

## Method measurement of Ar isotopes in He stream (conflo) for K/Ar geochronology

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Mass-spectrometric methods of measurement of Ar isotopes for K/Ar geochronology after of some key development (Inghram *et al.*, 1950, Standacher *et al.*, 1978) are developed on a way of perfection low background equipments. Achievement low background conditions measurement of Ar isotopes is extremely a challenge, requires greater efforts and a lot of time. Here, we report a new laser GC-MS method that incorporates helium carrier gas and chromatography methods (conflo) that allow for rapid analyses for small samples. The Ar gas is swept into the mass spectrometer in a helium carrier gas, allowing for extremely small samples to be quantitatively transferred ( $<5 \cdot 10^{-13}$ g). The laser GC-MS technique consists of six components: the overall high vacuum extraction line, the system of input tracer  $^{38}\text{Ar}$ , the sample chamber, the laser, the gas chromatograph, the interface to the mass spectrometer and the mass spectrometer MAT-253 (Thermo Electron, Bremen, GmbH). Three Faraday cup for simultaneous measurement of isotopes  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$  and  $^{40}\text{Ar}$  are installed in the ions receiver of mass-spectrometer. Electrometric amplifiers for mass 36, 38 and 40 have entrance resistance  $10^{-12}$ ,  $10^{-11}$  and  $10^{-11}$  Ohm accordingly. We used infrared ( $\lambda=1.064 \mu\text{m}$ , CW, 100W) Nd-YAG laser to heat samples up to 2000°C. Samples are placed into the chamber (10 - 18 samples, depending on weight). Extracted Ar together with tracer ( $^{38}\text{Ar} - 0.510^{-9}\text{g}$ ) passes through U-shaped a trap ( $T = -196$ ) and is adsorbed onto activated coal in a loop at temperature of liquid nitrogen. He is passed through the loop (He 99.9999) and the loop is heated up to 100°C. The Ar gas is entrained in a helium stream (1-2 mL He/min), passes through the gas chromatograph to separate the Ar from any other gas, and admitted into the mass spectrometer via a split interface (Matthews, Hayes, 1978). To separate the Ar from other gas we use the capillary chromatographic column (HP-MOLSIV). Samples are analyzed using a dynamically pumped mass spectrometer. In general, Ar extraction by laser can be made every 15-20 min. The laser GC-MS system has been used successfully to analyze samples containing  $<5 \cdot 10^{-11}\text{g}$   $^{40}\text{Ar}$ . Smaller samples can be analyzed with the use electron multiplier for  $^{36}\text{Ar}$ . Laser GC-MS method may be used and for  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology.

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## On the nebular origin of water in the Earth

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Although the chondritic or cometary origin of water in the Earth has been widely accepted, we explore another possibility that the Earth acquired water from the solar nebula. Several recent theories of the final assembly of the terrestrial planets in the solar system (e.g., Kominami and Ida 2002; Nagasawa *et al.* 2005) suggest that there existed the nebular gas until the formation of the terrestrial planets was completed. When that is the case, the planets collect large amounts of hydrogen from the solar nebula.

Our simulations of the structure of the atmosphere on terrestrial planets embedded in the solar nebula (Ikoma and Genda 2006) demonstrate that the planet's surface temperature is rather insensitive to the parameters and almost always higher than the melting temperature of silicate. In that situation the atmospheric hydrogen efficiently reacts with oxides contained in the magma ocean to produce water on the planet. From the chemical equilibrium constants (Robie *et al.* 1978), we find it possible that the reaction yields water comparable in mass to hydrogen. Although the exact amount of hydrogen that the primitive Earth acquired is unable to be determined at present because of the uncertainties in the heat flux and the grain abundance in the primitive atmosphere, our simulations show that production of water comparable in mass to the Earth's current sea water is possible for wide ranges of the values of the quantities.

We have also tackled the well-known problem of the discrepancy between the D/H ratios of the Earth's current sea water and the nebular gas (e.g., Drake and Righter 2002). We have simulated the evolution of the D/H ratio of sea water in the case the Earth had a relatively massive hydrogen atmosphere, which was neglected by previous studies, and found that the D/H ratio of the sea water increases by a factor of 3 to 9, depending of the escape rate of the atmospheric hydrogen (Genda and Ikoma 2007); this is consistent with the current D/H ratio of the Earth's sea water.

In the presentation we will discuss the advantages and disadvantages of the nebular hypothesis about the origin of water in the Earth.

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## Time-series analysis of Magnesium isotopes in speleothems

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Magnesium-isotope time series MC-ICP-MS analyses from NW Africa (Morocco) speleothems are reported. In addition, high-resolution C, O and Sr-isotope data, and Mg and Sr element abundances were compiled. The analytical results show clearly co-variant, systematic and cyclical fluctuations for all proxies collected along the growth axis and - with respect to the analytical error - invariant data within one growth increment. Magnesium-isotope ratios ( $\delta^{26}\text{Mg}$ ) fluctuate between  $-4.39\% \pm 0.02\ 2\sigma$  and  $-4.17\% \pm 0.05\ 2\sigma$ . The difference of 0.22‰ is significantly beyond the error of the external reproducibility of  $\pm 0.03\% \ 2\ \sigma$  for  $\delta^{26}\text{Mg}$ . Considering the analytical error, neither a purely kinetic nor an equilibrium fractionation process explains the observed isotope pattern. Two external factors might drive the speleothem Mg-isotope cyclicity: (1) climate-driven (arid versus humid) variances in the precipitation rate of a carbonate phase from meteoric water; and (2) changing rates of silicate versus carbonate weathering. Both of these processes fractionate the Mg-isotopic composition of runoff/seepage water.

## Fractionation of iron isotopes in shallow-marine ferromanganese concretions

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Fe-isotope data for ferromanganese concretions indicate a trend from positive to negative values going from the freshwater environment, via the Arctic Ocean to the Atlantic and Pacific Ocean nodules, possibly following the redox related separation pathway of Fe from Mn in the exogenic cycle. However, the database is still small and additional Fe-Mn concretion data is needed, especially from continental margins, to verify if such a trend exists.

Shallow marine Fe-Mn concretions from the Baltic Sea and the Barents Sea analysed in this study show large variations in  $\delta^{56}\text{Fe}$ , from -1.55 to +1.0, thus spanning the whole range of  $\delta^{56}\text{Fe}$  values presented so far for ferromanganese concretions. There are also large variations in  $\delta^{56}\text{Fe}$  in concretions from the same area. Large positive  $\delta^{56}\text{Fe}$  values are obtained only close to the reduced-oxidised interface in the sediment. Samples taken at some distance from the reduced-oxidised interface with low Fe/Mn ratios generally show negative values. It can be concluded that the local redox conditions strongly influence the Fe-isotope signal in the concretions.

This study indicates that dissolved heavy Fe-isotopes preferentially are trapped close to the reduced-oxidised interface and any dissolved Fe that might escape from the sediment up into the bottom water during early diagenesis should have a clear negative  $\delta^{56}\text{Fe}$  value. Hence, early diagenetic cycling of Fe-oxyhydroxides in shallow marine sediments acts as a sink for heavy Fe-isotopes and as a source of lighter ones.

## A U-series study on groundwaters from southwestern France

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U-series have been investigated in groundwaters from one demonstrative water body named the Eocene sands aquifer (Adour-Garonne district, southwestern France). This work was done in the framework of a research project (CARISMEAU, Négrel *et al.*, 2007), related to the UE Water Framework Directive (WFD, 2000/60/EC). The Eocene sands aquifer extends north and south of the Garonne River. Groundwaters have been recovered both in spring and fall, in order to check for seasonal variations.

The  $^{234}\text{U}/^{238}\text{U}$  activity ratios are in any case higher than 1 (equilibrium value), some of them being very enriched in  $^{234}\text{U}$  (up to 11 in the northern part). Only slight isotopic variations of the  $^{234}\text{U}/^{238}\text{U}$  activity ratios have been evidenced between spring and fall waters. In the southern part, the highest  $^{234}\text{U}/^{238}\text{U}$  activity ratios correlate roughly with the oldest measured  $^{14}\text{C}$  ages ( $> 25$  ka, André *et al.*, 2005) while recharge areas have the lowest  $^{234}\text{U}/^{238}\text{U}$  activity ratios, closer to the equilibrium value. Hence it is not possible to apply a "simple" model featuring a decay of excess  $^{234}\text{U}$  through time during groundwater circulation to put chronological constraints on the residence time of waters in the aquifer.

Thorium isotopes have been measured successfully in some of these groundwaters, due to recent analytical improvements in Th isotopic analysis (Innocent *et al.*, 2006).  $^{230}\text{Th}/^{232}\text{Th}$  activity ratios range between 0.4 ( $^{230}\text{Th}$  deficit) and 9.2 (large  $^{230}\text{Th}$  excess).  $^{230}\text{Th}/^{234}\text{U}$  activity ratios are very low ( $\leq 0.01$ ), except for recharge areas (0.6). High  $^{230}\text{Th}/^{232}\text{Th}$  roughly correlate with  $^{234}\text{U}/^{238}\text{U}$  close to the equilibrium. A open-system model, combining these three activity ratios is presented, potentially constraining groundwater residence times in the aquifer.

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## Spatial and temporal variation of anthropogenic lead inputs to the western Pacific

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A continuous record of anthropogenic lead affecting on the western Pacific has been less studied compare to the North Atlantic. In this study, Pb contents and isotopic compositions in the annually banded coral (*Porites* sp.) from Ogasawara, Japan was used for reconstruction of Pb variation since the late 19<sup>th</sup> century. We also determined Pb in corals collected from several sites in the western Pacific to examine spatial distribution of Pb in sea surface. Determinations of Pb contents and isotope ratios were conducted using inductively coupled plasma mass spectrometer (ICP-MS) and multiple collector ICP-MS, respectively (Inoue *et al.*, 2006; Tanimizu and Ishikawa, 2006). The spatial distribution of Pb showed a clear dilution pattern of Pb from Asian continent to the open ocean. In addition to the spatial distribution, Pb contents in Ogasawara coral have gradually increased during last 108 years. Although Pb emitted from Japan seems to be main source during the period of 1960 – 1980, that from China might be predominant source of Pb affecting on the western Pacific for the last 20 years based on the variation of Pb isotope ratios in the coral core.

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## Peridotite xenoliths from the andesitic Avacha volcano, Kamchatka – Any signatures of subduction metasomatism?

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We report chemical data, Os- and Li-isotope ratios, PGE abundances and  $fO_2$  estimates for peridotite xenoliths from the active Avacha volcano in southern Kamchatka peninsula, Russia. The rocks are large, fresh and homogeneous spinel harzburgites that contain accessory interstitial cpx and amphibole as well as highly variable amounts of fine-grained, second-generation orthopyroxene (opx). None of the samples have intrusive magmatic or metasomatic veins.

Major and trace element compositions were obtained for 17 peridotites. The whole-rocks contain 0.4-0.9%  $Al_2O_3$ , 0.5-0.9% CaO,  $\leq 0.03\%$   $Na_2O$ ,  $\leq 0.01\%$   $K_2O$ ; Mg# = 0.906-0.916. They are highly refractory rocks produced by high degrees of melt extraction, but their Mg# are lower than in many other (Ca,Al)-poor mantle peridotites. The Avacha xenoliths have low HREE and are depleted in LREE and MREE relative to HREE. The rocks show minor enrichments in Rb, Ba, U and Sr relative to adjacent REE but no significant Zr, Nb or Ti anomalies. Overall, they show no enrichment patterns considered typical of “subduction” metasomatism.

The rocks have 2.7 to 9.6 ppb Os;  $^{187}Os/^{188}Os$  range from 0.1235 to 0.1319 and are positively correlated to Al contents. This “alumichron” is not likely to be related to ancient melt extraction. Rather, it may reflect a correlation between the amounts of slab-derived radiogenic Os and those of late-stage amphibole and pyroxenes added by percolating fluids. Li abundances in whole-rocks, olivine and opx range from 0.8 to 1.8 ppm, i.e. match estimates for melting residues.  $\delta^7Li$  range from -2 to +4.7‰, with averages for olivine, opx and WR from +1.7 to +2.7‰, i.e. are within the range reported for oceanic basalts and “normal” mantle.  $\Delta \log fO_2$  determined using measured  $Fe^{3+}/Fe^{2+}$  in spinels are FMQ +0.1 to +1.8.

Relatively high  $fO_2$ , Os abundances and  $^{187}Os/^{188}Os$  in several Avacha peridotites might be related to enrichments by slab-derived fluids but these are decoupled from trace element and Li-isotope signatures, which show no or little evidence for metasomatism. The slab-derived fluids may be largely consumed by reaction with wall-rocks in the lower mantle wedge, with only small amounts of residual fluids occasionally reaching the shallow uppermost mantle sampled by the Avacha xenoliths.

## Re-Os evidence for ancient mantle beneath the Ontong Java Plateau

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We have carried out a Re-Os isotope study of a suite of peridotite xenoliths from Malaita, Solomon Islands in order to better understand the nature and formation of oceanic lithosphere beneath the Early Cretaceous Ontong Java Plateau (OJP). Thermobarometric and petrochemical evidence reveal that the xenoliths represent virtually the entire section of subplateau lithospheric mantle (<120 km) which is stratified in compositional [1]. Os isotope data have been obtained for samples covering the whole range of  $P$ - $T$  and depletion.

Whole-rock analyses of peridotites from the shallow part of the lithosphere (<95 km) yield an average  $^{187}Os/^{188}Os$  ratio of 0.1247 (n=15) and a range from 0.1223 to 0.1272, illustrating an affinity with abyssal peridotites (whole-rock mean ~0.1246) [2]. This is consistent with previous Sm-Nd results indicating a recent (Jurassic) mid-oceanic ridge origin for the shallow lithosphere [3]. By contrast, the deep-seated peridotites (>95 km) show much greater variation in Os isotope composition that is correlated with differences in rock types: garnet lherzolites have limited  $^{187}Os/^{188}Os$  variations (0.1244-0.1254); spinel harzburgites record unradiogenic  $^{187}Os/^{188}Os$  ratios (0.1174-0.1196); Fe-rich garnet lherzolite from the deepest portion possesses the most unradiogenic ratio (0.1156). These unradiogenic ratios yield Proterozoic model  $T_{RD}$  ages of 1.2-1.8 Ga, demonstrating the existence of ancient mantle in the basal section of subplateau lithosphere.

