

Quantifying denudation rates with vertical relief fission track profiles

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Apatite fission track analysis can identify differential vertical movements of the crust by recording the cooling that results from the denudation that is caused by tectonic uplift, by local relief changes or by changing climate. This can be most tightly constrained and quantified if vertical relief profiles are available. The full potential of vertical relief profiles is achieved if the palaeogeothermal gradient and denudation rates are calculated directly from these profiles.

Knowledge of the palaeogeothermal gradient is crucial for further quantification of the denudation history (i.e. converting palaeotemperature information into palaeodepth information). The magnitude and timing of denudation can be directly derived if modelling techniques are applied, and information about the palaeogeothermal gradient can be extracted.

When samples are collected from an undisrupted vertical relief profile, the resulting data can be modelled to produce an internally consistent thermal history. The palaeogeothermal gradient at a certain time can be reconstructed by plotting the maximum palaeotemperature versus present elevation of the sample. The gradient of this slope displays the palaeogeothermal gradient at that particular time. The gradient of a linear slope between apparent fission track age, and elevation provides a direct estimate of the denudation rate over this time interval.

Due to the excellent exposure of the Brandberg Igneous Complex, the highest mountain in Namibia with 2573 m, we can provide the first empirical estimates of the palaeogeothermal gradient in this region, which is a key parameter for the calculation of amounts of denudation from thermochronologic data. A palaeogeothermal gradient of approximately 27°C/km was determined to have prevailed in central Namibia in the Late Cretaceous. The net amount of denudation calculated using the geothermal gradient information is about five kilometres for the Brandberg region. An independent measure of the denudation rate between 80-60 Ma ranges in the order of 120 m/my..

Careful analysis of apatite fission track data provides detailed information of the exact timing and magnitude of crustal cooling. For Namibia, a phase of rapid cooling in the Late Cretaceous was triggered by a global change in spreading geometry, evident in other areas within Africa and the conjugated margin in South America too.

Combining information from vertical relief profiles and regional time-temperature information derived by thermal modelling of fission track data, long-term denudation models can be constructed and are also shown here.

The composition of Mid Atlas lithospheric mantle

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The metasomatic events which modified the geochemical signatures of the subcontinental lithospheric mantle beneath Ibalrhathene (Mid Atlas, Morocco) have been reconstructed by means of a combined EMP+LA-ICP-MS study of ultramafic xenoliths enclosed in the Plio-Quaternary alkaline basalts.

The collected xenoliths are characterised by a large compositional and textural variability. Amphibole ($\geq 3\%$)-bearing spinel peridotites show porphyroblastic textures; whereas amphibole ($\leq 1\%$)-poor spinel peridotites have protogranular to porphyroclastic textures. Wehrlites are medium to coarse-equigranular; spinel (\pm garnet) websterites have granular to coarse-granular textures, and clinopyroxenite/ hornblendite samples show cumulus textures. Poikiloblastic texture has been found only in one composite harzburgite/wehrlite xenolith.

Most lherzolites have clinopyroxenes (Type 1) with REE patterns from slightly LREE-depleted ($La_N/Yb_N \sim 0.6$) to LREE-enriched (spoon-shaped: $La_N/Yb_N = 1.3-17.2$); cpx from harzburgites and a few lherzolite samples possess more strongly fractionated REE patterns (La_N/Yb_N up to 32.8, Type 2). Cpx from websterites, clinopyroxenite and orthopyroxene-free wehrlites (Type 3) display LREE/MREE-enriched upward-convex patterns ($La_N/Yb_N = 1.5-6.8$). Cpx from the harzburgite/wehrlite composite xenolith are richer in REE than Type 2 & 3, and show upward-convex patterns (Type 4).

The different geochemical features of cpx can be ascribed to migration of successive and different metasomatic agents. Type 1 & 2 can be ascribed to a unique event related to the migration of alkaline melts fractionated by reactive porous flow through the lithosphere. The abundance of large orthopyroxene porphyroblasts in the peridotites suggests interaction with SiO_2 -saturated melts. Type 3 samples are probably related to the successive magmatic venue of relatively undifferentiated, SiO_2 -undersaturated magmas, probably circulating through magmatic conduits. Metasomatism operated by either a carbonate melt or CO_2 - H_2O rich fluids is documented by Type 4 samp.

Preliminary Sr-Nd isotopic results on cpx show an overall homogeneity of the compositions in the different groups of samples.

Preliminary results from FT dating of the Adula nappe: late tilting or not?

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The Alpine evolution of the Adula nappe proposes at least three regional phases leading to multiple metamorphic overprints: A series of eclogitic rocks found at the E side of the crystalline nappe body (HEINRICH 1986) reveals a strong P-T gradient (MEYRE et al. 1998) during the time of Eocene HP metamorphism (BECKER 1993). This gradient reveals that during subduction the nappe must have been in a strongly inclined position. The Oligocene intrusion of the Bergell granodiorite causes contact metamorphism at the SE end of the nappe, leading locally to the formation of granulite facies rocks. Finally, the middle Tertiary Lepontine metamorphism causes regional greenschist to amphibolite facies metamorphism (ENGI et al. 1996), showing a trend of increasing temperatures along the N-S extension of the nappe.

Exhumation of the nappe is primary the result of obduction after HP metamorphism, isostatic rebound around the Bergell intrusion body, vertical displacement along the Insubric line S of the Adula nappe (HURFORD 1986), and finally the doming and denudation of the Lepontine area. So far, the temporal frame of exhumation is only vaguely determined, in particular because of an ongoing debate about the age of early Alpine HP metamorphism and the age of the Lepontine overprint.

