

Studies of the source of laser-induced isotopic bias in LA-MC-ICP-MS

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Coupling laser ablation sampling with MC-ICP-MS analysis allows Cu and Fe isotopic compositions to be measured rapidly in sulphide minerals with 2% precision as low as 1 part per 10,000 (1 epsilon unit). This precision is much smaller than the variation typical in many sulphide ore deposits, allowing isotopic variations to be detected in a wide variety of mineralised systems on single-grain to deposit-wide scales [1,2,3]. These data offer, for the first time, a direct approach to identifying the source of metals in hydrothermal deposits. Potentially, they also allow isotopic fingerprinting of particular ore depositional environments, which may possess important exploration significance.

A major obstacle to performing laser-based metal isotopic analyses is a systematic and ablation-time-dependent bias (up to 40%) in the isotopic measurements. Correcting this bias can be achieved by referencing to analyses of an isotopically homogeneous, matrix-matched standard. However, the requirement for isotopic mineral standards severely limits the applicability of the technique, and frequent external standardisation reduces sample throughput.

To determine whether the bias in the laser-based analyses occurs during ablation (i.e., non-isotopically stoichiometric ablation) and/or during post-ablation processes occurring in the ICP, a copper target was ablated under a range of analytical conditions (wavelength, pulse energy, ablation gas). The ablated particulates were filtered from the gas stream, dissolved and analysed on a Neptune MC-ICP-MS, employing external normalisation using Ni to correct instrumental mass bias. Biases in the measured isotopic composition of the dissolved particles relative to the target material indicate that isotopic fractionation occurs during the ablation process, but only to a small extent. This leaves open the possibility that isotopic fractionation takes place to a significant degree in the ICP, as demonstrated for elemental fractionation [4], perhaps through the interplay of incomplete ionisation of ablated particulates and a systematic change in ablated particle size distribution during ablation.

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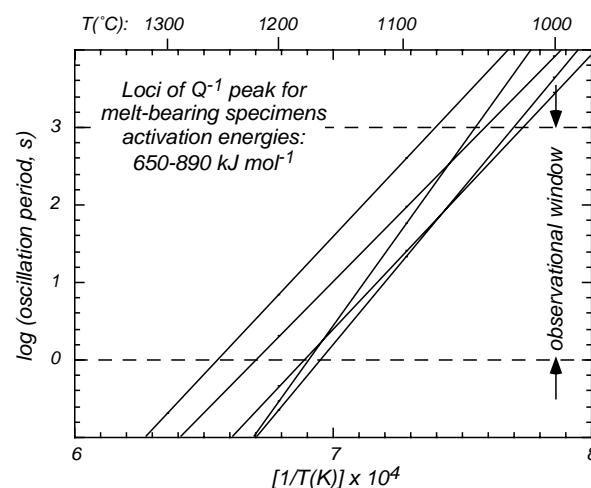
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Systematics in the seismic wave attenuation of partially molten olivine aggregates

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A suite of melt-bearing olivine specimens has been prepared by hot-isostatic pressing of natural or synthetic Fo_{90} powders mixed with powdered basaltic glass. The resulting specimens have been tested with torsional forced oscillation/microcreep methods at 50°C intervals during staged cooling. Relatively narrow grain-size distributions determined after testing by EBSD indicate a generally high degree of textural equilibrium with mean grain sizes of 9-52 μm . Melt fractions vary from 0.4 to 3.7% at the highest temperatures (1240-1300°C) reached during hot-pressing and mechanical testing. SEM and TEM observations indicate that the melt is distributed throughout an interconnected network of grain-edge tubules, some larger pockets and wetted grain boundaries – in accord with previous observations. Re-equilibration of one sample after testing showed that between 1300°C and 1200°C the melt distribution survives largely unaltered, most of the crystallisation occurring between 1200°C and ~1130°C.



The dissipation (Q^{-1}) measured at high temperatures on each of these specimens consists of a broad peak superimposed upon a monotonic background that is enhanced relative to that for melt-free materials. The peak moves across the observational window from 1 to 1000 s period without changing its shape as T decreases from 1170-1260°C (specimen dependent) to 1020-1080°C (Figure). The peak height is positively correlated with melt fraction, whereas its width remains essentially constant. Such systematics allow evaluation of alternative microscopic models for the melt-related enhancement and localisation of attenuation - including stress-induced melt redistribution and melt-facilitated grain-boundary sliding.

Lu-Hf isotopic systematics of subducted ancient oceanic crust: Roberts Victor eclogites

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The possible role of eclogite in mantle melting received increasing attention during the last years. However, this entity is difficult to constrain by theoretical modelling as effects of subduction and mantle metasomatism that are likely to change the composition of subducting oceanic crust are not well known. Eclogite xenoliths from the Roberts Victor kimberlite, South Africa, were among the first for which an origin as subducted altered oceanic crust was proposed. This hypothesis is based on oxygen isotopic studies as well as on trace element characteristics that revealed striking similarities to oceanic gabbros and basalts that experienced seawater alteration at different temperatures. Many of the Roberts Victor eclogites yield late Archean ages (2.7 to 3.2 Ga, by different methods) and Hf_(CHUR) model ages from this study confirm these. Thus, they may represent some of the earliest oceanic crust available for study.

Here, we report on Lu-Hf isotopic data from an ongoing study on diamondiferous and non-diamondiferous eclogitic xenoliths. The data are combined with evidence from $\delta^{18}\text{O}$, major and trace elements as well as Sr and Nd isotopic ratios to arrive at constraints on the reservoir of subducted oceanic crust within the Earth's mantle and to speculate on its role in melting processes. The samples show a large range of ϵ_{Hf} and ϵ_{Nd} values of -9.2 to 166 and -22 to 484, respectively, at the time of kimberlite eruption (120 Ma). Most samples plot below the mantle array, but the variation extends to more unradiogenic ϵ_{Nd} values, typical of continental crust. These very unradiogenic samples show evidence of cryptic metasomatism, unrelated to the kimberlite, that affected the Sm-Nd isotopic system, while the Lu-Hf system remained undisturbed. Two eclogites have extremely radiogenic Nd and Hf isotopic composition, very unradiogenic, identical $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70091 and depleted trace element patterns, indicating that these samples are residues of melting early in their history. Our first results show that the reservoir of subducted oceanic crust in the mantle may have a very variable composition. However, given the good correlation between Nd and Hf isotopes in terrestrial basalts, the contribution of eclogite melts to these basalts has to be relatively minor.

Comparison of isotope dilution and laser ablation REE measurement of Geochemical Standard Reference Materials

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The rare earth elements (REE) are important to our understanding of many geochemical processes, including mantle evolution, origin of volcanic and metamorphic rocks, sedimentary systems, and oceanography. In many of these systems, REE abundances vary on small spatial scales. In such cases, it is often important to use in situ micro-analysis techniques such as laser ablation ICP-MS (LA-ICP-MS) or secondary ion mass spectrometry (SIMS), where it is possible to analyse REE abundances with high spatial resolution. However, in situ analysis relies heavily on homogeneous matrix-matched standards such as the NIST- 610 and 612 glasses. Uncertainties in accepted values for these standard glasses translate directly to the accuracy in measured REE abundances. For high precision REE analyses, particular where the anomalous behaviour of individual REE is used as a tracing tool (e.g. Eu, Ce anomalies) uncertainties in accepted standard values may contribute to considerable inaccuracy. One way to test the accuracy of LA-ICP-MS analysing method is to compare the data with high precision data obtained from isotope dilution (ID). We present isotope dilution MC-ICP-MS analysis of REE in a number of geochemical reference materials: NIST- 610, 612, and 614, BIR-1, BCR-1, BCR-2, BHVO-1, BHVO-2, BHVO-2G, SCR-2G, W-2, and WS-E powders and glasses. We also present data from LA-ICP-MS Quadrupole analyses of glass reference materials. Our data shows that there are discrepancies between LA-ICP-MS and isotope dilution data, an artefact inherited from calibration and not from isobaric interferences.

Laser micro-sampling (offline) for ID and $^{143}\text{Nd}/^{144}\text{Nd}$ analyses is also a potentially powerful tool for rapid and precise high spatial resolution analysis of the REE and Sm-Nd isotopic compositions. Little is known about possible mass fractionation of REE laser ablation sampling. With this technique it may also be possible to decouple elemental fractionation occurring in the plasma from fractionation occurring during laser ablation. As such, we have explored the potential of offline laser sampling of silicate glasses and minerals directly into acid spiked with Sm-Nd or REE mixture spikes and subsequent analysis by MC-ICP-MS after chemical separation of LREE.