There are several potential explanations for the diversity of ancient Os signatures found in these OJP peridotites. (i) Continental mantle was tectonically incorporated to the newly forming oceanic plateau, analogous to the scenario suggested for the Kerguelen plateau mantle [4]. (ii) The OJP lithosphere may be sampling the inherent isotopic variability of the oceanic mantle as represented by abyssal peridotites, which overlaps the range reported here (extending to  $^{187}Os/^{188}Os$  as low as 0.110 in sulfide grains from abyssal peridotites [5]). (iii) The depleted Os isotope compositions may reflect recycled heterogeneity within the upwelling plume source, as suggested recently for Hawaii [6]. Option (iii) may best explain the absence of old continental materials around the OJP, the contrasting Os isotope ratios between shallow and deep lithosphere, and the presence of recycled pyroxenite of Proterozoic age in the basal lithosphere [7]. Thus, the OJP may have been generated by mantle plume consisting of a mix of ancient, depleted, recycled Proterozoic lithosphere.

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## **Amphibolite-facies metamorphism of the subducted slab and boninite magma genesis: An inference from the Oman ophiolite**

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The Oman ophiolite contains boninite and other arc-related volcanic rocks generated after the magmatism of spreading-ridge ceased. The initiation of subduction of a young, hot oceanic lithosphere (and obduction of the future Oman ophiolite) near the spreading ridge and the resultant melting of the hydrous shallow mantle wedge represent the most favorable mechanism for the genesis of the Oman boninites. On the other hand, this ophiolite is underlain by a thin sliver of amphibolite-granulite-facies metamorphic rocks. These rocks (metamorphic sole) are believed to represent oceanic crust overridden and “ironed” by the ophiolitic lithosphere, and may be analogous to the subducted slab that contributed to producing the geochemical signature of the boninites. Thus the Oman ophiolite provides a best opportunity for investigating the link between the amphibolite-facies metamorphism of the slab and the boninite magma genesis in the mantle wedge.

The amphibolites in the 230 m-thick metamorphic sole in Wadi Tayin area show significant variation in fluid-mobile element concentrations across the transect of the sole. The observed variations suggest that the amphibolites (>600°C in peak metamorphic temperature) near the contact with the overlying peridotite were equilibrated with evolved, B-Rb-K-Ba-rich fluids formed through successive fluid-rock interactions during prograde metamorphism. The estimated amphibolite-derived fluids are characterized by striking enrichments of B, Rb, K and Ba and moderate to minor enrichments of Sr, Li, Be and Pb. It is also suggested that at higher temperature (up to 700 °C), the fluids become considerably enriched in light REE and Nb in addition to the above elements. Model calculations showed that the trace element characteristics of the Oman boninites, including their U-shaped REE patterns and relatively low Ba/Rb ratios, are successfully explained by partial melting of the highly depleted mantle that had been metasomatized by the amphibolite-derived fluids. The Sr and Nd isotope compositions of the boninites and related volcanic rocks in the Oman ophiolite are also consistent with the involvement of such fluids. The compositions of the fluids liberated from the amphibolite-facies slab are likely to vary dependent on the metamorphic temperature, and the evolution and hybridization of such fluids may produced considerable variations in trace element and isotope compositions observed in the boninites.

## **The magmatic plumbing of the submarine volcanic chain of an oceanic island arc volcano: Long distance lateral magma transport?**

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Recent geophysical observations on basaltic composite volcanoes in Izu arc reveal the process of long distance lateral magma transport within the arc crust. Such intrusion events sometimes caused flank fissure eruption and also triggered a formation of collapsed caldera (Miyakejima 2000). To clarify a long-distance magma transport system of the basaltic volcano in volcanic arc from geological and petrological aspects, we investigated a submarine volcanic chain (Hachijo NW chain) and satellite cones nested Hachijo Nishiyama volcano, a frontal composite volcano in the northern Izu arc.

Basalts from the Hachijo NW chain generally have more primitive composition compared to those from the Nishiyama. The bulk compositional trend of Hachijo NW chain magma is controlled by crystal fractionation while plagioclase accumulation was indicated by aluminum-rich character of the Nishiyama volcano and its subaerial and submarine satellite cones other than NW chain edifices.

Trace element ratios unaffected by melting or crystal fractionation (e.g., Nb/Zr) and isotopic compositions are not significantly different between the Nishiyama and the Hachijo NW chain. This implies that the sources of magma for these volcanic systems are identical. However, Hachijo NW chain shows lower LREE/HREE and Zr/Y. These differences in trace element ratios could be ascribed to difference in degree of partial melting of the source or crustal assimilation. Assuming difference in degree of partial melting, Nishiyama magma, which is much more voluminous than Hachijo NW chain magma, should have lower degree of melting relative to Hachijo NW chain. Instead we prefer a model considering larger extent of crustal assimilation for Nishiyama magma, where assimilated crust is expected to have higher LREE/HREE and Zr/Y, but similar isotopic composition to basaltic primary magma.

Nishiyama magma is assumed to form shallow crustal magma chamber where it experienced crustal assimilation and plagioclase accumulation. Satellite cones other than NW chain can be explained by magma transport from this magma chamber in the shallow crustal level. On the other hand, Hachijo NW chain was tapped by the same primary magma as Nishiyama volcano, but experienced much less crystal fractionation and assimilation in the crust during ascent without forming shallow magma chamber. Long distance magma transport is assumed to have occurred in the lower crustal level, which is consistent with the depth of hypocenters of seismic event in 2002.

## Adsorption of As(III) and As(V) onto vivianite – Evaluation as a sink for arsenic in Bengali aquifers

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Although microbially mediated reduction of Fe(III) oxyhydroxide phases is thought to be critically implicated in the mobilisation of arsenic in shallow aquifers in Bengal (Islam *et al.*, 2004), Cambodia (Rowland *et al.*, 2004) and other parts of world, there is substantial evidence that mobility of arsenic in such aquifers is also controlled by the nature and distribution of secondary Fe-bearing phases. Secondary Fe-sulfides, magnetite, siderite and vivianite have all been suggested as potential arsenic sinks. Whilst there are considerable data on the adsorption and/or incorporation of arsenic into Fe-sulfides (Farquhar *et al.*, 2002; Wolthers *et al.*, 2005) and magnetite (Dixit and Hering, 2003; Coker *et al.*, 2006) there is a dearth of such data for vivianite. In this study, we report the sorption behaviors of both arsenite and arsenate on vivianite under anaerobic conditions as a function of solution pH and dissolved arsenic oxidation state and concentration

Natural well crystallised vivianite was characterised by ESEM/EDS, XRD, EPMA and BET and then mixed (1:8 wt/wt) with 1, 10 and 100 µM of As(III) or As(V) in a background electrolyte of 0.1 M NaNO<sub>3</sub> with pH adjusted from 3 to 11 with HNO<sub>3</sub> or NaOH. Solutions were purged with nitrogen and the studies were conducted under a modified atmosphere of 5% H<sub>2</sub> + 95% N<sub>2</sub> in an anaerobic cabinet at ambient temperature (T = 23 +/- 3°C) and pressure. Fe, P and As in the aqueous phase after 40 hours were measured by ICP-AES.

The adsorption of As(III) was found to be pH dependent, increasing from 10% of a 100 µM solution at pH 3 to 33 % at pH 10 and 75% at pH 11. Implications for the scavenging capacity of vivianite for As(III) in shallow reducing groundwaters in Bengal are discussed.

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## Fossilized microorganisms from Emperor Seamounts: Evidence for a deep sub-seafloor biosphere

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Fossilized microorganisms have been observed in drilled samples of seafloor basalts collected during ocean Drilling Program (ODP) Leg 197. During that leg three different seamounts belonging to the Emperor Seamounts in the Pacific Ocean were drilled: Detroit (81 Ma), Nintoku (56 Ma) and Koko (48 Ma) Seamounts respectively. A wide variety of microbial-like structures were found in veins, attached to mineral surfaces and embedded in minerals like calcite, aragonite and gypsum. Morphologically, the microfossils vary a lot. Globular cell-like coccoids, sheaths, segmented filaments, twisted filaments and branched filaments were found. With ToF-SIMS (Time of Flight Secondary Ion Mass Spectrometry) fatty acids and lipids were detected in the microfossils. This is, to our knowledge, the first time such compounds have been found in association with microbial remnants from sub-seafloor environments. ToF-SIMS further showed concentrations of C<sub>2</sub>H<sub>4</sub> and PO<sub>3</sub> in the microfossils. The biogenicity was also supported by dyeing the microfossils with the pigment PI (propidium iodide) that binds to dead bacteria cells and remnants of DNA. EDS-analyses showed that they contain slight amounts of elements like Si, Al, Mg, K and Na but very high amounts of carbon (~10-50 wt % C) and iron (~10-50 wt % Fe). The high iron content as well as a close association with iron oxides and deposition of iron oxides onto the filaments indicate that the microorganisms were involved in iron oxidizing reactions and that iron probably served as an energy source for the metabolism of the microorganisms.

Our observations show that all three seamounts drilled during ODP Leg 197 have been supporting a deep sub-seafloor biosphere during their volcanically active period of time when hydrothermal activity was present and fluids circulated the rocks.

## Determination of production rates of cosmogenic nuclides based on data from large landslides in the Alps

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We are analyzing samples from boulder and bedrock surfaces associated with large prehistoric landslides in the Alps for <sup>10</sup>Be, <sup>26</sup>Al and <sup>36</sup>Cl. In addition to determining the ages for undated landslides, we are examining cosmogenic nuclide production rates based on results from landslides with independent age constraints (for example Flims, Graubuenden Switzerland and Koefels, Tirol, Austria). We focus on <sup>10</sup>Be, <sup>26</sup>Al in crystalline regions with abundant quartz, while <sup>36</sup>Cl is used in areas underlain by calcareous rocks. Potential complications include pre-exposure, post-slide rock fall, and shielding by soil or snow. Results from several sites as well as the problems encountered will be discussed.

## Independent component analysis of isotopic compositions of oceanic basalts

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Isotopic variations in oceanic basalts indicate possible interactions among several distinct mantle components, such as DMM, EM, FOZO, C, HIMU, etc. Increasing number of data for various isotopic systems now allows us to systematically search the structure hidden in the multivariate compositional space by independent component analysis, ICA [1]. Principal component analysis (PCA) has been regarded to be the most efficient way to display the extreme mixing end-components. However, it has a fundamental problem: PCs are independent only when the data distribution follows the Gaussian distribution, which is not in this case. ICA is the method to deconvolute a data set into independent components that maximize the non-Gaussianity of the projected distribution of the data. Based on ICA, we have explored the isotopic compositional space of the oceanic basalts from Atlantic and South Indian Oceans, based on the data from literature [21] and GEOROC database. We show that the two independent compositional vectors/directions (referred to as independent components or ICs) are involved to create the variations with six isotopic ratios of Pb, Sr, Nd and Hf. One of the two ICs clearly divides OIBs and MORBs, while another IC distinguishes the geographical distribution including DUPAL anomaly. This feature supports that the two ICs are indeed independent. We also show that the conventional mantle end-components are not appropriate to represent the compositional space. Instead, two independent processes that create vectors parallel to DMM-FOZO or towards EM are proposed to explain the independent compositional space. Since the average composition of the oceanic basalts is similar to that of the average DMM, around which MORBs and OIBs are roughly symmetrically distributed in the IC space, we argue that these processes occur as two dominant but independent differentiation processes within the depleted mantle domain. Considering these nature, one IC is likely to be produced by recycling and stirring of MORB and its residue, while another IC is possibly created by the subduction zone processes. According to the ICs, the criterion of DUPAL anomaly is re-defined. As a result, distribution of the enriched region is modified, showing that the enriched signature disperses into the northern hemisphere.

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## The simulation experiments on hydrothermal formation of organic globules in carbonaceous chondrites

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Organic globules were found in the Tagish Lake meteorite (carbonaceous chondrite fallen in 2000). Since then, further characterizations of these globules in meteorites have been conducted. However, the formation processes of organic globules remain unclear. In order to simulate the globule formation processes, a series of hydrothermal heating experiments of an OH-bearing amino acid (threonine: Thr) have been conducted in the presence of some rocks (rhyolite, basalt).

40 ml of Thr solution with a rock piece was heated in a hydrothermal vessel at 160°C for 4 days, globules of 2 to 20 micrometers in size were observed under Scanning Electron Microscope (SEM) on the rock surface. By elemental analysis of the globules, they are found to be carbon rich substances. This result suggests that the organic globules found in Tagish Lake meteorite might be formed by organic-inorganic interactions during the aqueous alteration of the chondrite parent body.

In order to study quantitatively the globule formation processes, hydrothermal heating experiments of Thr solutions have been conducted with the silicate glass slide having smooth surfaces. SEM images of glass surfaces showed that diameters and numbers of globules increased with the heating duration and with the temperature. By image analyses, grain size distributions and mean diameters of globules have been determined. Growth rates of organic globules at different temperatures were evaluated by means of their mean diameters. Based on these results, formation of globules of about 300 nm in diameter would need several hundred years under the temperature of aqueous alteration (20°C). These results can be used to estimate temperature conditions and time scales of organic globule formation in the meteorite parent body.

## Processes of biomineralization in freshwater cultured pearls

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Freshwater cultured pearls formed by the mussel *Hyriopsis* represent excellent examples to study processes of biomineralization in molluscs. They are grown by inserting a piece of epithelial tissue from the mantle lobe into the mussel where processes identical to those forming the mussel shell occur.

Resonance Raman Spectroscopy of polished pearl cross-sections revealed that ca. 50% of the samples contain vaterite in addition to aragonite. Vaterite is the thermodynamically most unstable polymorph of CaCO<sub>3</sub> and is often discussed as a precursor phase in the mineralization of aragonite or calcite by organisms (Weiss *et al.*, 2002). Vaterite forms relatively small areas in high quality pearls (1-1.5 mm diameter) which are spherical to irregular and always in close proximity to the center of the pearl. However, in low-quality pearls, they can be much larger, sometimes comprising the major part of the pearl, including the surface (Ma and Lee, 2006; Qiao *et al.*, 2006).