The here presented study aims to reveal the amount and precise timing of late tilting or thermal relaxation of the Adula nappe by fission track (FT) dating. For this purpose, the crystalline body was sampled along its maximum N-S and E-W extension. At present, only apatite data are available and are discussed in the light of the addressed tilting and cooling processes. Apatite FT data (ages and track length distributions) do not show any significant patterns of late tilting after cooling below a temperature of 120 °C. A further step into the past will be given by zircon FT data, and eventually white mica Ar/Ar data.

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The Deuterium Anomaly in Stratospheric Molecular Hydrogen

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Molecular hydrogen (H₂) is the second most abundant reduced gas in the atmosphere (after methane) and has a globally averaged mixing ratio of ~ 530 ppbv. Its recognized sources include: photochemical oxidation of CH₄ and non-methane hydrocarbons (NMHC); biomass burning, fossil fuel burning, nitrogen fixation, and ocean degassing. The stable isotopic composition of H₂ can help quantify the relative importance of these various sources and balancing sinks. The average δD_{SMOW} of H₂ in the surface atmosphere is ca. +100 ‰ — strongly D enriched compared to that measured for atmospheric CH₄ ($\delta D_{SMOW} \sim -90$ ‰), expected for NMHC's, and known for combustion sources of H₂ (δD_{SMOW} of ca. -200 to -300 ‰) [Gerst and Quay, 2001; Rahn et al., 2002]. The D/H ratios of H₂ from ocean degassing and nitrogen fixation are poorly known but are likely to have δD_{SMOW} values of ca. -700 ‰, in near thermodynamic equilibrium with local H₂O. Thus, all major sources of atmospheric H₂ are hundreds of permil poorer in D than H₂ itself. Either the loss processes (photo-oxidation and/or soil uptake) must discriminate against reaction with HD and/or isotopic fractionation associated with photo-oxidation of CH₄ must favor production of HD over HH. Our current understanding of the global H₂ budget depends strongly on the exact contribution of each of these effects to observed D enrichment.

We analyzed concentration and D/H of H₂ in a suite of stratospheric air samples in order to investigate the photochemical processes influencing the deuterium content of H₂. We find that although the concentration of H₂ is nearly constant in the lower stratosphere, its δD_{SMOW} varies up to +440 ‰ after ~6 years of stratospheric residence time. To our knowledge, H₂ in the lower stratosphere is the most D-rich, natural material on earth. In order to account for this extreme D enrichment of H₂, we have determined that the reaction chain from CH₄ to H₂ involves an isotopic fractionation of $\alpha_T = k_{CH_3D \rightarrow HD} / k_{CH_4 \rightarrow H_2} = 1.31$; this is in addition to the enrichment due to the known slower oxidation of HD [Ehhalt et al., 1989]. Return flux of this exceptionally D-enriched H₂ from the stratosphere must be accounted for to correctly balance the isotopic budget of tropospheric H₂. The process we document also influences the overall distribution of deuterium in the upper atmosphere.

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Cosmogenic ^{10}Be as a high resolution correlation tool for climate records

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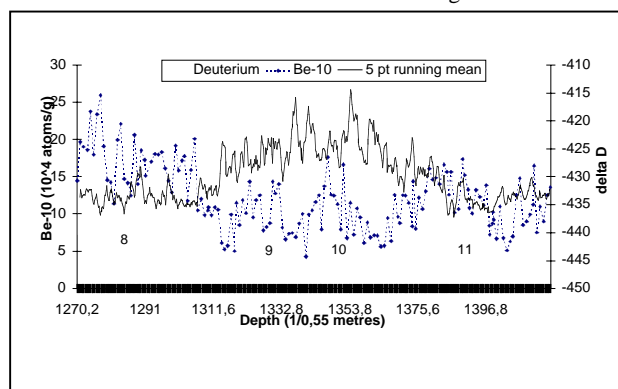
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Precise correlation of climate records is of critical importance for the themes of the present symposium. Because the controlling parameters (solar activity, geomagnetic field intensity, primary cosmic ray intensity) act globally and synchronously, identification and matching of distinctive features in cosmogenic isotope production rates in the climate records is one way of making such correlations. One of the most dramatic and reliably identified of these production variations is the enhanced production occurring ~40,000 years ago, first discovered in the Vostok ice core. This ^{10}Be “peak” was subsequently detected in other Antarctic and Greenland ice cores, and tentatively identified in several sediment cores. We report here a new high resolution profile of the ^{10}Be peak measured in the recently recovered EPICA ice core from Dome C Antarctica, together with a $\delta^2\text{H}$ profile in the same core. We then discuss the implications regarding the relative phasing of northern hemisphere vs southern hemisphere climate records during the last glacial period.

The ^{10}Be measurements were made at 11 cm (~9 year) resolution but are plotted as a 5 point running mean. The peak is centred at 740 m, almost 100 m less than in an earlier core at Dome C. As we already observed in similar high resolution measurements in a Vostok core, the peak shows structure even on decadal time scales. This enhances its potential for high resolution correlation. The $\delta^2\text{H}$ profile, made at 55 cm resolution, has 4 features that, based on their position and pattern, we identify as subdued analogues of interstadial (Dansgaard-Oeschger) events 8-11 observed in Greenland. The ^{10}Be peak straddles event 10, exactly as seen in the GRIP core. This implies that, within our ability to resolve, which we presently estimate as 200 years, the GRIP and EPICA climate records at this time are synchronous. This is in contradiction with conclusions based on methane records, which show Vostok climate leading Greenland by >2000 years in this period. If our analysis is correct, it implies either that there is a significant error in the modelled methane-ice age differences at Vostok, or that the phase relationship between the East Antarctica and Greenland climate records changes with time.



Cadmium anomalies in oolitic carbonates of Bajocian and Oxfordian/Kimmeridgian age in the Swiss and French Jura Mountains

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Positive anomalies in cadmium concentration of up to 8.15 ppm were discovered in oolitic carbonates of Bajocian and Oxfordian/Kimmeridgian age, in the Swiss and French Jura (Benitez-Vasquez, 1999, Veuve, 2000). The cadmium enrichment is restricted to the cortex of the ooids, or to entire ooids in the case they are micritized (Veuve, 2000).