^{182}Hf - ^{182}W , accretion of the Earth and the origin of the Moon

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The time scale and functional shape of Earth's accretion and core formation may be investigated using the ^{182}Hf (half-life: 9 Ma)- ^{182}W extinct nuclide chronometer (Jacobsen and Harper 1996, Harper and Jacobsen, 1996) because the Hf/W ratio is fractionated both strongly and uniquely by core formation. W is partitioned into the metal phase and Hf into the silicate mantle during the formation of the Earth. The core will develop a deficit in ^{182}W , while the silicate Earth will develop a ^{182}W excess during the early stages of accretion. If the accretion process continues for more than 50 Ma then this difference may be erased. Here we present new model results for the Hf-W system, as the two most important parameters used for such calculations in the past have now been drastically changed by the new results of Yin et al. (2002). First, according to the new results, the silicate Earth has a radiogenic W isotope signature of $\epsilon_{\text{W(CHUR)}} = +2$ (in contrast to the previous value of $+0.2 \pm 0.3$ of Lee and Halliday (1996)), and second, the initial solar $^{182}\text{Hf}/^{180}\text{Hf}$ has been lowered from 2.75×10^{-4} (Lee and Halliday, 1996) to 1.0×10^{-4} (Yin et al., 2002). The models are based on isotopic and chemical mass balance between a primitive nebular reservoir, the primitive mantle and the core. The results of using a variety of accretion histories from dynamical accretion models have the following features in common: 1) they can produce the observed ϵ_{W} anomaly in the silicate Earth provided the initial growth stage of the Earth is rapid ($> \sim 65\%$ completed in the first 10 Ma), 2) the remaining growth must be effectively finished in another 20-40 Ma. The W isotope composition of the Moon has now been revised from $\epsilon_{\text{W}} = +6$ down to a value of only 1.3 ϵ_{W} -units higher than the Earth (Lee et al., 2002). As late (> 50 Ma) giant impacts result in a ϵ_{W} anomaly in the Earth of less than 0.5 ϵ_{W} units higher than chondrites, it is necessary to have the Moon form by a giant impact at ~ 25 -40 Ma. A scenario in which the Earth's core is formed after 60 Ma and the Moon simultaneously by a giant impact is now implausible.

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Trace-metal dynamics in wetland sediments; Laboratory measurements and numerical simulations

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Mobility of trace metals in wetland sediments is controlled by the vertical redox profile that develops in these sediments. This profile is determined by the reactive transport of different electron acceptors in the sediments. Transport is affected by diffusion and advection, and for oxygen also the transport through the roots of wetland plants. Reactions affecting the electron acceptors include their utilisation by bacteria during the degradation of organic matter. The objective of our research is to obtain a mechanistically based understanding of the dynamics of trace metals in wetland sediments. The long-term goal is to assess how changes in either water quality or vegetation affect the sequestration or release of trace metals in wetland sediments. For this purpose we are conducting laboratory experiments and developing a numerical model, to gain a better understanding of the processes that affect the redox profile in wetland sediments and the fate of contaminant metals in these same sediments. Vertical concentration profiles of the key redox species, as well as that of trace metals, are being measured in microcosms maintained in a greenhouse in which cattails are planted at different densities in a sandy soil. A solution containing nutrients, various terminal electron acceptors, and trace metals is pumped at a constant rate into the microcosms. Water level above the sediment surface is maintained constant by allowing the excess fluids to drain from the microcosms. Infiltration is controlled by draining water from the bottom of the microcosms at a constant rate using peristaltic pumps. To determine the effect of the carbon load, acetate is applied to one microcosm as an external carbon source, while another microcosm relies only on root exudates as a carbon source. The vertical concentration profiles are being monitored in all microcosms using gold-amalgam microelectrodes and cyclic voltametric techniques. This is done over several diurnal cycles in order to determine the effect of plant activity on these profiles. A reactive transport model has been developed, consisting of a set of coupled, steady state mass balance equations, accounting for advection, diffusion, bioturbation and reaction of an organic substrate, electron acceptors, corresponding reduced species, and contaminant metals of interest. The model accounts for the effect of plants including the release of oxygen and uptake of nitrogen by plant roots, as well as flow induced by evapotranspiration. Model outputs are then compared to the measured concentration profiles to provide guidance for further model refinement.

Pb-U-Th isotopic evolution of the D'Orbigny angrite

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In order to understand the early evolution of our solar system high resolution dating of meteorites is necessary. Since most of the meteorite classes were formed in the first 50 Ma (1%) of our solar system's history, high precision dating is necessary. In particular, relative dating using extinct isotopes like the Mn-Cr system hinges on an absolute calibration. Only the Pb-Pb system can serve this purpose, but few such high precision Pb-Pb ages have been reported (1-3). Some of them have been reported with an age precision of 0,01%, which requires a measurement precision of 0.03% for the ²⁰⁶Pb/²⁰⁷Pb ratio--reached only by using the faraday collector and a tight control of the mass fractionation.

In the D'Orbigny meteorite for which we have obtained Pb-Pb ages, such a high precision has not yet been achieved because the Pb concentration in the dated pyroxene is extremely low (between 7 and 17 ppb). Four pure mineral separates of clean pyroxenes (of about 15 mg each) yielded only 100 to 250 pg of Pb that was too little to run on the faraday collector. Instead, measurement was made with an ion counter giving a typical error for the ²⁰⁶Pb/²⁰⁷Pb ratio of 0,1 to 0,2 % and translating into an age error of 2 to 4 my.

D'Orbigny is the sixth angrite to be identified and the largest of this rare meteorite class. Until now high-precision Pb-Pb data only has existed only for Angra dos Reis and LEW 86010 (1). Two of the D'Orbigny pyroxenes are from the groundmass and the other two are idiomorphic and grew inside druses-like cavities. The latter are considered to be 100% pure while the former may contain some inclusions. Also, we analysed one sample of anorthite, which had a Pb isotopic composition close to that of terrestrial Pb, and may be dominated by terrestrial Pb.

The Pb-Pb age of the two matrix pyroxenes are 4549 ± 2 Ma and 4557 ± 2 Ma; however, the U-Pb ages are distinctly discordant for the younger pyroxenes. The druses pyroxenes gave Pb-Pb age of 4555.4 ± 1.9 Ma and 4556 ± 4 Ma, with ²⁰⁶Pb/²⁰⁴Pb ratios of 522 and ~2000, respectively. Furthermore, the U-Pb ages for both these pyroxenes are, within the uncertainties of the correction parameters, concordant, as is a Th-Pb age for the second analysis. Unfortunately, the relatively large error of its Pb-Pb age reflects the small amount of Pb on the filament.

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Including stagnant zones in order to model overlapping redox processes occurring in a shallow sandy aquifer

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Partial equilibrium was used by Jakobsen and Postma (1999) to model a sequence of redox processes in a shallow aquifer using the 1-D transport capability of PHREEQC (Parkhurst and Appelo, 1999). Partial equilibrium implies overall kinetic control, due to slow breakdown of complex organic matter, while the anaerobic terminal electron accepting processes (TEAP's) are determined and controlled by the thermodynamics of the system. The TEAP's approach equilibrium showing small (negative) Gibbs energies that are close to constant for a given process in a given system.

The model in Jakobsen and Postma (1999) did not simulate the observed H₂ levels, due to the assumption of equilibrium, and could not fully simulate the observed overlap of sulfate reduction and methanogenesis. If a minimum energy yield, rather than true equilibrium, is used for the different TEAP's, there is no increase in the simulated overlap, but reasonable H₂ levels are obtained, though the modelled H₂ span is too wide, with values that are too high in the methanogenic zone. This corresponds to the apparent lack of available energy for methanogenesis if the observed concentrations of H₂ are used for calculating the available energy. This, and the lack of overlap in the model, indicate the presence of stagnant zones featuring more reduced conditions, next to zones with active groundwater flow.

Stagnant zones are readily included in PHREEQC, and the current model features stagnant zones in which the organic matter is added, leading to high H₂ concentrations and methanogenic conditions in these. H₂ and methane diffuse into the zones with flowing water where oxidation by sulfate or Fe-oxides may take place. If the oxidation of methane is controlled by the same K-value used for methanogenesis it would imply an energy loss for the microorganisms, which is not realistic. Furthermore the model fails to simulate the overlap of sulfate reduction and methanogenesis. Therefore it is necessary to implement a method in which both methanogenesis and methane oxidation are controlled by thermodynamics, but only occur if energy is gained from the process. The current version of the model is able to simulate the observed overlap of the redox processes, and the match to the observed H₂ concentrations is improved.

