performed at 200 MPa in CSPV at 800 and 850°C, and in IHPV at 900, 925 950 and 1000°C with run duration varied from 7 to 25 days. The water activity (a_{H_2O}) of the experimental charges was varied by adding a fluid composed of a mixture of H₂O and CO₂. In CSPV the oxygen fugacity was monitored by adding a solid Ni-NiO oxygen buffer, whereas in IHPV all experiments were conducted at intrinsic oxygen conditions, corresponding to NNO+2.6 under H₂O-saturated and to ~QFM at nominally dry conditions. Water concentrations in the experimental glasses were determined using infrared spectroscopy (FTIR). At 1000°C rhyolitic melt coexisted with magnetite in the range of all studied melt H₂O concentrations (H₂O^m). With decreasing temperature magnetite was followed by the crystallization of sanidine in runs with up to ~ 1 wt % H₂O^m. In nominally dry run (<0.5 wt% H₂O^m) at 950°C and in the runs with H₂O^m < 1.4 wt% at 900°C quartz, pigeonite and clinopyroxene were observed. Fayalite and plagioclase were stable at temperatures below 900°C and H₂O^m < 1.5-2.0 wt %. In these two experimental runs (T=850°C, H₂O^m = 0.3 wt %, H₂O^m = 1.5 wt %) the maximum number of minerals was crystallized, corresponding to multiple saturation conditions of the natural rhyolite. The experimental phase relationships demonstrate that the natural mineral assemblage Pl+Fsp+Cpx+Pig+Mt+ Qtz±Fa was reproduced only in the runs with low H₂O^m (< 1.5 wt%) below 850°C. The low H₂O^m required to reproduce the natural mineral association in CPT rhyolite are in agreement with previous ideas [1-3] on the nearly anhydrous character of the SRPY silicic magmatism. However, our new results (conditions of multiple saturation in CPT rhyolite) contradict with relatively high (950-1000°C) pre-eruptive temperatures obtained as a result of mineral thermometry in previous studies [1,2].

[1] Cathey & Nash (2004) *J. Petrology* **45**, 27-58. [2] Honjo *et al.* (1992) *Bull. Volc.* **54** 220-237. [3] Perkins & Nash (2002) *Geol. Soc. Am. Bull.* **114**, 367-381.

U-bearing quartz veins and related waters from Mondego Sul mine (Central Portugal)

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About 61 uranium mine were exploited in central Portugal in the past. The Mondego Sul open pit mine is located in the Mondego river and produced about 75 t of uranium oxide (U₃O₈) between 1987 and 1991.

At Mondego Sul area, the Variscan coarse- to very coarse-grained porphyritic biotite granite intruded the Cambrian schist-metagraywacke complex, which consists of alternating phyllites and metagraywackes with marble intercalations. The uranium deposit consists of brecciated U-bearing quartz veins which intersect phyllites and are 400 m away from the granite. The U-bearing quartz veins fill faults showing N40-50°W alignment and are subparallel to phyllite cleavage and granite-country rock contact. The uranium mineralization occurs mainly in the interception of this fault system with late N-S faults, but is also disseminated in phyllite. The U-bearing quartz veins contain the U-bearing phases zircon, monazite and xenotime, which occur as inclusions in quartz, muscovite and chlorite. The U-bearing quartz veins also contain the secondary U-phosphates autunite, torbernite, saleeite and uranocircite surrounding Fe oxides-hydroxides along microfractures in several minerals. Pyrite has fractures filled by Fe oxides-hydroxides.

Autunite and torbernite were exploited at the Mondego Sul mine. Tailings and rejected materials (400000 t) were deposited on ground and form three dumps. There has not been any significant development in the area. A lake was formed in the open pit. Ten sampling points were selected, 4 in the pit lake and 6 in the Aguieira dam. Waters from the pit lake are acid (pH = 4.5), have the highest electrical conductivity value (240 µs/cm) and the highest contents of U (131 ppm), SO₄²⁻ (113 ppm) and Mn (0.2 ppm). These waters are of magnesian-sulphated type, whereas waters from Aguieira dam are of mixed type. The abandoned mine is about 10 m away from the reservoir of Aguieira dam. The acid water from the pit lake and dumps flows directly to this reservoir.

Computer simulations of the interaction of bio-molecules with hydroxyapatite surfaces in aqueous environment

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In view of the importance of the hydroxyapatite/ collagen composite of both natural bone tissue and in synthetic biomaterials, we have employed a combination of electronic structure calculations based on the Density Functional Theory and Molecular Dynamics simulations to investigate the interaction with two major hydroxyapatite surfaces of the three amino acids that largely make up the collagen matrix, as well as a peptide strand of the same residues (glycine, proline and hydroxyproline).

We have performed full geometry optimisations of the hydroxyapatite surfaces with adsorbed amino acid molecules to obtain the optimum substrate/adsorbate structures and interaction energies, both *in vacuo* and in a liquid water environment. An aqueous environment is added through the explicit introduction of water molecules in the simulation of the dynamic behaviour. The calculations show that the amino acids, as well as the complete peptide are capable of forming multiple interactions with surface species, particularly if they can bridge between two surface calcium ions. The binding energies range from 291 kJ mol⁻¹ for glycine on the (0001) surface to 610 kJ mol⁻¹ for hydroxy-proline on the (01 $\bar{1}$ 0) surface. The large adsorption energies are due to a wide range of interactions between adsorbate and surface, including proton transfer from the adsorbates to surface OH or PO₄ groups. Similar to the amino acids, the Gly-Pro-Hyp peptide also binds more strongly to the hydroxyapatite (01 $\bar{1}$ 0) surface; indeed, in an aqueous environment only binding at this surface is thermodynamically favourable, which suggest that, in the presence of the collagen matrix, the hydroxyapatite crystal would grow more rapidly in the (0001) direction than in the (01 $\bar{1}$ 0) direction, in agreement with the naturally observed bone morphology.

A thrust for early skeletal evolution provided by ocean chemistry

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The advent of biomineralization at the end of the Precambrian (~ 550 Myr ago) produced fundamental changes in biology, ocean chemistry and sedimentary rocks. Mineral skeletons are thought to have arisen as protective armours in response to an increase in predation pressure, or as a means to maintain cellular calcium below toxic levels in the face of increasing oceanic calcium concentrations. I describe and additional thrust for early skeletal evolution provided by oceanic chemistry. I reconstructed the CaCO₃ saturation state (Ω_{CaCO_3}) and total alkalinity (TA) of the ocean during the advent of biomineralization from the sedimentary distribution of calcified cyanobacteria. The calcification of cyanobacteria is dependent on the Ω_{CaCO_3} of benthic cyanobacterial mats and the Ω_{CaCO_3} of the overlying ocean. With a recently developed numerical model of Ω_{CaCO_3} in cyanobacterial mats [1], the relative contribution of microbially-induced Ω_{CaCO_3} shifts and ocean chemistry can be disentangled, providing some constraints on the carbonate system of the ancient ocean. This approach indicates that when the first skeleton-producing animals appeared and diversified, the CaCO₃ saturation state and the alkalinity of the ocean were extremely high. This agrees with paleogeographic reconstructions, the strontium isotope record of marine carbonates and the geological record of marine clays which indicate intense continental weathering at that time, implying large fluxes of dissolved calcium and bicarbonate to the oceans. In most marine organisms that build CaCO₃ skeletons, the rate of calcification is positively related to the CaCO₃ saturation state of ambient waters, to the concentration of bicarbonate, or both, implying that oceanic chemistry during the advent of biomineralization favoured CaCO₃ skeletogenesis. High continental weathering rates would have delivered also dissolved phosphate and silica to the ocean, favouring the development of phosphate and silica skeletons.

[1] Aloisi (2008) *Geochim. Cosmochim. Acta* **72**, 6037-6060.

Bioenergetics in archaea/sulfate-reducing bacteria aggregates

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Recent studies of sediments from methane seep and vent sites using fluorescence *in situ* hybridization with group-specific ribosomal RNA probes provide detailed, microscopic portraits of microbial aggregates composed of archaea and sulfate-reducing bacteria (SRB). These aggregates are widely assumed to engage in syntrophic methane oxidation, but the actual metabolic processes mediated by the archaea and SRB remain poorly understood. We used a spherical diffusion-reaction model that incorporates thermodynamic controls, realistic aggregate morphology, and essential elements of cell structure to determine how cellular energy yields are affected by aggregate size and morphology, and to investigate the impact of organic matter remineralization on archaea and SRB in the aggregate.

The model provides the following insights: (a) archaea and SRB engaged in syntrophic methane oxidation face a substantial energetic cost for aggregating (a doubling of aggregate size reduces the average energy yield of archaea and SRB by factors of about 5 and 2, respectively); (b) direct contact between archaea and SRB engaged in syntrophic methane oxidation provides only a modest energetic advantage compared to a loose association; (c) remineralization of sedimentary organic matter can have a profound impact on reaction rates and energy yields in archaea/SRB aggregates; and (d) sulfidogenic-methanogenic aggregates that take advantage of fermentation products released during organic matter decay have a substantial energetic advantage over aggregates that rely exclusively on syntrophic methane oxidation.

Moreover, the model calls attention to a discrepancy between the observed sulfate reduction rate at a well-characterized methane-seep site and the theoretical upper-limit rate of syntrophic methane oxidation involving interspecies transfer of H₂, formate, acetate, or other chemical intermediates. An analysis of possible errors, ambiguities, and artifacts in modeling and experimental techniques leads us to a surprising conclusion: that archaea/SRB aggregates in methane-seep sediments may be methanogenic rather than methanotrophic.

Heavy metal contents in growth bands of *Porites* corals: Record of anthropogenic and human developments from the Jordanian Gulf of Aqaba

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To assess pollutants and impact of environmental changes in the coastal region of the Jordanian Gulf of Aqaba, concentrations of six metals were traced through variations in five years growth bands sections of recent *Porites* coral skeleton. X-radiography showed annual growth band patterns extending back to the year 1925. All metal profiles (except Fe and Zn) recorded the same metal signature from recent coral (1925-2005) in which low steady baseline levels were displayed in growth bands older than 1965, similar to those obtained from fossil and unpolluted corals. Most metals showed dramatic increase (ranging from 17 to 300 %) in growth band sections younger than 1965 suggesting an extensive contamination of the coastal area since the mid sixties (Fig.1). This date represents the beginning of a period that witnessed increasing coastal activities, constructions and urbanization. This has produced a significant reduction in coral skeletal extension rates. Results from this study strongly suggest that *Porites* corals have a high tendency to accumulate heavy metals in their skeletons and therefore can serve as proxy tools to monitor and record environmental pollution (bioindicators) in the Gulf of Aqaba.

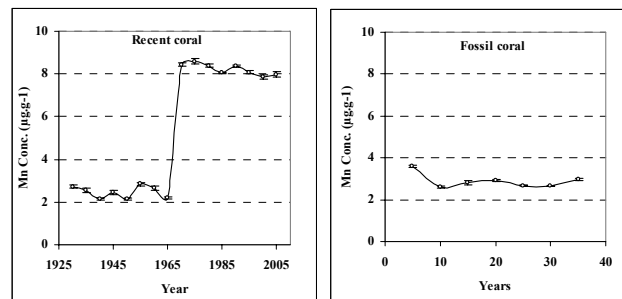


Figure 1: Time series record of Mn concentrations ($\mu\text{g}\cdot\text{g}^{-1}$) measured in recent (1925-2005) and fossil (35 years long) *Porites* coral sp. collected from the northern Gulf of Aqaba.

Evidence for the Toarcian oceanic anoxic event in the Southern hemisphere (Los Molles Formation, Neuquén Basin, Argentina)

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The Early Jurassic, Toarcian, Oceanic Anoxic Event (~180 m.a.) was characterized by emplacement of a large igneous province, (e.g. Karroo Ferrar) high sea-surface temperatures (~6°C warmer than present), mass extinction, and the deposition of sediments rich in organic carbon thought to be associated with a global oceanic anoxic event. Most chemostratigraphic studies of the event have focused on the northern hemisphere, leading some researchers to question its global nature. Here we report results from a combined sedimentological, biostratigraphic and geochemical study of a southern hemisphere Pliensbachian-Toarcian black-shale succession, the Los Molles Formation of the Neuquén Basin, Argentina, in order to assess the global extent of the Oceanic Anoxic Event. Preliminary results show a negative -7‰ carbon isotope excursion, as well as a ~2% relative enrichment in TOC over the OAE interval. These new data have been compared with those from Lower Toarcian sections in southern Europe, and show a strictly comparable step-wise negative carbon-isotope excursion. The preliminary results support the hypothesis that Toarcian oceanic anoxia and the attendant carbon-cycle perturbation was a phenomenon of global significance.

Geochemical processes in carbonate and silicate-dominated reservoirs of deep geothermal systems: Insights from coupled thermal-hydraulic-chemical modeling

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We use reactive-transport models patterned after the geothermal systems at Bad Blumau, Austria, and Basel, Switzerland to track the fate of fluids that originate from a carbonate and a silicate-dominated geothermal reservoir, respectively, on their passage through the geothermal system. We explore 1) mineral scaling and the rate at which it occurs, 2) borehole corrosion and geochemical fingerprints indicating incipient corrosion, 3) chemical and hydrological implications of reinjecting the fluid into the deep aquifer. P-T changes of the circulating fluid and the extraction of heat modify the chemical state of the fluid and induce the precipitation of mineral phases. The latter are primarily dictated by the composition of the reservoir fluid. The distribution of minerals is a function of the flow and reaction rates, as well as of the temperature dependence of solubilities. We use our model to explore the effect of corrosion on the fluid composition and on mineral precipitation to identify chemical fingerprints that could be used as corrosion indicators. Thus, incipient corrosion could be detected early on during regular chemical monitoring. Any modification of the fluid composition caused by mineral precipitation means that the reinjected fluid is no longer in equilibrium with the aquifer rock. Thus, rock-water interaction and fluid mixing at the base of the injection well drive chemical reactions that cause changes in porosity and permeability of the aquifer, potentially compromising the efficiency of the geothermal system.

Iodargyrite (AgI) in supergene zones of argentiferous Cu deposits in the Atacama Desert, Chile: Involvement of I-rich waters?

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We document the occurrence of inclusions of a (Ag,I)-rich mineral in supergene chalcocite from the Mantos de la Luna argentiferous stratabound Cu deposit in the Coastal Range of northern Chile. In this deposit, located 30 km south of Tocopilla, Cu mineralization occurs preferentially in the lower levels of amygdaloidal and porphyritic horizons. Mineral paragenesis is simple and composed exclusively of Ag-bearing supergene chalcocite (digenite), atacamite, and chrysocolla.

EMPA observations reveal the presence of discrete, micron-sized (1-10 µm) inclusions of a Ag iodide mineral in supergene chalcocite. The inclusions were identified as iodargyrite by means of EDS and WDS elemental mapping. The Ag concentrations in the inclusions vary from 1.0-67.6 wt% and they are contaminated by Cu and S from chalcocite. The small size and the beam-sensitivity of the Ag-I inclusions precluded the precise description of its chemical formula. However, the Ag and I elemental maps strongly correlate with the inclusions, whereas the WDS maps of Cu and S correlate well with the chalcocite sulfide host.

The occurrence of iodargyrite inclusions in supergene chalcocite suggests the involvement of iodine-rich waters during supergene enrichment at the Mantos de la Luna Cu deposit. Considering the fact that the occurrence of iodargyrite is restricted to extremely arid environments [1], our observations strongly suggest the prevalence of hyperarid conditions during the latest stages of supergene enrichment of the Mantos de la Luna argentiferous Cu deposit in northern Chile. This suggests that supergene enrichment processes of Cu deposits in the hyperarid Atacama Desert are dynamic in nature and do not exclusively require the presence of meteoric water. Further studies are needed not only to address the isotopic signature (and age) of iodine-rich waters involved in supergene enrichment of these deposits (e.g. deep formation waters), but also to constrain the origin of iodine in the extensive nitrate deposits occurring in the eastern flank of the Coastal Range.