These elevated cadmium contents in the rock substratum lead to cadmium enrichments in the soils, which reach values of up to 10.4 ppm. These concentrations largely exceed the official guideline values in Switzerland (0.8 ppm) and France (2 ppm).

Our topic is to characterize, map and date more precisely these anomalies, by studying complete sections in Bajocian and Oxfordian carbonates (Swiss Jura; Bourgogne/Lorraine - France) and by analysing selected samples for cadmium content (by ICP-MS), mineralogy (by XRD), and facies (by thin sections). Another part of our research consists in the analysis of carbonates of similar facies but of different ages in the Jura Mountains and northern Alps, and the analysis of the types of rock substratum underneath soils with established cadmium enrichments (Bourgogne/Charente - France).

With this research we hope to elaborate the sedimentary and paleoenvironmental conditions and changes that led to cadmium enrichment in carbonate oolites, as well as to develop predictive tools for other facies types.

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Mantle Sources Generating Recent Volcanism Along the Perimeter of the Colorado Plateau

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Continental basalts erupted along the transition zone between the Colorado Plateau and the Basin and Range Province retain variable isotopic and trace element signatures that range between those expected for mantle asthenosphere and mantle lithosphere. We have analyzed a suite of these basalts (whole-rocks) for (²³⁰Th)/(²³²Th) by TIMS and will present comparable results obtained using the ThermoFinnigan Neptune® MC-ICP-MS at the GeoAnalytical Lab at Washington State University.

Continental basalts erupted along the southern and western edges of the Colorado Plateau during the Pleistocene and Holocene have variable Th-enriched signatures with ²³⁰Th excesses that rival those observed in oceanic basalts. These basalts define a broad range of isotope and trace element characteristics that differ from oceanic basalts and that must originate from lithospheric mantle sources. In addition, only a limited number of these basalts reflect geochemical characteristics consistent with either silicic or mafic crustal contamination. It is, however, difficult to justify how ²³⁰Th "ingrowth" during mantle upwelling (similar to models that account for ²³⁰Th enrichments in oceanic basalts) can be responsible for ²³⁰Th excesses in these basalts as a result of the presence of variably thickened lithosphere underlying this portion of the western US which would act to impede mantle upwelling. If ²³⁰Th excesses were indeed the result of "ingrowth" during mantle upwelling, mantle lithosphere in this region would need to be dramatically thinner than current geophysical estimates and resulting melts would have to obtain their respective isotope and trace element signatures during transit through intervening mantle lithosphere. In contrast, ²³⁰Th enrichments in these basalts can be reasonably modeled as the result of small degree partial melts of a garnet lherzolite source containing variable amounts of clinopyroxene. Notable exceptions require higher source garnet contents, over-estimated eruption ages, or additional, although limited, "ingrown" Th inputs.

Paleoclimate Record of Variation of the organic carbon(TOC) in Chinese Loess Section since 0.15Ma B.P.

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1. Sampling and methods

Samples came from Luochuan Loess section in Shaanxi province. Samples involved S₀-L₁ and S₁. Samples were continuously obtained, and thickness of every sample was 10 centimeter. There were 91 piece of samples. The organic carbon was measured by sulfuric acid/dichromate oxidation.

2. Discussion of results

Mean value of the organic carbon (TOC) is 0.26% (Table 1) in Luochuan section, lower than Weinan section. This fact shows TOC concentrations gradually increase from north to south of Chinese Loess plateau, and implies that climate has

Table 1 Mean value (%) of the organic carbon in different layers of Luochuan and Weinan Section

layers	Luochuan section	Weinan section
S0	0.47(5)	0.35(29)
L1	0.25(75)	0.29(99)
S1	0.27(8)	0.33(93)
_S+L	0.26(91)	0.28(221)

an important effect on creatures. In addition, TOC concentrations in Luochuan loess section (S₀-L₁-S₁) gradually decrease from top to bottom. But TOC concentrations in paleosoil is usually higher than those in Malan Loess. Finally,

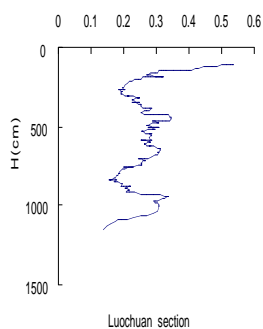


Fig.1 Distribution of TOC content(%) with depth in Luochaun Loess Section

Fig.1 shows that Variation of TOC in Luochuan section is similar to that in Weinan loess section^[1]. Variational curve of TOC of Chinese loess section represents great three change of climate, and there are little two fluctuations of climate in Malan loess(Fig.1). Variation of TOC is well consistent with Variation of magnetic susceptibility in Luochuan and Weinan loess section^[1].

3. Conclusion

Content of TOC has a good relation with climate change. Therefore, the organic

carbon can be a better character to record change of paleoclimate to some extent.

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Rheology of the Proterozoic massif anorthosites

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Introduction

Many investigators of the petrogenesis of Proterozoic massif anorthosites believe that extensive crystallization of a mantle-derived magma ponded at or near the base of the crust that produces suspension of plagioclase in Fe-rich, high-Al gabbroic liquids and later followed by the intrusion of the suspensions into the mid-Upper crust where they form complex magma chambers (1).