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Deformation assisted fluid migration in rocks

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The layman's notion that a solid rock is impenetrable to fluid flow is probably in many cases a more correct conception than the view expressed by geophysical textbooks listing finite, but often ridiculously small permeabilities for metamorphic and igneous rocks. In the absence of tectonically produced deformation with associated dilation and porosity generation, or porosity inflation due to devolatilization, most metamorphic and igneous rocks are probably impermeable. This also applies to well consolidated sedimentary rocks such as carbonates and evaporites as well as to many shales. Even in the presence of a finite porosity, the wetting properties of many natural fluid-rock systems prevent the formation of a connected porosity in the absence of cracks. Yet, introduction of external fluids to dry and impermeable volumes of the Earth's crust is a prerequisite for retrogressive metamorphism and may cause significant changes of the crust's physical properties, notably its density, rheology, and elastic properties. Clearly fluid migration through impermeable rocks must be intimately associated with porosity generation.

We present field observations and modelling results illustrating fluid migration promoted by hydrofracturing and reaction enhanced permeability respectively.

The early evolution of the Earth : core formation, mantle differentiation and volatile evolution.

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The early evolution of the completed Earth has been conditioned both by the building material and by the great impact which led to the formation of the Moon. This event has marked the final differentiation of the core and produced the mantle differentiation by the formation of a magma ocean. The present expression of that magma ocean is the upper mantle: the problem is to identify the present limits of this upper mantle. In a simple model it could be the fraction "above 650 km". However this probably conflicts with some characteristics of the present Earth as well as with energy fluxes and chemical mass balance considerations and with the result of recent two-level convection experiments.

The present trace of the early upper-lower mantle boundary is more likely to be identified with the tomographic surface at around 1000km depth, which corresponds to mantle mass fractions of 0.44 and 0.56 respectively for the upper and lower mantle. That separation corresponds to a chemical boundary for major elements, the upper mantle being silica-depleted. This difference is also apparent in isotopic signatures of some trace elements, notably the rare gases.

The silica depletion of the upper mantle is due both to the uptake of silicon, between ~10 and 24 Gpa, by the metal migrating to the core, and to the effect of partial melting on silicates, enriching the liquid in magnesium.

The Earth has been completed by a late veneer of material bringing the siderophile element content of the upper mantle and also part of the volatile elements. If we believe recent osmium isotopic data, that veneer resembled ordinary and enstatite chondrites but was unable to bring all the terrestrial volatile inventory, especially the water.

Hence it had to be followed by another veneer, probably of cometary origin, of much smaller size, which brought about half of the water and part of the terrestrial carbon and nitrogen.

The main differences between the Earth and Venus lay in the absence of a great impact, hence of a doubly convecting mantle, which led to complete mantle outgassing, and to the very small size of the cometary veneer.

Water mass pathways off the Argentine coast traced by REE concentrations and Nd isotopic composition

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Ocean circulation off the Argentine coast reflects the interactions between the energetic Deep Western Boundary Current originating from the northern Atlantic, recirculation loops involving different water masses such as the South Atlantic Central Water and the Antarctic Intermediate Water and Mode Waters recently formed in the Subantarctic Zone. Surface waters are also influenced by the freshwater discharge from the Rio de la Plata. As a result, water circulation in this region is very sensitive to variations in global circulation patterns on decadal or larger timescales, and monitoring these changes could provide an early warning system of impending changes in global circulation.

In addition to classical hydrological parameters, Nd isotopic composition of seawater is a powerful tracer to reconstruct present day pathways of water masses; furthermore, the imprint of this tracer in metalliferous sediments, fish teeth, or foraminifera shells is a good tool to reconstruct paleocirculations

We present here the Nd characteristics on vertical profiles collected at 13 stations between 35 and 40°S, in the framework of the Confluence 4 cruise (October 1994) and 4 stations collected along a section from Punta Arenas to 47°S-54°6' W, during ANTXVII/4 (Polarstern, 2000). Profiles obtained by Jeandel et al (EPSL, 1993) at 33°S-41°W and 49°39'S-33°23'W stations are also linked to the present work, in order to give the largest view of the Nd behavior in this area. Nd concentrations are oceanographically consistent, varying between 1.5 ng/l at the surface and more than 4 ng/l in deep waters. Nd isotopic compositions vary broadly, from $\epsilon_{Nd}(0) = -6.8 \pm 0.2$ (characterizing Rio de la Plata Waters) to -12.5 ± 0.3 (NADW at the northern entrance of the Brazil/Malvinas confluence area). The effect of the Rio de la Plata waters on the studied area is quantified. The change affecting NADW flowing southward ($\epsilon_{Nd}(0)$ values vary from -12.5 ± 0.3 at 30°S to $-11.3 \pm$ at 48°S) is due to a mixing of 81% of NADW with 19% LCDW. Similar mixing processes explain the Nd signal variation along the LCDW pathways. The conservative behaviour of the Nd signatures emphasizes the potential use of this proxy as tracer of past circulation.

Li isotope fractionation in the mantle

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Li is the lightest non-volatile element, with the largest relative mass difference between its stable isotopes, ⁷Li and ⁶Li. Alteration of the oceanic lithosphere both increases Li concentrations and its ⁷Li/⁶Li. Mixing of this material back into the mantle should impart a distinct Li isotope signature on sources that contain recycled material. Realisation of this promise has become more tangible with recent developments in plasma ionisation multicollection mass spectrometry (PIMMS). The Thermo Finnigan *Neptune*, PIMMS shows excellent stability and sensitivity for Li. Using rapid sample-standard bracketing, Li isotopes can be measured with better than 0.5 per mil reproducibility, at low concentration 10-20 ppb, with intense ⁷Li beams of 5-20 V. In tandem a chemistry that very effectively and rapidly separates Li from silicate matrix but quantitatively recovers Li has been developed using a two-column procedure with inorganic acid-methanol mixtures.

However, one further important issue needs to be addressed before Li isotopes can be effectively used as tracers of recycled material. It is possible, as has been well documented for oxygen, for example, that significant equilibrium isotope fractionations occur between host mantle phases and melt. Interpreting the Li isotope signature of mantle-derived melts requires a quantification of such fractionations. Work by Tomascak et al, 1999 and co-workers have demonstrated no systematic variation (within ± 1.5 per mil errors) within a suite of lavas related by olivine fractionation. This places some constraints on the possible magnitude of olivine-melt Li isotope fractionation, but significant isotope fractionations remain permissible within the bounds of the natural experiment. Tighter controls can be obtained studying the Li isotope compositions of co-existing phases from mantle xenoliths. We will present Li isotope data for olivine-opx-cpx-aluminous phase for garnet and spinel lherzolites, together with melt-olivine pairs for mafic lavas.

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Sr-isotope diffusion profiles from Alpine marbles: what do they mean?

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We have measured Sr-isotope profiles in calcite across phlogopite-bearing bands in marbles from the Central Swiss Alps (e.g. Figure 1).

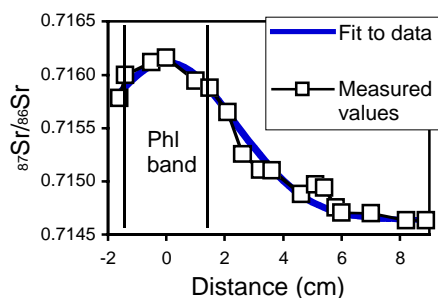


Figure 1. HT15, Lago del Naret, Ticino, measured by laser ablation multi-collector ICP. Most errors are within the size of the plotting symbols.

The integrated area beneath the profiles, coupled with the Rb/Sr of the mica bands, suggests that they contain ⁸⁷Sr built up since deposition of the limestones in the Triassic. However, the flat background to the profiles is higher than would be expected for Triassic seawater, indicating early diagenetic homogenisation.

The symmetry of the profiles, with inflection points at the edges of the mica bands, suggests fluid advection was negligible and exchange took place by diffusion alone. The data fit well to diffusion profiles that assume all the ⁸⁷Sr in the profile was originally contained in the high Rb/Sr mica bands. The Dt product for the exchange is $2.5\text{--}0.15 \times 10^{-4} \text{ m}^2$. Assuming exchange takes place by combined volume diffusion and grain boundary diffusion only, then the calculated time for exchange exceeds the age of the rock, and is unfeasible. Therefore exchange must have taken place *via* a faster process such as diffusion through a fluid phase on the grain boundaries. However, assuming an interconnected fluid, even with a low porosity, gives high D values, with consequently short exchange times of $\sim 10^{-2} \text{ Ma}$. This is very short compared with times envisaged for Alpine metamorphism (5–10 Ma?). Such discrepancies are also apparent from a limited number of similar studies elsewhere.

Either 10^{-2} Ma is the duration of fluid connection along the grain boundaries, or exchange took place over a longer duration due to a variety of causes. Sr-isotopic profiles across individual calcite grains are flat within error. Do these allow us to choose between these possibilities?