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Vacuum extraction of volatile organic compounds from water for compound-specific stable carbon isotope analysis at the sub-µg/L level

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A new method (VacEx) for the vacuum extraction of volatile organic compounds (VOCs) from water samples was developed. Following protocols for noble gas analysis (1) allowed determination of carbon isotopic compositions of VOCs, increasing the sensitivity of compound-specific stable carbon isotope analysis (carbon-CSIA) to the sub-microgram per liter level. VacEx was developed to extract and pre-concentrate VOCs for later carbon-CSIA by the standard extraction technique purge-and-trap (2). The $\delta^{13}\text{C}$ signatures determined by using the new VacEx-P&T-mass spectrometry (MS) and the standard P&T-MS were in good agreement (<1‰). Limits of detection for carbon-CSIA are now for *trans*-DCE and *cis*-DCE 0.21 µg/L, for TCE 0.24 µg/L, for MTBE 0.02 µg/L, for benzene 0.15 µg/L, for toluene 0.03 µg/L, for ethylbenzene and m-p-xylene 0.06 µg/L and for o-xylene 0.03 µg/L.

Using noble gas analytical protocols in water allowed, for the first time, to determine VOCs isotopic compositions at the very low typical concentrations in natural waters. This analytical development brings carbon-CSIA closer to field applications in assessing *in situ* VOCs transformation.

[1] Beyerle *et al.* (2000) *Environ. Sci. Technol.* **34**, 2042-2050.

[2] Zwank *et al.* (2003) *Anal. Chem.* **75**, 5575-5583.

Microbial survival mechanisms in the cold subsurface

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Viable micro-organisms have been recovered from ancient permanently frozen environments (i.e. ice sheets and permafrost) that have been isolated from the Earth's surface for millions of years. Macromolecular components of the cell (e.g., DNA) would be expected to incur damage over extended periods of frozen dormancy, and the question remains whether it is possible for microorganisms to repair under these extreme conditions. Using cryomicroscopy, we observed that cells are partitioned into liquid-filled veins along ice crystal junctions [1]. Within this highly saline microenvironment, bacteria and yeast isolated from permafrost and glacial ice are capable of synthesizing up to 370 proteins and 4.5 % of their total DNA length per year and per cell under laboratory conditions at -15°C (Fig. 1). Ability of microbes to remain active in frozen matrices opens the possibility that cells may repair macromolecular damage as it occurs and before a lethal threshold is achieved. Measurements of background ionizing radiation were used to estimate the inferred increase in cell longevity if populations were metabolically active under frozen conditions. Our data and related calculations imply that microbial survival and longevity would only be limited by nutrient availability in a frozen subsurface if cells remain metabolically active.

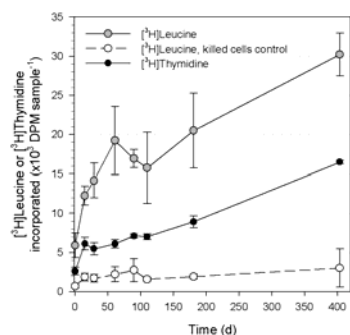


Figure 1: Incorporation of [3H]leucine and [3H]thymidine by frozen suspensions of *Psychrobacter cryohalolentis* K5 at -15°C ($2.0 \pm 0.9 \times 10^6$ cells mL⁻¹ in 0.1 mM M9 mineral medium (solid lines) or in 5% TCA (controls, dashed line)).

[1] Amato *et al.* (2008) *Environ. Microbiol.*, doi:10.1111/j.1462-2920.2008.01829.x.

Modeling large scale geogenic contamination of groundwater, combining geochemical expertise and statistical techniques

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Consumption of groundwater with high arsenic or fluoride concentrations poses a health threat to millions of people around the world [1-3]. In this study we used a large database of georeferenced arsenic (20,000) and fluoride (60,000) measurements in groundwaters from around the world as well as a global multi-layer GIS database including soil, geology and climate to model probability of arsenic and fluoride concentrations exceeding their respective WHO thresholds. A knowledge-based statistical procedure was developed and used to combine the available data and expert knowledge to delineate regions with similar geochemical properties. Arsenic and fluoride concentrations were then modeled in each region using adaptive neuro-fuzzy inferencing system followed by Latin hypercube sampling for uncertainty propagation to produce probability maps. Using some proxy surface information, the models explained between 30 to 70% of fluoride variation in different regions [3]. While for arsenic the developed models explained around 60% of variation [2]. The global arsenic and fluoride models could benefit from more accurate geological information and further information regarding chemistry and physics of the aquifers. The probability maps based on the above models correspond well with the known contaminated regions around the world and delineate new, untested areas that have a high probability of fluoride or arsenic contamination. Although the probability map does not replace fluoride testing, it gives a first indication of a possible contamination and thus may support the planning process of new drinking water projects.

[1] Winkel *et al.* (2008) *Nature Geosci.* **1**, 536-542. [2] Amini *et al.* (2008a) *Eviron. Sci. Technol.* **42**, 3669-3675. [3] Amini *et al.* (2008b) *Eviron. Sci. Technol.* **42**, 3662-3668.

The Ca isotope composition of bulk Earth: Revisited

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The Ca isotope composition of Bulk Earth is an important parameter for many models of global Ca cycling. The $\delta^{44/40}\text{Ca}$ value for Bulk Earth has previously been inferred from analyses of various meteorites and terrestrial silicate rocks yielding $-0.9\pm 0.2\%$ relative to seawater [1;2]. Estimating Bulk Earth using meteorites is hampered by potential Ca isotope heterogeneity in the solar nebula [3], and terrestrial silicates have recently been shown to vary much more widely than previously believed, particularly, mantle peridotites, whose $\delta^{44/40}\text{Ca}$ values may range as low as -0.7% [4].

In this study, we reevaluate the $\delta^{44/40}\text{Ca}$ of Bulk Earth with new analyses of (1) Primitive and differentiated meteorites that cover various regions of the solar nebula and degrees of planetary differentiation, including carbonaceous chondrites, eucrites and SNCs, and (2) Mantle xenoliths that are 'fertile' with respect to their refractory, lithophile, major element compositions (spinel peridotites previously used to constrain the composition of the Earth's primitive mantle [5]). $\delta^{44/40}\text{Ca}$ analyses were performed by TIMS using a 43/42-double spike, and are reported in delta notation relative to modern seawater with an analytical uncertainty of $<0.1\%$ (2sd). The $\delta^{44/40}\text{Ca}$ value for BHVO-2 measured in our laboratory is $-0.99\pm 0.04\%$.

Five different mantle xenoliths cluster around an average $\delta^{44/40}\text{Ca}$ value of $-0.93\pm 0.04\%$ suggesting a homogeneous Ca isotope composition for the upper mantle. The eucrite Camel Donga is identical to this within the quoted uncertainties (-0.92%). The carbonaceous chondrites Orgeuil and Allende are shifted to lower $\delta^{44/40}\text{Ca}$ values by up to 0.3% . SNC meteorites range from -0.66% to -0.99% . The range of Ca isotope variation in these Martian meteorites is consistent with the range of $\delta^{44/40}\text{Ca}$ values in terrestrial silicate rocks reported in [4], suggesting that Ca isotope fractionation is associated with igneous differentiation processes on Earth and Mars. Although the fractionation mechanism is not understood, the primitive compositions and uniform $\delta^{44/40}\text{Ca}$ values of the xenoliths point to a Bulk Earth value of -0.9% .

[1] Russell *et al.* (1978) *GCA* **42**, 1075-1090. [2] Skulan *et al.* (1997) *GCA* **61**(12), 2505-2510. [3] Simon & DePaolo (2007) *AGU Fall meeting* V34F-05. [4] Amini (2007) PhD thesis. [5] Jagoutz *et al.* (1979) *10th LPSC* 2031-2050.

Absolute diffusion rates in MgSiO₃ perovskite and post-perovskite

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Diffusion controls most physical and chemical processes in the solid Earth. While experiments are limited to conditions of the shallow lower mantle, ab initio calculations allow us to probe conditions at any pressure and temperature. By applying harmonic transition state theory (Vineyard-theory [1]), we have calculated self-diffusion coefficients of MgO and MgSiO₃ perovskite and post-perovskite at conditions of Earth's lower mantle from first principles. This is, to best of our knowledge, the first time that diffusion coefficients of complex materials such as MgSiO₃ perovskite and post-perovskite have been calculated from first principles. Our approach relies on determining exact migration pathways using the climbing-image nudged elastic band method [2].

Our analysis shows that magnesium and oxygen in MgSiO₃ perovskite migrate via simple single jumps to nearest neighbour sites. For silicon we propose diffusion via a six-jump cycle on the silicon-magnesium-B2 sublattice. In this mechanism, silicon diffuses by making use of vacated magnesium sites and magnesium uses vacated silicon sites. We investigated the rate of this mechanism using mean first passage theory [3] and the kinetic Monte-Carlo method [4].

We compared our absolute diffusion rates with experimental data of magnesium and oxygen diffusion in MgO at temperatures between 1873 K and 2273 K and at pressures ranging from 7 GPa to 35 GPa. Our calculated diffusion rates of magnesium, silicon and oxygen in MgSiO₃ perovskite have also been compared with experiments at 25 GPa with temperatures ranging from 1259 K to 2273K. All our diffusion rates are in perfect agreement with all the available experimental data.

The six-jump cycle mechanism works also in MgSiO₃ post-perovskite allowing both cations to cross the octahedra-layers. However, diffusion in MgSiO₃ post-perovskite remains very anisotropic.

[1] Vineyard (1957) *J. Phys. Chem. Solids* **3**, 121-127.
[2] Henkelman, Uberuaga & Jonsson (2000) *J. Chem. Phys.* **113**, 9901-9904. [3] Arita, Koiwa & Ishioka (1988) *Acta Metall.* **37**, 1363-1374. [4] Voter (2005) In: *Radiation Effects in Solids*, Sickafus & Kotomin (eds). Springer, NATO Publishing Unit.

Altitude dependence of the production rates of terrestrial cosmogenic nuclides

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Terrestrial cosmogenic nuclides (TCN) are continuously produced in the uppermost layer of the Earth's surface due to nuclear interactions with cosmic rays. The application of TCN as chronometers has revolutionised research in the field of geomorphology in the last decade. For accurate application of this methodology the altitude and latitude dependence of TCN production rates needs to be known accurately [1-6]. We will present results of a study on the altitude dependence of ²¹Ne, ³⁶Cl, (and ¹⁴C) production rates in sanidine.

Samples from three trachitic lava flows from the north western flank of the volcano Payun Matru in Argentina (36°25' S and 69°12'W) have been analysed. These flows overlap at an altitude of 2500 and cover a profile of about 1300 m, from 1878 to 3149 m above sea level. The overlap of the altitude range of the lava flows allows the determination of the relative altitude dependence of the production rates even if the ages of the flows are unknown. The lower flow has been dated with K-Ar to be 15±1 ka [7].

Preliminary data show that the relative ²¹Ne and ³⁶Cl production rates increase with altitude, and for ³⁶Cl an apparent attenuation coefficient of about 140 g/cm² can be calculated. It is planned to analyze ¹⁴C in the sanidine as well, and it is expected that initial results will be presented at the conference.

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Chromium isotope data for the Yorkshire 'Jet Rock': Transition metal isotope analysis of the Toarcian OAE from NE England

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A new approach for the investigation of palaeoclimatic and palaeoenvironmental changes from sedimentary records is now made possible by recent advances in mass spectrometry that permit the routine measurement of a very wide range of stable isotope ratios. Chromium has particular advantages as a tracer of past ocean-water oxygenation because its two principal stable oxidation states exhibit dissimilar chemical properties in the natural environment and responds to a changing redox state by a different degree than other elements. Consequently, Chromium-isotope stratigraphy may offer information on past seawater chemistry and global volumes of anoxic/euxinic waters on timescales of <10,000 years, its present day oceanic residence time. For comparison, Molybdenum, which has oceanic residence times ~800,000 years, shows an ~2 permille excursion in the ⁹⁸Mo/⁹⁵Mo ratio across the Early Jurassic (Toarcian) Oceanic Anoxic Event (OAE) interpreted as a drawdown of marine Mo into a sediment sink as euxinic conditions envelop the water column [1].

Accurate and precise isotope ratio measurements demand a method for extracting chromium from rock samples that delivers a high yield to ensure that the natural signal is not masked by any isotope fractionation induced by the separation process. We have recently developed a method which consistently delivers chromium yields of >95% for sedimentary samples. Preliminary results for chromium abundance and ⁵³Cr/⁵²Cr isotope ratios across the Jurassic, Toarcian OAE, from the 'Jet Rock' section at Hawsker Bottoms, Yorkshire, UK are presented.

[1] Pearce *et al.* (2008) *Geology* **36**, 231-234.

Recent progresses in the mineral encapsulation of cells

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The encapsulation of cells within mineral hosts is of interest for both fundamental aspects related to geomicrobiology and cell-material interactions and for applications in the design of biosensors and bioreactors [1].

For a long time, the long-term viability of immobilized bacteria within inorganic matrices was only achieved in silica-based materials [2]. Recently, we have evaluated novel nanostructured gels based on aluminium-, iron- and zirconium-oxyhydroxide colloids as hosts for *Escherichia coli* immobilization [3, 4]. In all cases, the viability rates after encapsulation were lower than for silica. However, in the presence of an organic additive, the preservation of biological activity over one month in the absence of nutrients was possible.

Attempts to correlate the properties of the inorganic colloids and resuting gels with observed viability rates suggest that two main factors, *i.e.* mineralisation kinetics and particle/cell membrane interactions, may be responsible for observed difference between the mineral gels. The possible effect of the rheological properties of the gels should also be considered.

Based on these data, the immobilization of bacterial cells can now be envisioned in a wide range of inorganic materials of geological, biotechnological and medical interest.

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The influence of humic acids on microbial Fe(III) reduction rates and iron mineral formation

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Microorganisms change the mineralogy of iron minerals in the environment by catalyzing Fe(II) oxidation or Fe(III) reduction. Mineral transformation influences magnetic properties of soils, porosity of aquifers, availability of nutrients or toxic elements and the reactivity of iron minerals. Humic substances can influence electron transfer between bacteria and Fe(III) minerals by either shuttling electrons between cells and the mineral surface, by complexing and thus solubilizing Fe(III) or by sorption to the mineral surface.

In this study 2-line ferrihydrite, a poorly crystalline Fe(III) hydroxide, was microbiologically transformed in the presence of different humic acid concentrations by the iron reducing strain *Shewanella oneidensis* MR-1. Depending on the humic acid concentration, these redox-active organic molecules were shown to either sorb to the iron mineral and hinder electron transfer by limiting the bioavailable mineral surface via aggregate formation or to function as dissolved electron mediators between cells and the mineral surface thus stimulating iron mineral reduction. The amount of adsorbed and dissolved humic acids was shown to play a key role for the competition between inhibiting or accelerating effects. Additionally, the identity of the formed mineral precipitates was determined using sequential extraction, μ -XRD and Moessbauer spectroscopy. In the presence of humic acids the formation of less crystalline iron mineral phases was observed compared to minerals formed in the absence of humic acids. This change in crystallinity potentially affects the reactivity of the minerals and the bioavailability of iron in anoxic environments.