It is not clearly known why did a highly buoyant mantle-derived magma pond at or near the base of the crust and subject to extensive crystallization leading to the production of high-Al Opx megacrysts which preserve a record of high pressure stage. In fact the buyant magam should have intruded into the mid-Upper crust through rifts in the crust and crystallized as it happened in the case of Labrador anorthosites (which show little or no deformation) . It implies that mantle - derived magmas were forced to pond at or near the base in the crust due to lack of rifts for intrusion into the crust in the Grenville and Sveconorwegian provinces. Similarly it is not known what forced the crystal mushes after their formation from the lower to mid-Upper crust (through a distance of 20-25Km)

The Petrogenetic Scheme

Therefore the author (4) presents the view that the mantle-derived magmatic melts ponded at or near the base of the crust due to lack of rifts for upward movement, experienced Soret effect (3) above they liquidus due to which certain elements (Fe, Ti, P, Ca, Mg, etc.) migrated and concentrated at or near the cooler margins of the magma pools while the hot regions of the magma pool got enriched in Si, Al, Na, K, Mn, etc., On crystallization high Al -Opx megacryst were produced at depth. The bulk of the remaining hyperfeldspathic magma crystallized at depth and remained there at very high lithostatic pressure. The deep seated anorthosite plutons which were under enormous lithostatic pressure(>30km) moved upwards as rheological solids in response to destressing (removal of pressure) due to extensive and intensive removal of a few tens of km of over-burden. The destressing of plutons provided the required driving force for the upward movement of the Plutons (which are now found in deeply eroded mid-Proterozoic orogenic belt in the Grenville province. This forced moment produced melting of the pluton at its margins and also contact rack and variable contamination of the margins and also remelting of the Fe, Ti, P enriched margins of the pluton and other features like domical structure of many massifs, protoclastic structures etc.,

Conclusion

The upward movement of the deep seated plutons, may be the cause for the origan and occurrence of tectonic earthquakes in orogenic belts.

Geochemistry and age of the European CAMP basalts

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The Central Atlantic Magmatic Province (CAMP) is Earth's largest Phanerozoic continental igneous province, with tholeiitic basalts cropping out over about 7 million km², around the Central Atlantic Ocean. The CAMP event occurred at about 200 Ma and preceded the break-up of Pangea. The northernmost CAMP is represented by basaltic lava flows, dykes and sills occurring in Portugal, Spain and France.

⁴⁰Ar/³⁹Ar step-heating ages on plagioclase separates from the European CAMP lava flows have been obtained (age of neutron-fluence monitor Fish Canyon sanidine = 28.02 Ma) for lava flows of southern Portugal. The plateau ages range from 195.6 ± 1.2 Ma to 198.6 ± 0.6 Ma (2σ errors) and are undistinguishable from the age of peak magmatic activity throughout CAMP. Therefore, this brief and simultaneous igneous event includes the European occurrences.

Major and trace elements composition of European basalts and basaltic andesites are similar to those of low-Ti basalts (TiO₂ < 2.0 wt.%) from the entire CAMP. They are moderately evolved (MgO 10-5 wt.%) tholeiites characterized by moderately enriched light REE and LIL elements relative to heavy REE (mantle-normalized La/Yb = 1.8-3.5; Ba/La = 9.2-25.5), with negative Ti, P and Nb, and positive Pb anomalies. Initial Sr, Pb and Nd isotopic compositions define a relatively limited compositional field (⁸⁷Sr/⁸⁶Sr = 0.70528-0.70652; ²⁰⁶Pb/²⁰⁴Pb = 18.19-18.77; ²⁰⁷Pb/²⁰⁴Pb = 15.59-15.75; ε_{Nd} = 0.24 to -2.88) particularly when compared to CAMP basalts from Africa, South and North America. In general, relatively homogeneous isotopic and trace element ratios suggest a common signature for the European CAMP basalts, despite the large sampling area and despite locally different crustal and tectonic settings, suggesting that these basalts issued from an enriched mantle source.

Nonetheless, local effects are observed, such as relatively low ²⁰⁷Pb/²⁰⁶Pb and ε_{Nd} displayed by lava flows from southern Portugal and moderate correlations of isotopic and major and trace element compositions for basalts from the 550 km long Messejana dike. These characteristics suggest that geographically defined basaltic suites evolved from slightly heterogeneous mantle sources, and locally assimilated moderate amounts of distinct lower (trend towards low ε_{Nd}) or upper crustal rocks (trend towards high ⁸⁷Sr/⁸⁶Sr), as is consistent also with preliminary ¹⁸⁷Os/¹⁸⁸Os analyses (measured ¹⁸⁷Os/¹⁸⁸Os = 0.159-0.392).

A genetic relationship between Archean TTG granitoids and eclogitic and peridotitic xenoliths from the subcratonic mantle? experimental evidence at 2-4 GPa

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Models for the origin and growth of the continental crust and the chemical evolution of the subcratonic lithosphere in the Archean require a general understanding of the genetic relationship between Na-rich TTG (tonalite-trondhjemite) granitoids comprising the earliest continental masses and their deep roots or "keels" in the underlying mantle. Partial melting of hydrous basalt in the laboratory at pressures of 1-4 GPa produces liquids that, in terms of major-element composition, closely resemble early-mid Archean TTGs. These melts are in equilibrium with eclogitic residual assemblages. Reaction between TTG melts and mantle peridotite produces hybridised granitoid melts compositionally comparable to late-Archean sanukitoids, in equilibrium with garnet websteritic reaction residues (Rapp et al., 1999). We have used the ion microprobe to geochemically fingerprint, in terms of an array of trace elements (Ba, Rb, Th, U, Nb, Sr, Zr, Y, Cr, REEs), coexisting granitoid liquids, and crystalline residues of melting (eclogite) or melt-rock reaction (peridotite) in these experiments, generating mineral-melt partition coefficients relevant to partial melting and melt-rock reaction in the process. Because the measured data are at natural abundance levels, we can make direct geochemical comparisons with (1) Archean TTG granitoids (e.g., trace element abundance patterns of liquids at 2-4 GPa match nearly perfectly those of TTG granitoids from the Kaapvaal craton), (2) eclogite xenoliths interpreted as residues from partial melting and TTG magmatism in the Archean (e.g., Barth et al., 2001), and (3) cratonic peridotites showing evidence for metasomatism by Si-rich (i.e., TTG) melts.