To further study the micro-structure of the vaterite zones, cross-sections were etched with Mutvei's solution (Schoene *et al.*, 2005). This etching method dissolves the calcium carbonate surface with acetic acid, while the organic matrix is stabilized with glutaraldehyde and Comassie Blue colours the organic material in intensities which correspond to the concentration of the organics. SEM analyses of the etched surfaces show that growth rings transect the vaterite areas, implying that vaterite and aragonite grew simultaneously, and that vaterite may not have been an initial template for aragonite growth.

LA-ICP-MS and electron microprobe were used to quantify minor and trace elemental differences between the calcium carbonate polymorphs. Vaterite areas have about 1400 ppm Mg and 1000 ppm Na, versus around 30 ppm Mg and 1650 ppm Na found in aragonite. The Sr concentration in vaterite (250 ppm) is about half of that found in aragonite, while for Mn, Zn and Ba no significant differences were detected.

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## Thermodynamic assessment of the magnesium-olivine-pyroxene system using a lattice vibrational technique

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We are currently constructing a thermodynamic database providing phase diagrams, thermophysical and thermochemical properties for materials with a geophysical relevance, applicable in the pressure and temperature regime of the Earth's mantle. The computational technique is based on Kieffer's (1979) approach to model the vibrational density of states of a substance, a key property to derive the Helmholtz energy. It allows the calculation of  $V_P$  and  $V_S$  sound wave velocities. The developed thermodynamic framework uses model input properties related to Raman and infrared spectroscopic data. It puts tighter constraints on thermodynamic properties compared to methods based on polynomial parameterisations of thermal expansivity, heat capacity and isothermal bulk modulus. Jacobs and de Jong (2005) and Jacobs *et al.* (2006), showed that this framework entails a description of properties free from physical anomalies for close-packed materials. In addition it discriminates, based on internal consistency, between the quality of disparate sets of experimental thermochemical, thermophysical and phase diagram data.

The present work focuses on the application of vibrational modeling to the magnesium-olivine-pyroxene system, which constitutes over 90% of the Earth's mantle and which is intimately linked to the magnesium-olivine system by the common phases wadsleyite, ringwoodite and perovskite. We show how our approach is used in a thermodynamic assessment of experimental data. The results, presented here, were used in a numerical model of convection in the Earth's mantle to reveal, effects of phase transitions on the degree of layering, mineral distribution and sound wave velocities in the transition zone, around 660 km depth in the Earth.

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## Accretion and early differentiation history of the Earth based on extinct and long-lived chronometers

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Jacobsen and Harper (1996) showed that isotopic variations due to decay of extinct nuclides (<sup>129</sup>I, <sup>244</sup>Pu, <sup>182</sup>Hf and <sup>146</sup>Sm) could be used to study early evolution of terrestrial reservoirs and provide observational constraints on the timescale of accretion of the terrestrial planets. Measurable variations in <sup>182</sup>W/<sup>183</sup>W, <sup>142</sup>Nd/<sup>144</sup>Nd, <sup>129</sup>Xe/<sup>130</sup>Xe and <sup>136</sup>XePu/<sup>130</sup>Xe in the Earth (compared to bulk planetary values inferred from primitive meteorites) provide a preserved record of accretion, core formation, early crust, atmosphere formation and evolution. The <sup>182</sup>Hf-<sup>182</sup>W system is the best accretion and core-formation chronometer because it is identifiable with chemical fractionation during the accretion process itself. This system yields a mean time of Earth's accretion and core formation of 10 Myr, with a total timescale of accretion being 30 Myr. New experimental data pertaining to the conditions that existed in the Earth's deep mantle ( $P > 100$  GPa and  $T > 6000$  K) subsequent to the giant Moon-forming impact show that metal-silicate equilibration will be rapid enough for the Hf-W chronometer to reliably record this timescale (Petaev *et al.* 2007). Although the <sup>207</sup>Pb-<sup>206</sup>Pb chronometer has been used to argue for a more protracted timescale (~100 Myr) of accretion and core formation, Yin and Jacobsen (2006) showed that these data do not require a longer time scale. Using the coupled <sup>146</sup>Sm - <sup>147</sup>Sm chronometer, the age of the initial silicate differentiation in the mantle source region of some of the Earth's oldest surviving crustal rocks can be constrained to ~4.47 Ga. Attempts to use this chronometer for dating proto-crust formation at ~30 Myr are unreliable because of the uncertainties in the initial Nd isotopic composition inferred from heterogeneities in Ba and Nd isotopes in primitive meteorites (Ranen and Jacobsen 2006). The presence of a large <sup>129</sup>Xe excess in the deep Earth is consistent with a very early formation and a short time interval for the accretion of the Earth.

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## $\delta^{44}\text{Ca}$ evolution during water-rock interaction in a carbonate aquifer

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To improve understanding of Ca isotope transport during water-rock interaction on the continents, we measured  $\delta^{44}\text{Ca}$  values along a 236 km flow path in the Madison aquifer, South Dakota, where fluids have chemically evolved according to dolomite and anhydrite dissolution, calcite precipitation, and Ca-for-Na ion-exchange over a timescale spanning ~15 kyr. We use a reactive transport model that employs rate data constrained from major ion mass-balances to evaluate the extent to which calcite precipitation and ion-exchange fractionate Ca isotopes. Elevated  $\delta^{44}\text{Ca}$  values during the initial and final stages of water transport may result from calcite precipitation under supersaturated conditions and Ca-for-Na ion-exchange, respectively. However, for the bulk of the flow path,  $\delta^{44}\text{Ca}$  values evolve by mixing between dolomite and anhydrite dissolution, with no fractionation during calcite precipitation under saturated conditions. We attribute the absence of Ca isotope fractionation to the long timescale of water-rock interaction and the slow rate of calcite precipitation, which have enabled fluids to chemically and isotopically equilibrate with calcite. We therefore conclude that the equilibrium Ca isotope fractionation factor between calcite and water ( $\Delta_{\text{cal-w}}$ ) is very close to zero. We further reason that instances of  $^{44}\text{Ca}$  enrichment attributed to calcite precipitation must stem from kinetic isotope effects. To the extent that the Madison aquifer typifies other groundwater systems, our study suggests that groundwater  $\delta^{44}\text{Ca}$  values can be modelled according to simple mixing theory, without the need to invoke isotope discrimination during calcite precipitation. We suggest that groundwater may play an important role in transmitting the pristine isotopic signature of Ca mineral weathering to the oceans, by way of surface-groundwater interactions in tributary networks of large rivers.

## Diatom $\delta^{13}\text{C}$ , $\delta^{15}\text{N}$ , and C/N since the Last Glacial maximum in the Southern Ocean: Evidence for regional and ecological influences

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The carbon and nitrogen isotopic composition ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) and C/N ratio of diatom-bound organic matter is commonly used to reconstruct oceanographic processes that contribute to variations in atmospheric  $\text{CO}_2$  over glacial-interglacial cycles. This organic material is presumed to be part of the diatom cell wall and the template for biomineralization, entombed upon silicification and protected from diagenesis. However, this material has not been well characterized and there is no strong sense yet for how variable its composition is between species or among members of the same species growing under different conditions. In addition, the studies that have been carried out on isotopic fractionation by diatoms have focused on the "whole cell" isotopic composition and not specifically that of the material occluded within the matrix of the silica. Some investigation of this matters would go a long way towards refinement of these proxies for nutrient utilization and primary production.

Towards this end, measurements of  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and C/N on diatom-bound organic matter were made over the Holocene and Last Glacial Maximum (LGM) from 3 piston cores in the Southern Ocean, one from each of the three sectors. The site in the Atlantic sector differs considerably from the other two sites by having markedly lower  $\delta^{13}\text{C}$ , more variable  $\delta^{15}\text{N}$  and C/N ratios, and a sedimentary diatom assemblage that is never dominated by *Fragilariopsis kerguelensis*. The proportion of *F. kerguelensis* in the samples, and to a lesser degree, the carbon content of the organic matter, have a strong influence on  $\delta^{13}\text{C}$ . Extreme values of  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and C/N at the Last Glacial Maximum are also related to the abundance of resting spores of *Eucampia antarctica*. These results suggest that methods for the separation of specific diatom species out of opal sediments would considerably aid in the reconstruction of paleoceanographic conditions from diatom stable isotope and elemental records.

## Formation of hydrozincite, Zn layered double hydroxide and Zn phyllosilicates in contaminated calcareous soils

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The incorporation of Zn into layered mineral structures such as layered double hydroxides (LDH) or phyllosilicates may reduce its mobility and bioavailability in soils. The quantity and structure of Zn bearing layered phases forming in soils depend on soil physicochemical properties and contamination level. To date, most spectroscopic studies on the speciation of Zn considered neutral to acidic non-calcareous soils. In this study, we investigate the reactivity and speciation of Zn in contaminated soils developed from calcareous and dolomitic parent material.

Five soils developed from limestone and one developed from dolomite were sampled below power line towers made from galvanized steel that had been constructed 30 to 50 years ago. All soils have been contaminated by input of runoff water containing dissolved Zn from corrosion. The soils cover a wide range in clay content (90-450 g/kg), inorganic carbon content (10-89 g/kg), and Zn concentration (1'300 - 30'000 mg/kg). They have pH values between 6.1 and 7.5. The molecular scale speciation of Zn in the soil matrix was investigated by Zn K-edge EXAFS spectroscopy on powdered soil samples. Thin sections from two calcareous soils (1'300 and 30'000 mg kg<sup>-1</sup> Zn) and the dolomitic soil (1'400 mg kg<sup>-1</sup> Zn) were further studied by  $\mu$ -X-ray fluorescence ( $\mu$ -XRF) and  $\mu$ -EXAFS spectroscopy. Principal component analysis and target testing indicated that octahedrally coordinated Zn in layered minerals and tetrahedrally or octahedrally coordinated sorbed Zn are likely candidate species. In the dolomitic soil, pure Zn-phyllosilicate was identified in Zn-rich spots. In the calcareous soil containing 30'000 mg kg<sup>-1</sup> Zn, the Zn was diffusely distributed in the soil matrix with a spectrum similar to Zn-LDH. Crusts on calcite particles from the same soil were identified as hydrozincite using powder X-ray diffraction and EXAFS spectroscopy. Linear combination fits to the bulk EXAFS spectra indicate that LDH- and phyllosilicate-type precipitates account for a considerable fraction (17-53%) of the total Zn in all soils. To quantify the reactivity of Zn, the soils as well as synthetic references were fractionated using a 7-step sequential extraction procedure (SEP). Between 32-65% of the total Zn in the soils was extracted in the first two fractions (1M NH<sub>4</sub>NO<sub>3</sub> and 1M NH<sub>4</sub>-acetate at pH 6.0, respectively), suggesting that most Zn occurred in labile species. Zn-LDH, Zn-phyllosilicates and hydrozincite showed similar chemical reactivity with 46 to 84% of the total Zn mobilized in the first two fractions.

## Solving the mystery of SNC meteorites

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Rb-Sr, Sm-Nd and U-Th-Pb isotopes have been intensively studied on SNC meteorites. There is a general consensus that these meteorites are magmatic rocks. While in terrestrial magmatic rocks the Rb-Sr system usually shows a greater melt-residue fractionation than the Sm-Nd system, it is just the reverse in the case of the SNC meteorites. While the whole rock SNC meteorites scatter along a 4.5Ga Rb-Sr reference isochron showing only a slight disturbance, the Sm-Nd isotopes for the same whole-rocks are strongly fractionated, with a considerable depletion of Nd for the shergottites and an enrichment of Nd for the nakhlites. One would expect that a magmatic fractionation would cause a strong enrichment in Rb in the melt, but only a moderate enrichment in Nd. The shergottites, however, which clearly originally crystallized from melts, show no significant enrichment in Rb but, by contrast, a strong depletion in Nd. The nakhlites, which are mafic cumulates with a residual major element chemistry, experienced a significant Nd enrichment. Model-calculations that are able to explain the Sm/Nd evolution cannot be extended to the other REE and completely fail to explain the observed Sm/Yb and La/Nd ratios. A mixing model reveals the need for three components to explain the composition of shergottites and nakhlites, but does not contribute to an understanding of a realistic magmatic process.

Recently we developed a magmatic model that consistently explains the observed petrographic and isotopic data for SNC meteorites. It is based on the premise that the basaltic shergottites, Shergotty, Zagami, and Los Angeles, have typical crustal compositions and were differentiated very early at 4.4 Ga, while nakhlites and olivine-bearing shergottites, Que, SAU, Y89, and others, derive from a nearly homogeneous mantle source [1].

Minor heterogeneities in the Sr and Pb isotopes are insufficient to argue against a common mantle source, and reported W isotopic differences might be caused by terrestrial contamination (the intrinsic W contents of the olivine shergottites, as estimated from the W/La in these meteorites, may be unmeasurable). To explain their unusual fractionation pattern, we postulate the presence of two phosphates in the Martian mantle: xenotime and monazite. At the time of fractionation, xenotime partitions into the olivine bearing shergottites while monazite partitions into the nakhlites. This phosphate chemistry has little effect on the Rb-Sr systematic, strongly fractionates between the light and heavy REE. Because in such an environment the trace-elements do not follow Henry's law, commonly employed melting models cannot be applied.

## Differences between preserved vs. delaminated lower crust: Evidences from the Kohistan arc

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Delamination and foundering of the lower continental crust (LCC) into the mantle are important crust forming mechanisms. However, knowledge of the composition and mineralogy of the preserved and/or delaminated LCC remains scarce. We provide a synopsis of recent research within the Kohistan arc (Pakistan). We show that hydrous and “less-hydrous” liquid lines of descent related to flux and decompression melting, respectively, produced compositionally different lower crustal rocks in the Kohistan arc. These observations allow a new model for CC formation where delaminated and preserved LCC differ in mineralogy and composition.

Within the Kohistan arc two mantle-lower crustal sections are exposed: the older Jijal section and the younger, rifting-related Chilas section. We describe lithologies of these sections and argue that fractionation mechanisms that produced them document two liquid lines of descent with largely differing initial water contents. The Jijal liquid line of descent is typical for a hydrous, high-pressure fractionation sequences (e.g. pyx, grt, Fe/Ti-oxides, amph, An-rich plag). The composition of the Jijal lower-crustal gabbroic rocks differs markedly from bulk lower crust estimates but is complementary to silica-rich rocks (tonalite, granite etc.), exposed within the Jijal section and within the so-called Kohistan Batholith.