Overall it can be concluded that a better understanding of microbially catalyzed mineral transformations, specifically in the presence of natural concentrations of humic substances, helps to evaluate and predict the reactivity of iron minerals in natural environments.

SOA formation via aqueous reactions of phenols from wood combustion

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Introduction

While secondary organic aerosol (SOA) is generally considered to arise from the gas-phase oxidation of volatile organics, recent work has shown that aqueous-phase reactions can also form low volatility products that remain in the particulate phase after drop evaporation. This aqueous formation of SOA has been shown to be important for molecules such as small carbonyls, and other work has suggested that phenols might also be important. Large amounts of gaseous phenols are emitted from wood combustion, but little is known about the kinetics of phenol oxidation in the aqueous phase or about SOA yields.

In this project we examined the kinetics and SOA yields of three representative phenols in aqueous solution: phenol, 2-methoxyphenol (guaiacol), and 2,6-dimethoxyphenol (syringol). We examined the transformation of each compound in the dark, with simulated sunlight, and with a combination of simulated sunlight and OH (formed via photolysis of hydrogen peroxide).

Results

All three of the phenols are degraded in the presence of OH and/or light to form SOA; no phenolic loss or SOA formation was observed in the dark. Lifetimes of the aqueous phenols with respect to reaction with OH (and light) under atmospheric conditions are on the order of a few hours (syringol and guaiacol) to a few days (phenol). For guaiacol and syringol, most of this decay is due to direct photoreaction, while for phenol it is all due to OH reaction. In contrast to this wide range of kinetic reactivities, all three of the phenolic compounds very efficiently formed SOA. At pH 5, the SOA yields (defined as mass of SOA formed per mass of phenol reacted) ranged between 1.0 - 1.5 for all three compounds. The SOA yields at pH 7 were somewhat lower, 0.7 - 1.2, but still close to unity. These exceptionally high SOA yields, combined with the fast kinetic reactivity and large emissions, suggest that phenolic compounds from wood combustion are a significant source of SOA via aqueous-phase reactions.

Lu-Hf dating of metamorphism

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Lu-Hf garnet geochronology potentially offers an excellent tool for dating metamorphism. Advanced mineral separation and chemical sample pre-treatment, despite some problems (e.g. chemically induced parent/daughter fractionation) proved to be very helpful in recovering the *true* isotopic ratios of the analysed minerals and helped to achieve high age precision. While achieving high precision is not particularly difficult, the meaning of the obtained ages can be problematic even for garnet, commonly assumed to be relatively easy for linking its age with metamorphic conditions. Inheritance, multiple and prolonged growth or involvement in the retrograde reactions influence accuracy of garnet ages. However, *in situ* trace elements studies along with careful petrography and high spatial resolution dating help to provide not only better age interpretation but also information on rates and duration of metamorphism.

Separate core and rim dating of a garnet crystal from high grade gneisses from the Broken Hill area showed that, at least in some geological settings, garnet may grow for as long as 15 Ma. Such long growth has important consequences for, the most commonly applied, bulk garnet dating technique. High precision growth ages obtained for bulk garnet do not take into account the prolonged crystallisation time and thus underestimate age uncertainty. Another consequence of applying bulk garnet dating technique to such slowly crystallizing garnets is that mixing different proportions of older cores with younger rims will result in higher scatter of data points in isochron diagram, lowering age quality or even in preventing obtaining a well defined date.

Garnet dating may be biased already at mineral preparation stage. In the case of eclogites from the Sanbagawa belt, cleaner cores were picked preferentially to inclusions rich rims, which resulted in an age c.25 Ma older than accepted time of eclogite facies metamorphism. Petrographical and trace element studies proved that the obtained age represents, earlier, epidote amphibolite facies, garnet growth phase represented by much cleaner garnet core.

Whereas trace elements studies were very successful in explaining the Lu-Hf ages in the Sanbagawa belt, they appeared insufficient in explaining age inconsistencies in more complex polymetamorphic rocks of the Scottish Highlands.

The Zn isotopic composition of diatom frustules, a proxy for Zn availability in ocean surface seawater

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Zinc is among the essential trace-metal micronutrients for phytoplankton. In common with some other bio-active trace metals, Zn concentrations are highly depleted in those parts of the surface ocean that are replete in the major nutrients (so-called High Nutrient-Low chlorophyll, or HNLC, zones), including the Southern Ocean. The release of these HNLC zones from trace metal limitation may be key for explaining lower atmospheric CO₂ during glacial periods. The preferential incorporation of light Zn isotopes into phytoplankton organic material is expected to leave residual surface seawater Zn isotopically heavy. Thus the degree of trace metal depletion in surface oceans in the past could be tested with a suitable archive of surface seawater Zn isotopes.

We are investigating the reliability of diatom opal as a recorder of the Zn isotopic composition of surface seawater, and have measured Zn isotopic compositions in cleaned diatom frustules from a sequence of core-top samples across the Southern Ocean. All diatom opal exhibits heavy Zn isotopic compositions, as expected from surface waters in highly trace metal-depleted HNLC zones, and the Zn isotope composition tracks decreasing diatom opal burial rates with progressively heavier Zn isotope compositions. Furthermore the measured Zn isotope and Zn/Si ratios, a potential proxy for the free Zn²⁺ content in surface water, are consistent with a model of Zn isotope evolution of the surface ocean in response to the fractionation of Zn isotopes into phytoplankton organic material as measured in experiments [1]. These results suggest that Zn isotopes in diatom frustules record trace metal availability in HNLC zones. Our initial down-core results also show a clear correlation between Zn isotopes and opal burial rates.

[1] John *et al.* (2007) *Limnol Oceanogr.* **52**, 2710-2714.

Sedimentary ²³¹Pa/²³⁰Th ratios are not a proxy for Atlantic meridional overturning circulation

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Sedimentary ²³¹Pa/²³⁰Th ratios are receiving growing use as a kinematic proxy to estimate changes in the rate of Atlantic Meridional Overturning Circulation (AMOC). We will present evidence that this use is misdirected. In the Atlantic Ocean today, dissolved ²³¹Pa/²³⁰Th ratios in deep waters increase from north to south, as expected given that water masses are ventilated in the north and deep waters age as they move southward. However, in contrast to the southward increase in dissolved ²³¹Pa/²³⁰Th ratios, a survey of core top samples shows that the highest sedimentary ²³¹Pa/²³⁰Th ratios generally occur in the northernmost North Atlantic, in the region of best-ventilated deep waters. Furthermore, at mid latitudes, sedimentary ²³¹Pa/²³⁰Th ratios off NW Africa are nearly twice as large as at corresponding latitudes off North America. Overall, the spatial pattern of sedimentary ²³¹Pa/²³⁰Th ratios indicates control by biological productivity; specifically, by diatom productivity and by the flux of biogenic opal exported to the deep ocean. This relationship is governed by the strong preference for scavenging of dissolved Pa by biogenic opal. Sedimentary ²³¹Pa/²³⁰Th ratios do not reflect AMOC in the modern Atlantic and should not be used as a quantitative proxy for past changes in the rate of overturning circulation.

We do not contend that AMOC was unaffected during Heinrich Events. To the contrary, we propose that it was the reduction of AMOC that allowed the North Atlantic to be flooded with Si-rich water supplied from the Southern Ocean. If winter mixing penetrated deep enough to entrain Si-rich southern-source water, then this source of Si to surface waters would have stimulated the production of diatoms and increased the flux of opal that enhanced the scavenging of Pa from the water column. This view is supported by the peak during Heinrich Event 1 in the accumulation rate of diatoms in Bermuda Rise sediments [1] that coincided with the interval of elevated ²³¹Pa/²³⁰Th ratios there [2].

[1] Gil, Keigwin & Abrantes (submitted) *Paleoceanography*.

[2] McManus *et al.* (2004) *Nature* **428**, 834-837.

The importance of river water inflow and shelf sediment-sea water exchange in the East Siberian Sea for the Nd isotopic composition of Arctic Ocean water

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With data generated from cruises to the Canada Basin in 2000, to the Eurasian and Central Arctic Ocean basins in 2001, to the Fram Strait in 2002 and to the Chuckchi Sea in 2005 we now have a good general view of the distribution and isotopic composition of Nd (ϵ_{Nd}) in the Arctic Ocean [1, 2]. The restricted Arctic Ocean basin is surrounded by large continental shelves, covering more than 50% of its total area.

Distinct from other oceans, with surface water Nd depletion, there is throughout the Arctic a pattern of high Nd concentrations, up to 58pM, at the surface that gradually diminish with depth to 15-18pM in the deep waters. A range of isotopic variations across the Arctic and within individual depth profiles reflects the different sources of waters. The dominant source of water and Nd is the Atlantic ($\epsilon_{Nd} = -10.7$). Radiogenic isotope Nd signatures can be traced in Pacific water flowing into the Canada Basin and further into the Eurasian Basin (up to $\epsilon_{Nd} = -6.5$). The variation of ϵ_{Nd} and concentration in the Arctic Ocean suggest that Nd input from rivers and shelf sediments is also of great importance.

Improving our understanding of the vast Siberian Shelves influence on Nd and trace element behaviour in the Arctic Ocean was one of the main objectives of the International Siberian Shelf Study 2008 (ISSS-08). The ISSS-08 cruise recovered filtered water (<0.2 μ m), particles and sediments from the Laptev and East Siberian Seas as well as estuarine and river water from Lena, Indigirka and Kolyma. Crucial processes, including loss of river water Nd in the estuarine region and shelf sediment-sea water exchange will be discussed in terms of controlling the Nd concentration and isotopic composition of sea water.

[1] Andersson *et al.* (2008) *GCA* **72**, 2854-2867. [2] Porcelli *et al.* (2009, in press) *GCA*.

A methodology to estimate Pitzer interaction parameters

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Most of the geochemical aqueous speciation models of electrolytic systems are based on the "ion pairing and complexing approach", only suitable for aqueous solutions with ionic strengths up to about 0.8 eq/kgw. For highly saline solutions, an approach based on "specific-ion interactions" (named "Pitzer approach") provides more accurate results.

Various thermodynamic databases supporting the "Pitzer approach" exist but they are often inconsistent and poorly documented. The number of chemical elements is limited because of the difficulties to measure relevant parameters for large ranges of temperature, ionic strength and pH. These limitations prevent from satisfying applications of the Pitzer formalism to simulate the geochemical behaviour of solutions and gas-brine-rock interactions in deep reservoir conditions. Consequently, databases have to be continuously updated and improved to better represent these geochemical processes.

This study presents the development of a new methodology for determining Pitzer interaction parameters. This methodology is based on the use of PEST [1], a nonlinear parameter estimation and optimization package, coupled to the PHREEQC code [2]. PEST takes control of PHREEQC, running it as many times as necessary while adjusting the Pitzer interaction parameters. The fitting procedure stops when the discrepancies between selected model outputs and a complementary set of field or laboratory measurements are reduced to a minimum.

This methodology was applied with success to different saline solutions (NaCl, KCl, HCl...). The computations were performed using measurements of water activities and mineral solubilities. All these calculations demonstrate that, if the number of measured data is sufficiently important, Pitzer interaction parameters can be determined for temperatures ranging between 25 and 300°C. Over the good fitting of calculation results with measured data, the smooth and monotonous variations of the interaction parameters values with temperature confirm the consistent adjustment of the determined parameters, allowing extrapolation potential to higher temperatures. This methodology to determine Pitzer interaction parameters is also applied to divalent salts and ternary interaction coefficients.

[1] Doherty (2004) *User Manual*: 5th Edition. [2] Parkhurst & Appelo (1999) *Wat. Res. Investigations Report* 99-4259.

Natural and anthropogenic aerosols and their effects on clouds, precipitation and climate

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The aerosol in today's atmosphere is a blend of particles of natural and anthropogenic origin. Because the lifetime of aerosol particles is comparable to the time scale of intra-continental and intercontinental transport, anthropogenic aerosols are ubiquitous and the natural 'background' aerosol is difficult to observe and quantify with confidence. From *in situ* measurements of aerosol concentrations at remote sites, together with data on appropriate pollution tracers, estimates of the natural concentrations of aerosols can be derived. The concentrations of cloud condensation nuclei (CCN) can be obtained using either direct measurements or information on size spectra and aerosol hygroscopicity. Adding remote sensing information makes it possible to up-scale the *in situ* observations to a global picture of the natural continental aerosol and its anthropogenic perturbation. The results show that natural CCN concentrations are low over both oceans and continents, which implies that cloud processes in much of today's atmosphere are substantially different from those in the pre-anthropogenic system. A conceptual model to describe the effects of these perturbations on precipitation and cloud dynamics, as well as examples of observations of these effects will be presented.

Experimental study of carbon sequestration reactions controlled by the percolation of CO₂-rich brine through peridotites

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Carbonation of ultramafic rocks in geological reservoirs is, in theory, the most efficient way to trap CO₂ irreversibly; however, possible feedback effects between carbonation reactions and changes in the reservoir permeability must be considered to assess realistically the efficiency and sustainability of this process. We investigated changes in the hydrodynamic properties of sintered dunite samples by means of percolation experiments, under conditions analogous to that of *in situ* carbonation [1].

Our results show that carbonation efficiency is controlled by the local renewal of the reactants and the heterogeneity of the pore structure. Preferential flow zones are characterized by the formation of magnetite and of a silica-rich layer at the olivine surfaces, which eventually inhibits olivine dissolution. Conversely, magnesite and siderite are formed, together with Mg-TOT-phyllsilicates, within reduced-flow zones. Thus, carbonate precipitation decreases porosity, but only in zones where diffusion-controlled transport is dominant, which does not affect sample permeability (controlled by the main flow paths). Consequently, while high flow rates will decrease the carbonation efficiency of the reservoir and low flow rates may reduce the permeability irreversibly close to the injection point, moderate injection rates will assure a partial carbonation of the rock and maintain the reservoir permeability.

[1] Andreani *et al.* (2009) *Envir. Sci. Technol* **43**(4), 1226-1231.

The ^{205}Pb - ^{205}Tl and Cd isotope systematics of ordinary chondrites

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This study investigates the early history of the ordinary chondrite parent bodies using the ^{205}Pb - ^{205}Tl decay system. The presence of short-lived ^{205}Pb ($t_{1/2}=15.1$ Ma) in the early Solar System [1-2] and large variations in the Pb/Tl ratios of ordinary chondrites make the ^{205}Pb - ^{205}Tl system suitable for chronological studies of these bodies. To minimize the problem of terrestrial Pb contamination, only meteorite falls have been selected for study. The LL-chondrites analysed give a Pb-Pb age of 4.53 ± 0.11 Ga, suggesting that their Pb budget is not dominated by terrestrial lead.

The ordinary chondrites display a spread in $^{204}\text{Pb}/^{203}\text{Tl}$ ratios from 1.7 to 152, primarily controlled by a large variation in Tl concentration (from 0.3 to 19 ppb). Lead concentrations vary less, but still differ by a factor of 7. The Tl isotopic composition of unequilibrated chondrites (type 3) indicates radiogenic in-growth of ^{205}Tl , suggesting a relative Pb-Tl age similar to that of the IAB iron meteorites [1]. Equilibrated LL and L chondrites (type 4-6), on the other hand, show no evidence of radiogenic ^{205}Tl . This indicates that their high Pb/Tl ratios were established later than 4.45 Ga, suggesting a longer cooling history for the LL chondrite parent body than seen for the H-chondrite parent body [3-4], or a resetting of the Pb-Tl system after this time, perhaps due to impact-induced thermal metamorphism [5].

The element Cd has approximately the same volatility as Tl. Hence, Cd stable isotope analyses are used to identify samples where the Tl isotope compositions were altered by stable isotope effects from mobilization of Tl during thermal metamorphism [6].