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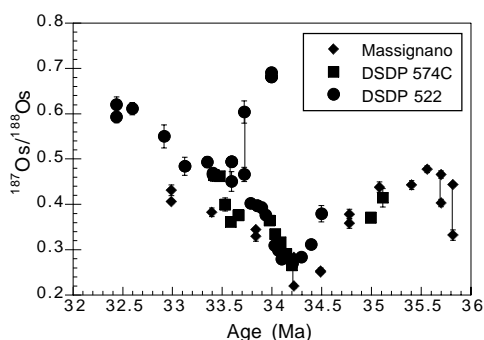
The marine Os isotope record of the Eocene-Oligocene transition

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Osmium isotope analyses of bulk sediment samples from the South Atlantic (DSDP 522), Equatorial Pacific (DSDP 574C) and the Italian Apennines (Massignano) are used to construct a composite record of seawater ¹⁸⁷Os/¹⁸⁸Os variations across the Eocene-Oligocene (E-O) transition. Between 34 and 34.5 Ma all three records display a pronounced excursion to very low ¹⁸⁷Os/¹⁸⁸Os (0.29 to 0.26) from higher late Eocene ¹⁸⁷Os/¹⁸⁸Os ratios (0.4 to 0.45). Following the local minimum ¹⁸⁷Os/¹⁸⁸Os rises rapidly to approximately 0.6 by 32.5 Ma. Both the late Eocene ¹⁸⁷Os/¹⁸⁸Os excursion and the asymmetry about this minimum are also apparent LL44-GPC3 record of Pegrarn and Turekian (1999).



We contend that these data reflect large changes in the ¹⁸⁷Os/¹⁸⁸Os of seawater across the E-O transition. Direct comparison of the Os isotope record to benthic foram oxygen isotope variations, a proxy record of ice volume change, shows that rising ¹⁸⁷Os/¹⁸⁸Os is correlated with the growth and decay of the first major Antarctic ice sheet. This coupling provides evidence of glacially enhanced continental weathering that is globally significant. A large excursion to low seawater ¹⁸⁷Os/¹⁸⁸Os precedes major Antarctic ice sheet formation. If this excursion is not the result of increased influx of cosmic dust, then the Os isotope record suggests that dramatic shifts in global weathering patterns may have played a primary causative role in the first major Antarctic glaciation.

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A Chlorine Isotope Effect for Biochlorination

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Recent studies have identified several chlorinated organic compounds (COCs) accumulating in marine animals, which may be derived from natural or anthropogenic sources (Vetter *et al.*, 2001). To determine whether isotope ratios could be used to identify different sources, we investigated the chlorine isotope effect for biochlorination. We chlorinated 1,3,5-trimethylbenzene (TMB) and 3,5-dimethylphenol (DMP) with a chloroperoxidase isolated from the fungus *Caldoromyces fumago*. Each experiment was performed in triplicate in solutions of H₂O₂ and excess KCl with a known chlorine isotopic composition (-1.4‰). Extraction and analysis by gas chromatography revealed that the DMP was trichlorinated (~75%) and dichlorinated (~25%). The TMB was almost fully dichlorinated (90%) with traces of the mono- and trichlorinated isomers. Bulk δ³⁷Cl values of the extracts were -12.06 ± 0.18 ‰ and -11.08 ± 0.08 ‰ for the TMB and DMP halogenated products, respectively, and indicate that chlorine isotopes may be useful in identifying natural versus anthropogenic sources of COCs. For example, natural COCs synthesized by this enzymatic pathway will have δ³⁷Cl values that are approximately -13 to -9‰ assuming a δ³⁷Cl of natural Cl from -2 to 1‰ (Jendrzejewski *et al.*, 2001). These products should be easily distinguished from anthropogenic COCs with δ³⁷Cl values of -5.10 to +1.22 ‰ (Drenzek *et al.*, 2002).

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Transitions and twin wall conduits: controls on chemical transport in minerals

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Many rock-forming minerals display symmetry-changing structural phase transitions in response to changing temperature, pressure or chemical composition. As a consequence a hierarchical microstructures of transformation twins may develop [1]. It has long been recognised that these offer the potential for modifying the diffusion rates and transport characteristics of chemical species within the host minerals. Using the α - β phase transition in quartz as a model example, we have investigated the significance of a fairly typical structural phase transition on the rates and mechanisms of ionic diffusion.

Using β -eucryptite as a Li^+ ion source [2], we have measured diffusion of Li^+ into a natural single crystal of quartz as a function of temperature through the phase transition from low (trigonal) quartz to high (hexagonal) quartz. As this transition is encountered, a changing pattern of Dauphiné twins develops, with the twin wall density increasing on heating towards the transition temperature, T_c , and an incommensurate phase stable with a couple of degrees of the transition. We find that Li^+ ion transport peaks in the vicinity of the incommensurate phase, and the temperature dependence of diffusion indicates that the activation energy for diffusion in the high-temperature phase is around half that measured in the low-temperature phase.

The increase in Li diffusion into quartz very close to T_c can be explained in terms of the increased density of domain walls, if Li^+ diffuses faster in the domain wall than in the bulk α -quartz structure. This implies that domain walls act as conduits for diffusion, as has been noted previously in measurements of Na^+ into the WO_3 perovskite structure. Additional effects due to changes in elasticity through the structural phase transition may also modify the transport behaviour in the bulk, and account for the differences in diffusion coefficients in the low- and high-temperature phases.

In materials science applications, the phenomenon of domain wall transport could be exploited in device fabrication at mesoscopic scales. In Earth sciences, domain wall transport could be envisaged as a significant process in those phases which display transformation twin (ferroelastic) microstructures, ranging from numerous framework silicates in the crust, to silicate perovskites in the lower mantle.