Late Archean komatiites and BIFs, Woodburn Lake Group, Churchill Province, Nunavut

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Komatiites and banded iron formations (BIFs) of the Woodburn Lake Group (WLG) comprise a metallogenically important component of a so-called platform greenstone belt, an assemblage of komatiite, iron formation, intermediate to felsic volcanics, and volcanoclastic-epiclastic sedimentary rocks, which formed in a subaqueous to shallow marine paleodepositional environment. WLG komatiites include texturally well-preserved lava flows (thin/distal) with massive, fine-grained B zone cumulates (MgO >40 wt%) overlain by coarse, random, olivine spinifex-textured A zone flow units (MgO >27 wt%). Locally B1 zones are also present. The BIFs occur in oxide, silicate and sulphide facies intimately associated with the komatiites, felsic volcanics and silicified tuffs and mudstones. A Re-Os isotopic and geochemical study of these late-Archean komatiites and BIF has as its goals the magmatic age and source characteristics of the komatiites and the relationship of komatiite to BIF/BIF-hosted gold mineralization, as typified by the possibly world-class Meadowbank and Meliadine occurrences.

Komatiites analyzed for Re-Os have high MgO (>30 wt%) in both spinifex and cumulate portions. Re and Os contents of some of the spinifex-textured komatiites are typical of komatiitic magmas, whereas; the cumulates have exceptionally low Re (0.05 ppb) and high Os (3.2–6.7 ppb) contents leading to exceptionally low ¹⁸⁷Re/¹⁸⁸Os (0.04 to 0.1) for komatiitic whole-rocks.

Re-Os isochron systematics are complex. Four cumulate B zone komatiites and a subset of the BIFs form a $2690 \pm 41 \text{ Ma}$ isochron in good agreement with a U-Pb zircon age on a interlayered rhyolite. The initial ¹⁸⁷Os/¹⁸⁸Os of this isochron is 0.1074 ± 0.0091 and establishes the BIFs as Archean and the WLG mantle source as having a slightly subchondritic time-averaged Re/Os typical of depleted Archean upper mantle. Spinifex-textured komatiites, some cumulates and mineralized BIFs fall on secondary subparallel arrays with 2450 Ma age and an elevated initial Os. This suggests that some spinifex textured rocks may have been preferentially reset by by crustal fluids 200–300 Ma after crystallization.

Biotite oxidation in the weathering profiles of granitic rocks: chemistry, mineralogy, and implications for elemental behavior

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Biotite was oxidized in the deep saprolitic weathering profiles of granitic rocks in a humid temperate climate. The mineralogy and chemistry of oxidized biotite were characterized by chemical analysis, electron microscopy, X-ray diffraction, thermal analysis, and radiogenic Ar analysis. The results showed that b_0 -dimension decrease, radiogenic Ar loss, and vermiculite formation are fairly synchronized with oxidation degree of ferrous iron. The chemical composition of oxidized biotite was modified by a non-stoichiometric removal of cations in the order $Fe > Mg \sim K$ to compensate for the charge imbalance induced by iron oxidation. The pervasive loss of cations and radiogenic Ar suggests their diffusion through oxidizing biotite in a non-expanded state. Iron oxidation and cation loss caused decrease in the b_0 -dimension with the formation of discontinuities as a conduit of the weathering solutions, resulting in partial vermiculitization (< 10%). The iron oxidation was nearly completed at the lower part of the profile concomitantly with rapid mineralogical and chemical modification to oxidized biotite which persists throughout the profile without further notable modification. Less-soluble oxidized biotite persisting in the weathered profiles may be one of the factors related to the discrepancy between laboratory and field dissolution rates of biotite. Cation release from biotite is governed in early stage by the formation of oxidized biotite, and later by its decomposition.

Correlation between Morphology and Isotopic Composition of Oxygen and Carbon of Calcite from Mezica Mines, Slovenia

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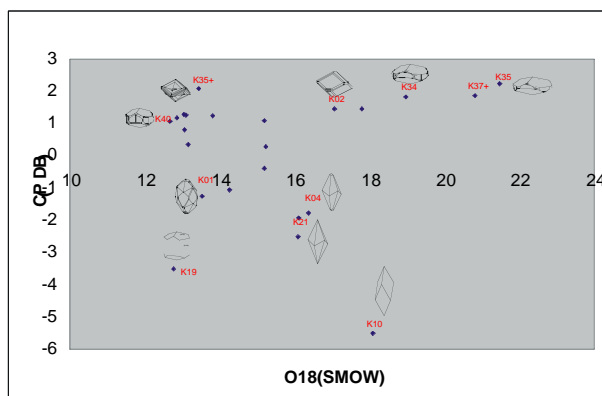
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Stable oxygen and carbon isotopic analyses of calcite from open carbonate veins, also containing wulfenite crystals, in Pb-Zn deposit Mezica indicate a close connection between morphology of calcite crystals and their isotopic composition (Fig.1).

Calcite crystals enriched with light oxygen isotope, which most probably precipitated from relatively high temperature hydrothermal solutions of non magmatic origin, show much more developed forms relative to low temperature calcites enriched with heavy oxygen as well as light carbon isotope.

Figure 1. Morphology of calcite crystals related to isotopic composition of oxygen and carbon.



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Nd-Sr-Pb isotopic compositions for red residua underlying dolomites in Karst Terrains of Guizhou Province

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Well-developed, clay-rich soils are widespread in the global karst terrains, for their genesis has been debated for several years. The article presents the Nd-Sr-Pb isotopic composition for Pingba red residua profile underlying dolomites in the Triassic karst terrains of Yunnan-Guizhou Plateau, provide strong constrains on the material sources of regolith, and also acquirement into isotopic fractionation in the chemical weathering processes. It is suggested the insoluble residues from underlying Triassic dolomites as the domination of parent materials for the red residua.

The results of isotope analysis for bulk samples showed that the ⁸⁷Sr/⁸⁶Sr ratios varied relatively greatly, from 0.708 to 0.747, but the ¹⁴³Nd/¹⁴⁴Nd ratios displayed a little variation, from 0.5121 to 0.5124 ($\Sigma Nd_{(0)} = -9.6 - -11.5$). The isotopic compositions of Pb belonged to "ordinary lead" which was derived from feldspar minerals, and ²⁰⁶Pb/²⁰⁴Pb was little change, about from 19.0 to 20.6. The ratios of Pb isotopes in this study were clearly different from the ratios of Pb isotopes from the average crust, the background of research regions and aerosols in China. The sample points of Pb isotopes were fallen on a mixed line, and the reason for their formation had been suggested in this study.

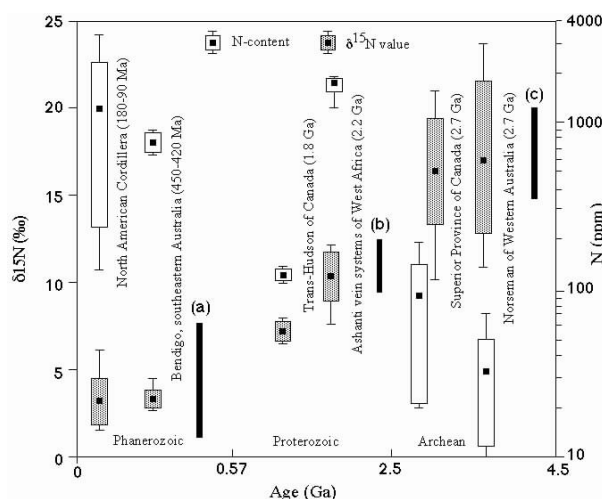
With increasing weathering intensity, ⁸⁷Sr/⁸⁶Sr and Sm/Nd ratios in the weathering front showed a decreased and increased variation, respectively. The change with Sr and Nd isotopic system, were chiefly derived from the early stage of weathering, either the water rock interaction or preferentially weathering the different Rb/Sr ratios of the minerals. From the element balance calculation and variation of ⁸⁷Sr/⁸⁶Sr ratios, the leaching weathering of dolomite, rare earth minerals and feldspar minerals were been discovered during rock-soil alteration processes, respectively. The Pingba profile had experienced a primary weathering process and the two-stage nature of weathering could be distinguished precisely, which determined the processes of dissolution and resetting for Nd-Sr isotopic system.

A ¹⁵N-enriched Archean crust

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New measurements of the N-isotope composition of 2.7 Ga Archean metasedimentary rocks, and K-micas in hydrothermal systems that sample average crust, both yield $\delta^{15}N$ values of 16 to 24‰, compared to 7 to 10‰ in Paleoproterozoic and 2 to 6‰ in Phanerozoic counterparts, implying a secular decrease in crustal $\delta^{15}N$ (Fig. 1).