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Silicate and salt (Li, Na, F) melts of the Dzarta Khuduk rare-metal occurrence (Central Mongolia)

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Using electron and ion microprobe analysis, we investigated inclusions of mineral-forming media in minerals from the rare-metal (Nb, Zr, and REE) alkali-rich felsic rocks of the Late Paleozoic bimodal volcanic association of the Dzarta Khuduk occurrence (Central Mongolia). Dzarta Huduk paleovolcano occupies an area of more than 120 square kilometers. A sequence of felsic agpaite volcanics rests on subalkali basalts and consists of intercalating alkaline trachydacites, pantellerites, and comendites. Their mineralogical and chemical characteristics correspond to silicic peralkaline rocks of the K-Na series with an agpaite coefficient (K_a) of >1 and high contents of F, Zr, Li, Rb, and REE. Primary solid and melt inclusions were determined in quartz of the comendites and comendite tuffs. Aegirine, fluorite, ilmenite, and chevkinite (rare REE di-orthosilicate with 21 wt % Ce_2O_3 , 17 wt % La_2O_3 , 1 wt % Nb_2O_5 , and 0.5 wt % Y_2O_3) were found as single-phase inclusions. The melt inclusions in comendites are composed of glass, gas phase, and a fine-grained villiaumite (NaF)-griceite (LiF) aggregate.

The melt inclusions in comendite tuffs are composed of homogeneous glass and can be considered as residual melts formed during the crystallization of comendite magma.

Thermometric experiments with melt inclusions in comendites were conducted using a microscopic heating stage allowing fast quenching (within 1-2 s). The complete homogenization of melt inclusions was observed at 800–1030°C. The glasses of homogenized inclusions are chemically similar to the host comendites and contain (wt %): 72–80 SiO_2 , up to 5 FeO, 4–7 Na_2O , 3.6–4.7 K_2O , and 7.8–11.0 Al_2O_3 . A conspicuous feature of these melts is extremely high Li and Zr contents, up to 1800–1900 and 1300–3700 ppm, respectively. In addition, the melts show high Rb (300–600 ppm), Nb (100–235 ppm), Y (110–240 ppm), Ce (up to 290 ppm), and La (up to 120 ppm), but very low Sr (2–5 ppm) and Ba (5–9 ppm) abundances. The contents of volatile components are 0.4–1.4 wt % H_2O , 0.8–2.8 wt % F, and up to 0.3 wt % Cl. The glasses from comendite tuffs are even stronger enriched in Zr, Th, Rb, and Sr. The concentrations of Zr in glasses from the tuffs are higher than 1 %. The majority of trace elements (Rb, Pb, U, Ta, Y, Th, and almost all REE) show direct correlations with Nb. Thus, our study of melt inclusions in quartz from comendites and comendite tuffs revealed the occurrence of strongly evolved rare-metal alkaline melts enriched in Na, F, Li, Zr, and REE and allowed us to distinguish main magmatic processes responsible for their formation. The evolution of the comendite melt was controlled by the processes of crystal fractionation and silicate-salt liquid immiscibility.

Multi-factorial analysis of surface interactions in single species environmental bacteria and model surfaces

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Environmental bacterial populations consist of diverse communities with differences in cell surface physiology and surface chemistry. Subsurface environments are made up of a heterogeneous mineralogy which also has a range of surface chemistries. Biofilm formation and structure in environmental bacteria was examined in relation to the surface chemistry of both the micro-organisms and the substrata. A set of bacteria isolated from subsurface environments were used, some Gram positive and some Gram negative. The attachment and proliferation into biofilms of these strains was tested on 3 surfaces with different surface chemistries polystyrene (hydrophobic), Tissue culture treated polystyrene (less hydrophobic, negatively charged), and Quartz (hydrophilic, negatively charged).

The surface chemistry of bacterial isolates was shown to be either hydrophobic or hydrophilic but this appeared to have no predictable influence on cell attachment and biofilm proliferation. A multi-factorial cell attachment experiment showed that attachment of bacterial cells to surfaces is highly variable and dependent on a combination of factors. The extent of attached growth differs by organism and substratum, but planktonic growth does not. The hydrophobic model surface (polystyrene) is related to greater attached growth while only two strains of organism show substantial attached growth on the hydrophilic, negatively charged mineral surface of quartz *Pseudomonas putida* Pse1 and *Sphingomonas xenophaga* strain Sph2.

These studies show that general characterisation of cell and substratum properties (i.e. hydrophobicity) do not strongly distinguish between the tendency for attachment and proliferation of growth or otherwise. Furthermore, genetically similar strains exhibit very different and unpredictable attachment profiles.

Comparison of the biogeochemical influences of angiosperm-only, gymnosperm-only, and mixed forest trees on Critical Zone processes

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Forests play a vital role in regulating many processes occurring in the Critical Zone, including weathering, element uptake, complexation, transport, and sequestration. A greater understanding of the impact of two broad groups of trees, the angiosperms and the gymnosperms, on critical zone processes is needed. Potential differences between the tree types with regard to mycorrhizal fungal associations, leaf chemistry, litter seasonality, rooting architecture and organic exudates may affect these processes. Our previous study of well-separated angiosperms and gymnosperms indicates these trees may have different interactions with some elements (e.g. Ca, Mg, Fe, K). Here, we examine an expanded element suite and use soil profiles beneath single tree types to assess the impact of a mixed forest on Critical Zone geochemistry.

Field sites A and B are in the western Cascade Mountains of Washington State, USA. Each has shallow soils underlain by granodiorite parent material. Site A contains angiosperms (*Alnus rubra* and *Acer macrophyllum*) on one half of the study transect, and gymnosperms (*Pseudotsuga menziesii* and *Thuja plicata*) on the other half. Site B is a more complex grove: the center of the 21m study transect is composed of conifers only, while each end of the transect contains both conifers and maple, but in different proportions at each end.

Plotting soil chemical data as mass change versus depth allows comparison of geochemical profiles between sampling sites. We use the site A angiosperm and gymnosperm element profiles as endmembers when interpreting the profiles of mixed vegetation at site B. For most of the element profiles examined (Al, Na, Ca, P, Fe, Mg, Mn, Ni, Co, and Pb), the coniferous middle section of site B resembles the gymnosperm profile from site A. The profiles of the two end sections appear to be intermediate between the angiosperm and gymnosperm endmembers with regard to extent of element depletion or accumulation with depth. Other elements (K, Zn, Mo) have more complicated profiles. These data indicate that at field scales, the full biogeochemical impact of a mixed forest on soil geochemical profiles may potentially be interpreted as a mixing model of the net influences of endmember tree types.

Investigation of the light-induced degradation of glutamic acid and stabilisation of glucose on the surface of iron-bearing minerals

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Soil organic matter (SOM) is the most important factor for the maintenance of soil fertility. It is essential to understand the processes that mineralise or stabilise organic matter in soils. Iron-bearing minerals are ubiquitous in soils and the presence of iron is connected to higher concentrations of organic matter [1]. For the purposes of this study, our hypothesis was that photochemical reactions that occur on the surface of iron-bearing minerals, such as haematite [2, 3] and olivine, could play a role on the mineralisation or stabilisation of SOM. As a simple analogue we used glutamic acid and glucose.

In batch photochemical experiments, separate solutions of glutamic acid and glucose have been irradiated with UV light of wavelength 254 nm or 365 nm in the presence of haematite or olivine. These studies have shown that glutamic acid is degraded in the presence of these minerals while, on the other hand, glucose is stabilised [4]. The understanding of the mechanisms that cause the degradation of glutamic but stabilise glucose is of great significance.

Here, we present results of an investigation of the adsorption of the two organics on crystal surfaces of haematite and olivine with Atomic Force Microscopy (AFM).

We used AFM to investigate the adsorption behaviour of the organics, molecular orientation on the surface and yield evidence about the modified rate of photochemical reactions when the organic molecules are adsorbed on the surface of the minerals.

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Relation between chlorophenol and chloroanizol cork content and soil chemical composition

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The natural environmental decay of persistent organic pollutants is a critical environmental concern. The chemical and reactions that lead to pollutant dispersion and dilution process on the soil matrix are uncountable. Those persistent pollutants namely the pentachlorophenols (PCP) present a great problem for some Industries that use their products in the food Industry. For cork industry, the PCP precursor of 2,4,6 - tetrachlorophenol (TCA) in a few concentrations (10 ppt) is a cause to the exclusion of the cork to produce stoppers, because it is one of the causes of cork wine taint.

The content of chlorophenols in cork plates was evaluated in 11 cork piles that provenance from different stands. The chemical characteristics of the soil of those stands were evaluated in terms of: pH, organic matter content, assimilated phosphorus, assimilated potassium, chlorates, calcium; magnesium, sodium, potassium, Ca/Mg ratio.

Chromatographic analyses were carried out on Agilent technology equipped with a mass spectrometry detector and the compounds evaluated was: PCP; 2,4,6 – trichlorophenol (TCP); 2,3,4,6-Tetrachlorophenol (TeCP); TCA; pentachloroanizol (PCA) in the 11 previously piles.

That methodology gives the possibility to the identification of regional zones with probability to have TCA in the cork and that data are very important for the cork industry because the cork that provide from that stands could be have other kind of uses and other kind of methodologies for storage in the factory.

Principal Components Analysis indicated a good correlation between chlorates content and Ca/Mg ratio and the concentration of TCA and PCA. The organic matter in the soil influences the TCP content.

This is a preliminary approach about the possibility of correlation between the content of chlorophenols of the analyzed cork plates and the soils of their origin, but other studies are in progress to evaluate and validate that relation.

Anion disorder in calcite and nitratine

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There is considerable interest in the phase transitions in calcite (CaCO_3) and the related mineral, nitratine (NaNO_3). The transition in both isotopic calcite and NaNO_3 involves orientational disorder of the CO_3 or NO_3 groups. The temperature dependences of the crystal structure and intensities of the (113) and (211) reflections in calcite, CaCO_3 , and nitratine, NaNO_3 , were studied using Rietveld structure refinements based on synchrotron powder X-ray diffraction data. Calcite transforms from $R\bar{3}c$ to $R\bar{3}m$ at about $T_c = 1240$ K, whereas nitratine transforms at 552(1) K. A CO_3 or NO_3 group occupies, statistically, two positions with equal frequency in the disordered $R\bar{3}m$ phase, but with unequal frequency in the partially ordered $R\bar{3}c$ phase. One position for the CO_3 or NO_3 group is rotated by 180° with respect to the other. The unequal occupancy of the two orientations in the partially ordered $R\bar{3}c$ phase is obtained directly from the occupancy factor, x , for the O1 site and gives rise to the order parameter, $S = 2x - 1$. In calcite, the a cell parameter shows a negative thermal expansion at low T , followed by a plateau region at higher T , then a steeper contraction towards T_c , where the CO_3 groups disorder in a rapid process. In nitratine as well, the a axis contracts towards T_c , where the NO_3 groups disorder rapidly. Using a modified Bragg-Williams model, fits were obtained for the order parameter S , and for the intensities of the (113) and (211) reflections.

Two contrasting Ordovician and Variscan plutons at Central Iberian Zone (central Portugal)

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In the Central Iberian Zone (CIZ) of the Iberian Massif, most granitic plutons are related to the last ductile deformation phase D3 of the Variscan orogeny. Ordovician granites are rare.

The Oledo pluton consists of Early Ordovician granitic rocks (479 - 480 Ma), ranging from tonalite to granite, whereas the Castelo Branco pluton consists of late-D3 Variscan granodiorites and granites (310 ± 1 Ma). The U-Pb ages were determined on zircon and monazite by ID-TIMS. The former pluton was intruded by the latter pluton.

At the Oledo pluton, biotite granodiorite contains biotite tonalitic and granodioritic microgranular enclaves. They are of I-type. Granodioritic enclaves and host granodiorite were derived from tonalitic magma by fractional crystallization. Biotite > muscovite granodiorite shows a sharp contact with biotite granodiorite and is of hybrid origin. Biotite = muscovite granodiorite has tonalitic and granodioritic enclaves. The granodioritic enclaves result from mixing of relatively primitive granodiorite magma with magma derived from crustal melting. Tonalitic enclaves are globules of a more mafic relatively primitive magma. Muscovite > biotite granite is of S-type.

The reversely zoned pluton from Castelo Branco consists of S-type granitic rocks. It has a muscovite > biotite granite at the pluton's core surrounded successively by biotite > muscovite granodiorite, porphyritic biotite > muscovite granodiorite grading to porphyritic biotite = muscovite granite and by muscovite > biotite granite. Porphyritic granodiorite and biotite = muscovite granite were derived from the granodiorite magma by a fractional crystallization process. Both muscovite > biotite granites resulted from two distinct pulses of granite magma.

Surface speciation of sulfate at a water-ferrihydrite interface

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Surface speciation is important for understanding the adsorption mechanisms and the long-term behavior of dissolved toxic species as well as the bioavailability of nutrients. In addition, the speciation influences the physicochemical property of the minerals, such as solubility of nano particles [1] and dissolution rate of mineral [2]. Ferrihydrite is low crystalline ferric hydroxide widely distributed in soils and rivers. It is also thought to be an effective anion adsorbent because of its high-specific surface area and positively-charged surface in natural water. Sulfate (SO_4^{2-}) is common anion in soils and rivers. It is reported that sulfate competes with phosphate, carbonate, trace metal and organic acid adsorption [3,4]. The present study aims to reveal the surface speciation of sulfate at the electrolyte solution-ferrihydrite interface under various pH and ionic strength conditions by means of *in situ* IR spectroscopic analysis (ATR-FTIR) and surface complexation modeling (Extended Triple Layer Model: ETLM [3, 5]).

IR spectra of sulfate adsorbed on ferrihydrite were fitted by Gaussian functions based on the assignments by Peak *et al.* [4]. The number and position of the peaks from IR spectra showed there are inner-sphere and outer-sphere sulfate complexes. Outer-sphere complex is dominant under the examined pH (4 to 9) and ionic strength ($I = 0.01$ to 0.1) conditions, although the contribution decreases with increase of ionic strength and decrease of pH. The coordination environment was estimated by ETLM analyses of independent surface charge data of ferrihydrite in Na_2SO_4 solutions as function of pH and ionic strength. The coordination environment of outer-sphere species was determined to be $(>\text{FeOH}_2^+)_2\text{SO}_4^{2-}$ (bidentate deprotonated outer-sphere species) while that of inner-sphere species was $>\text{FeOSO}_3^-$ (monodentate deprotonated inner-sphere species). ETLM prediction using these two sulfate surface species and these reaction equations quantitatively reproduced the surface speciation as function of pH and ionic strength obtained by the ATR-IR analyses.

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Modeling cesium diffusion in a claystone formation

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Diffusion experiments performed at different scales with reactive tracers provide a good opportunity to test and verify reactive transport models. Recently, considerable progress has been made to describe the diffusion of cations and anions in clay media [1] by accounting for the different porosities and diffusivities 'seen' by the different ionic and uncharged species. Thus, simultaneous diffusion of tritium, iodide and sodium from an *in situ* experiment in Opalinus Clay was successfully modeled using the PHREEQC code with the newly developed multicomponent diffusion option [1].

Cesium, a safety-relevant radionuclide is known to sorb rather strongly to claystone, but on the other hand displays a high effective diffusivity. Two *in situ* diffusion experiments (DI-A1 and DI-A2), in which a number of tracers including also Cs^+ were carried out in the Mont Terri URL. The results of these were modelled with simple diffusion models and empirical expressions for sorption (e.g. [2]). Here we report the refined modelling of the Cs^+ diffusion data from the two *in situ* experiments using the multicomponent diffusion model of [1] and accounting for recent laboratory Cs^+ diffusion data on small-scale samples [3].