The Chilas liquid line of descent is typical for a “less-hydrous” fractionation sequence (e.g. ol, pyx, plag, amph). Gabbro-norite to diorite rocks are dominantly composed of plagioclase, clinopyroxene and orthopyroxene ( $\pm$ quartz,  $\pm$ amphibole). Despite the similarity of the Chilas gabbroic rocks to typical lower crust compositions, the “less hydrous” fractionation results in massive amounts of gabbroic material and small volume of silica-rich rocks. This mass balance and their mineralogy precludes them to represent the magmatic equivalent of the upper crust.

We propose that the upper, non-sedimentary CC is dominantly formed by hydrous high-pressure fractionation with subsequent delamination of the complementary garnet-pyroxene-amphibole-rich LC cumulates. This LC The delaminated amphibole-rich lower Jijal crust has trace element content and mineralogy adequate to explain certain characteristics of OIB. In contrast, the LCC, which is preserved over geological timescales, is formed by “less-hydrous” parental melts. We suggest that the bulk crustal composition is a mixing between these two compositional end-members.

## Plastic deformation of orthoenstatite and the ortho- to high-P clinoenstatite transition studied by atomistic simulation

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Atomistic computer simulation techniques are used to study plastic deformations of orthoenstatite, MgSiO<sub>3</sub>, at high pressure, P, and high temperature, T. The combination of molecular dynamics with metadynamics allows the direct observation of the structural changes at the atomic scale during the creation of stacking faults in the (100) planes. The respective slip deformations consist of at least four partial deformations crossing high energy intermediate structures. Although the low energy structures that may be observable experimentally suggest a dominant (100)[001] single slip system, the partial deformations also have contributions in (100)[010] direction.

Choosing conditions in the stability field of high-P clinoenstatite (T=1000 K, P=15 GPa), one sequence of plastic deformations in orthoenstatite leads to reformation of perfect orthoenstatite, whereas a second sequence results in the formation of the thermodynamically stable high-P clinoenstatite. From experiments (Lin, 2003; Kung *et al.*, 2004) it is known that due to the high kinetic barrier of the partly reconstructive phase transition, the formation of high-P clinoenstatite is prevented at ambient T in a wide pressure range up to at least 22 GPa. We are able to identify some of the possible metastable high-P polymorphs of orthoenstatite, which lead to anomalous behavior of the elastic properties (Kung *et al.*, 2004) and to changes in the Raman spectra (Lin, 2003).

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## The influence of metasomatized mantle wedge related to flat-subduction processes in extra back-arc basalts in Patagonia, Argentine

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During the Cenozoic age, there were relatively large volumes of basaltic lava eruptions in the eastern Andes along the Chile trench, South America, which generated extensive volcanic plateaus in a geotectonic environment of continental "extra" back-arc. The outcropping volcanic products in the studied area are displaced from 34°S to 46°30'S and host ultramafic xenoliths. Twenty-three samples of volcanic basalts from 11 different localities were analyzed. These rocks are basanites-tefrites, trachybasalts and basalts of the alkaline series, with phenocrysts and/or xenocrysts of olivine, orthopyroxene and clinopyroxene. In general, REE patterns for these rocks present similar variation with an expressive enrichment in light REE in relation to the heavy REE. The multi-elemental diagram analyses allow the individualization of the basalts into two groups with distinct behaviors. Group I shows OIB-like characteristics with Th enrichment and Pb depletion, while Group II presents OIB-like characteristics with Pb, Ba and Sr enrichment, which is related to some influence of the subduction zone. Isotopic data for both group present low <sup>87</sup>Sr/<sup>86</sup>Sr isotopic ratios (0.7031-0.7049) and moderate <sup>143</sup>Nd/<sup>144</sup>Nd values (0.512689 to 0.512983) that are comparable to typically mantelic basalts with OIB characteristic, according to Hart and Zindler (1989). However, Group I generally exhibit higher <sup>143</sup>Nd/<sup>144</sup>Nd and lower <sup>87</sup>Sr/<sup>86</sup>Sr isotopic ratio compared to the majority of samples from Group II. These characteristic are similar to the ones observed to Pliocene-Pleistocene post-plateau basalts studied by Gorrington and Kay (2001). However, our data suggest that some of these basalts in Group II are generated from depleted mantle wedge with some influence of the subduction event when flat-subduction of Nazca plate might be temporally occurring under the South American plate during the Miocene. Our conclusions are very close to the one reached by Stern *et al.* (1990) who classified the basalts in "cratonic" and "transicional" observing a geographic distribution for them. However, our basalts from both groups resemble the "cratonic" basalts of Stern *et al.* (1990), and we address the difference from one to the other to different contribution proportion of fluids originated from the subducting slab. We do not observe samples with "transitional" characteristic or any geographic distribution for them.

## Controls on weathering rates by reaction-induced hierarchical fracturing

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Weathering takes place through several stages that include mechanical disintegration of the rocks, and subsequent interactions between the exposed rock surface, the hydrosphere and the biosphere. Here we demonstrate how physical and chemical weathering processes are intimately coupled during weathering of basaltic intrusions (dolerites) in the Karoo Basin in South Africa. Incipient chemical weathering of the dolerites occurs around water-filled fractures originally produced by thermal contraction or by externally imposed stresses. This chemical weathering causes local expansion of the rock matrix, which generates elastic stresses. On mm to cm scales, these stresses lead to mechanical layer-by-layer spalling, producing the characteristic spheroidal weathering patterns. However, our field observations and computer simulations demonstrate that in confined environments, chemical weathering drives a much larger scale hierarchical fracturing process in which fresh dolerite undergoes a continuous domain division that effectively regenerates fresh surfaces in a self-accelerating manner. This process produces the characteristic weathering patterns seen in Karoo and a wide-range of other geological environments, and provides a first-order control on the total weathering rate.

## **The mechanism of oxidation and “leaching” of ilmenite during natural and experimental alteration**

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Ilmenite ( $\text{FeTiO}_3$ ) undergoes weathering through oxidation and removal of Fe to form an apparently continuous series of compositions from ilmenite to pseudorutile (ideally  $\text{Fe}_2\text{Ti}_3\text{O}_9$ ), and with further weathering, to leucoxene (essentially rutile and/or anatase). We have carried out an experimental study of ilmenite alteration in autoclaves at  $150^\circ\text{C}$  in HCl solution, and studied the resulting products by X-ray diffraction, scanning and transmission electron microscopy, electron microprobe and Raman spectroscopy. In some experiments the solution was initially enriched in  $^{18}\text{O}$  and the distribution of the isotope in the alteration products mapped from the peak shift in the Raman spectra. The results indicate that the alteration proceeds in two distinct stages, each with a sharp interface between the parent phase and the product. The alteration begins at the original ilmenite crystal surface and along cracks through which the fluid can migrate. The first alteration product is pseudorutile – no phases intermediate between ilmenite and pseudorutile were detected. The textural relationship between ilmenite and pseudorutile suggests a coupled dissolution-precipitation mechanism rather than a solid state continuous oxidation and Fe diffusion mechanism. The second stage involves a further dissolution-precipitation step to form rutile. Raman spectroscopy shows that the  $^{18}\text{O}$  is incorporated in the rutile during the recrystallisation. Throughout the alteration process the original morphology of the ilmenite is preserved although the product is highly porous. The rutile inherits crystallographic information from the parent ilmenite, resulting in a triply-twinned rutile microstructure.

## **The role of crustal assimilation and fractional crystallization in the generation of a hybrid composite dikes suite in the Arabian-Nubian Shield, southwest Jordan**

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A suite of hybrid composite dikes from the Arabian-Nubian Shield (ANS) in southwest Jordan is investigated. The petrogenesis of these dikes is discussed on the basis of field, petrographic, geochemical and Rb-Sr isotopic data. These dikes originated from the interaction between basaltic magma and the granitic basement. This interaction ranges from brecciation and partial assimilation of the host alkali feldspar granite to almost complete assimilation of the granitic material. Field structures range from intrusive breccia (i.e. angular granite fragments in a mafic groundmass) to hybrid composite dikes. The rims are mafic (basaltic andesite) in composition with alkali feldspar ovoids (up to 1 cm in diameter) ; while the central parts are of trachydacitic to dacitic in composition again with alkali feldspar ovoids and xenoliths of the dike rims.

A seven points Rb/Sr isochron from one the composite dikes yields an age of  $560 \pm 7$  Ma and an initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.70332 \pm 0.00004$  ( $2\sigma$ ) and MSWD value of 0.59.

Geochemical modelling using major, trace elements and isotopes suggest the generation of the hybrid composite dikes through the assimilation of 30% granitic crustal material by the basaltic magma, while the latter was undergoing fractional crystallization deep in the continental crust.

## Changes in the $\delta^{15}\text{N}$ of nitrate in Greenland ice: Implications for source changes over the last 500 years

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Recent increases in atmospheric nitrogen oxides may have a profound effect on terrestrial and lacustrine ecosystems through increases in the deposition of nitrogen. These nitrogen oxides, emitted from both anthropogenic (e.g., fossil fuel combustion) and natural (e.g., biomass burning, lightning, and soil emissions) sources, also affect the lifetimes of greenhouse gases such as methane and carbon dioxide through atmospheric interactions with ozone and OH. Developing an understanding of natural variations in atmospheric nitrogen oxides over the Holocene will aid in the interpretation of long-term records of climate and ecosystem change. One possible source of such information is the record of nitric acid ( $\text{HNO}_3$ , or nitrate,  $\text{NO}_3^-$ ), the primary sink of nitrogen oxides, obtained from ice cores in polar ice sheets.

We present isotopic measurements of nitrate ( $^{15}\text{N}/^{14}\text{N}$  and  $^{18}\text{O}/^{16}\text{O}$ ) deposited and preserved in ice at Summit, Greenland. Previous studies have suggested that the  $\delta^{15}\text{N}$  of nitrate in precipitation contains a source signal while the  $\delta^{18}\text{O}$  of nitrate contains information regarding chemical pathways of nitrate production prior to deposition. Our measurements from a 100-meter ice core, which contains approximately 300-500 years of climate information, show a large shift in  $\delta^{15}\text{N}$  between the top and bottom of the core. We discuss the possibility that this shift is indicative of changing sources of nitrogen oxides to the atmosphere over the industrial transition. This would imply that our ice record can be used to evaluate the contribution and extent of influence of pre-industrial sources of nitrogen oxides, providing an important constraint on the interpretation of other records of environmental change.

## Trials into the effect of manganese oxide addition to composted municipal solid waste

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### Procedure

Trials were carried out into the effects of amending the compost-like output (CLO) from the aerobic digestion of municipal solid waste with varying levels of waste manganese oxides. It was theorised that manganese oxide could affect humification of the decomposing CLO, with potential improvements in carbon storage in the material. Carbon emission data was recorded over the five week period of the study, and  $E_4/E_6$  ratios of a sodium pyrophosphate extraction were measured from CLO samples after five weeks of composting to assess levels of humic matter. Sand was included in the study as a control amendment with the manganese oxide, which was itself a granular material coated onto sand grains.

### Results

A statistically significant effect was found between manganese oxide level and carbon flux rate, with flux rate increasing with increasing manganese oxide level. The effect was not significant between all levels however. The level of sand amendment included for comparison was found to be a significant factor only in one of the two trials carried out, where flux rate increased with sand addition. The  $E_4/E_6$  ratio for the CLO extractions were found to be unaffected by the addition of manganese oxide. The absorbancies at both wavelengths (465nm and 665nm) were found to increase significantly with increasing manganese oxide level.

### Conclusions

The effect of the manganese oxide was found to have an effect on the rate of flux, although the confounding nature of environmental variations means that further work would be needed to quantify this effect with greater confidence. Attributing the increase in flux rate with manganese oxide to the physical or chemical properties of the amendment is difficult with the data collected to date.

The results from the absorbance analysis suggest that while the degree of humification of the humic matter was unchanged by the presence of manganese oxide, more humic matter in total seems to have been formed.

## Deciphering the record of early life in Precambrian oceans using combined microscopy and microchemistry of organic-walled microfossils.

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Organic-walled microfossils (acritarchs) can be exquisitely preserved in fine-grained siliciclastics and chert through the Proterozoic and conceivably in the Archean. These fossils record crucial steps in the early evolution and diversification of complex ecosystems, and their morphology indicates the evolution of major biological innovations. However, the taxonomy of these fossils is often impossible to resolve beyond the level of domain.

Acritarchs are conventionally interpreted as algal cysts but most probably include a larger range of organisms such as prokaryotic sheaths, heterotrophic protists or even parts of multicellular beings. The organic remains can be studied in thin sections with optical microscopy and with Raman micro-spectroscopy to prove endogenicity. They can then be isolated from the rock by gentle acid maceration to be further studied by FTIR micro-spectroscopy, SEM and TEM microscopy to reveal morphological and ultrastructural details, and biopolymer composition, permitting in some cases to determine their biological affinities by comparison with extant clades. We present how combining microscopy (light microscopy, Scanning and Transmitted Electron Microscopy) with micro-spectroscopic analyses of individual Proterozoic microfossils (FTIR and Raman micro-spectroscopy) offers further insights into the paleobiology and evolution of early microorganisms in Precambrian oceans.

Such a multidisciplinary approach offers new possibilities to investigate the record of early life on Earth and beyond.

## The most probable Earth composition

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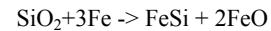
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Redox and isotopic criteria for Earth primitive materials clearly select a unique chondrite family, which, whatever its conditions of formation, can be modelled simply by a mixture in variable proportions of three mineral types: silicates (enstatite with minor amounts of oligoclase and free silica), metal (Si-bearing kamacite) and sulfides of Fe, Ca and Mg (evolving to metal, oxides and silicates with increasing temperature and decreasing  $f_{S_2}$ ).

The modelling of a million such mixtures results in well defined elemental correlations, which can be used efficiently to test the obtained compositions versus high pressure mineralogy and seismological data. About a quarter of them have Fe contents compatible with the Earth's Core/Mantle ratio and mantle range of densities. Their composition is perfectly compatible with the geophysical constraints in their present state of accuracy

They predict Lower Mantle features long advocated (eg enrichment in silica and/or iron).

In our model mantle iron derives largely from the reaction:



This results in a strong correlation between bulk mantle iron content and core silicon content ( $\text{Si}_n = 1.5 \text{ Fe}_m - 5.9$ ).