Present-day atmospheric N₂ of 0‰ is sequestered by microorganisms, converted to N-bearing kerogen in sediments with average $\delta^{15}N$ of 3 to 4‰, and a proportion retained as NH₄⁺ substituting for K in crustal rocks, giving a crust-atmosphere fractionation of 3 to 4‰. Consequently, if N-isotope fractionation between them in the Archean is the same as at present, then the ¹⁵N enriched 2.7 Ga Archean crust is consistent with an atmospheric value of 13 to 21‰.

These results endorse the model of the Earth's secondary atmosphere forming by late accretion of volatile rich C1 carbonaceous chondrites ($\delta^{15}N = +30$ to $+42$ ‰) and comets at ~ 4.5 Ga. Consequently, the present atmospheric N-isotope composition can be accounted for by progressive sequestration of atmospheric N into crustal rocks, as tracked by the secular variation of crustal $\delta^{15}N$.

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The Mantle Source of the Aegaitic Lamprophyre in Northeastern Hunan Province, China

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Geologic setting and time of the rock formation

A group of aegaitic lamprophyres has been detected in Mesozoic continental extension belt within South China Plate. It intruded along the NE trending deep fault belt. It intruded into 136.61Ma granite in dikes swarm and the Rb-Sr whole rock isochron age is 136.61Ma.

Major, Trace Element and Sr-Nd Isotope Geochemistry of the Aegaitic Lamprophyres

The SiO₂ is 46.49%~51.63% and rich in Na₂O, FeO, TiO₂ and LREE. Na₂O is 3.0~4.08%, K₂O/Na₂O rate is 0.44~0.79, TiO₂ is 1.75~3.17, fEu=1.02~1.06. It is belong to sodium-rich lamprophyre in the classification diagrams of the lamprophyre. The LILE were not rich very obvious, some samples even show K/Sr slightly depleted. Within HFSE, Ta/Nb/Nd/P were enriched slightly and Ti/Zr/Hf were not changed obviously, but Yb, Y were depleted. All the patterns of trace elements show the aegaitic lamprophyres have characteristics of typical oceanic island basalt magma source, which very different from the high K/Ti-low Ti apotassic lamprophyres related with the zone of subduction. Initial ⁸⁷Sr/⁸⁶Sr isotope ratio is 0.705332 in average, Initial ¹⁴³Nd/¹⁴⁴Nd isotope ratio is 0.512646 and Σ_{Nd}(t)= +3.5~ +3.8, express the slightly depletion mantle source and different with the enriched mantle source of the apotassic lamprophyres.

Discussion and Conclusion

The aegaitic lamprophyres have slightly depletion mantle source and magma come from asthenospheric mantle. The aegaitic lamprophyres were formed in the mantle hot spot tectonic setting caused by asthenospheric mantle diapirism. The asthenospheric mantle diapirism or mantle plume may be the main controlling factors about the continental extension. The aegaitic lamprophyre usually formed in the tectonic conversion epoch from compression to extension.

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Niobium in planetary cores

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Introduction

Nb/Ta ratios of all major terrestrial silicate reservoirs appear to be lower than the chondritic value of 17.5 (Jochum et al, 2000; Mezger et al., 2001). Propositions for a reservoir containing the missing Nb include subducted, refractory eclogites (Rudnick et al., 2000) and the Earth's core (Wade and Wood, 2001). The latter hypothesis is based on experimental evidence that Nb has siderophile character at high pressures and temperatures and within the range of oxygen fugacities in the Earth's mantle.

Results and discussion

In search for a reservoir containing the missing niobium, we used spark source mass spectrometry to analyze magmatic iron meteorites, thought to be fragments of metallic cores of asteroid-sized bodies. We found significant and variable Nb concentrations (7 – 40 ppb) that are correlated with V and Cr. Published estimates for V and Cr abundances in the Earth's core lie on the V-Cr correlation line (McDonough and Sun, 1995). Ta abundances are very low (< 0.2 ppb), thus confirming the non-siderophile behaviour of this element.

Using estimates on Nb/Ta for Earth (14), Mars (16), the Eucrite Parent Body Vesta (17), we obtain mass fractions of the Nb budget of 20%, 9% and < 2% for the cores of Earth, Mars and Vesta, respectively. The Nb depletion in the bulk silicate phases of planets may be correlated with the V depletion. The Earth's mantle shows a significant V depletion of 0.73, whereas the Eucrite Parent Body appears to be undepleted. The bulk silicate Mars having a Nb depletion of 0.91 may have a similar depletion for V (0.9).

Metal/silicate partition coefficients of Nb were calculated for the different planetary bodies by using the bulk silicate estimates for Nb/Ta in Earth, Mars and Vesta and the mean Nb abundances in the magmatic iron meteorite groups. They increase strongly with increasing pressure and the results are consistent with the experimental data (Wade and Wood, 2001).

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The use of cement to control the mobility of heavy metals in wastes:

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Cement is often used to stabilise nuclear and non-nuclear wastes. The aim is to reduce the release of potential contaminants to the environment. These contaminants may be radionuclides or ionic species of metals and metalloid components. Understanding their binding in the cement matrix enables us to optimise prediction of the behaviour of cement/waste mixes.

Studies show that in hydrated cementitious matrices, metal mobility is generally low due to physical factors, such as a low permeability, and by geochemical binding within the cement matrix. There appear to be three basic types of binding mechanism. A metal ion may (i) be bound in the alkaline cement matrix as an oxide, mixed oxide or other solid phase, (ii) sorbed onto surfaces or (iii) be incorporated into hydrated cement minerals. The precipitation of heavy metal containing solid phases does seem to be a limiting factor with regard to the second and third mechanisms. However, for heavy metals that are sufficiently soluble in basic media, such as Zn, Pb or Cr(VI), incorporation in hydrated cement minerals appears to be significant.

Calcium silicate hydrate ($\text{CaOSiO}_2 \cdot x\text{H}_2\text{O}$ or CSH) is the most abundant component of hydrated portland cement (~60%), has a large capacity for ion uptake and is thus a prime candidate for heavy metal binding. Basic Ca sulphoaluminates such as monosulphate ($3\text{CaOAl}_2\text{O}_3\text{CaSO}_4 \cdot 12\text{H}_2\text{O}$) or ettringite ($3\text{CaOAl}_2\text{O}_3 \cdot 3(\text{CaSO}_4) \cdot 32\text{H}_2\text{O}$) also have a potential for heavy metal uptake. Their structures are relatively tolerant of substitution without a change in structure. A number of ions are reported to substitute at the different sites in ettringite, namely divalent cations such as Pb^{2+} , Cd^{2+} or Zn^{2+} for Ca^{2+} , trivalent cations such as Cr^{3+} , Ni^{3+} or Co^{3+} in place of Al^{3+} and diverse anions in exchange for SO_4^{2-} .

The different processes that control the solubility of heavy metal and metalloid ions in contact with cement minerals can be illustrated by the example of cement stabilised municipal solid waste incinerator air pollution control residues. Here it is probable that dissolved Zn concentrations are controlled by sorption to CSH. Less soluble heavy metal cations, such as Ni^{2+} and Cu^{2+} may be immobilised as $\text{Ni}(\text{OH})_2$ and CuO respectively, and the solubility of MoO_4^{2-} and WO_4^{2-} are probably controlled by their respective Ca metallates. Components that are highly soluble in the basic pH range, such as Pb(II), may be incorporated in CSH or ettringite.

The Thermal Stability of Hydrogen in Feldspars

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Introduction

Feldspars are the most common crustal minerals, and contain fluid inclusions and trace amounts of structural OH, H_2O , and NH_4^+ . Trace H in feldspars could be used as a record of fluid history, but to do this an understanding of the behavior of each species at temperatures of geologic interest is needed. Infrared (IR) spectroscopy is a sensitive method for determining speciation of H, and, when calibrated, can be used to determine the concentration of individual hydrous species. We investigated the thermal stability of structural OH and H_2O and fluid inclusions in feldspars from a variety of geological environments at 1 bar using IR spectroscopy.

Methods

For samples containing structural H, polarized IR spectra were taken parallel to principal optical directions on polished slabs. Unpolarized spectra were used for samples containing fluid inclusions. Polarized spectra were summed to determine total band area. Absolute concentrations of H were determined using the IR calibration from Johnson and Rossman (2001) for structural species and the absorption coefficient of water for fluid inclusions. Samples were dehydrated in air.

Results

The diffusion coefficient (D) of H at 1000°C in plagioclase containing structural OH is estimated to be $1\text{--}2 \times 10^{-12} \text{ m}^2/\text{s}$ using a one-dimensional diffusion model for an infinite slab. This is similar to the D ($2.2 \times 10^{-11} \text{ m}^2/\text{s}$) determined at 900°C for adularia containing structural H_2O (Kronenberg et al. 1996). The D determined for plagioclase suggests the retention of initial [OH] by volcanic feldspars could range from >90%–0% depending on the transport time (hours to weeks) during an eruption at 1000°C. Natural volcanic phenocrysts contain low but variable amounts of OH (0 to 300 ppm wt. H_2O).