A dual porosity model, which is consistent with structural data of the clay, is shown to be necessary to describe the *in situ* data. Moreover, the results show the importance of including the specific hydraulic properties of the borehole filter and the annular space between filter and rock in the modeling description. When these effects are accounted for, then a remarkable consistency in diffusion and sorption parameters between the different *in situ* tests and the small-scale lab tests is obtained. Also, the results are consistent with batch sorption data performed at low solid/liquid ratio, thus indicating the same cesium sorption capacity at high S/L ratios at different spatial scales.

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Global model studies on the composition and distribution of atmospheric ice nuclei

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Black carbon (BC) and mineral dust particles are among the most important atmospheric aerosol types forming ice crystals by heterogeneous nucleation (so called ice nuclei). When emitted, most BC and dust particles are externally mixed with other aerosol compounds. Through coagulation with particles containing soluble material and condensation of gases, externally mixed particles gain a liquid coating and are, therefore, transferred to an internal mixture.

This aging process is essential for the direct and indirect effect of BC and dust particles on climate, since the coating changes the radiative and hygroscopic properties of the particles and, therefore, their cloud activation ability and lifetime. Moreover, laboratory studies have shown that a liquid coating influences the freezing properties of the particles and hence their behaviour as ice nuclei [1, 2].

Due to large computational resources required, global climate models mostly parameterize the particle aging by using estimated turnover times, rather than simulating the aging processes explicitly.

In the present study, the global aerosol-climate model ECHAM5/MESSy1/MADE was extended by new aerosol modes to represent BC and dust particles and their different states of mixing as well as the relevant aging processes of externally mixed particles. The extended model setup was applied to particularly simulate the mass and number concentration as well as the composition of potential ice nuclei in the global atmosphere. Additionally, the timescales of transforming externally mixed BC and dust particles into the internal mixture was quantified.

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Asymmetry in crustal and thermal evolution of the Moon

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Understanding of lunar origin and evolution has been advanced with synergies of sample analysis and remote sensing. Apollo ferroan anorthosites (FAN) with high plagioclase abundance (>90 vol%) and low Mg/(Mg + Fe)[=mg#] ratio (typically 50–65) have been the basis of the magma ocean model, where lunar feldspathic crust formed by floated plagioclase cumulates from an evolved, Fe-enriched magma ocean [1]. Recent discovery of magnesian anorthosite (MAN) (mg#=75-77, 96.5 vol% plagioclase) and spinel troctolite (ST) (mg#=84-85, 72.0 vol% plagioclase) in lunar meteorite Dhofar 489 and paired rocks suggests a greater range of mg# in lunar feldspathic crust than previously thought. The presence of magnesian and ferroan granulites from Apollo [2], and mg# of feldspathic lunar meteorites [3] are consistent with this implication. FAN rocks are mostly noritic, whereas MAN and ST are troctolitic. The mineralogical contrast between FAN and MAN/ST further suggests a bimodal crustal composition, ferroan noritic and magnesian troctolitic.

The extremely low contents in Th, Fe, and REEs of Dhofar 489 and siblings [4, 5] indicate a probable origin of farside highland [5]. Apollo FAN from nearside highland and Dhofar MAN from farside highland imply the bimodal crust composition of the nearside and farside crust. Mineralogical and mg# distribution estimated based on Clementine ultraviolet-visible multispectral data also hints the asymmetric nearside-farside crust composition [6, 7].

MAN/ST and FAN may be products of a series of liquid line of descent during a magma ocean crystallization [8]. The crystallization sequence of olivine, anorthite, and orthopyroxene to produce ST/MAN, and following FAN requires a more Al₂O₃-rich magma composition [9] than a terrestrial mantle-like bulk-Moon composition [10]. The asymmetric crust composition might be attributed to different thermal conditions of the nearside and farside.

The composition of a magma ocean will be further constrained from the mineral distributions/compositions and thickness of the global crust by Multiband Imager and Spectral Profiler of Kaguya. The thermal condition of the global crust will be defined by gravity field data of Kaguya.

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Antimony isotopic fractionation during adsorption on ferrihydrite

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Antimony is a potentially toxic trace element, though its physiological function is not known well. In industry, about two-thirds of all Sb production is consumed as Sb₂O₃, added to plastics to act as a flame retardant. The environmental impact by the leaching of Sb into natural water system is concerned. Knowledge of the chemical factors controlling the distribution and mobilization of Sb species in the aqueous systems is therefore important for environmental control and monitoring of Sb as well as for understanding of their geochemical and biological cycling.

Here, we developed a precise isotopic analysis technique of antimony and applied to an adsorption experiment on a mineral surface. Antimony has two stable isotopes of mass number 121 and 123 with relative abundances of 57.362% and 42.638%, and high precision isotopic analysis is possible by a recent introduction of multiple collector ICP-MS. An equilibrium adsorption experiment of pentavalent Sb in aqueous solutions on synthetic ferrihydrite was carried out with a wide range of pH.

Results from XANES and EXAFS analyses indicate Sb⁵⁺ is present as an inner-sphere complex of octahedral Sb species on the surface [1]. Resultant isotope ratios revealed that ¹²³Sb/¹²¹Sb values in the aqueous phases were enriched in heavy isotopes slightly. This Sb isotopic trend was confirmed by the analysis of an interstitial solution from sediments near a stibnite mining area.

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Towards a global calibration of the *G. ruber* (white) Mg/Ca paleothermometer

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Paired planktonic foraminiferal Mg/Ca and δ¹⁸O analyses are commonly applied to jointly estimate sea surface temperature and δ¹⁸O_{seawater}, a proxy for ocean salinity. Our recent findings from an Atlantic meridional coretop sample transect revealed a significant temperature-independent, influence on *G. ruber* (white) shell Mg/Ca. This effect leads to much higher Mg content than is predicted from traditional SST-Mg/Ca calibration equations and a large, systematic offset between shell derived and observed δ¹⁸O_{seawater} values. The 'excess Mg/Ca' (residual of observed Mg/Ca – expected Mg/Ca at the δ¹⁸O calcification temperature) appears to be highly correlated to salinity and is similar to that found by Ferguson *et al.* (2008). However, culture studies indicate a much lower dependence of shell Mg/Ca on salinity.

A global database (n=122), consisting of coretops of late Holocene age were selected from trigger weight cores in the Pacific, Indian, and Atlantic basins. SEM images of specimens from each basin and from a range of salinities, indicate there are no overgrowths or obvious morphological differences to account for the observed 'excess Mg/Ca'. Flow-through ICP-MS analyses from a global subset of samples yielded similar Mg/Ca ratios as results from batch method analyses, indicating that incomplete cleaning cannot account for the 'excess Mg/Ca' signal either. This implies the 'excess Mg/Ca' signal derives from the primary shell chemistry.

Shells from all coretop samples were cleaned for Mg/Ca using the full oxidative-reductive procedure. Data from these analyses were used to determine new calibration equations for surface ocean temperature and salinity using shell Mg/Ca, δ¹⁸O, bottom water ΔCO₃²⁻, and surface CO₃²⁻ as potential predictors. The relationship of shell Mg/Ca to salinity appears to be non-linear. These results indicate good predictive skill and were validated using published coretop data from all basins.

Mo isotope proxy for ancient anoxia: Insights from a modern anoxic basin

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Insights into biogeochemical cycling in ancient anoxic environments can be gleaned from studies of their modern day analogues. One such setting is the Golfo Dulce, a ~200 m deep semi-restricted basin on the Pacific coast of Costa Rica. As a result of limited exchange with the open ocean, the deeper parts of the basin experiences sub-oxic to anoxic conditions, but little or no sulphate-reduction, for the majority of the year. The Golfo Dulce thus provides a natural laboratory to study biogeochemical cycling of redox sensitive trace metals, such as molybdenum (Mo), under conditions that are perhaps analogous to those of Archaean/Proterozoic oceans. Mo, and its isotopes, have recently emerged as potentially powerful proxies for reconstruction of past oceanic and atmospheric redox state^{1,2}. The palaeoproxy power of Mo rests on its redox-bimodal aqueous geochemistry and associated isotopic fractionation during removal to oxic or euxinic sedimentary environments.

Here we focus on Mo systematics in both pore waters and sediments, obtained from 50cm sediment cores across the basin. Mo cycling is investigated across pronounced down-core redox gradients and variable bottom water redox conditions, as suggested by corresponding Fe and Mn pore-water profiles. At the deeper anoxic site, $\delta^{98}\text{Mo}$ begins increasing, by 2‰ in total, at the sediment/water boundary. The same pattern is seen in the core retrieved from beneath oxic bottom water, but in this case further down-core. With the isotopic variation there is a corresponding decrease in Mo concentration. Such a correlation could be explained by removal of Mo from the pore waters as a thio-molybdate species, in the presence of low dissolved sulphide. This process is thought to preferentially remove light Mo isotopes³. These data will be interpreted in light of their accompanying solid phase systematics, along with emerging data on experimental controls on Mo isotope fractionation during early diagenesis.

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Reaction pathways for rising hyperalkaline groundwater in a bentonite mine in the Philippines

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The Zambales Ophiolite in the Philippines comprises a thick ultramafic sequence overlain by gabbro, diabase complex, a pillow basalt unit and overlain by tuffaceous siltstone and sandstones referred to as the Aksitero Formation. A hyperalkaline spring called the Manleluag Hyperalkaline Hot Spring (pH 10-11) found within the gabbro section of the ophiolite, is postulated to be associated with the hydrous reactions with gabbros at depth and interaction upon rising with a bentonite deposit formed from the tuffaceous sandstone and siltstone nearby (i.e. Akistero Formation). The reaction pathway for rising hyperalkaline groundwater that interacts with the overlying bentonite deposits is illustrated in a rock core taken from a continuous section from the bentonite connecting to the underlying basalt deposit. Stratigraphically-oriented geochemical and mineralogical analyses of the sliced cores indicate a mixture of smectite and zeolite formed from the progressive alteration of the basalt with hyperalkaline water. This study highlights a natural analogue site located in the Philippines.

Under what conditions is weathering maximized?

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According to Edmond and Huh [1] current global weathering rates are at a kinetic minimum due to a low atmospheric CO₂ content. It is hypothesized that this minimum in atmospheric CO₂ has been reached through a recent high consumption of CO₂ by enhanced silicate weathering due to tectonic uplift of the Himalayas [2]. To determine a range of possible global silicate weathering rates, we need to characterize the role of the processes, which control global spatial variability of weathering rates and to pinpoint conditions under which weathering is maximized or minimized.

Here, the concept of a dynamic model of soil genesis and associated rock weathering rates is presented and tested globally in order to find conditions under which weathering is maximized. In the model formulation the state of the soil system, i.e. temperature, water balance, depth, composition and CO₂ partial pressure, determines the outflow of weathered elements to rivers and ultimately the ocean. This allows us to quantify and model the influence of climate, uplift, erosion, soil age, and the direct and indirect effects of vegetation on silicate weathering rates.

The geographic variation of weathering rates and soil state can be examined and possible maximum weathering regimes recognized through a set of sensitivity simulations of weathering output to variability in vegetation, uplift and erosion. The outcome of such a set of experiments is presented and discussed.

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Constraining the ³⁶Cl/Cl ratio of seawater and its sources

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AMS Analysis of ³⁶Cl/Cl ratio of Seawater

Cosmogenic ³⁶Cl found in seawater is produced via spallation of atmospheric ⁴⁰Ar [1] and neutron capture of secondary cosmic-ray neutrons by dissolved ³⁵Cl [2]. The long residence time of chloride in the ocean and relatively long half life of ³⁶Cl compared to the oceanic mixing time should result in a homogenous ³⁶Cl/Cl ratio throughout the ocean.

Until recently, attempts to measure the ³⁶Cl/Cl ratio were unsuccessful due to insufficient analytic sensitivity. Modern AMS technology now allows us to measure ³⁶Cl/Cl ratios down to values close to 10⁻¹⁶ [3]. We have recently analyzed seven seawater samples from the Pacific and five commercially available NaCl salt samples at the ANU 14UD Pelletron. The average ³⁶Cl/Cl ratio of our seawater samples was 7.6 +/- 1.6 x 10⁻¹⁶, and the blanks averaged 0.5 +/- 0.4 x 10⁻¹⁶.

Discussion of Results

Preliminary calculations to determine how well this value correlates with expected atmospheric and oceanic sub-aqueous production indicate a discrepancy. Using values calculated by Masarik & Beer [1], estimated contribution to the ³⁶Cl/Cl ratio of seawater from atmospheric production is 2.9 x 10⁻¹⁶. Using the neutron flux values in seawater calculated by O'Brien [4], the contribution to the ³⁶Cl/Cl ratio via neutron capture by ³⁵Cl is estimated to be ~1.0 x 10⁻¹⁶. These two primary sources of ³⁶Cl sum up to a ratio of ~3.9 x 10⁻¹⁶. Future work will focus on identifying and quantifying the source of this discrepancy.

Acknowledgments

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Interlayer structures and binding conformations in the interaction of a tetracycline antibiotic with a smectite clay

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Interactions of antibiotics with soil particles can influence their environmental fate and the extent of their potential effects on soil and aquatic sensitive organisms. Of specific interest are their sorption mechanisms within smectite clay interlayers [1]. We employed a combination of experimental and modeling techniques to investigate the molecular interactions of Oxytetracycline (Oxy) with montmorillonite. Sorption experiments were conducted with a synthetic Fe-free Na-montmorillonite [2] at pH 4, pH 6, and pH 8. The pH-dependent changes in the clay interlayer structures as a function of adsorbed Oxy was revealed through X-ray diffraction pattern analyses of the Oxy-clay systems. These XRD results in conjunction with molecular modeling Monte Carlo simulations were used to probe for the binding conformations of the different Oxy species within the clay interlayer. This study provides for a mechanistic depiction of the sequestration of antibiotics within soil clay particles.

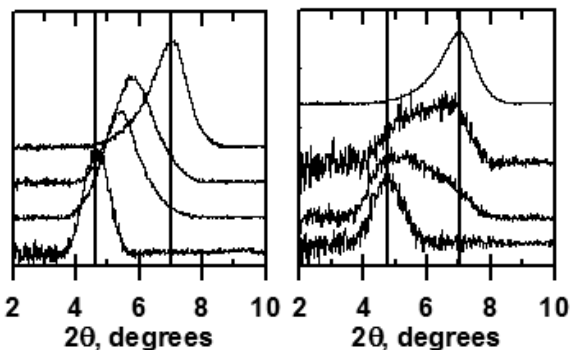


Figure 1: Selected X-ray Diffractograms: Interstratification at pH 4 (left) versus segregation at pH 6 (right). Amount of adsorbed Oxy (mmol Oxy/kg of clay) from top to bottom: 0.0, 40.7, 78.4, 284.2 at pH 4 and 0.0, 80.5, 99.6, and 221.7 at pH 6.

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Carbonate ooid formation in a modern freshwater lake: How determinant is the biological role?

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Shallow water sediments in western Lake Geneva, Switzerland, are composed of more than 90% of ooidal sands. The presence of biofilms lining depressions on ooid surfaces has been previously appointed as starting sites for low Mg calcite cortex formation [1]. Field- and laboratory-based experimental results indicate a dominant role of biological versus purely physicochemical processes in the early stages of ooid development.