There is also a well marked anticorrelation between silica saturation and iron content of the lower mantle (Perovskite% = 100 (1.07-0.015 $\text{Fe}_m$ %)). That is, the denser it is, the softer it is.

Finally the Lower Mantle is strongly depleted in major radioactive elements (U~7ppb).

From the presently available experimental high pressure melting experiments a primitive pyrolytic upper mantle is obtained by an average 25-40% partial melting of the original solid silicate part

Earth envelopes' compositions hence are as follows:

Primitive Upper mantle: pyrolytic

Lower Mantle:  $\text{Mg}_{0.81}\text{Fe}_{0.15}\text{Al}_{0.03}\text{Ca}_{0.01}\text{Si}_{10.97}\text{Al}_{0.03}\text{O}_3$

Core: 85.3% Fe, 5.7% Ni, 6% Si, 3% O.

## A multiproxy approach to constrain the origin of the natural fertilisation on the Kerguelen plateau

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The Kerguelen Ocean and Plateau compared Study (KEOPS) took place during the austral summer (19 Jan-13 Feb 2005, R/V "Marion-Dufresne", 68°-78°E/ 49°-52°S sector). One of the KEOPS objectives was to determine the mechanisms responsible for the bloom occurring on the Kerguelen plateau and allocated to natural fertilisation due to island inputs.

Coupled with physical measurements, a multi-proxy investigation was carried out in order to better constrain the sources of iron, but also the water mass and particle pathways. REE concentration and Nd isotopes suggest that weathering of Heard Island brings significant amounts of iron to plateau waters (Zhang *et al.*, in rev.), in agreement with radium isotopes (van Beek *et al.*, in rev.) and consistent with total dissolvable and particulate iron results. The isotopes allow the quantification of particle settling velocities on and off the Kerguelen plateau and the identification of strong boundary scavenging along the south-east Kerguelen slope, likely due to the occurrence of nepheloid layers (Venchiarutti *et al.*, *in rev.*). Slow particle settling velocities are observed on the Kerguelen plateau, consistent with the high mineralization rates characterizing this area, deduced from the barite concentrations which were used as proxy for twilight zone mineralization of organic matter (Jacquet *et al.*, in rev.).

This talk highlights the main results deduced from each proxy, underlining both coherences and contradictions. A synthetic and simplified scheme of the potential sources and sinks of iron over the plateau is finally discussed.

### References

All the papers cited in revision will be published in the KEOPS special issue, Deep Sea Research II.  
Venchiarutti C., Jeandel C. and Roy-Barman M., <sup>230</sup>Th and <sup>232</sup>Th isotopes in the wake of Kerguelen *Deep Sea Res.* (submitted)

## Geochemical monitoring of CO<sub>2</sub> storage: Natural analogues studies using isotopic composition of gases and travertines

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Studies of natural analogues can be used to understand long-term processes affecting CO<sub>2</sub> in geological storage, because CO<sub>2</sub> can remain trapped for geologically significant times.

Noble gases are useful tools for tracing CO<sub>2</sub> and track its leakage toward surface. They also provide information about the origin of CO<sub>2</sub>; its migration, physical processes such as diffusion, solubilization in water and residence time.

We collected gas samples from natural CO<sub>2</sub> reservoirs and surface seeps in French carbo-gaseous province: Sainte Marguerite seeps (Allier, France), Montmiral natural CO<sub>2</sub> field (Drôme, France), and in the Colorado Plateau (Green River seeps (Utah), Springerville St Johns natural CO<sub>2</sub> field (Arizona)).

The preliminary results obtained provide strong evidence for a mantle-derived magmatic source for CO<sub>2</sub> in all sampled accumulations, and show various physical processes affecting CO<sub>2</sub> during its migration.

For example, natural CO<sub>2</sub>-degassing springs near Sainte Marguerite, Allier, France show evidence of Rayleigh fractionation on argon, neon isotopes and elementary ratio of atmospheric-derived noble gases. This distillation process highlights rapid migration of CO<sub>2</sub> toward surface, consistent with small accumulation of radiogenic/nucleogenic isotopes.

The Helium concentrations range between 0.28 and 8.22 ppmv, consistent with a magma degassing at depth. Such low concentrations imply that solubilization of CO<sub>2</sub> in water occurs at shallow depth, thus CO<sub>2</sub> migration mainly occurred in the gaseous state.

Active and fossil travertines were present in all sampled areas. They represent geological record of the movement and discharge of CO<sub>2</sub> and associated fluids to the Earth's surface. They also provide information about the origin of CO<sub>2</sub> from which they precipitate. We present here our first petrographical observations as well as isotopic results for the travertines, including  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . The samples from Green River have  $\delta^{13}\text{C}$  values typical of thermogene carbonates and presumably associated with deep magmatic degassing. On the contrary in Montmiral, the  $\delta^{13}\text{C}$  values are more typical of the meteo-gene travertines, associated with atmosphere-derived CO<sub>2</sub>.

## Nitrate reduction, sulfate reduction and sedimentary iron-isotope evolution during the Cenomanian-Turonian Oceanic Anoxic Event (OAE2)

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Organic-carbon rich shales from localities in England, Italy and Morocco, which formed during the Cenomanian-Turonian Oceanic Anoxic Event (OAE), have been studied for their total organic carbon values (TOC) together with their carbon-, nitrogen- and iron-isotope ratios. Carbon-isotope stratigraphy ( $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$ ) allows accurate recognition of the strata that record the Oceanic Anoxic Event, in some cases allowing characterization of isotopic species before, during and after the OAE. Within the black shales formed during the OAE, relatively heavy nitrogen-isotope ratios, which correlate positively with TOC, suggest nitrate reduction; extant sulfur-isotope data and molecular fossils of green sulfur bacteria signify the development of free  $\text{H}_2\text{S}$  in the water column by sulfate reduction. Black shales deposited before the onset of the OAE in Italy have unusually low bulk  $\delta^{57}\text{Fe}$  values, unlike those found in the black shale (Livello Bonarelli) deposited during the Oceanic Anoxic Event itself: these latter conform to the Phanerozoic norm for organic-rich sediments. Pyrite formation in the pre-OAE black shales has apparently taken place via dissimilatory iron reduction (DIR), within the sediment, a suboxic process that causes an approximately -2 ‰ fractionation between a lithogenic Fe(III)oxide source and  $\text{Fe(II)}_{\text{aq}}$ . In contrast, bacterial sulfate reduction (BSR), at least partly in the water column, characterized the OAE itself and was accompanied by only minor iron-isotope fractionation. This change in the manner of pyrite formation is reflected in a decrease in the average pyrite framboid diameter from  $\sim 10\ \mu\text{m}$  to  $\sim 6.5\ \mu\text{m}$ . A gradual, albeit irregular increase in Fe-isotope values during the OAE, as recorded in the Italian section, may demonstrate limited isotopic evolution of the dissolved iron pool, consequent upon ongoing water-column precipitation of pyrite under euxinic conditions.

An important implication of the low  $\delta^{57}\text{Fe}$  values measured in this study is that they decrease the gap between the lowest values observed for Phanerozoic sediments in which DIR is indicated to exert a strong control of isotopic fractionation and the very low Fe-isotopic compositions observed for Archaean rocks.

## Speciation of arsenic in the coprecipitated As(V)-Fe(III) solids

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Lime neutralization and coprecipitation with ferric iron is the common method for the removal and immobilization of arsenic from industrial mineral processing effluents. The nature of the arsenate in the coprecipitated  $\text{As}^{\text{V}}\text{-Fe}^{\text{III}}$  solids is not fully understood though it is generally believed that arsenate is adsorbed as surface complex on ferrihydrite. In this study we used infrared spectroscopy and X-ray diffraction to characterize the coprecipitates with an attempt to shed some more light on this issue.

A suit of  $\text{As}^{\text{V}}\text{-Fe}^{\text{III}}$  coprecipitates were synthesized by neutralization of acidic solutions of various Fe/As molar ratios to pH 4-8 using both sodium hydroxide and slaked lime as base. The synthesized samples were subjected to powder X-ray diffraction and Fourier transformed infrared analyses. Lab synthesized scorodite, poorly crystalline ferric arsenate and 2-line ferrihydrite were used as reference materials. The speciation of arsenate was determined based on the As-O stretching vibration bands located at 650-950  $\text{cm}^{-1}$  and the characteristic XRD bands of poorly crystalline ferric arsenate and ferrihydrite.

Both infrared spectroscopic and X-ray diffraction data showed that poorly crystalline ferric arsenate is the dominant arsenate phase in the  $\text{As}^{\text{V}}\text{-Fe}^{\text{III}}$  solids coprecipitated at pH 4 using NaOH as base. At pH 8 the arsenate is present basically as adsorbed surface complex in ferrihydrite. The results are similar to the arsenate-ferrihydrite adsorption system in which poorly crystalline ferric arsenate surface precipitate is formed at acidic pH while bidentate surface complex is the major arsenate species on the surface of ferrihydrite. Crystalline yukonite ( $\text{Ca}_2\text{Fe}_3(\text{AsO}_4)_4(\text{OH})\cdot 12\text{H}_2\text{O}$ ) was generated in the coprecipitated solid when the CaO neutralized system was subjected to heat treatment at 75 °C.

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## Geochemistry and genetic models for tin deposits in South China

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South China is one of the most important tin producers in the world. Except for the classical granite-related magmatic-hydrothermal tin deposits, there are many other types of tin deposits in this region, such as sediment-hosted massive sulfide type and migmatitic hydrothermal-related tin deposits. In addition, A-type granite related tin deposits are also found in South China recently.

The Dachang tin deposit in Guangxi Province is the secondary largest tin producer in China. Although some researchers have suggested that this deposit is a skarn or replacement type associated with the Yanshanian magmatic hydrothermal event, our detailed geochemical investigation including major, trace, rare earth elements, Pb, S, Sr, Nd, B, H, O, He, and Ar isotopes have indicated a submarine exhalative-hydrothermal origin for the bedded and massive sulfide ores in the deposit.

The Yunlong tin deposit in Yunnan Province is a medium-sized tin deposit, which occurs mainly as cassiterite-quartz-tourmaline ore veins hosting in a suite of metamorphic rocks and migmatite. Previously many researchers considered this deposit as a typical granite-related tin deposit, with a blind granite body at depths or it is genetically related to a S-type granite body occurring just outside the deposit. Our recent fluid inclusions, geochemical and isotopic (H-O, S, Pb, B) studies in the deposit indicated that metamorphic hydrothermal fluids generated by dehydration of the regional Chongshan group rocks were possibly responsible for the formation of this tin deposit. Hence, we proposed that the Yunlong tin deposit belongs to a new type of tin mineralization, i.e., migmatitic-hydrothermal type.

The Furong tin deposit in Hunan Province is a newly discovered large tin deposit. Tin mineralized bodies mainly occur as veins in the crush zone of the Qitianling granite that genetically related to chlorite alteration, although less important small greisen and skarn orebodies also occurred in the contact of granite with country rocks. Our study shows that the Qitianling granite is distinctly different from common S-type tin granite in the world but rather similar to A-type granite. Tin mineralization is suggested to be related to post-emplacement chloritization of the Qitianling granite. Sn-rich mafic minerals (amphibole, biotite and titanite) in the granite released tin and other metals (e.g. Ti) into the hydrothermal fluids when these minerals were altered to chlorite. Then cassiterite and rutile precipitated together when the physical and chemical condition of Sn- and Ti-rich fluids changed. It is a special model for granite-related tin mineralization.

## Geochemistry of Late Mesozoic lamprophyre dikes from the eastern North China Craton: Implications for subcontinental lithosphere evolution

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Mineral chemical, element geochemical and Sr–Nd–Pb isotopic data have been determined for the late Mesozoic lamprophyre dikes from the Jiaodong and Liaodong Peninsulas. Together with the published data, three late Mesozoic lamprophyre belts in the eastern North China Craton (NCC) could be grouped, from the Sulu Orogenic Belt towards the northwest, are the Sulu lamprophyre belt (belt 1), Guojialing–Linglong lamprophyre belt (belt 2) and Dashiqiao–Laizhou lamprophyre belt (belt 3), respectively. These lamprophyre dikes are potassic and ultra-potassic rocks and have high MgO and compatible element contents. They are all enriched in LREE and LILE and depleted in HFSE. The belt 3 lamprophyre dikes have similar Sr–Nd–Pb isotopic compositions to the EM 2-type mantle. From the belt 3 through belt 2 to belt 1, the lamprophyre dikes show a trend towards the EM 1-type mantle in terms of Sr–Nd–Pb isotopic compositions. In addition, the Sr–Nd–Pb isotopic compositions of each lamprophyre belt show a trend towards those of MORB. Furthermore, the belt 1 lamprophyre dikes have super-chondritic Nb/Ta ratios (>17.5) whereas the belt 2 and belt 3 lamprophyre dikes show sub-chondritic Nb/Ta ratios (<17.5). All these features, together with comparison to the Late Triassic (201 Ma) Sulu mafic dikes that have similar Sr–Nd isotopic compositions to the EM 1-type mantle and also show super-chondritic Nb/Ta ratios, suggest that the eastern NCC lithospheric mantle near the Sulu Orogenic Belt was hybridized by the melt derived from the subducted Yangtze continental slab during the Triassic collision of the Yangtze Craton with NCC and then all the subcontinental lithosphere beneath the eastern NCC was metasomatized by slab-derived fluid during the late Mesozoic Palaeo-Pacific plate subduction. Detailed elemental and isotopic data, together with our recent studies on the origin of the late Jurassic (160–153 Ma) Linglong suite and Early Cretaceous (130–126 Ma) Guojialing suite in the northwestern Jiaodong Peninsula, also suggest that the Early Cretaceous lamprophyre dikes were derived from partial melting of the delaminated lithospheric mantle plus additional input from the upwelling asthenospheric mantle. Such a delamination is a consequence of the progressive slab roll-back associated with the subduction of the Palaeo-Pacific plate.