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Coordination of some metals sorbed at the calcite-water interface

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Metal incorporation into calcite has been shown to be strongly site selective on the common (10.4) face. Multiple surface sites are distinguished by different geometrical arrangements of CO_3 groups, and the nonequivalent sites are segregated between structurally distinct surface steps. Adsorption of metal species at the calcite-water interface is an essential step in the overall incorporation process, and it may also be an important mechanism for sequestration of toxic metal species in natural waters. In view of these surface site differences, individual coordination preferences of various metal species may control both their site preferences and their extent of uptake. We have used EXAFS spectroscopy to characterize the coordination of Zn(II), Cu(II), and Pb(II) species sorbed at the calcite-water interface at pH 8.3. Our results show distinct surface site coordinations that differ from the coordination of these same species substituted into calcite, and allow us to explain surface site preferences.

Zn(II), Cu(II), or Pb(II) was added to pre-equilibrated calcite suspensions at pH 8.3 with maximum metal concentration below saturation with respect to possible solubility-limiting phases. Calcite solids were recovered by filtration after 48 h; moist paste samples were loaded into sealed sample holders for EXAFS data collection at beamline X11A or X18B at NSLS. Fitting was done using WinXAS and theoretical phases and amplitudes calculated with FEFF7.

EXAFS fit results for adsorbed Zn(II) show a Zn-O first-shell distance of 1.95 Å, consistent with tetrahedral coordination by four oxygens. A fitted Zn-Ca distance of 3.45 Å confirms that Zn(II) forms an inner-sphere complex at a Ca surface site. Adsorbed Cu(II) atoms are Jahn-Teller distorted, with the equatorial oxygen atoms located at a radial distance of 1.95 Å. No axial oxygen contribution could be identified, but a Cu-Ca shell was found at $R=3.9$ Å, which indicates the formation of inner-sphere Cu(II) complexes at the calcite surface. Incorporated Cu(II) atoms occupy the Ca site within the calcite surface as Jahn-Teller distorted octahedra with the equatorial oxygen shell at 2.01 Å. Fit results for Pb(II) yield a first shell of approximately four oxygens at 2.36 Å. A Pb-Ca distance of 4.05 Å verifies that metal binding at the mineral surface takes place via inner-sphere complexation.

The coordination of adsorbed Zn(II) and Pb(II) differ from their regular octahedral coordination when substituted in the Ca site of calcite, and differences in coordination also occur between the adsorbed and incorporated Cu(II). We note that Zn, Pb, and Cu exhibit similar site preferences on calcite (10.4) surfaces. It remains to be determined if and how these preferences for surface coordination may influence distribution coefficients.

From process-oriented laboratory experiments to the modelling of complex natural systems: Incorporation of microbial dynamics in a Biogeochemical Reaction Network Simulator based on the concept of a 'Knowledge Base'

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Knowledge about key reaction processes involved in the biogeochemical dynamics of natural environments is continuously expanding. Field- and laboratory-based experiments are being conducted to identify reaction pathways, quantify reaction kinetics and elucidate the interactions between biotic and abiotic processes. An important challenge is to develop theoretical and computational tools that allow the systematic integration of new knowledge about the coupled biogeochemical processes which, together, determine the cycling of elements in environmental systems. In this framework, a Biogeochemical Reaction Network Simulator (BRNS), based on the novel concept of an evolving 'Knowledge Base' (KB) has been developed. In this approach it is no longer the model itself, but an easily accessible, open resource element, the KB, which contains the conceptual and quantitative understanding of biogeochemical pathways and their interactions. It is through the KB that a continuous learning process and information exchange between experimentalists and modelers can be conducted. In addition to the KB, a newly developed automatic code generator and associated numerical engines constitute the BRNS.

Our current research aims at merging microbial ecology into existing geochemical models of early diagenesis, using the results from process-oriented laboratory experiments. Because essential parameter values are scarce and poorly constrained for many microbial groups, especially anaerobic bacteria, a continuous feedback loop between process implementation and model simulations is needed. Our modeling approach based on the 'Knowledge Base' concept offers the necessary flexibility for this implementation. The BRNS allows to evaluate alternative process formulations, to develop diagnostic indicators of biogeochemical pathways that can be measured in the field or in experimental set-ups, and to assess the propagation of model and experimental uncertainties in predicted system behavior.

Secular variation of Tl isotopes in ferromanganese crusts?

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In a recent study we reported that the surface layers of ferromanganese (Fe-Mn) crusts have Tl isotope compositions that differ from seawater by ~2% (Rehkämper et al., 2002). This difference is thought to result from the isotope fractionation that accompanies the adsorption of Tl onto ferromanganese particles.

We have measured time-resolved Tl isotope compositions in six serially sampled Fe-Mn crusts: BM 1969.05 (N. Atlantic, 0-55 Ma), Alvin 539 (N. Atlantic, 0-30 Ma), Antipode 109 D-C (Indian Ocean, 0-14 Ma), DODO 232D (Indian Ocean, 0-17 Ma), D11-1 (Pacific, 0-55 Ma) and CD-29-2 (Pacific, 0-45 Ma). For most Fe-Mn crusts, we did not attempt to obtain high-resolution profiles and one sample was analyzed per 10-15 Ma. One higher resolution 0 to 4 Ma time series for BM 1969.05, however, does not show any significant short-term (0.3 Ma) variations in Tl isotope composition.