A special device was placed in the ooid-rich bank of the lake. It contained frosted glass (SiO₂) slides, while quartz (SiO₂) is the most abundant mineral composition of ooid nuclei that acted as artificial substrates to favour microbial colonization [2]. Microscopic inspection of the slides depicted a seasonal pattern of carbonate precipitates, which were always closely associated with biofilms that developed on the surface of the frosted slides. They contain EPS, cyanobacteria, diatoms and heterotrophic bacteria. Carbonate precipitation peaks during early spring and late summer, and low-Mg calcite crystals mostly occur in close association with filamentous and coccoid cyanobacteria. Further SEM inspection of the samples revealed low-Mg calcite with crystal forms varying from anhedral to euhedral rhombohedra, depending on the seasons.

In situ biofilms communities were harvested and cultivated under laboratory conditions. Liquid and solid cultures corroborate the field observations and demonstrate that under the same physicochemical conditions the absence of biofilms prevents low-Mg calcite precipitation. The lack of evidence for the presence of sulphate-reducers further indicate that photosynthetic activity through increasing pH in EPS is the main factor triggering the early precipitation of low-Mg calcite. Hence, these results support the hypothesis of external microbial precipitation of low-Mg calcite as the main mechanism involved in the early stage of ooid formation in freshwater Lake Geneva. Total DNA extractions on natural ooids, biofilms harvested from the *in situ* glass slides, and cultured biofilms in the laboratory indicate a comparable microbial diversity supporting this model.

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Mississippian seawater temperature and ice volume variations revealed by $\delta^{18}\text{O}$ and Mg/Ca values of brachiopod shell calcites (late Viséan, SW Spain)

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Introduction

The late Palaeozoic ice age, one of the most remarkable palaeoclimatic crises in Earth history, was characterized by significant seawater temperature variations as well as by notable glacier fluctuations that were registered in the chemical and isotopic compositions of marine carbonates. In order to record palaeoclimatic changes occurred during the Mississippian, a total of 21 exceptionally well-preserved [1] brachiopod shell calcites were analysed for their elemental and stable isotope composition. Combination of $\delta^{18}\text{O}$ and Mg/Ca proxies could provide an effective method for estimation of ancient seawater temperatures and continental ice sheet formation [2]. The samples were collected along two stratigraphic levels from late Viséan [3] carbonate platform deposits of the Guadiato unit (Pedroches basin, SW Spain).

Interpreting $\delta^{18}\text{O}$ and Mg/Ca Values

On one hand, mean $\delta^{18}\text{O}$ values of the brachiopod shell calcites ($\delta^{18}\text{O}_c$) show an overall increase of $\sim 1\text{‰}$ from oldest to youngest samples (from -3.8‰ V-PDB to -2.9‰ V-PDB), which in terms of palaeotemperature implies a drop of seawater temperatures of $\sim 5.5^\circ\text{C}$. However, this positive $\delta^{18}\text{O}_c$ shift ($\sim 1\text{‰}$) can be interpreted to reflect variations in seawater palaeotemperature and/or alternatively differences in continental ice volume. On the other hand, mean Mg/Ca molar ratios of the brachiopod calcites show a $\sim 30.3\%$ decrease through the studied time interval (from 12.13 to 8.46 mmol/mol). This decline in Mg/Ca ratios indicates a temperature drop of $\sim 3.3^\circ\text{C}$, suggesting that other processes besides temperature may have accounted for the $\delta^{18}\text{O}_c$ shift. According to the ΔT obtained from the Mg/Ca data a positive shift in seawater $\delta^{18}\text{O}$ of about 0.4‰ can be calculated, which may contribute in the remaining $\delta^{18}\text{O}_c$ shift and likely reflects increasing storage of continental ice.

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Silicon isotopes in achondrites and the light element in Earth's core

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Silicon has long been suggested as a major light element in the core, partly due to the superchondritic Mg/Si of the bulk silicate Earth [1]. This is supported by high temperature and pressure experiments [2]. If silicon has entered the core we may expect a fractionation of the isotopic composition because of the major difference in bonding relative to silicates [3].

Georg *et al.* [3] analysed a series of different meteoritic, lunar, and terrestrial samples and found that the Si composition of the Earth and Moon are heavier, by $\sim 0.2\text{‰}$, than both chondritic and achondritic meteorites. This points to some fractionation event that has only affected the Earth-Moon system such as high temperature and pressure core formation. Silicon isotopic measurements of experimental silicate-metal charges are in accord with this conclusion [4].

There have been a number of subsequent Si isotope studies comparing analyses of terrestrial and meteoritic samples [5-9]. Some find differences between BSE and meteorites which are smaller than 0.2‰ and some that claim that the difference is irresolvable. Chondrites, as representing Earth's precursor material, have been the focus of most of these meteorite analyses. However, the Si isotopic signatures of achondrites are important in constraining whether the Earth-Moon system suffered a unique event.

Measurements made at Oxford using the Nu Plasma HR for a suite of Martian and HED meteorites give an average differentiated achondrite value of $\delta^{30}\text{Si} = -0.43 \pm 0.05\text{‰}$ (1SD) which is within error of our chondrite average of $-0.45 \pm 0.06\text{‰}$. The offset between our meteorite values and the BSE value of $\delta^{30}\text{Si} = -0.27 \pm 0.04\text{‰}$ (1SD) [9] points to some process in Earth's history such as high pressure core formation that does not extend to some smaller differentiated bodies.

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The role of magma ‘fertility’ in the formation of magmatic sulfide deposits

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A well-entrenched idea is that magmatic ore deposits in mafic-ultramafic rocks, such as the Ni-sulfide deposits of Noril'sk in Russia or the PGE deposits of the Bushveld Complex in South Africa, require parental magmas that are ‘fertile’, or unusually rich in ore metals. The magmas that formed the Bushveld Complex, for example, are thought to have had unusually high contents of platinum group elements (PGE). The idea has led to questionable models in which the parental magmas of these and other deposits acquire high metal contents from unusual sources such as metasomatised lithospheric mantle. Counter arguments are: (1) the vast range of Ni contents in magmas parental to Ni sulfide deposits, from about 1500 ppm in komatiites to about 80 ppm in the Sudbury melt sheet; (2) the comparable PGE contents in alkalic and tholeiitic mafic-ultramafic magmas, even though only the latter contain major ore deposits. Here I argue that the metal contents of primary mantle-derived magmas play only a minor role in the ore-forming process and that the important processes are those that act at upper crustal levels. Almost all mantle-derived magmas contain sufficiently high Ni, Cu, Cr and PGE contents to form a deposit; what is required is that the ore metals are efficiently extracted from a large volume of magma. In practice this requires that (a) a small fraction of the ore mineral is efficiently concentrated from a high-flux magma as it passes a ‘choke-point’ where changes in geological context or physico-chemical conditions cause segregation of the ore mineral, and/or (b) the ore minerals segregate at deeper crustal levels and are then remobilised and transported upwards, to become re-concentrated at a shallower level in the magma system.

Geochemical evolution of the global ocean during a Mid-Cretaceous OAE: Model development and sensitivity analysis

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The Mid-Cretaceous OAEs are witnesses of major perturbations of the Earth climate, which resulted from important changes in the biogeochemical functioning and structure of the ocean-atmosphere system. They are globally well documented by the ubiquitous presence of organic carbon-rich black shale layers characterized by unique geochemical and isotopic signatures. Nevertheless, numerous outstanding questions remain, not only concerning the general mechanisms that lead to the development of anoxic and/or euxinic conditions in the global ocean, but also regarding the influence of these particular environmental conditions on the enhanced carbon burial in marine sediments.

Here, we present a new version of the coupled Earth system model GEOCLIM. The new version combines a climate model (FOAM 3-D GCM) with a vertically resolved diffusion-advection box model of the global ocean, a pelagic biogeochemical model and a fully formulated diagenetic model (BNRS). The model is extended by coupling the sulphur and nitrogen biogeochemistry to the existing description of the carbon and phosphorus cycles. This structure allows investigating the dynamic interplay between the simulated oceanic conditions and sedimentary burial and recycling fluxes. The new model is thus particularly suitable to examine the feedbacks between climatic conditions, oceanic geochemical dynamics and diagenesis.

The model is used to explore the biogeochemical response of the global ocean to climate change during the Mid-Cretaceous A sensitivity study helps identify the most sensitive processes and parameters that control the development and the evolution of ocean anoxia and euxinia. Model results show that ocean anoxia can easily develop into euxinia if nutrient availability is high enough to sustain enhanced primary production. High production rates deplete oceanic oxygen concentrations and enhance sulphate reduction rates leading to a sulphide build up in the water column.

Retracing diagenetic pathways in diffusion controlled marine sediments: hydrogeochemical modelling with PHREEQC

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Marine sediments undergo a wide range of early diagenetic processes. Controlling factors for these processes like sulphate reduction, iron reduction or methanogenesis are for example the primary mineralogy of sediments and the amount and kind of organic matter.

Major conversion products of early diagenetic processes are carbon dioxide and methane. So far, hydrogeochemical models to simulate carbon mass balance and species distribution as results of coupled equilibrium and irreversible reactions are lacking. Therefore, we are developing a hydrogeochemical model, which will enable us to retrace and predict hydrochemical composition of pore waters, conversion of mineral phases, and composition of coexisting gas phases.

In our approach, diagenetic signals in sediments will be retraced by modelling the redox-conversion of metabolizable organic carbon. Diagenetic signals to be retraced are aqueous solutions, mineral and gas phases. The theoretical background is based on chemical thermodynamics and the applied hydrogeochemical modelling tool is PHREEQC [1].

Successful modelling results were obtained for the open, diffusion controlled system of Hydrate Ridge sediments, ODP Leg 204 Site 1246 [2]. Modelled pore water concentration profiles reach measured pore water concentrations in the zone of sulphate reduction as well as in the methanogenic zone. Furthermore, modelled contents of secondary diagenetic phases like methane and greigite (Fe₃S₄) in specific sediment depths were consistent with measured values. With PHREEQC it was also possible to calculate the gas composition in different sediment depths. Beside methane (>93 mol%) up to 1 mol% CO₂(g) and 6 mol% N₂(g) are present in sediments of the methanogenic zone.

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Sources and properties of carbon in Earth's oldest rocks

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Elemental carbon in the oldest known sedimentary rocks on Earth - organogenic, terrestrial inorganic and potentially meteoritic, are investigated with the ultimate purpose of establishing the earliest traces of life on Earth. Evidence for the origin and mode of formation is sought in the carbon ultrastructure. Meteoritic carbon is distinguished from terrestrial organogenic (= biogenic) carbon by the accompanying concentrations of platinum metal elements. The oldest known supracrustal rocks on Earth in Greenland (ISB) contain several genetic types of carbon. One appears in iron carbonates with carbon as graphite precipitated by disproportionation of the siderite. Another type of carbon occurs in the banded iron formation, commonly accepted as a sedimentary deposit. A third source of ISB carbon, potentially biogenic, is a carbonaceous shale discovered by Rosing and with spatial extent recently explored by coring. The 3.4 to 3.2 Ga deposits in the Barberton Greenstone Belt (BGB), S.Africa offer exceptional opportunities for the study of carbon in an early Archean sedimentary environment and contain objects that deserve analysis as possible organic structures. Both Barberton sediments and shungites are extensively permeated by mobile bitumen, obscuring primary sedimentary carbon features.

Properties of natural biogenic aerosols measured at the Amazonian Aerosol characterization Experiment (AMAZE-08)

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The main objectives of AMAZE-08 were to understand the sources and regulators of organic particle mass in a pristine continental environment and the connections between particle chemistry and particle optical and hygroscopic properties. The AMAZE-08 tower measurements were conducted during the wet season. The site was 60 km NNW of Manaus and located within a mostly pristine rainforest. The site allowed the study of pristine biological aerosol particles, although there were several episodes of long-range transport from Europe and Africa and more infrequent regional transport from Manaus and northerly biomass burning. Particle instrumentation included two high-resolution aerosol mass spectrometers (HR-ToF-AMS) with thermodenuder, two cloud condensation nuclei counters (CCNC), a continuous flow diffusion chamber (CFDC) for ice nuclei measurements, three OPC, an UV-APS for measurement of biologically active particles, two TEOMs, two SMPS, two multiwavelength nephelometers, three CPC, a MAAP, an aethalometer, coarse- and fine-mode filters for elemental and ion analysis as well as particle imaging. Gas instrumentation included a PTR-MS, and measurement of O₃, CO, CO₂, NO, and NO_x. Very low values of BC, light scattering, fine mode aerosol mass, and other properties were observed. The combination of this diversity of instruments allowed to observe the influence of sulphur in CCN activity, and to quantitatively apportion the effect of aerosol species on light scattering and absorption. Natural biogenic aerosol particles dominates more than 80% of aerosol mass and most of the observed optical activities. Secondary organic aerosol dominates the fine mode aerosol fraction.

Geochemical variations in the Erlend volcano, Faroe-Shetland channel

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Sr, Nd and Pb isotope ratios together with REE, other trace and major element measurements in the Paleogene Central Volcanic Complex, Erlend, situated in the Faroe-Shetland Channel evidence a complex petrological genesis. A detailed stratigraphic sampling of cores and cuttings in three exploration wells situated on this volcano have been investigated.

The volcano consists of mainly dacitic-rhyolitic extrusives with a basaltic lava succession on top, interleaved with sedimentary units.

The basaltic lavas are divided into three distinct groups, based on trace element and isotope ratios. Two groups of low-Ti basalts and one high-Ti are recognized. The low-Ti basalt groups are distinguished based on REE patterns and incompatible trace element ratios. The low-Ti 1 group shows a MORB trend, with depleted LREE, whereas the low-Ti 2 group shows a flat LREE trace. The high-Ti basalt group has a strongly LREE enriched signature with La/Sm of 3.5 to 4.5.

New Sr, Nd and Pb isotopic data on these basalts show a wide range of ratios similar to basalts in continental settings. Crustal contamination is thus an important factor to consider in the interpretation of these. Most of the lavas show trends towards East Greenland and Scottish Archaean crustal values in ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb and ⁸⁷Sr/⁸⁶Sr.

Trace element modelling of melting shows relatively high degree melting in the low-Ti 1 group ranging to lower degree in the low-Ti 2 group, and the smallest degree in the High-Ti group.

When data from the Erlend basalts are compared to those from the adjoining Faroe Island Basalt Group, it is evident that the Erlend basalts show several distinct features of the latest extrusive activity, the Enni formation and the latest dykes. This suggests that earlier correlations of the Erlend basalts to the earliest pre-breakup igneous activity are questionable. Furthermore, the new data imply that the volcano situated in the Faroe-Shetland Channel was active after the breakup between the Faroe Islands and East Greenland.

Sound velocity measurements in water at high pressures: Application to water at lower mantle conditions

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Introduction

Water is one of the fundamental elements of Earth and icy large planets. Therefore, the knowledge of its thermodynamic equation of state is a key to understand many phenomena in the interior of these planets. Sound velocity measurement in a diamond anvil cell is one of the potential methods to obtain density of liquid water under static conditions up to lower mantle pressures. In this study, we extend the experimental pressure and temperature range to 25 GPa and 900K using a laser heated diamond anvil cell with a combined system of Brillouin scattering and synchrotron X-ray diffraction at SPring-8, Japan [1].

Results

Simultaneous measurements of Brillouin scattering and X-ray diffraction were conducted at the range of pressure and temperature, 5-25 GPa and 550-900 K, along the melting curve of ice.

Obtained sound velocities in water were in good agreement with previous data obtained by external heating experiments [2, 3]. The sound velocities were converted to density with Murnaghan's equation of state and bulk modulus of water at 1 GPa (after [4]) by fitting a parameter of its pressure derivative. Results are in good agreement with the prediction by the previously reported equation of state for water based on sound velocity data up to 6 GPa [2].