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## Shallow crystallization and deep magma storage: Insights from U-Th and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology

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Precise  $^{40}\text{Ar}/^{39}\text{Ar}$  age determinations and  $^{238}\text{U}$ - $^{230}\text{Th}$  analyses from volcanoes atop vastly different thicknesses of crust in four subduction zones reveal new insights about the temporal and physical development of arc magmatic systems over several tens of thousands of years. Analytical advances yield  $^{40}\text{Ar}/^{39}\text{Ar}$  ages and U-Th mineral isochrons for latest Pleistocene to Holocene lavas and tephra with uncertainties of only a few thousand years. Thus, quantifying the length of time between crystallization and eruption has become more robust and crystallization-eruption intervals may be calculated over the lifetime of an individual volcano; this represents a significant advance in linking volcanic evolution to magmatic processes as compared to restricting U-Th geochronology to historical eruptions. Our most compelling discovery is that minerals (opx, cpx, mt, plag, ol), matrix glass, and whole rocks measured in dozens of basaltic to rhyolitic lava flows and pyroclastic deposits erupted over the last ~150 ka define  $^{238}\text{U}$ - $^{230}\text{Th}$  isochrons whose age cannot be distinguished from that of the eruption. This finding indicates that the observed phenocrysts began to grow less than 1 to 2 ka prior to eruption and that processes including crystal fractionation and magma mixing—required to explain the spectrum of basaltic to rhyolitic compositions erupted at these volcanoes—took place *prior* to growth of the erupted crystals. The short crystal residence times are consistent with inferences from trace-element zoning and diffusion profiles in phenocrysts and  $^{226}\text{Ra}$ - $^{230}\text{Th}$  disequilibrium data from recent eruptions at several volcanoes, each of which likely reflect exceptionally rapid transit of evolved melt through the crust, during which crystallization of the erupted phenocrysts occurs *en route* due to decompression.

The duration of magma storage and processing in the deep crust, although more difficult to constrain, can be tracked using initial ( $^{230}\text{Th}/^{232}\text{Th}$ ) ratios in sequences of lavas and tephra erupted over  $10^4$ - $10^5$  year periods of volcano growth that have been precisely dated using  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology. Our large set of  $^{238}\text{U}$ - $^{230}\text{Th}$  data suggests that the duration of deep crustal storage, differentiation and mixing of magma may vary greatly, ranging from a few thousand years to longer than 100 ka. In most cases, it appears that the deep crust buffers mafic magma flux from the mantle, which may explain our finding that long-term arc volcano growth rates are modulated to within a narrow range, despite gross differences in crustal thickness or age.

## Oxygen isotope record of Devonian and Carboniferous biogenic apatite

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Oxygen isotopes of conodont apatite (n=1286) were studied in order to reconstruct the palaeotemperature and ice volume history during the Devonian and Carboniferous. Oxygen isotope ratios are around 18‰ V-SMOW in the Early Devonian, increase gradually during the Pragian and Emsian, show comparatively high values around 20‰ V-SMOW in the Middle Devonian, decrease during the early Frasnian to minimum values around 18‰ V-SMOW at the Frasnian-Famennian transition, and increase again to 19‰ V-SMOW in the Famennian. The Early Carboniferous record is characterized by a first major increase to values around 21‰ V-SMOW in the middle Tournaisian to earliest Viséan, high values around 21‰ V-SMOW in the Viséan and a second major increase in the Serpukhovian to maximum values around 23‰ V-SMOW. Oxygen isotope values of Pennsylvanian and Early Permian conodont apatite vary between 19 and 22‰ V-SMOW.

The  $\delta^{18}\text{O}$  fluctuations recorded in the Devonian are interpreted as palaeotemperature changes with the Early and Late Devonian revealing relatively warm climatic conditions, whereas the Middle Devonian is characterized by a cooler climate. The positive shifts in the oxygen isotope ratios in the Tournaisian and Serpukhovian are too large to be explained solely by a change in sea water temperature and/or salinity. Instead, the 2‰ positive shift in the Tournaisian argues for a first major cooling and glaciation event in the Tournaisian with ice masses persisting into the Viséan. The 1.5‰ shift in the Serpukhovian points to an intensified ice build-up during the latest Mississippian. The relatively large variance in the oxygen isotope ratios of Pennsylvanian conodonts is explained by the waxing and waning of Gondwanan ice sheets.

The comparison of the conodont apatite with published brachiopod calcite  $\delta^{18}\text{O}$  records (taking into account the different thermodynamic oxygen isotope fractionations for apatite and calcite) reveals that  $\delta^{18}\text{O}$  values of apatite are in many cases significantly higher than calcite  $\delta^{18}\text{O}$  values. Apatite  $\delta^{18}\text{O}$  values translate into realistic palaeotemperatures by assuming a modern  $\delta^{18}\text{O}$  value for Palaeozoic sea water and do not support the idea of a secular change of the oxygen isotope composition of sea water.

## **Reactive fluid flow in slabs – A metamorphic view on the origin of the slab component**

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Subduction zones are the places on Earth where quantitatively the largest mass transfer rates exist and element fractionation occurs between crust and mantle. The agents, which are central to these processes, are aqueous fluids, supercritical fluids, and melts. Field evidence found in formerly subducted rocks shows that the preferential flow field of released slab fluids is highly channelized and that these fluids tend to react with parts of their wall rocks. Thereby they are able to serve as agents for mobilization and transport for most trace elements. I will describe a model for fluid flow within slabs that suggests that slab melting must not necessarily be invoked for mobilization of so-called fluid-immobile trace elements. For this model it is critical that permeabilities in the subducting slab appear to be too low and dihedral angles between fluid and relevant minerals too high to allow for pervasive porous flow, hence the fluids tend to localize while flowing. I will outline how fluid channelization controls reaction rates and element redistributions during metamorphism of the subducting plate as well as trace element composition of subduction-related fluids during flow. Channelized fluid flow predicts that most formerly subducted material will show only very limited evidence for fluid flow, consistent with the rarity of observed high fluid fluxes in subduction-related rocks. Aqueous fluid produced by dehydration reactions will not percolate through large rock volumes, but rather will be carried away from the dehydration sites by a veining network. Indeed evidence for significant aqueous-fluid fluxes have been found in high-pressure veins with adjacent selvages. In such selvages, LILE's generally show the highest mobilities, followed by light REE's and then heavy REE's and HFSE's. Equilibrium between aqueous fluid and surrounding rock will only be approached at sites of fluid production and mineral reaction. However, this fluid can be significantly modified while moving upwards through a veining network where the wallrocks are out of equilibrium with the passing fluid. In a subducting slab, such reactive fluid flow can preferentially dissolve minerals and release their trace elements. The degree of change in aqueous fluid composition will depend on the fluid composition itself, the amount of fluid–mineral surface interaction and the ratio between the kinetics of the mineral reactions and the velocity of the passing fluid. In this talk I will focus on field evidence for reactive fluid flow in localized channel networks in high-pressure metamorphic terranes and its distinct chemical signature that is a direct counterpart to that in arc magmatism.

## **Interplay of deformation, fluid infiltration and eclogitization**

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It is a common observation that during increasing metamorphic conditions dry coarse-grained rocks often fail to react because of sluggish mineral reactions. The crucial trigger mechanism to start the delayed metamorphic reactions is the infiltration of fluids. But how do fluids flow within dry rocks with very low permeability and how fast do the system react? The Kråkenes Gabbro is a partially deformed and transformed igneous body located in the Western Gneiss Region (Norway). The body is transected by a swarm of cm-wide hydrous eclogite-facies shear zones. The shear zones have cores of intensely deformed material surrounded by a dm-wide reaction halo where deformation is less obvious. The water-bearing minerals are highly concentrated in shear zones and their modal abundance progressively decreases with increasing distance to the deformation front. Fluid infiltration into the undeformed parts apparently occurred both along grain boundaries and through reactive minerals. Thereby, olivine appears to have been too reactive and thus shielded by corona formation, whereas clinopyroxene mainly reacted along its grain boundary and the magmatic plagioclase reacted to a micron-sized hydrous symplectite. It is interesting to note that these symplectites lack deformation features, indicating that they formed under static conditions. The subdomains can be regarded as tiny batch-experiments in which the fluid was rapidly supersaturated in the precipitating mineral phases, so that the replacement products inherited the chemical variations of the subdomains. In this manner magmatic zoning of plagioclase grains have been preserved. These findings imply that the kinetics of the reactions were faster than the fluid flow. From less transformed subdomains it is evident that element transfer was controlled by discrete transport pathways. At the terminations of such transport pathways the stable mineral assemblage precipitated. Real eclogite formed only if the element exchange between different subdomains was efficient, otherwise “metastable” phases formed. Obviously, the dynamic formation of porosity and permeability is crucial for the described observations, because it allows fluid access to the reaction interfaces and mass transfer even in undeformed parts. However, even though the suggested fluid pathways are wide, in cases up to several hundred microns, the final effective porosity is low. Thus, beside the deformation enhanced fluid infiltration along the shear zones effective porosities only exist while minerals react – then the newly formed mineral assemblage closes the pathways. Formation of porosities is either reaction enhanced along grain boundaries or occurs in form of porosity waves associated with mineral reactions through reactive domains.

## Iron isotopes constrain the roles of biologic and abiologic processes in formation of banded iron formations

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Iron isotope compositions of 2.5 Ga banded iron formations (BIFs) from the Hamersley Basin and Transvaal Craton identify the iron sources and formation pathways during BIF genesis. <sup>56</sup>Fe/<sup>54</sup>Fe ratios for magnetite reflect a strong inheritance from Fe(III) hydroxide precursors, with a peak about  $\delta^{56}\text{Fe}=0$ . Near-zero  $\delta^{56}\text{Fe}$  values for the Fe(III) hydroxide precursors may be produced by complete or near-complete oxidation of Fe(II)<sub>aq</sub> derived from marine hydrothermal fluids, suggesting the existence of a significant oxidant in the upper water column at 2.5 Ga. Transformation of the Fe(III) hydroxide precursors to magnetite occurred through several diagenetic processes that produced a range of  $\delta^{56}\text{Fe}$  values: 1) addition of marine hydrothermal Fe(II)<sub>aq</sub>, 2) reduction by bacterial dissimilatory Fe(III) reduction (DIR), and 3) interaction with excess low- $\delta^{56}\text{Fe}$  Fe(II)<sub>aq</sub> that was produced by DIR.

The range in  $\delta^{56}\text{Fe}$  values for siderite reflects a mixture of iron sources including seawater Fe(II)<sub>aq</sub> and Fe(II)<sub>aq</sub> produced by DIR. The inferred Fe sources and pathways for magnetite and siderite from adjacent bands, however, are distinct, and these minerals did not generally form in Fe isotope equilibrium. Instead, the Fe isotope variability of magnetite and siderite document fine-scale isotopic heterogeneity that reflects a strong component of diagenesis. Support for an important role of DIR in siderite formation in BIFs comes from previously published C isotope data on organic carbon and siderite, which may be explained as a mixture of C produced by bacterial and seawater sources.

Several factors likely contributed to the important role that DIR played in formation of the 2.5 Ga BIFs from the Hamersley Basin and Transvaal Craton, including high rates of ferric hydroxide formation in the upper water column, delivery of organic carbon related to photosynthesis, and low clastic input. We infer that DIR-driven Fe cycling was much more important during deposition of these BIFs than in modern marine systems. Low pyrite contents in oxide-facies BIFs suggests that bacterial sulfate reduction (BSR) was minor, and the absence of sulfide allowed preservation of magnetite and siderite; low BSR also provided a competitive advantage for DIR. When compared to BIFs that formed prior to 3.0 Ga, the Fe isotope signature for DIR is absent in the older sequences, suggesting that this metabolism may have been absent in the Early Archean. Moreover, the generally positive  $\delta^{56}\text{Fe}$  values for the older BIFs suggests that oxidants were more limited, which in turn would limit DIR activity.

## Slab dehydration beneath central Mexico inferred from melt inclusions and geodynamic modeling

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To investigate volatiles (H<sub>2</sub>O, CO<sub>2</sub>, S, Cl) and magma formation in subduction zones, we have analyzed olivine-hosted melt inclusions from 10 basaltic centers at varying distances from the trench in the Michoacan-Guanajuato Volcanic Field in central Mexico. Our data from these primitive basaltic cones (most contain Fo87-90 olivine) reveal the surprising result that H<sub>2</sub>O contents are high (3.0-5.2 wt%) from the volcanic front to ~140 km behind the front. The high H<sub>2</sub>O across the arc, combined with high S and Cl, suggest that flux of volatiles from the subducted plate has affected a broad region of the underlying mantle.

To understand the depths over which subducted slab components dehydrate beneath the arc, we have modeled the thermal structure of the mantle wedge and slab using a 2D numerical model (Manea *et al.*, 2005). We then use phase equilibria to evaluate dehydration of subducted sediment, altered oceanic crust, and hydrated lithospheric mantle in the slab (Rupke *et al.*, 2004). An important constraint is that volcanism has migrated towards the trench over the last 3 Ma, suggesting an increase in slab dip angle. Thus our studied cones farthest from the trench are older than those closer to the trench, and their volatile contents likely reflect mantle hydration resulting from a different slab geometry than the present-day configuration.

For the present-day slab model (13 Ma oceanic crust at trench), maximum mantle wedge temperatures beneath the volcanic front (1200-1300°C) agree with petrological calculations. The model results predict dehydration of subducted sediment and altered oceanic crust beneath the forearc, the volcanic front, and extending ~50 km behind the front. Subducted lithospheric mantle, if hydrated, would undergo dehydration beneath the arc ~50 km behind the volcanic front. In addition, chlorite formed by hydration of the overlying mantle wedge would no longer be stable ~100 km behind the volcanic front. Thus the width and high magmatic H<sub>2</sub>O in the Quaternary arc may be due partly to dehydration of subducted serpentinized mantle and the stability of chlorite in the overlying mantle wedge. For the 3 Ma slab model, subducted sediment and oceanic crust dehydrate largely beneath the wide forearc during near-horizontal subduction. The main source of H<sub>2</sub>O to flux the wedge beneath the volcanic front at 2-3 Ma comes from dehydration of serpentinized lithospheric mantle in the slab. Thus our results for both the present-day and 3 Ma slab configurations suggest a role for deserpentinization of the downgoing slab in magma generation beneath Mexico.

## Springtime Deposition and Emission of Mercury from Arctic Snow

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Atmospheric mercury depletion events (MDEs) provide a pathway for gaseous elemental mercury ( $\text{Hg}^0$ ) to be rapidly oxidized to  $\text{Hg}^{2+}$  and deposited to terrestrial surfaces. MDEs occur between polar sunrise and spring melt in many high-latitude locations. Projected changes in the Earth's climate this century will alter contaminant transport pathways (Macdonald, 2005) and may enhance Hg deposition and bioavailability in high latitude ecosystems (Lindberg, 2002).