Upon heating a pegmatitic albite from Brazil to 300°C, the intensity of a band due to fluid inclusions (3440 cm^{-1}) decreases and absorbance at 3050 cm^{-1} increases. No such transformation is observed in other feldspars. Fluid inclusion water is lost from plutonic feldspars by 700°C. The high concentration of fluid inclusions in plutonic feldspars (up to 2 wt% H_2O) is much larger than the concentration of structural OH in plagioclase or H_2O in microcline (up to 0.14 wt% H_2O). Fluid inclusions in plutonic feldspars must be principally derived from hydrothermal fluids.

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Cd Partitioning in Metal-Mineral-Bacteria Systems: Testing the Surface Complexation Approach

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Minerals and bacteria represent some of the most reactive surfaces in geologic systems and adsorption onto mineral surfaces and bacterial cell walls can determine the fate, transport and bioavailability of aqueous heavy metal cations. Therefore, it is crucial to develop geochemical models that accurately account for the partitioning of metals between these surfaces and aqueous solutions. Surface complexation models are successful in two-component systems (metal-mineral or metal-bacteria); however, their ability to account for metal distribution in mixed metal-mineral-bacteria systems has not been tested. In this study, we measure partitioning of cadmium between three interacting reservoirs: an aqueous phase, and bacterial and mineral surfaces. We compare partitioning estimates from surface complexation modeling to the observed partitioning, thereby conducting a rigorous test of the applicability of the surface complexation approach to mixed metal-mineral-bacteria systems.

Two types of two-component batch adsorption experiments were performed: 1) metal-bacteria experiments in which a 10 ppm Cd solution was placed in contact with 1 g/L (wet wt.) of the gram-positive bacteria, *Bacillus subtilis*, and 2) a 10 ppm Cd solution was placed in contact with 5 g/L hydrous ferric oxide (HFO). Two types of three-component batch adsorption experiments were also conducted: 1) ones in which *B. subtilis*, HFO, and 10 ppm Cd solution were allowed to equilibrate in contact with each other, and 2) ones in which the HFO was physically, but not chemically, isolated by placing it in a sealed dialysis tube. This set-up enabled determination of the extent of Cd partitioning between the bacteria and the iron oxide surfaces.

The experiments indicate that adsorption in systems containing both bacteria and minerals can be dominated either by bacterial surfaces, by mineral surfaces, or by both types of surfaces, depending on the pH and on the bacteria:mineral ratio. The data from the two-component system adsorption experiments were used to determine stability constants for each of the important surface complexes. Using FITEQL, we use these stability constants, along with stability constants for the other surface and aqueous species in the experimental systems, to independently predict the extent of adsorption and the partitioning of Cd in the bacteria-mineral-metal systems. Results from these comparisons suggest surface complexation modeling can be used successfully to account for metal partitioning in multi-sorbent geologic systems.

Cr Stable Isotopes: Measurement, Systematics and Applications

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We have developed a method to measure mass-dependent fractionation of Cr isotopes, determined the amount of fractionation during Cr(VI) reduction, and observed Cr isotope ratio shifts in reducing groundwaters. Toxic Cr(VI) can be highly mobile and is a common contaminant in most major industrial areas.

We use double-spiked TIMS measurements to obtain a precision of $\pm 0.2\%$ or better on $^{53}\text{Cr}/^{52}\text{Cr}$, using 200ng Cr. We purify Cr for analysis via a two-step Cr(VI)/Cr(III) ion exchange method.

In anaerobic experiments with a magnetite suspension and two sediment slurries, abiotic Cr(VI) reduction to Cr(III) occurred over a period of several days and induced an instantaneous $^{53}\text{Cr}/^{52}\text{Cr}$ shift of $3.4 \pm 0.1\%$. Experiments now in progress will measure microbial Cr isotope fractionation.

Samples of three basalt standards, a commercial CrO₃ supply, two reagent Cr compounds, and three Cr plating baths yielded $\delta^{53}\text{Cr}$ values between -0.07% and $+0.37\%$ relative to NIST SRM-979. These data suggest that igneous rocks, Cr ores, commercial Cr supplies, and contaminants originating from plating baths are all isotopically close to the bulk earth. The plating bath result is intriguing. Cr(VI) reduction occurs in the electroplating process but apparently does not fractionate the isotopes greatly in this case.

We analysed eight groundwater samples from two sites where Cr(VI) contamination was likely attenuated by reduction, which produces insoluble, less toxic Cr(III). $\delta^{53}\text{Cr}$ values ranged from $+1.08\%$ to $+5.79\%$. This enrichment in the heavier isotope strongly suggests that Cr(VI) was removed from the water by reduction. We estimate 30% to 80% removal had occurred prior to sampling. Provided variability in the instantaneous isotope fractionation is not too great, and sorption does not greatly fractionate the isotopes, Cr isotopes will provide a great improvement over current methods for assessing natural attenuation of Cr(VI) in contaminated groundwater.

Cr isotopes may be useful in other geoscience studies. For example, Cr(VI) is the dominant inorganic species in the modern oceans, but Cr(III) is present and reduction may be important in the global Cr cycle. Under mildly reducing conditions, Cr speciation and cycling could change greatly.

Experimental constraints on Fe isotope fractionations during biogeochemical cycling of Fe

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Experimental calibration of Fe isotope fractionation factors in the system Fe(II)-Fe(III)-Fe₂O₃/FeOOH in both inorganic and biologic systems allows us, for the first time, to quantify the “vital” effects that are associated with biological processing of Fe during both Fe reduction and oxidation. Equilibrium isotope fractionation between hexaquo Fe(III) and Fe(II) varies from +2.7 to +3.5 per mil for ⁵⁶Fe/⁵⁴Fe from 22 to 2 °C, and is independent of Cl substitution into the inner hydration sphere up to a stoichiometry of [Fe(III)(H₂O)₅Cl]²⁺ for ferric Fe. In contrast, equilibrium isotope fractionation between hexaquo Fe(III) and Fe₂O₃ at low temperatures is nearly zero, which is distinct from the significant (~ 1 per mil) kinetic fractionations that may be produced by rapid precipitation of ferric oxides. Combining these results indicates that equilibrium isotope fractionations between Fe(II) and ferric oxides is ~ -3 per mil for ⁵⁶Fe/⁵⁴Fe.

Fe isotope fractionation produced during dissimilatory Fe reduction, as well as anoxygenic photosynthetic Fe oxidation, produces remarkably similar fractionations in ⁵⁶Fe/⁵⁴Fe between ferrous and ferric components of ~ -1.5 per mil, which is half that measured for “equivalent” inorganic systems. We may define this contrast as a “vital” effect, and we interpret this to reflect the unique organic ligands that are involved in complexing ferric and ferrous Fe during biological processing of Fe.

Combined, the experimental data explain several aspects of Fe isotope variations observed in nature, as well as those expected during biogeochemical cycling of Fe:

- 1) The moderately positive δ⁵⁶Fe values of primary hematite in some Late Archean Banded Iron Formations are best explained by Fe oxidation by photosynthetic bacteria,
- 2) The low δ⁵⁶Fe values for ferrous-rich fluids and minerals are consistent with both inorganic or biological processing of Fe,
- 3) The δ⁵⁶Fe values of oxide minerals are likely to directly reflect the Fe isotope compositions of Fe(III) in ancient fluids,
- 4) Redox cycling of Fe by bacteria will produce Fe deposits that are strongly zoned in Fe isotope compositions.

Grain formation, processing and survival in, and transport through, the ISM

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The major dust-forming environments are the circumstellar environments of ‘old’ stars, principally asymptotic giant branch (AGB) stars and supernovae (SNe). While AGB stars seems to dominate the galactic dust budget, in terms of the variety (crystalline and amorphous silicates, amorphous aliphatic/aromatic hydrocarbons and SiC) and the quantity of the dust that they produce, the SNe dust input contribution is not entirely clear. The total dust input rate to the Galaxy is of the order of $8\text{-}30 \times 10^6 M_{\text{Sun}} \text{ kpc}^{-2} \text{ yr}^{-1}$ (Jones 2001). If we assume that dust makes up some 1% of the galactic gas mass then it would take of the order of 3 billion years to replenish the entire galactic dust mass.

Interestingly, not all of the dust materials formed in AGB and SNe circumstellar environments are, however, detected in circumstellar regions or in the interstellar medium (ISM). Some of them, e.g., SiC, graphite, Al₂O₃ and Si₃N₄, have been extracted from primitive meteorites and have been extensively analysed but are never seen in the ISM.