The Tl isotope time series of most Fe-Mn crusts show a coherent trend of increasing $\epsilon^{205}\text{Tl}$ with time ($\epsilon^{205}\text{Tl}$ is the deviation of the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio of a sample from the NIST SRM 997 standard in parts per 10⁴). For the two Pacific samples, the trends of $\epsilon^{205}\text{Tl}$ with time are almost identical: $\epsilon^{205}\text{Tl}$ increases smoothly from ~+6 at about 50 Ma to present-day values of ~+14. The time series of the Indian Ocean Fe-Mn crusts are very similar: $\epsilon^{205}\text{Tl}$ increases from ~+11.5 at 15 Ma to ~+13.5 at 0 Ma. The two samples from the North Atlantic show trends that differ somewhat from the Indian and Pacific Ocean results. For BM 1969.05, $\epsilon^{205}\text{Tl}$ increases from ~+5 at 55 Ma to ~+14.5 at 30 Ma. Following this, $\epsilon^{205}\text{Tl}$ is relatively constant to 15 Ma, then it decreases to ~+11.5 at 8 Ma after which $\epsilon^{205}\text{Tl}$ is almost constant again to the present day. In Alvin 539, $\epsilon^{205}\text{Tl}$ decreases continuously from ~+13.5 at 30 Ma to ~+11.5 today.

An evaluation of the significance of the Tl isotope time series results is difficult at present. Three interpretations of the data are possible. (1) The trends are signatures of diagenetic alteration of the Fe-Mn crusts. In this case, the $\epsilon^{205}\text{Tl}$ variations do not reflect changes in paleoceanographic conditions. (2) The Tl isotope variations in the Fe-Mn crusts are due to changes in the fractionation factor of Tl between seawater and ferromanganese particles. Such changes could be due to, for example, variations in ocean temperatures or the mineralogy of the Fe-Mn crusts. (3) The temporal trends of $\epsilon^{205}\text{Tl}$ reflect a change in the Tl isotopic composition of the oceans. This would indicate that the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio of seawater increased significantly during the Cenozoic, by nearly 10 ϵ -units.

Fast ligand controlled goethite dissolution kinetics under non-steady state conditions in the presence of siderophores and oxalate

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Ligand controlled dissolution of goethite

Non-steady state weathering processes are commonly observed in natural systems. Iron stressed plants, for instance, mobilize iron from poorly soluble iron (hydr)oxides by diurnal pulse-release of siderophores into the rhizosphere.

This study investigates the mechanism of non-steady state dissolution of goethite (α -FeOOH) in the presence of oxalate and pulsed additions of the microbial siderophore desferrioxamine B (DFO-B). All experiments for this study were carried out in batch reactors at pH 6 with a constant oxalate concentration of 100 μ M. In a series of batch experiments, spikes of 40 μ M DFO-B were added to the oxalate-goethite system after defined initial pre-equilibration times, whereby in each batch the addition times of the spike were different. In another experiment, multiple spikes of DFO-B were successively added to one single batch. The additions of the siderophore spikes led to very fast dissolution reactions with subsequent steady state dissolution. It was observed that the magnitude of the fast dissolution reaction was a function of the pre-equilibration time of the oxalate-goethite system. The experiment involving multiple spikes of DFO-B revealed that the fast dissolution reaction occurred reproducibly with every added DFO-B spike.

In analogous experiments, oxalate was replaced by malonate and citrate, respectively. Similar results were observed, verifying that this effect is not exclusive to oxalate.

Discussion and conclusion

Due to the low solubility of goethite at pH 6 little dissolution of iron is observed in the oxalate-goethite system. However, the addition of DFO-B causes a disequilibrium in the system that leads to fast dissolution of iron. Since the magnitude of the fast dissolution reaction is a function of the pre-equilibration time, it seems likely that the adsorbed oxalate destabilizes the surface sites of the goethite in a slow reaction that leads to the accumulation of labile iron centers at the mineral surface. Thus, the observed fast dissolution corresponds to the release of labile iron which is triggered by the disequilibrium caused by the addition of DFO-B.

Identifiability Analysis of a Diagenetic Model

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Introduction

Due to the large base of scientific knowledge, the description of environmental systems is often based on complex simulation models, which contain parameterizations of a large number of processes. The parameters of such models are typically not identifiable from a data set available for a specific system. In such situations, identifiability analysis techniques are useful in order to find identifiable subsets of parameters and to gain insight into the degree of non-identifiability (Brun et al., 2001). Such techniques have not been applied to diagenetic models so far.

Results

Based on such techniques, it has been shown that for a diagenetic model of Lake Zug, Switzerland (Dittrich et al., 2002), an exceptionally large number of parameters (more than 20) can be identified from the available data. This is due to the availability of a comprehensive data set consisting of measured sediment profiles of 9 dissolved (pH, HCO₃⁻, NH₄⁺, HPO₄²⁻, SO₄²⁻, Mn²⁺, Fe²⁺, CH₄, Ca²⁺) and 6 particulate (POC, PON, MnO₂, FeOOH, CaCO₃, FeS) substances. Major uncertainties remain with respect to time-dependent boundary conditions at the water-sediment interface (due to the lack of measurements over the 200 year simulation period), to oxic and denitrifying mineralization rates (due to the lack of oxygen and nitrate at the sediment water interface during the past 50 years), to the precipitation rates of vivianite and manganese carbonate (due to the absence of measurements of these compounds), and to joint determination of maximum degradation rates and half-saturation concentrations (due to the small spatial variability of important substrates).

Conclusions

It is shown that identifiability analysis techniques are very useful in order to determine the lack of uniqueness of the values of model parameters and the conditional dependence of fitted parameters of the values of parameters that were kept constant during the fit. The determination of effective mineralization rates of different mineralization processes can be a first step towards a more universal mineralization model that considers the density of the bacteria responsible for mineralization.

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The determination of diffusion profiles in small samples: a comparison of micro-beam techniques

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The determination of chemical diffusion profiles in high pressure samples produced in multi-anvil experiments requires a micro-analytical technique with high spatial resolution such as secondary ionisation mass spectrometry (SIMS) or laser ablation inductively couple plasma mass spectrometry (LA-ICP-MS). Experiments were carried out in order to investigate the transport properties of silicate liquids at high pressure and temperature. Under investigation were both ionic self-diffusion and the chemical diffusion of trace elements.