We investigated net Hg deposition by MDEs to the Arctic cryosphere near Barrow, Alaska by (1) monitoring Hg concentrations in surface snow for 18 days, (2) quantifying emission of total gaseous mercury (TGM) from snow in flux chambers and (3) applying a newly developed analytical technique to measure Hg isotopic fractionation during (photo)chemical reactions. A nine-day MDE occurred during our intensive sampling campaign.

Daily monitoring of the upper 1 cm of the snowpack at two locations showed an increase in total Hg concentration throughout the MDE to maximum levels of 147 and 237 pg/g Hg. Twice-daily sampling at one site revealed a secondary trend of night-time Hg deposition. Mercury concentration in surface snow typically rose after exposure to darkness (~12 hours), while it remained unchanged or slightly decreased after exposure to daylight (~12 hours). Within two days of MDE cessation, Hg in surface snow returned to near-baseline levels and is probably the result of both  $\text{Hg}^0$  emission and physical mixing of the snowpack (high-Hg surface layer diluted by low-Hg snow column).

Flux chambers were employed to elucidate the rate and mechanism of TGM emission from natural snow. The TGM emission pattern was typical of light and/or temperature dependent reactions: emission peaked shortly after solar noon and ceased overnight. Peak TGM emission from MDE and non-MDE snow reached  $> 15 \text{ ng/m}^2/\text{hr}$  and  $\sim 8 \text{ ng/m}^2/\text{hr}$ , respectively. Blocking direct UV radiation decreased TGM emission by only 25%;  $\text{UV}_B$  was not wholly responsible for this flux. Hg isotopic ratios of snow samples before and after flux chamber incubation are being measured to help identify an isotope signature of Hg (photo)chemical reduction.

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## Modeling glyphosate and metal-glyphosate speciation at solution-mineral interfaces

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Glyphosate (N-(phosphonomethyl)glycine, PMG,  $\text{H}_3\text{L}$ ) is a widely used organophosphorous herbicide. It interacts with metal ions and mineral surfaces, which may affect its mobility, degradation and bioavailability in the environment. However, so far these interactions are far from fully understood.

This paper is a discussion on the complexation of PMG with metal ions in aqueous solution and the adsorption of PMG and Cd(II) on different mineral surfaces. EXAFS, ATR-FTIR, and XPS measurements showed that PMG adsorbs to the surfaces of goethite ( $\alpha - \text{FeOOH}$ ), aged  $\gamma$ -alumina ( $\gamma - \text{Al}_2\text{O}_3$ ) and manganite ( $\text{MnOOH}$ ) through one oxygen of its phosphonate group to singly-coordinated OH-surface sites.

The coadsorption of PMG and Cd(II) on the surfaces of goethite and manganite results in the formation of ternary mineral-PMG-Cd(II) surface complexes, as suggested from EXAFS results. In addition to the surface reactions in the binary Cd(II)-mineral and PMG-mineral systems, a single ternary complex with the stoichiometry  $\equiv \text{MeLCd}(\text{OH})^{1.5-}$  was sufficient to explain coadsorption data.

Surface complexation models consistent with the different spectroscopic results were fit to adsorption data using the 1pK reaction formalism involving charge distributions.

## Sorption of arsenic under oxic and anoxic conditions: Possible origins of elevated arsenic in groundwater

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In Bangladesh and West Bengal, millions of people are using groundwater with elevated (> 50ppb) concentrations of arsenic. The origin of the elevated arsenic levels is still unclear. Both As(V) and As(III) are strongly sorbed to iron(III) (hydr)oxides. We have developed surface complexation models for sorption of As(III) and As(V) on goethite and ferrihydrite. These models predict that sorption should limit As concentrations to acceptable levels even when As(V) is reduced to As(III) and ferrihydrite transforms to goethite. One hypothesis for the elevated As concentrations is that sorbed As is released during bacterial reductive dissolution of Fe(III) (hydr)oxides. However, this should yield a strong correlation between dissolved Fe and As but this is not observed. The formation of secondary Fe(II) or mixed Fe(II)/Fe(III) minerals such as siderite (FeCO<sub>3</sub>), green rust (GR) and magnetite has been suggested to reduce the aqueous concentration of Fe while leaving the concentration of As high in the Bangladesh and West Bengal aquifers. To test this hypothesis we have studied the adsorption of arsenite and arsenate to siderite, carbonate GR and magnetite as a function of pH using EXAFS and batch adsorption experiments.

EXAFS spectra show that As(V) sorbs to GR, magnetite and siderite by forming bridging bidentate inner-sphere surface complexes. The adsorption is similar to that of As(V) on Fe(III) (hydr)oxides and the adsorption decreases with increasing pH. No evidence of As(V) reduction is found. Hence, reduction of iron(III) (hydr)oxides could release As(V) into solution but the formation of GR, magnetite or siderite would immediately re-adsorb the released As(V), keeping the aqueous As(V) concentration low.

EXAFS spectra show that As(III) forms strong inner-sphere surface complexes on magnetite and GR, similar to that of As(V). No evidence of As(III) oxidation is found. On siderite, however, As(III) sorbs only by forming a weak outer-sphere complex and adsorbs much less strongly than to GR, magnetite or Fe(III) (hydr)oxides.

We propose that the elevated groundwater concentrations of As in West Bengal and Bangladesh result from the reduction of iron(III) (hydr)oxides to siderite in conjunction with the reduction of As(V) to As(III).

## Magnesite dissolution in the presence of organic and inorganic ligands

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Quantitative and predictive modelling of CO<sub>2</sub> sequestration in deep aquifers requires precise knowledge of carbonate mineral reactivity at conditions pertinent to CO<sub>2</sub> storage. Whereas the effect of temperature, salinity, pH, and pCO<sub>2</sub> on Ca- and Mg-carbonate dissolution is extensively studied, the understanding of the influence of organic and inorganic ligands, omnipresent in deep sedimentary basins, remains very limited. Organic and inorganic molecules can exert various influences on the kinetics of growth and dissolution of crystals. The ligands can promote or inhibit growth and dissolution and can control crystal morphology.

Here, a combination of mixed-flow reactor experiments and in-situ hydrothermal atomic force microscopy experiments has been used to investigate the effect of organic (acetate, oxalate, citrate, succinate, EDTA) and inorganic (sulphate, phosphate, borate) ligands on the surface morphology of magnesite and on the molecular mechanism and kinetics of magnesite dissolution at different pH values and NaHCO<sub>3</sub> concentrations.

Since AFM enables to observe monolayer step motion on the surface as well as the step formation frequency by pit nucleation, the effect of ligands on the rate of detachment at specific surface sites can be determined. Thus, AFM data can be interpreted towards a determination of the consequences of adsorption at specific sites on the dissolution kinetics of magnesite in a molecular scale. Comparisons of these data with the dissolution rates of the (104) surfaces and with the dissolution rates of entire crystals (obtained by mixed-flow reactor experiments) allow one to link the molecular-scale effects to the macroscopic effects of ligands on magnesite dissolution.

At circum-neutral pH, the experiments showed a most pronounced effect in citrate- and EDTA-bearing solutions. For citrate, the modification of the reactivity of a distinct kink-site could be detected. More pronounced than the effect of organic ligands was the effect of 0.01 M NaHCO<sub>3</sub> (at pH around 8) which caused a general decrease in reactivity at far from equilibrium conditions. The ligands phosphate, oxalate, citrate, and EDTA were found to weaken but not to fully compensate the retardation of the reactivity generated by NaHCO<sub>3</sub>.

## Voltammetric determination of Te(IV) and Te(VI): Sorption behaviour on Fe and Mn oxides

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Sorption experiments by Koschinsky *et al.* (2004) had shown an extremely fast and effective enrichment of tetravalent tellurium (Te(IV)) on Mn and Fe oxides, but no comparable enrichment of the geochemically very similar Se(IV). This Te enrichment was related to a surface oxidation process of Te(IV) to Te(VI) on the Fe-Mn oxide surfaces, which apparently does not take place for Se(IV). In order to compare the behavior of tetravalent and hexavalent Te and Se species, which can both exist in natural waters, new sorption experiments were carried out with the hexavalent species of Te and Se.

Te(IV) was determined by differential pulse cathodic stripping voltammetry (DPCSV) using a 0.1 M HCl and 1 mg L<sup>-1</sup> Cu<sup>2+</sup> medium according to Ferri *et al.* (1998). As Te(VI) cannot be reduced electrochemically, a UV-reduction step was required after the sorption experiments and before the voltammetric analysis. For the UV-irradiation procedure, best results were obtained by using a 0.4 M HCl medium for 3 ½ h irradiation time at 90°C (Hg-high pressure lamp, 500 W).

The results of the sorption experiments indicate sorption of Te(VI) on all Mn and Fe oxides used in the experiment, however, the sorption rate was significantly lower than in the experiments with Te(IV). This supports our assumption that Te(IV) is preferentially removed from aqueous solution by Fe and Mn oxide phases compared to Te(VI) and compared to Se(IV) and Se(VI). Comparison of solid phase concentrations of Te and Se in marine oxides indicates that this different sorption behaviour leads to a significant fractionation of the two elements in the marine environment.

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## Trace element distributions in hydrothermal quartz: Fluid or structural control?

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Quartz is probably the most common hydrothermal vein mineral and its isotopic composition and the chemical composition of its included fluids are widely used for petrogenetic interpretations. In contrast, its own chemical composition is often close to being pure SiO<sub>2</sub>. A number of studies have, however, shown that some trace elements may enter its structure. While the factors governing such an incorporation are, as yet, not clearly understood, it is obvious that they can potentially be useful for petrogenetic interpretations.

A number of Alpine fissure quartz crystals having formed from chemically different fluids were analyzed for a range of possible trace elements (Li, Na, Mg, Al, P, K, Ca, Ti, Fe, Ge, and H) using different *in situ* methods (electron and ion microprobes, LA-ICP-MS, and FTIR spectroscopy) after cathodoluminescence (CL) analyses to determine the growth zones. CL bright zones were associated with high Al (up to 7000 ppm), Ge, and Li contents, these elements being strongly correlated, in particular within zones of discontinuous grown crystals. No correlation was found between Al and Na and K. The Al-Li-Ge correlation remains the same in quartz analyzed from different localities as well as along the same growth sector within any one crystal, suggesting that differences in the chemical composition of the fluids (also monitored through the oxygen isotope compositions of the quartz) do not control this correlation. However, the Li/Al ratio (i.e. compensating ion/ substituting ion) can be changed along a growth sector and within different crystals and it never appears to approach unity. While significant quantities of H (deduced from OH<sup>-</sup> absorption spectra) are also present within the quartz, with high amplitude IR-spectra corresponding to Al-Li rich zones, the H-content alone does not compensate for the charge difference between a Si<sup>4+</sup> and (Al<sup>3+</sup>,Li<sup>+</sup>) coupled substitution. Also, while no significant differences in trace element content have been observed between the two rhombohedral faces (*r* and *z*, where *z* generally grows faster than *r*), the prismatic face (*m*) always has lower trace element content compared to *r* and *z*.

It can be concluded that the incorporation of trace elements into hydrothermal quartz is strongly influenced by the growth mechanism, structure, and probably by surface effects, but less so by the chemical composition of the fluid.

## Considerations in dating impact craters using the $^{40}\text{Ar}/^{39}\text{Ar}$ method: The problem of inherited $^{40}\text{Ar}^*$

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A large number of impact structures on Earth remain to be dated accurately and precisely (e.g. <http://www.unb.ca/passc/ImpactDatabase/index.html>) and [1]. A very versatile and powerful chronometer is the  $^{40}\text{Ar}/^{39}\text{Ar}$  method, because of its sensitivity to thermal input, the availability of internal reliability criteria such as age plateaux and/or isochrons, and the possibility to obtain compositional parameters (i.e., Ca/K, K/Cl and  $^{40}\text{Ar}^*$ ). Apart from alteration and/or metamorphic processes that can strongly bias the measurement of the age of a sample, accurate  $^{40}\text{Ar}/^{39}\text{Ar}$  age determinations are often challenged by the presence of inherited  $^{40}\text{Ar}^*$  (i.e., Ar not completely degassed from the target rock during the impact) in the sample.

Here, through the study of 2 impact structures (Tswaing, South Africa and Jänisjärvi, Russia) and comparison with results from 4 other structures, we study the cause and consequence of the presence of inherited  $^{40}\text{Ar}^*$ . For example, in the case of Tswaing impact glass particles, no ages approximating the previously accepted impact age of  $250 \pm 104$  ka [2] could be obtained, whereas the Jänisjärvi impact melt rock yielded a statistically robust global isochron age of  $682 \pm 4$  Ma.

The main characteristic controlling the apparent age bias (for a given proportion of inherited  $^{40}\text{Ar}^*$ ) is the age difference between the impact and the target rocks. The buffer effect for a given crater structure can be predicted knowing the age of the impacted basement and having a rough estimation of the age of the crater structure itself. The occurrence of  $^{40}\text{Ar}^*$  inherited is likely influenced by (1) the degree of polymerization (i.e., silicate structure complexity) of the target rock and presumably related to the diffusivity of Ar in the melt/glass, (2) the Ar partial pressure at grain boundaries, (3) the quantity of energy involved in the impact, and (4) the porosity of the target rocks. In addition, the degree of polymerization will control the degree of homogenization of the melt and the rate of  $^{40}\text{Ar}^*$  diffusion in the melt. Homogenization of the inherited  $^{40}\text{Ar}^*$  ratio at the grain scale (i.e. 150-250  $\mu\text{m}$ ) facilitates accurate age determination through isochron analysis, although in completely melted rocks a homogenization of atomic scale environments for inherited and radiogenic Ar eliminates the possibility to resolve the two components thermally, i.e., by step-heating.

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## Zn isotopic fractionation during complexation with organic matter

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Organic matter (OM) is of great importance for the speciation, mobility and bioavailability of metals in the environment. The knowledge of zinc isotopic fractionation during complexation with OM is therefore crucial to understand zinc isotopic signatures in the environment.

Zinc isotopic fractionation during adsorption onto humic acid, an analogue of OM, has been investigated experimentally as a function of pH. Two different techniques were used to isolate free zinc in solution from zinc bound to OM.