Present results can apply the water generated by dehydration of hydrous phases in subducting slabs at lower mantle conditions.

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Quantification of microbial communities in groundwater using real-time PCR

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On deep geological environment, microbes affect the changes in the redox of groundwater which is one of the most important properties to estimate the condition of a geological disposal system for high-level radioactive waste. It is necessary to quantify microbial biomass on the geological environment as input data in numerical model to evaluate the redox condition. The real-time PCR assay will apply to rapid and simple method as one of the quantification methods. Thus, we applied this method to estimate microbial biomass related to microgeochemical processes in groundwater.

The groundwater was obtained at the depth of -35m and -500m from the borehole H17-1-01 and HDB-10, respectively at Horonobe area, Hokkaido, Japan. SYBR Green-based real-time PCR assay using the LightCycler Systems (Roche) was performed to quantify based on the gene copy number of nitrite reducers (*nirS* and *nirK* gene), denitrifiers (*nosZ* gene), Geobacteraceae including Mn(IV)- and Fe(III)-reducers (16S-rRNA gene), sulphate reducers (*dsr* gene), methanogens (*mcrA* gene), Bacteria (16S-rRNA gene) and Archaea (16S-rRNA gene).

The dominant members of microbes at the depth of -35m (H17-1-01) were Mn(IV)- and Fe(III)-reducers and sulphate reducers. On the other hand, the dominant members of microbes at the depth of -500m (HDB-10) were sulphate reducers and methanogens. The results of real-time PCR assay showed the same tendency as seen in the results of the cultivation-based methods and 16S-rRNA clone analysis. This result suggested that the real-time PCR will be useful for quantification of microbial biomass on the geological environment.

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Analysis and interpretation of microbial fossils in extreme environment of Dry Valley rocks, Antarctica

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The presence of indigenous microflora colonising the inside of Antarctic desert rocks [1] is a landmark for extreme environment microbial ecology. Some minerals in Antarctic rocks are formed by induced biomineralization and/or transformed by microbial activity [2]. These minerals are examples of inorganic biomarkers – traces left by living microorganisms due to their biological activity. However, if extensive biomobilisation of elements occurs when microorganisms are biologically active and/or after their decay, the microorganism fossil formation could be observed [3]. Careful interpretation of SEM-BSE images revealing the ultrastructural features of mineralized cells is the most important criteria for the interpretation of fossilized microorganisms. In addition, Raman spectroscopy had confirmed previous analysis obtained with EDS regarding to the composition of the mineralized cell and their mineralized environment. Thanks to Raman application in this study, the presence of jarosite filling the pore is definitively confirmed in all the analyzed cases.

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Clinopyroxene eclogite-peridotite thermobarometry of the large Yakutian kimberlite pipes.

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Universal monoCPX barometer with (Nimis & Taylor 2000) CPX thermometers [1] reveal agreement with experiments to 100 kbar (~7 kbar) for peridotites (~10 kbar) for eclogites, with Opx estimates and new mono-garnet thermobarometry (Ashchepkov & Vishnyakova 2009). TP position of eclogites pyroxenites and diamond inclusions in mantle columns beneath the large pipes of Yakutia. Large pipes contain HT diamond bearing eclogites (Sobolev *et al.* 1996, Beard *et al.* 1996, Taylor *et al.* 2006, Shatsky *et al.* 2008) ~55-40 kbar in several clusters and more rarely TP estimates of eclogites refer to the convective branch >60 kbar. Pyroxenite TP trace LT branch, TP for ilm PXT coincide with inflection in lithosphere base. TP for Cr-diopsides of diamond inclusions of metasomatic affinity mark HT branches while orthopyroxene and Cr- pyrope (G10) diamond inclusions reflect LT conditions.

Eclogites melted by the rising plume melts produced hybrid Al-Cr-Na metasomatites in Alakite, Upper Muna and Mirninsky fields. Eclogites and hybrids signify the diamond potency as well as Cr- rich (G9-10) garnets.

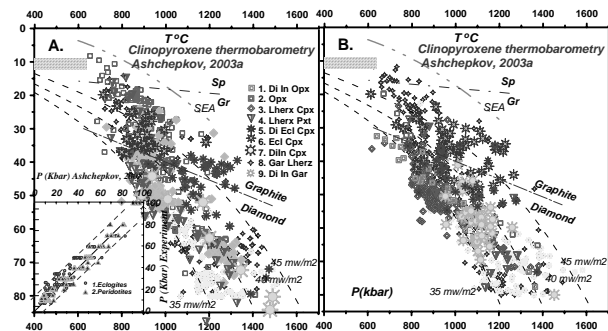


Figure 1. Mono TP estimates for eclogites, pyroxenite

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Quataron concept of nanoparticles formation and crystal growth

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Previously [1, 2] we have described a set of ideas and principles dealing with structural self organization of substance in the nanorange. These ideas have been collectively referred to as the 'quataron concept'. Central in this new concept is the idea that there are specific nanosize clusters arising under non-equilibrium conditions. These clusters cannot be described in terms of known states of substance and represent a separate intermediate phase ('hidden' phase) at the nanolevel. Clusters of 'hidden' phase named as a 'quatarons'.

Quatarons are dynamic structures constantly changing their forms. They are quasi-spherical in shape and have no symmetry restrictions. Quatarons are the basis for all kinds of equilibrium nanostructures from ordinary tetra- and octahedral groupings to the widely known fullerenes or dense dodecahedral and icosahedral clusters, colloidal, fractal particles. In particular, quatarons are fullerenes predecessors.

Physically quatarons are pre-crystallization clusters of the 'transient' phase. It has been found that clusters more than ~1.2 nm in size can become potential centers of crystallization. Only such clusters contain a minimal number of atoms necessary for crystal nucleation. At the same time, crystals grow by smaller clusters (quatarons), which are transformed to 'two-dimensional' nuclei already on the growing crystal surface. Quatarons are ideal as growth units: chemical composition of quatarons is the same as that of crystals, topologically quatarons are close to structural modules of crystals, variability of the structure allows quatarons to join any crystal surface. As a result we have to revise a number of outdated ideas on crystal growth theory.

Quatarons as objects which properties are determined by quantum-mechanical laws, on the one hand, and laws of classical physics, on the other hand, determine the originality of the nano-state of matter. Uniqueness of quatarons consists in that they bear lines of live organisms and live matter. In particular they as well as live cells are capable to divide at achieving certain sizes. Their role as nano-reactors of concentration and synthesis of new compounds, including biomolecules of the elementary elements of live matter is unique [3].

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[3] Askhabov (2008) *Doklady Biological Sciences* **418**, 50-52.

Arsenic mobilization in acid mine drainage from the Tinto Santa Rosa Mine, Iberian Pyrite Belt, Spain

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The waters and sediments of the acidic discharge of the Tinto Santa Rosa abandoned mine in the Iberian Pyritic Belt (SW, Spain) were studied to characterize the natural processes controlling arsenic attenuation in acid mine drainage waters.

Variation in water composition and pH from the acid mouth downstream was characterized by a pH decrease, accompanied by a systematic decrease in ferrous iron, total iron, As(III), As(V) and total arsenic concentrations. This evolution indicates that along the stream As(III) and Fe(II) were respectively oxidized to As(V) and Fe(III), and the latter precipitated as schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_{5.5}(\text{SO}_4)_{1.25}$), goethite (FeOOH) and jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), which partially sorbed the aqueous As(V).

The total arsenic content associated with the bed-stream sediments was determined by total acid digestion. Results showed a high arsenic content in the solids, present mainly in its pentavalent state based on arsenic K-edge XANES analysis. Least-squares fitting (LSF) of XANES spectra yielded evidence of changes in As speciation along the stream and in depth in the sediments. Comparison of the sediment mineralogy, arsenic concentration, and arsenic speciation showed that the highest arsenic concentrations were associated with sediments made up mainly of schwertmannite.

Reactive transport modelling coupling advective flux and the main chemical reactions observed in the field was performed using the PHREEQC code [1]. Despite the simplicity of the considered model, the kinetic expressions of the processes related to arsenic attenuation reproduced well the observed arsenic mobilization data along the Tinto Santa Rosa acid discharge.

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Calcite cleavage surface reactivity in sulphate-rich waters

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Passive treatment systems use limestone to remediate Acid Mine Drainage (AMD) waters with high metal and sulphate contents. Geological sequestration of CO₂ in rock formations containing brines rich in sulfate has also been proposed. Gypsum precipitation on dissolving calcite surfaces may occur in both types of systems.

In this study, the dissolution of the (104) calcite cleavage surface was investigated by means of ex situ VSI (Vertical Scanning Interferometry) measurements using flow-through and batch experiments at pCO₂ = 10^{-3.4} and (1) pH ranging from 1 to 7 in sulphate-free (HCl) and sulphate-rich solutions and (2) pH 3 in metal-free sulphate and metal-sulphate solutions. Also, solutions equilibrated with gypsum have been used.

In sulphate-free solutions, the dissolution of the calcite (104) cleavage surface follows the same trend previously reported from powder experiments (rate decreases from pH 2 to 6, becoming pH independent at pH 6-9), but the magnitude of the rates is about one order of magnitude smaller. Moreover, the calcite dissolution mechanism controlled by the formation and coalescence of rhombohedral pits that promote an overall surface retreat is observed. In the sulphate-rich solutions at highly acidic pH, the calcium released reacts with sulfate, yielding a solution that is supersaturated with respect to gypsum. The precipitation of gypsum forms a dense but porous layer of needle-like crystals that allows diffusion of products and reactants between the calcite surface and the solution.

At pH 3 and metal-free sulphate and metal-sulphate solutions, calcite (104) cleavage surface dissolution is similar than the rates at pH 3 in HCl solutions. The presence of divalent cations (Fe(II), Cu, Zn, Cd) in sulfate-rich solutions does not show a significant effect on calcite dissolution rate, regardless of gypsum precipitation.

Occurance of iron skarns in relation to A-type granites in SE Saqqez, western Iran

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The study area is located in southeast of Saqqez in the north of the Kurdistan Province, western Iran. In the southeast of Saqqez, there are two contrasting granitoid complexes (G₁ and G₂). G₁ granitoids are composed of alkali feldspar granite, syenogranite and quartz alkali feldspar syenite whereas G₂ granitoids are composed of monzogranite, granodiorite and tonalite. Geochemically, G₁ granitoids are peralkaline and their characteristics resemble the A-type granites, but G₂ granitoids are subalkaline (calc-alkaline) and metaluminous and their characteristics resemble the I-type granites. According to the geochemical classification scheme of [1], G₁ granitoids are ferroan alkali and ferroan alkali-calcic whereas G₂ granitoids are magnesian and calcic. Based on field geological evidence, petrographic studies and G₁ granitoids are ferroan, it seems that iron skarns are produced in contact with Permian limestones in south of Ranga-Rizhan and southeast of Hassan Salaran villages.

Ore minerals in the Ranga-Rizhan ore body are magnetite, hematite, pyrite, goethite and chalcopyrite. Magnetite is the predominant mineral and is produced in oxidation phase of high-temperature degree. Hematite is the production of supergene processes and according to [2] hematite mineral produce during martitization process from magnetite. Pyrite is the most abundant sulfide mineral in this ore and is produced after magnetite. Goethite is produced by atmospheric water during supergene process from the Fe-bearing minerals such as pyrite. Chalcopyrite minerals are seen very small but some of them are large.

Ore minerals in the Hassan Salaran deposit are magnetite, hematite, pyrite, goethite, chalcopyrite and rutile. The mineral assemblages in this deposit is very similar to the Ranga-Rizhan deposit except for existence of rutile. Rutile is produced in oxidation phase, but in the lower temperature degree than magnetite and after it.

[1] Frost et al. (2001) *Journal of Petrology* **42**, 2033-2048. [2] Ramdhor (1980) *Pergamon Press*, 1267P.

Validating geochemical models with isotopic data

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Numerical models are widely used to simulate biodegradation of organic contaminants. These models often involve complex redox conditions and degradation pathways. There is also a need to provide several degradation constants that are often poorly characterised in the field.

In order to verify the assumptions of numerical models, and the used parameters, we suggest to use isotopic data as an independent validating variable. The degradation constants used in the models are combined with laboratory enrichment factors to simulate plumes of light (^{12}C) and heavy (^{13}C) substances. The spatial distribution of the isotope ratio of each pollutant is calculated directly from the concentrations of light and heavy isotopes.

As an example we selected one of the few sites where numerical simulation were done and isotope data were measured : the Dover site (USA). The isotopic data are given only for PCE and TCE and show significant but small changes at only few points [1]. We compared a simulation done by Clement *et al.* [2] and a simulation done with our approach called MIKSS [3]. After a fitting procedure, both models are able to nicely reproduce the spatial distributions of PCE, TCE, cDCE and VC for a source active since 40 years. However as both model show some quite different degradation constants, the future evolution of the plumes will differ among the models. The simulated isotopic data are completely different between both models, with the MIKSS approach being much closer to field results than the simulation by Clement *et al.* In fact, in the MIKSS approach the degradation of the chlorinated products occur in a very small zone while it is supposed to occur over the whole plume for the Clement *et al.* model. This large zone of degradation produces a very important increase of $\delta^{13}\text{C}$ values, that does not exist in the field.

This work has also important consequences on the the treatment techniques that may differ according to the degradation hypotheses. Simulations at other sites, without $\delta^{13}\text{C}$ data, but with electron acceptors maps, show that very reduced degradation cores are the predominant pattern.

[1] Sherwood-Lollar *et al.* (2001) *Env. Sci. Technol.* **35**, 261-269. [2] Clement *et al.* (2000) *J. Contam. Hydrol.* **41**, 113-140. [3] Atteia *et al.* (2007) *Env. Sci. Technol.* **42**, 3289-3295.

The role of degassing processes on the helium paradox

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It has been observed that some OIB have a lower He content than MORB. This seems to be in contradiction with the observation that OIB have a more primitive and comparatively higher $^3\text{He}/^4\text{He}$ ratio than MORB. This has been named the helium paradox. Many hypotheses have been proposed to explain this observation. Recently, non-equilibrium degassing have been proposed to be the key mechanism responsible for the lower He content in OIB than in MORB [1].

Based on published data on Loihi and new data from Pitcairn and Society hotspots, I show that all measured OIB show equilibrium degassing with respect to major volatiles (a CO_2 and H_2O dominated gas phase). I show that a non-equilibrium degassing model such as the one presented by Gonnermann and Mukhopadhyay (2007) [1] cannot be applied to Loihi and OIB basaltic glasses. This can be easily explained by a larger initial volatile content in OIB than in MORB. A higher volatile content results in a higher vesicularity in OIB than in MORB (i.e., a larger contact surface area between the gas phase and the melt, promoting equilibrium between the two phases).

After a complete examination of possible processes that may decrease the volatile content of quenched submarine OIB and MORB glasses, I identify a combination of three processes that are at the origin of the preferential He depletion in OIB than in MORB: (1) open system degassing, (2) the vesicle bursting effect occurring during sampling and sample preparation, and (3) the post-eruptive preferential helium diffusion loss from high vesicularity OIB glasses than from low vesicularity, more massive MORB glasses.

Based on existing data, I show that it is not possible to demonstrate that OIB sources have less helium than the MORB source.