The derived lifetimes for grains in the ISM appear to be short (400-600 million years, e.g., Jones et al. 1996) compared to the time-scales for their re-formation. This discrepancy in timescales is about order of magnitude. Thus, a lifetime and propagation problem is posed for dust in the ISM. Apparently, it is necessary to re-form and grow grains in the ISM, through accretion and coagulation processes, in order to explain interstellar dust observations. Clearly we see presolar dust in meteorites and this dust must therefore have traversed the ISM before incorporation into primitive Solar System bodies. This paper will discuss: dust formation in circumstellar and interstellar environments, dust sources and their contributions to the galactic dust budget, and dust survival in, and propagation through, the ISM.

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Highly Siderophile Elements and Planetary Accretion

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Analyses of highly siderophile elements (HSE) in martian (SNC) meteorites indicate that Pt behaves indifferently during basalt genesis [1]. The SNC suite is a mixture of diverse lithologies: a dunite, augite cumulates, basalts, evolved basalts, and partial cumulates. But despite this diversity, the Pt in the SNC suite is remarkably constant (6.2 ± 3.1 ppb), and we therefore infer that $D^{Pt} \sim 1$ during basalt genesis/fractionation. This is in sharp contrast to Os and Ir, whose abundances in SNC's vary by $\sim 10^4$ X.

We attribute this Pt partitioning behaviour to its valence and ionic radius. Both quantum arguments and experiments [2] indicate that Pt in silicate systems exists as Pt^{2+} . Therefore, Pt can substitute into mafic silicates without requiring charge balance. Secondly, the ionic radius of Pt^{2+} is 0.80 \AA , which compares to 0.72 \AA and 0.61 \AA for Mg^{2+} and Fe^{2+} , respectively [3]. Therefore, Δr for Pt-Mg is about the same as that of Fe-Mg. Since Fe^{2+} behaves rather indifferently during basalt fractionation and petrogenesis, we should expect similar behaviour from Pt.

If D^{Pt} is truly ~ 1 , we may use the SNC Pt abundances to estimate the Pt content of the martian mantle, which would also be ~ 6 ppb. We compare this concentration to the Pt content of the Earth's upper mantle, 6.5 ± 0.8 ppb, and find these values are indistinguishable. The Pt concentration of the Earth's depleted mantle is also in this range [4], further supporting the indifferent nature of Pt during basalt genesis. Further, analyses of low-Ti mare basalts indicate that Pt in the Moon (7.7 ± 1.6 ppb) is very similar to the Pt concentrations of the Earth and Mars [5].

This similarity of HSE concentrations among the terrestrial planets is not expected from the late veneer (LV) hypothesis. Planets at different heliocentric distances are expected to have seen different fluxes of LV material. For the Earth and Mars, this difference is estimated to be 2 X [6]. And if the LV was well mixed into planetary mantles, geometry considerations dictate that smaller bodies will have proportionally higher HSE concentrations than larger bodies. The net effect of these considerations is that we expect the Moon and Mars to have ~ 4 X higher HSE concentrations than the Earth. Such is not observed, so it may be that we must find alternatives to the LV hypothesis.

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Modelling an in situ test of PCE oxidation using permanganate

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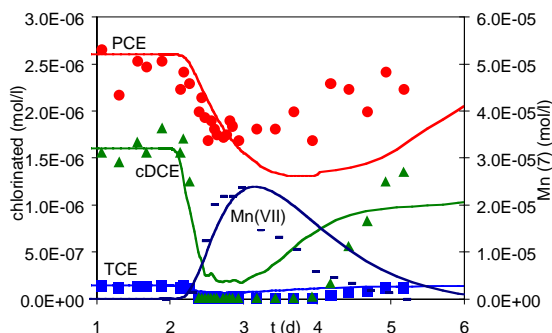
In situ experiment

We conducted a pilot test in an aquifer polluted by organic chlorinated solvents (PCE, TCE, DCE, see table) consisting of a concentrated injection of $KMnO_4$ and a long term pumping from a borehole 13 m downstream. The reactant slug was 10 kg of commercially available $KMnO_4$ injected during 3.2 h along with 680 l of water. Extraction rate was maintained constant for 10 d at a 4.75 l/s.

Modelling results

The experiment was modelled with PHAST (Parkhurst et al., 2000), the domain being a grid of $10m \times 10m \times 20m$. The hydrodynamic parameters were calibrated using the results of a tracer test. The chemical processes considered were the oxidation of the chlorinated ethylenes by Mn (VII) as described in Yan and Schwartz (1999). 2nd order kinetics reaction was used for PCE, while the rest followed a 1st order reaction. No other electron donors such as OM were considered and the injected Mn was adjusted for the modelling. The "best fit" parameters used in the model are listed below. The computed (line) vs. measured (dots) concentrations are shown in the plot below.

Parameter	PCE	TCE	cDCE
Mn_{max}/Mn_{min} (mol/l)	$10^{-5}/10^{-6}$	10^{-6}	10^{-6}
k_1 (sec ⁻¹)	10^{-5}	10^{-3}	$5.0 \cdot 10^{-3}$
k_2 (mol ⁻¹ /sec)	0.66	-	-
d.t. (mol/l)	10^{-8}	10^{-8}	10^{-8}
C_0 and C_{bc} (mol/l)	$2.6 \cdot 10^{-6}$	$1.4 \cdot 10^{-7}$	$1.6 \cdot 10^{-6}$
Mn_{injec} (mol/l)	$3.73 \cdot 10^{-2}$ (\approx of the actual)		



Conclusions

The model reproduces the drop down of the chlorinated but the recovery is poorly described. The kinetic reaction constants used have been calibrated to reproduce the data.

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Application of Reactive Transport Modelling to the Interpretation of pH Changes in Sediments

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A complex set of transport and reaction processes control geochemical conditions in sediments. Reactive transport models can account for the coupling of these processes. So far, however, existing models have not been able to reproduce satisfactorily observed pore water pH profiles. In order to understand the factors affecting pH changes in sediments, we adopt a systematic approach to modelling the relevant processes.

Process formulations, their corresponding parameters, as well as the fluxes of organic and inorganic carbon at the sediment-water interface are factors that influence the predicted pH profiles to varying extents. We evaluate the role of these factors through a Biogeochemical Reaction Network Simulator. This modeling framework provides an efficient and flexible modeling environment in which modifications of model formulations are easily implemented and tested.

Our current research focuses on the effects of solid deposition fluxes on the resulting pH profiles. Sediments from the deep sea and the continental shelf dominated by different organic carbon degradation pathways (oxic respiration/denitrification; iron reduction; sulfate reduction) are considered. For each of these redox systems, the buffering effect of calcite dissolution/precipitation on the pH profiles is evaluated quantitatively under contrasting conditions of inorganic carbon fluxes reaching the sediment-water interface.

Deuterium in the terrestrial water cycle: Present-day distribution and paleoclimatic applications

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Whereas the deuterium/hydrogen ratio is practically constant in the world ocean, the main water reservoir on Earth the situation differs for the atmosphere, the hydrosphere and the cryosphere. This is due to fractionation processes that occur at each phase change of the water (except sublimation and melting of compact ice) owing to slight differences in physical properties of HDO and H₂¹⁶O molecules, mainly their saturation vapor pressure and their molecular diffusivity in air. As a result, the deuterium distribution vary both spatially and temporally in the atmosphere, in the precipitation and, in turn, in the hydrosphere and of the cryosphere. Those isotopic variations have applications in such fields as climatology and cloud physics. More importantly, they are at the origin of two now well-established disciplines isotope hydrology and isotope paleoclimatology.

We will focus our presentation on the use of deuterium in paleoclimatology which is based on the observed relationship between δD and climatological parameters. Of primary interest is the linear correlation between annual values of δD and mean annual temperature at the precipitation site that is observed at middle and high latitudes and has given rise to the notion of "isotopic paleothermometer". We will first review the various models that allow to describe isotopic distributions in water vapor and precipitation, and their ability to account for present-day observations. We will then focus on paleodata and more specifically on Greenland and Antarctic deep ice cores with the longest record covering the last 420 000 years at the Vostok site in Antarctica, and discuss the calibration of the "isotopic paleothermometer" through the comparison with other methods allowing to estimate temperature changes in polar regions.

The measured coral oxygen isotopes result of the superimposition of two fractionations.

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Coral oxygen isotopes are regarded as a robust proxy of environmental variables. Despite the apparent isotopic disequilibrium of aragonite skeleton, there is a strong temperature dependence, the isotopic curve versus temperature being almost parallel to the "paleotemperature" of CaCO₃ deposited in isotopic equilibrium. When the slope, around -0.23‰/°C is used to assess the sea surface temperature (SST) increase recorded from the beginning of the last century, the calculated range of 1°C exceeds the instrumental observations, 0.3 to 0.4°C at the tropical latitudes.