Experiments were made with an insolubilized humic acid [1] that allows us to separate OM and the solution by centrifugation. Results show no fractionation at acidic pH (below pH 6) and a significant fractionation at higher pH (above 6) with an enrichment of heavy isotopes in the OM ( $\Delta^{66}\text{Zn}_{\text{OM-Solution}} = 0.52\text{‰} \pm 0.08$  for  $0.1 \text{ mol.L}^{-1} \text{ KNO}_3$ ). This result can be interpreted as a change of zinc complexation with pH, zinc being preferentially complexed by “carboxylic type groups” at low pH and by “phenolic type groups” above pH 6.

The insolubilization process may however alter partly the binding properties of the humic acid. We have decided to use another complementary approach with a Purified Peat Humic Acid (PPHA). The Donnan Membrane Technique (DMT) developed by Temminghoff *et al* [2] is used as a more efficient way to separate zinc complexed by untreated PPHA from free zinc in solution.

First tests in absence of PPHA have been done to check the eventual fractionation due to the complexation of zinc onto the membrane. Although less important than the fractionation observed in the previous experiments, it is not negligible ( $\Delta^{66}\text{Zn}_{\text{Membrane-Solution}} = 0.15\text{‰} \pm 0.03$ ). Despite this fractionation on the membrane, once fully validated for isotopic measurements this technique will be a powerful tool to measure zinc fractionation during its complexation with different kind of ligands like humic substances or organic chelating acids (i.e. siderophores). It can also be used for other elements as well as in situ measurements.

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## Plagioclase lamellae in peridotite-hosted orthopyroxene

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The solubility of low-Ca orthopyroxene (opx) in calcic clinopyroxene (cpx) and vice versa is temperature dependent. During cooling, pyroxenes develop subparallel exsolution lamellae. Deviations from this canonical behaviour are very rare. Here we present results from porphyroclastic plagioclase lherzolites from the Ozren ultramafic massif (Dinaride ophiolite belt) that contain plagioclase (plag), which seems to be texturally exsolved from opx.

Plag lamellae are parallel to cpx exsolution lamellae and occupy up to 10 vol-% of opx. Spacing is irregular between different porphyroclasts and within the single porphyroclast, but generally ranges between 30 and 500 µm. Some plag lamellae are interrupted by trace amounts of spinel, cpx or amphibole (very rare). In places, opx porphyroclasts are devoid of plag lamellae, but instead contain irregular plag blebs and trails. Opx have very well developed alumina concentration gradients around the Na-poor (An90) plag lamellae and blebs.

Opx-hosted plag exsolutions are very difficult to recognize, both in thin section and BSE images. They are easily overlooked and probably more widespread than commonly assumed. We have also observed them in harzburgite opx near a highly evolved gabbro dike (Central Indian Ridge). To our knowledge they have been described only in peridotites from the Ronda massif (Obata 1980). In contrast, cpx-hosted plag exsolution lamellae are apparently more widespread in peridotites (e.g. Rampone *et al.* 1993). Closed-pyroxene exsolution requires additional silica in form of Eskola component to produce plag ( $2\text{CaAl}_2\text{SiO}_6 + 2\text{Ca}_{0.5}(-)_{0.5}\text{AlSi}_2\text{O}_6 = 3\text{CaAl}_2\text{Si}_2\text{O}_8$ ), as known from HP and UHP mafic rocks. However, Eskola pyroxene is not expected in silica undersaturated rocks (Gasparik, 1985) and additionally non-stoichiometric pyroxenes don't occur in spinel facies at same massif. Alternatively, spinel exsolution from pyroxene could provide the Si to produce plag, but spinel contents are too low to balance all observed plag. A third possibility is that Si is brought in by a melt or fluid, reactively replacing pre-existing lamellar cpx (in the absence of olivine). This would require that the peridotites were lithospheric and that heating was sufficiently fast to reach near-solidus conditions to allow for grain boundary melt migration without rehomogenizing exsolved pyroxenes.

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## Speciation and long-term sequestering of Zn in a naturally enriched soil

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Recent XAS investigations of Zn-impacted soils have identified Zn-phyllsilicates, Zn/Al-Layered Double Hydroxides, Zn sorbed on Mn and Fe oxides and Zn complexed to soil organic matter as the most probable chemical forms for anthropogenic Zn in soils (e.g. Kirpichtchikova *et al.*, 2006 and reference therein). However, the long-term stability of these Zn species has been rarely investigated. This question, which is of primary importance to assess the fate of anthropogenic Zn, can be partly addressed by studying the chemical forms of Zn occurring in naturally Zn-enriched soils overlying geochemical anomalies. Such approach has already allowed us to identify chemical forms of lead and arsenic able to resist to long-term weathering (Morin *et al.*, 2001; 2002).

In the present study, the selected soil has developed upon sulfides mineralized sandstone (Ardeche, France) and exhibit Zn concentrations (up to 500 mg/kg) similar to those found in impacted soils. Molecular-level information gained by EXAFS indicate the occurrence of two main Zn species (Zn-bearing clay minerals and Zn-sorbed Fe oxides), with varying proportions as a function of depth. In the topsoil (A<sub>0</sub>- and B<sub>s</sub>-horizons), about 50 % of Zn is hosted by the clay minerals, whereas this proportion decreases to less than 10 % at depth (C-horizon) where no clay minerals could be detected by XRD. These results suggest that Zn-sorption onto Fe oxides represents the first-stage of weathering of the ZnS-mineralized sandstone (C-horizon). After longer weathering (A<sub>0</sub>- and B<sub>s</sub>-horizons), Zn is progressively incorporated in neofomed clay minerals which likely represent long-term hosts for this element in soils.

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## Trace element SIMS investigation of multistage garnet – Constraints on partial melting processes in crustal rocks

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The basement dominated granulite-facies part of the central Damara orogen (Namibia) hosts abundant migmatites that originated by partial melting of metapelitic or, less abundant, meta-igneous sources. A migmatitic orthogneiss shows the growth of garnet within the host gneiss (A), the leucosomes (B) and cross-cutting granite dykes (C). Based on microstructural features and microprobe data, garnet A is considered to be metamorphic and garnet B and C are considered to be anatectic and igneous, resp. Rb/Sr and Sm/Nd whole rock isotope data confirm the suggestion that the gneiss belongs to the Pre-Damara basement. Sr isotope data are heterogeneous but assigning an age of 550 Ma for the gneiss, 500 Ma for the leucosomes and 493 Ma for the dykes results in similar initial <sup>87</sup>Sr/<sup>86</sup>Sr ratios of ca. 0.730. These results suggest high-grade metamorphic conditions at ca. 550 Ma, followed by in-situ partial melting at ca. 500 Ma and intrusion of granitic dykes at ca. 493 Ma. All garnets have a 10<sup>4</sup>-10<sup>5</sup> CI-normalized range in REE abundances and steep LREE-depleted and HREE-enriched element patterns. Garnet from A, B, and C are zoned in Y, HREE, Sr and Ti in which garnet A shows a small core with HREE, Y, Sr and Ti enrichment and a broad rim with trace element depletion. Garnet B has a core enriched in Yb+Y but depleted in Er and Dy and an outermost rim even more depleted in these elements. Garnet C has a broad core with enrichment in Yb+Y and depletion in Er and Dy. The rim is enriched in HREE+Y. LREE (Sm, Nd) profiles are similar to HREE profiles for garnet B and C but garnet A shows the opposite of HREE zoning with a LREE-depleted core and a LREE-enriched rim. These features indicate that HREE fractionation of garnet A follows a Rayleigh fractionation scheme but Nd and Sm concentration profiles are modified by volume diffusion at high temperatures. Garnet B shows evidence for a two-step growth history (melt absent vs. melt-present?) evidenced by the marked hump between core and rim. The trace element pattern of garnet C can be explained by a combination of a Rayleigh fractionation process and a liquid diffusion controlled process. The data show that trace elements may potentially be more sensitive to chemical changes in rocks than major elements in which an accurate interpretation leads to an improved understanding of p-T paths of metamorphism and melting.

## High-precision Lu-Hf garnet ages from granulite-facies migmatites (Damara orogen, Namibia)

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The basement dominated granulite-facies part of the central Damara orogen (Namibia) hosts abundant migmatites formed by partial melting of metapelitic sources during intrusion of hot granitic melts. Centimeter-sized garnet is a common product of incongruent melting reactions and has been dated with the Sm-Nd and U-Pb methods. In addition, the U-Pb ages of matrix monazite have also been determined for the majority of the samples. In general, Sm-Nd garnet whole rock ages are precise (better than 1%) and agree with the Pb-Pb ages of the garnets, although the latter are relatively imprecise (2-8%) due to low <sup>206</sup>Pb/<sup>204</sup>Pb ratios. Collectively, the Pb-Pb garnet data define an age of 540±40 Ma, whereas the Sm-Nd garnet-whole rock ages range from 530±3 Ma to 506±2 Ma. These age estimates agree with previous Sm-Nd grt-WR ages and U-Pb monazite ages from elsewhere in the orogen and are interpreted to constrain the time span of high-grade metamorphism and melting. To better resolve the relationship between high grade metamorphism and melting and garnet growth, and to improve upon the precisions of the Sm-Nd and Pb-Pb age determinations, garnets were dated with the Lu-Hf technique. All garnets display similar Lu-Hf isotope systematics, with high Lu (16-40 ppm) and high Hf (0.9-1.5 ppm) contents, moderately high <sup>176</sup>Lu/<sup>177</sup>Hf ratios (1.7-7.3), and radiogenic <sup>176</sup>Hf/<sup>177</sup>Hf ratios (0.30059-0.35467). Due to these characteristics, the internal isochron ages are precise (0.2-1.0%), and range from 531±1 Ma to 514±5 Ma. For all samples, the Lu-Hf grt-WR ages are similar to—or lower than—the U-Pb monazite ages and are also similar to (with one exception) the Sm-Nd grt-WR ages from the same sample. The similarity among Lu-Hf and Sm-Nd grt-WR ages, Pb-Pb garnet ages, and U-Pb monazite ages imply relatively fast cooling rates immediately after the peak of regional metamorphism, which was probably related to fast uplift of the basement-dominated part of the orogen.

## Geochemical and isotope geochemical investigations on Palaeozoic sedimentary rocks

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Palaeozoic natural gas reservoirs in the Central European Basin (CEB) regionally contain high percentages of molecular nitrogen (N<sub>2</sub>). The highest nitrogen contents are found within Rotliegend reservoirs of the North East German Basin (NEGB) where thick, highly mature Palaeozoic sedimentary sequences are present.

The release of molecular nitrogen from coals and sedimentary rocks with low contents of dispersed organic matter was investigated by means of non-isothermal open system pyrolysis, elemental analysis and stable isotope mass spectrometry. The principal goal was to explore the contents, isotopic composition ( $\delta^{15}\text{N}$ ) and the speciation of nitrogen in organic and inorganic constituents of these sequences.

Total nitrogen contents of Namurian shales from four deep wells (4400 - 7000 m) in NE Germany ranged from ~500 to ~2700 ppm. Between 50 and 100 % of this nitrogen is inorganic and fixed as ammonium. Although there is a clear facies trend from marine sediments in the lower part to paralic and terrestrial sediments in the upper part of the Carboniferous sequence, the corresponding  $\delta^{15}\text{N}_{\text{fix}}$  values are within a narrow range (+1 to +3.5‰) along the entire profile while the isotopic composition of the thermally liberated nitrogen was consistently lighter (by 3-5‰). Low nitrogen contents (as low as 460 ppm) and high  $\delta^{15}\text{N}$  values (up to +5.6‰) in one well in the basin centre suggest a significant release of nitrogen (as NH<sub>3</sub> and/or N<sub>2</sub>) associated with <sup>15</sup>N enrichment in the residual nitrogen.

Open-system non-isothermal pyrolysis has revealed the presence of inorganic nitrogen species with relatively low thermal stability in marine Namurian A shales. Inorganic nitrogen components in the paralic Namurian B facies show a higher thermal stability range while nitrogen in kerogen and coals is fixed in very refractory compounds decomposing in the 700 – 1200°C temperature range. The presence of significant amounts of inorganic nitrogen is also reflected in the high N/C<sub>org</sub> (atomic) ratios (up to 0.108) of the Palaeozoic shales. Thus the on-line isotope analysis indicates the presence of precursor pools with different thermal stability and nitrogen isotopic composition.

The combination of laboratory data, field data and numerical simulations is expected to further constrain the time, temperature and fluid flow conditions and result in an improved understanding of this complex issue.

## Pit lakes in Kemerovo region, Russia: Geochemical composition and ecological risk

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The open pit mining and processing of polymetallic ores in XVIII-XX centuries resulted in rise of pits with high-sulfides wastes in all over the world and Russia particularly. The pit lakes arise after pits flooding with atmospheric and underground water and are characterized by low pH, high metal and SO<sub>4</sub><sup>2-</sup> concentrations. Unfortunately investigations on pit lakes composition, development and transformation haven't been carried out adequately in our country. The several pit lakes situated in the Salair ore field (Kemerovo region) are examined in this paper.

Results of the field researches in 2005-2006 and following analytical works allowed to ascertain the composition of water and bottom sediments in pit lakes situated in three ore deposits: Aleksandrovskoe, II Mine, III Mine. Slow interaction between water and oxidized ore bodies in the pit walls resulted in formation of acid solutions (pH=3-5) with high mineralization (5-8 g/l) and metals (Fe-up to 350 mg/l, Zn - to 100 mg/l, Cu, Cd and Pb - to 10 mg/l) and metalloids (concentration of arsenic is up to 0.3 mg/l). The concentrations of concerned elements considerably exceed the background and maximum allowable values with the greatest portion of Cu, Zn, Cd species is most toxic free ion.

The geochemical anomalies of various elements (Ti, Mn, V, Cu, Zn, Cd, Pb, As, Sb, Ag, Te) appear in the pit lake bottom sediments which are mainly in very soluble forms and of high mobility.

The data obtained point out not only an ecological risk but also indicate it is possible to extract the ore elements from these objects for the second time. But currently superficial lakes with transparent water and bottom sediments lacking in vegetation are very popular pleasure resorts for Salair's natives. The detailed research of circulation of toxic elements will be conducted in the system «pit wall – bottom sediments – water – biota» which is essential to forecast the subsequent changes in pit lakes and find the methods of improvement of these objects.