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Stable Zinc isotope fractionation between plant and growth water

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Understanding the mechanisms of zinc uptake, transport and storage by plants is of critical importance as plants represent the entrance to the food chain and because of the potential of plants to extract Zn from contaminated soil. Whilst elemental analysis allows to document the distribution of Zn in water, soil and plant, one potential way to improve our understanding of uptake of Zn by plant from water and soil is to use stable zinc isotope ratios. Our objective was to investigate the effect of Zn level in growth solution and we have selected to compare the behavior of two closely related *Arabidopsis* species that differ in their tolerance and in the level of translocation from root to shoot for that purpose. The first species is the zinc-hyperaccumulating and zinc-tolerant *Arabidopsis halleri* and the second one is the non-hyperaccumulating and zinc sensitive *Arabidopsis petraea*. The zinc-hyperaccumulating species was found to present a higher $\delta^{66}\text{Zn}$ in the root (by about 0.5‰) and slightly lower $\delta^{66}\text{Zn}$ (by about -0.1‰) in the shoot than in the growth solution. Due to high shoot/root Zn mass ratio, the isotope depletion between the whole plant and growth solution is close to that observed between shoot and solution. The temporal variation in $\delta^{66}\text{Zn}$ of the growth solution was found consistent with a Rayleigh model for Zn uptake. The Zn isotope fractionation between solution and root for the zinc-hyperaccumulating plant was found larger for non-hyperaccumulating species and thus to depend on zinc transfer between the solution, root vacuole and periderm.

Source and evolution of Mo in the porphyry-Mo(Nb) deposit at Cave Peak, Texas

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Although the general principles leading to porphyry-Mo mineralization are relatively well understood there is little agreement regarding the source Mo in these deposits. Based on the observation that basement rocks in the vicinity of Mo porphyries in the USA and Norway host local Mo impregnations of various age it has been suggested that these represent large-scale crustal anomalies and that the Mo contained in the porphyries was for the short term derived from the crust (and not from coexisting mafic magmas, as seems to be case in porphyry-Cu deposits).

At the Cave Peak deposit [1], which formed ~36 Ma ago during the initial stages of the Rio Grande Rift, anomalously high Mo concentrations in the mineralizing magmas can be linked directly to mafic alkaline rocks exposed in the nearby Marble Canyon stock. Melt inclusions hosted by apatite, olivine, clinopyroxene and quartz in rocks ranging from nepheline-bearing monzogabbro (50 wt% SiO₂) to rhyolite (76 wt% SiO₂) were analyzed by LA-ICP-MS for 27 major and trace elements. The most mafic melt inclusions analyzed are nepheline monzosyenitic in composition (~50 wt% SiO₂) and have a geochemical signature similar to that of ocean island basalts. Incompatible trace element abundances define continuous trends reaching up to 100 times average upper continental crust, indicating element enrichment through fractional crystallization of the mafic input magma. Molybdenum increases from 4 ppm in the most primitive melts to 10-12 ppm in melts immediately before Mo mineralization. During ore formation the Mo content of the melt decreased gradually back to 5 ppm, in accord with fluid/melt partition coefficients of 17-20 determined on coexisting melt and fluid inclusions in aplitic rocks of the Marble Canyon stock. A high sulfur fugacity in the mafic input magma is indicated by early pyrrhotite saturation. To account for the 0.4-1.5 Mt Mo present in the Cave Peak deposit a volume of $\geq 1.4\text{-}5.2 \text{ km}^3$ pre-mineralization melt (12 ppm Mo) is needed, or $\geq 3.4\text{-}12 \text{ km}^3$ of mafic input melt (4 ppm Mo).

[1] Sharp (1979) *Economic Geology* **74**, 517-534.

Tracking lower crustal events with Re-Os isotopes of granulite sulfides

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The composition of the lower crust, sampled by granulite xenoliths, provides critical constraints on the tectonothermal evolution of continents. Granulite whole rock Re-Os isotope systematics are corrupted by crustal assimilation and do therefore not yield meaningful ages [1]. While *in situ* U-Pb geochronology on zircon or monazite in granulites has proven to be a useful tool [2] to date events such as initial crust formation and later mafic underplating or accretion [3], not all granulites carry these minerals. We are analysing Re-Os isotopes and major-elements of single sulfides (pyrites) in kimberlite-entrained granulite xenoliths from the central Slave craton in order to assess whether useful age and petrogenetic constraints can be obtained from these minerals. The granulites have mafic to peraluminous compositions, with variable $\delta^{18}\text{O}$, SiO_2 and $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ [4].

Preliminary results show Ni contents of most sulfide grains <1 at%, whereas one grain has 6.7 at% Ni, compared to <<1 at% in kimberlitic pyrite. Re and Os contents are distinctly lower (median 135 and 9 ppb, respectively) and $^{187}\text{Re}/^{188}\text{Os}$ higher (140) than in sulfides in eclogite xenoliths from the same locality (620 and 70 ppb, respectively, $^{187}\text{Re}/^{188}\text{Os} = 50$), interpreted to have MORB protoliths.

In the Re-Os isochron diagram sulfides show some scatter likely due to assimilation of older crust, and several generations of sulfides may occur in a single xenolith. The Ni-rich grain lies on a trend of pre-entrainment (ca 90 Ma) sulfide introduction into a high-temperature mantle eclogite, possibly documenting trans-lithospheric effects of events precursory to kimberlite magmatism. Several sulfide grains lie along 3.3 or 2.65 Ga model isochrons corresponding to the age of lower crustal formation/metamorphism [5]. Others plot about a 2.2 Ga model isochron, the age of the Malley-McKay dike swarms previously linked to zircon growth in lower crustal xenoliths [3]. Lower Re and Os contents but higher $^{187}\text{Re}/^{188}\text{Os}$ may indicate that the protoliths to the granulites crystallised sulfides prior to emplacement in the central Slave lower crust.

[1] Saal *et al.* (1998) *Nature* **393**, 58-61. [2] Simonetti *et al.* (2006) *Int. J. Mass Spec.* **253**, 87-97. [3] Davis (2003) *Geology* **25**, 343-346. [4] C. Krauss, unpubl. data. [5] Davis *et al.* (2003) *Lithos* **71**, 541-573.

Thermobarometric implications of clinopyroxene chemistry in the Plio-Quaternary magmas of Gran Canaria (Canary Islands, Spain)

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New evidences on the Plio-Quaternary volcanism in Gran Canaria (4 Ma to recent) [1] have provided a complete framework of petrographic, chemical, isotopic and thermobarometric data that allows to reinterpret the recent evolution of this island. In this work, bulk rock and mineral chemistry have been used to define P-T paths of the ascending magmas based on clinopyroxene (cpx)-melt thermobarometric calculations following the model of Putirka *et al.* [2].

Plio-Quaternary pristine melts separated at mantle depths (P~13 kbar and T~1250 °C) and then rised towards the surface by early adiabatic ascent. Above the MOHO (located at ca. 15 km depth), a first group of magmas continued rising by the same P-T ratios but with a shift towards lower T (~1150°C). This is interpreted as the effect of intrusion in the colder fragile oceanic crust. Instead, a second group of magmas stagnated close to the mantle-crust discontinuity (P~4 to 6 kbar; 12 to 20 km depth). Most of the ponded pristine magmas are characterized by the presence of reverse zoned cpxs, with green cores of salitic composition surrounded by brown rims classified as diopsides. Petrographic and chemical features of such reverse zoned cpxs favour a xenocrystic origin of the green cores, likely related to magma mixing or mingling processes. Subsequent uprising of this second group of magmas through the crust was not continuous but occurred in a spread way.

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[1] Aulinas (2008) PhD Thesis, Univ. Barcelona. [2] Putirka *et al.* (2003) *Am. Min.* **88**, 1542-1554.

**‘Smart Water’ as wettability modifier
in carbonate and sandstone:
A discussion of similarities in the
chemical mechanisms**

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Waterflooding has for a long time been regarded as a secondary oil recovery method. In the recent years, extensive research on crude oil, brine, rock (COBR) systems has documented that the composition of the injected water can change wetting properties of the reservoir during a waterflood in a favorable way to improve oil recovery. Thus, injection of ‘Smart Water’ with a correct composition and salinity can act as a tertiary recovery method. Economically, it is, however, important to perform a water flood at an optimum condition in a secondary process. Examples of ‘Smart Water’ injection in carbonates and sandstones are:

1. Injection of seawater into high temperature chalk reservoirs
2. Low Salinity floods in sandstone reservoirs

The chemical mechanism behind the wettability alteration promoted by the injected water has been a topic for discussion both in carbonates and especially in sandstones. In this paper, the suggested mechanisms for the wettability modification in the two types of reservoir rocks are shortly reviewed with a special focus on possible chemical similarities. The different chemical bonding mechanisms of polar components from the crude oil onto the positively charged carbonate and the negatively charged quartz/clay indicates a different chemical mechanism for wettability modification by “Smart Water” in the two cases.

[1] Doust *et al.* (2009) Paper presented at: *The 15th European Symposium on IOR*, Paris 27-29 April.

**Trace element and Pb and Sr isotope
systematics in petroleum systems**

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The presence of trace metals in crude oils can cause severe problems in refineries as they may pollute the catalysts. However, relative and absolute concentrations of metals can provide further insights into source rock characteristics and have been used for oil-oil/oil-source correlations. To date, most studies have focused on Ni and V which are primarily present as metalloporphyrins which reside in the heavier organic fractions of the oil. The presence of other trace elements in petroleum studies is well understood, but considerable fractions might be entrained in the crudes as salts/brines, formation waters and/or mineral matter. Radiogenic isotope systematics (Sm-Nd and Re-Os isotopes) have also been used in the field of oil-source correlations and for dating of hydrocarbon accumulations.

In the current study a large number of trace elements and Sr and Pb isotopes were analysed in a selection of crude oils/condensates of variable maturity and degree of biodegradation, from several petroleum systems around the world. The oils were ashed in pressurised quartz vessels in a High Pressure Asher (HPA) system. Sr and Pb isotopes were measured by TIMS and MC-ICPMS, respectively, and trace element abundances by ICP-MS. Good accuracy and precision was obtained for V, Cr, Ni, Cu, Co, As, Rb, Sr, Ba, Pb, Mo, Th, U, Zr as inferred from replicate analyses of international oil and coal standards.

Most of the trace metals show negative correlations with API gravity, which may extend the use of metals in oils as potential correlation and classification tool beyond Ni and V. Pb and Sr isotope compositions of the oils are variable, even amongst oils from the same petroleum system, and show no obvious relation to provenance or age of the oils. The similarity between isotope ratios of a crude oil and its related formation water, but also between whole oils and acid leachates, poses the question of which phases contribute to the Sr and Pb isotope systematics of the oils. This will be discussed in more detail.

Chemical analyses of lipids preserved in Iron Age pottery from Bibracte, France

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Bibracte is a Late Iron Age *oppidum*, or fortified city, at the Mount Beuvray in Burgundy, France. Carbonized residues in recovered ceramic vessels suggest that they were used for cooking or storage of foodstuffs. Here we present the results of the first chemical investigation of organic residues from 11 potsherds. The lipids preserved in the interior of the vessels and those absorbed in the ceramic matrix were extracted with organic solvents, separated in fractions, derivatized and submitted to GC-MSD and GG-C-IRMS analyses.

The GC-traces of all samples show a series of straight chain fatty acids in the C₉ to C₂₄ carbon number range, excluding C₂₁ and C₂₃. The main saturated fatty acids are the C_{12:0}, C_{14:0}, C_{15:0}, C_{16:0}, C_{17:0} and C_{18:0} acids, maximizing at C_{16:0} with generally clearly greater abundance of C_{16:0} than C_{18:0}. These fatty acid distributions are typical of degraded fats, suggestive of animal origin. Small to trace amounts of C_{10:0}, C_{11:0}, C_{13:0}, C_{20:0} and C_{22:0} acids occur in all samples. The only unsaturated acids identified were C_{16:1} and C_{18:1}. Terminally, branched iso and anteiso b-C_{15:0} acids elute between C_{14:0} and C_{16:0}. Apart from trace amounts of C_{18:2}, no polyunsaturated fatty acids were detected. The δ¹³C values of the fatty acids for all samples ranged from -31.2 to -25.7‰ VPDB, which encompasses the range predicted for an ecosystem based on C₃-nutrition. The δ¹³C values of the major fatty acids were compared with the isotopic fields of preindustrial animal and vegetable fats (δ¹³C_{FA} value of modern material +1.6‰). Most samples plot in the δ¹³C_{16:0} vs. δ¹³C_{18:0} and δ¹³C_{18:1} vs. δ¹³C_{18:0} fields of preindustrial ruminant milk, and young suckling calf/lamb and pig adipose. The identification of plant and animal C₂₈₋₂₉ sterols (campesterol, β-sitosterol, cholesterol, cholestanol) and plant epicuticular waxes (C₂₅, C₂₇, C₂₉, C₃₁, and C₃₃ n-alkanes and C₂₂, C₂₄, C₂₆, C₂₈, C₃₀, C₃₂ and C₃₄ n-alkanols) in the TMS-derivatives indicate that the vessels contained both animal and plant material.

[1] Paunier *et al.* (2004) *Bibracte* **8**. [2] Spangenberg *et al.* (2006) *Jour. Arch. Sci.* **33**, 1-13.

Metal and isotope dispersion in an abandoned heavy metal mine: Callahan, Maine, USA

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The Callahan Cu-Zn-Pb mine produced ~800,000 tons of ore hosted by Cambrian volcanic and volcanoclastic rocks. The mine was sited in a marine estuary and is now a US-Environmental Protection Agency Superfund site [1]; ~5 million tons of sulfide-bearing waste and unprocessed ore remain on-site bordering ponds and tidal flats. Mineralogy, trace element, and Pb-Sr-Nd isotope geochemistry document metal redistribution among host rocks, ore, tailings and waste piles, stream and estuary sediments, and the aquatic biota.

Pyrite from waste piles is enriched in Cu, Pb, and As, and sphalerite is enriched in Cu, Pb and Cd. Sediment cores from open estuary ponds at the site contain <1-3% pyrite, and rare sphalerite; sediments vary in Zn (88-1590 ppm), Cu (14-268 ppm), Pb (4-1070 ppm), As (4-55 ppm), and Cd (up to 83 ppm). Bivalve shells from estuary sediments have variable contents of Cu (5-74 ppm), Zn (6-443 ppm), and Pb (1-76 ppm). Clam tissue at the site has 0.71 to 43 ppm Pb (US-EPA, 2008); some values exceed the US-FDA safety tolerance level (1.7 ppm Pb). Pb isotopes of estuary sediments (²⁰⁸Pb/²⁰⁷Pb = 2.4223-2.4696; ²⁰⁶Pb/²⁰⁷Pb = 1.1544-1.1965) [2, this study] span a range from host volcanic rocks (²⁰⁸Pb/²⁰⁷Pb = 2.4817-2.5466; ²⁰⁶Pb/²⁰⁷Pb = 1.2254-1.2537) to massive sulfide, and tailings (²⁰⁸Pb/²⁰⁷Pb = 2.4224-2.4350; ²⁰⁶Pb/²⁰⁷Pb = 1.1566-1.1646). Pb isotope data analyses of bivalve shells (²⁰⁸Pb/²⁰⁷Pb ~ 2.43-2.45, ²⁰⁶Pb/²⁰⁷Pb ~ 1.16-1.18) are within the range of the ores and tailings. Sr and Nd isotope compositions also link the host rocks, ore lenses and clam shells. The clams likely incorporated Pb and other metals by ingestion of fine sulfide and silicate particles in addition to dissolved metals. Within and immediately adjacent to the mine site the metals originated from sulfide weathering and metal mobilization. By contrast, at a distance of ~1 km from the mine site the impact of mining is essentially undistinguishable from the geogenic background.

[1] MACTEC Engineering & Consulting (2007) *Site Inspection Prioritization Report*, v. 1-3. [2] Boeckeler & Gaudette (1996) *Geol. Soc. America, Abs.* **28**, 40.