Very often, the oxygen and carbon isotopic signals from corals show a positive correlation which cannot be explained by the thermodynamical law. By performing a principal component analysis (EOF) on these data we identify a first component which explains more than 80% of the variance. This variability governed by a kinetic process, is controlled by SST which drives an isotopic variability around -1‰ per 1°C. This slope is likely dependent on the growth characteristics of each coral colony.

The signal obtained by removing pc1 from the measured oxygen isotopes corresponds with the paleothermometer, depending upon temperature and water isotopic composition. Since water isotopic composition and salinity obey to the same processes, O and C isotopic records allow accurate SST and SSS reconstruction.

In Pacific Ocean, interannual SST variations are governed by the zonal mode El Niño whereas interdecadal SSS fluctuations are influenced by the meridional mode Pacific Decadal Oscillation (PDO).

Zinc trapping in Layered Double Hydroxydes (LDHs) and phyllosilicates in contaminated soils from Western Europe.

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The FAMEST (Fundamental Aspects of METal Speciation and Transport in metal-contaminated soils and aquifers) program is aimed at assessing zinc speciation in European soils impacted by industrial activities. We will present results obtained in three soils (France, Switzerland and England) contaminated by pyrometallurgical activities or sewage sludge adding and differing in mineralogical composition (silty, carbonaceous clayey and sandy).

After conventional methods (XRD, SEM-EDS) failed at assessing zinc speciation in these soils, X-ray Absorption Spectroscopy (XAS) was successfully combined with selective chemical extractions to evidence the incorporation of Zn²⁺ in Zn/Al-layered double hydroxides (Zn/Al-LDHs) and/or Zn-bearing phyllosilicates, as well as its sorption onto hydrous iron oxides and humic substances. In the silty French soil and in the clayey carbonaceous Swiss one (pH ranging from 5.5 to 8.0), Zn/Al-LDHs and Zn-bearing phyllosilicates were the most abundant Zn-bearing components and their relative proportions were related to pH conditions. In the sandy English soil (pH 6.5), Zn-bearing phyllosilicates were found together with zinc sorption complexes on hydrous iron oxides, the latter dominating in surface horizons.

The ubiquity of LDHs and/or metal-bearing phyllosilicates in impacted soils studied, and the possible incorporation of a large range of transition elements (Cr, Mn, Co, Ni, Cu) in these structures, emphasizes their potential for *in situ* remediation techniques.

The Geochemistry of Hawaiian Plume Dynamics.

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Magmas erupted along the Hawaiian Island chain provide a detailed source of information about the dynamics and structure of a mantle plume. High resolution major, trace, and isotopic studies of these magmas (e.g., Frey and Rhodes, 1993; Kurz et al., 1996; Sims et al., 1999), in addition to their volume and eruption rate, provide constraints on the degree and rate of melting, the geometry of the melt zone, and the nature and extent of melt extraction in the underlying mantle. Previous coupled geodynamic-geochemical studies (Watson and McKenzie, 1991; Richardson and McKenzie, 1994), did not take into account the asymmetry of the plume caused by the motion of the overlying Pacific plate, or the effect of temperature dependent viscosity on mantle flow. Consequently, these studies could not, for example, use the variability in magma production rate and chemistry from the leading edge of the plume at Loihi, the main stage volcanics at Mouna Loa, and the late stage "rejuvenated" volcanics at Haleakala to constrain the plume dynamics. Any model for the large scale dynamics of the Hawaiian plume must be able to account for the observed variation in melt production and chemistry along the island chain.

Numerical models that include interaction between the mantle plume and the overlying plate (e.g., Ribe and Christensen, 1994; Ribe and Christensen, 1999) have provided an explanation for the variability in magma production rates along the island chain, but there has been no attempt to incorporate calculations of melt chemistry into these models. In order to determine the sensitivity of plume dynamics calculations to constraints from geochemical observations at the surface, we have developed a coupled geodynamic-geochemical model of the Hawaiian plume that builds on the variable viscosity, multi-grid code of Albers (2000). This model takes into account the effect of motion of the overlying Pacific plate, temperature-dependent viscosity, depletion buoyancy, and viscous shear heating, and also allows local grid refinements in the model domain. Preliminary results show that the late stage melting event is sensitive to boundary conditions of the model domain. We will present calculated rare earth element concentrations and uranium series disequilibria [$^{226}\text{Ra}/^{230}\text{Th}$ and ($^{230}\text{Th}/^{238}\text{U}$)] from our plume model and thus produce a "map" of the magma chemistry on the overlying plate as a function of position with regard to the underlying plume. These results will be compared to the chemistry of basalts from along the island chain, and recent data from the Hawaiian Scientific Drilling Project. If time permits, we will incorporate chemical tracers from a heterogeneous mantle source into our calculations.

Decadal-Centennial scale climate variations in the Arabian Sea during the Early Holocene

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The monsoonal system in the Arabian Sea area is highly sensitive to seasonal variations in solar insolation and is the subject of this study. Here we show that during the Early Holocene rapid $\delta^{18}\text{O}$ -change of the surface dwelling foraminifer *G. bulloides* of up to $\sim 0.6\%$ in Core 905 translates into temperature variations in the Arabian Sea of roughly $2\text{--}3^\circ\text{C}$ during summer. Within the resolution of the AMS ^{14}C -dating, these inferred temperature changes occur in phase with precipitation induced $\delta^{18}\text{O}$ -variations recorded in the Hoti Cave in Oman [Neff *et al.*, 2001] which are controlled by the monsoonal system. From this relationship we conclude that solar insolation affected the monsoonal system on a regional scale.

In addition we present stable O-isotope data from the benthic foraminifera *C. kullenbergi*. These data record an overall $\delta_{\text{--}}$ -reduction by 0.5% between 10 and ~ 6.5 kyr BP superimposed upon short-term $\delta_{\text{--}}$ -variations at a decadal-centennial time scale. We conclude from modelling experiments that the short-term $\delta_{\text{--}}$ -variations between 10 and ~ 6.5 kyr BP most likely document changes in the evaporation-precipitation balance in the central Red Sea. Changes in water temperature and salinity cause the outflowing Red Sea Water to settle roughly 800 m deeper than today. In summary our results show that the Early Holocene climate in the Arabian Sea was much more variable than previously believed down to a decadal resolution.

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U-Pb zircon, sphene and apatite ages from shear zone-hosted syenites: Implications on Pb retentivity in magmatic and metamorphic sphene

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An apparently paradoxical feature of orogenic cycles is the development of major extensional structures within overall compressive systems. Sometimes, intrusion of mantle-derived magmas, are connected with these zones of weakness. Consequently, the emplacement of these magmas into the crust has become a fundamental component of petrogenetic models and it is becoming increasingly apparent that there is a spatial and temporal coincidence of plutonism with major shear zones in many orogenic belts. In the Damara orogen (Namibia) Pb-Pb zircon ages obtained on some on-shear zone and off-shear zone syenites yielded consistent ages of c. 520 Ma which are interpreted as the age of intrusion of these syenites close to the peak of regional metamorphism. Pb-Pb sphene ages obtained on xenocrystic dark brown sphenes from off-shear zone syenites yielded significantly older ages between c. 700 and 730 Ma similar to zircon and sphene ages from syenites from the northern part of the orogen. Since the c. 730 Ma age is similar to the proposed age of sedimentation of the country rock metapelites the sphene ages are not interpreted as metamorphic ages, instead the xenocrystic dark brown sphenes are likely remnants of pre-existing igneous rocks in the deeper crust. Together these ages precisely define the onset of rifting and access of mantle sources during the early stages of orogeny at c. 730 Ma. Pb-Pb sphene ages obtained on light brown sphenes which occurred as mantles around the dark brown sphenes and as individual crystals define two groups with ages between c. 610 and 575 Ma and between c. 540 and 490 Ma. The older ages are interpreted as the age of sphene growth during regional metamorphism in the southern part of the Damara orogen which is structurally unrelated to the rest of the orogen. The younger ages correspond either to another peak of regional metamorphism or to intrusion of on-shear zone syenites which yielded consistent Pb-Pb sphene and apatite ages between c. 490 and c. 550 Ma. These data indicate activity of the shear zone at c. 700 Ma (onset of rifting) and between 490 and 550 Ma (regional metamorphism). Furthermore, for the off-shear zone syenites Pb retentivity in sphene is high indicated by the inheritance of older sphene in younger intrusive rocks and by the preservation of older metamorphic sphenes. Lastly, for the on-shear zone syenites the similarity of apatite and sphene ages suggests that these ages rather represent magmatic ages than metamorphic ages implying fast cooling rates during intrusion.