In this study, the determination of the chemical diffusion of trace quantities of Ni and Co and the self-diffusion of network-modifying ions Ca²⁺ and Mg²⁺ were carried out in samples of CaMgSi₂O₆ (diopside) composition liquid, synthesised at high pressure and temperature. The self-diffusion profiles were defined by changes in the abundance of enriched isotopes, in this case ⁴⁴Ca and ²⁵Mg. LA-ICP-MS and SIMS have been used to determine the self-diffusion of Ca²⁺ and Mg²⁺ while the chemical diffusion profiles of Ni and Co have been determined by LA-ICP-MS only.

Even with automated sampling, the acquisition time required for the analysis of a diffusion profile using point analyses is on the order of hours for both SIMS and LA-ICP-MS. In order to reduce the acquisition time of the analyses using LA-ICP-MS two different analytical procedures have been tested and compared: 1) traditional single spot analyses and 2) rapid line scanning. The latter technique reduces the acquisition time approximately 15 times compared to single spot analyses.

The two procedures produce profiles that are in good agreement with each other and also with those derived from point analyses using SIMS. These results indicate that the use of rapid line scans to determine diffusion profiles provides a power way to reduce analysis time.

Crystal ages as tracers of rhyolite differentiation and storage

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Besides providing evidence for magma residence times, the ages of individual accessory phases like zircon and allanite are passive tracers of silicic magma evolution. General observations for rhyolites from dating individual crystals (Reid et al., 1997; Brown and Fletcher, 1999; Reid and Coath, 2000; Vazquez and Reid, in press; Simon and Reid, this volume) include: 1) Late entrainment of crystals from earlier episodes of magmatic activity and from country rocks, likely during magma ascent and eruption, is evidenced by the lack of juvenile crystal rims and by the presence of inherited radiogenic Ar (major mineral phases; e.g., Gansecki et al., 1998). These factors emphasize the need to interpret "old" mineral ages with caution; 2) Similar-age populations between successive effusive eruptions (e.g., post-caldera Long Valley and Yellowstone) suggest repeated tapping of the same magma reservoir, but do not require the system to have been molten throughout the repose interval; 3) Lack of crystal memory from one eruption to the next in other cases (e.g., Bishop Tuff, Yellowstone) provides strong evidence for new episodes of rhyolite differentiation; 4) Accessory phases may have protracted, and probably episodic, growth histories (e.g., Whakamaru, Toba). Considered together with the likelihood that the main increment of accessory phase growth accompanies initial saturation, accessory phase sizes have uncertain value as indicators of their ages; 5) Ages of the oldest cognate crystals can approach those of the previous rhyolite eruption, suggesting renewed silicic magma differentiation and/or emplacement soon after evacuation of the magma reservoir; 6) Relatively youthful mean crystallization ages and evidence for resorption of the cores of older grains suggest that voluminous rhyolites may develop relatively rapidly with respect to the duration of silicic magmatism. Hence, average rhyolite accumulation rates are probably not equivalent to long-term eruption rates. Either major eruptive episodes are the product of a "grand cycle" of differentiation or regular silicic magma production is accompanied by a quasi-steady-state flux of melt from the molten to mushy portion of the magma reservoir.

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Intercalibration of zircon (U-Th)/He and K-feldspar $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronometry

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Deducing accurate thermal histories of rocks, especially over large temperature and time intervals, requires intercalibration of ages and cooling models from different thermochronometers. At low temperatures (e.g., ~300-50 °C), thermal histories are typically constrained by multi-diffusion domain modeling of K-feldspar $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra, fission-track (FT) cooling ages and track-length models, and (U-Th)/He cooling ages of various phases. While temperature dependent diffusivity is the fundamental interpretational basis for all of these systems, each is based on different diffusing species and domain configurations, and is subject to potential influences besides temperature. Here we focus on comparisons between the low-temperature (<200 °C) portion of $^{40}\text{Ar}/^{39}\text{Ar}$ K-feldspar cooling models, and (U-Th)/He cooling ages, primarily for zircon. Previous work has only constrained the closure temperature (T_c) for He in zircon (~160-210 °C) within fairly broad bounds, and raised questions about the effect of radiation damage on effective T_c . Our new He diffusion experiments for zircon ($E_a = 172 \pm 0.4$ kJ/mol (41.1 ± 0.1 kcal/mol); $D_0 = 1.1 \pm 0.3$ cm²/s) yield a closure temperature of 183 ± 4 °C (for $dT/dt=10$ °C /myr), and are consistent with diffusion domain and crystal size equivalence, as for titanite and apatite. However, we also confirmed higher He diffusivity in strongly radiation damaged zircon, raising the possibility that, at least in cases of highly radiation damaged zircons, (U-Th)/He closure may be a function of U-Th content and thermal history.

To compare these constraints with cooling ages and thermal histories of natural zircons from different geologic settings, we obtained detailed thermal histories from Pb, FT, Ar, and He systems for 4 samples (3 from New Zealand and 1 from Alaska) that cooled through ~200 °C between 9-85 Ma, at rates of ~10-75 °C/myr. Correlation factors (C_{fg}) for K-feldspar spectra (Lovera et al., 2002) in these samples vary from 0.88 to 0.94, suggesting good adherence of observed spectra to multi-diffusion domain hypotheses of the cooling models. Multiple replicates of laser-heated, single-grain zircon ages for most samples show 2- σ reproducibility of 5-10%, whose means are well within 1- σ of K-feldspar models (or their extensions) at 180 °C. Overall these data indicate good agreement for these chronometers and, assuming accurate K-feldspar models, restrict the zircon He T_c to 175 ± 25 °C for these samples, regardless of ages and U-Th contents that vary by factors of 10 and 3, respectively.

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The fate of wastewater indicator compounds during groundwater recharge

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Artificial recharge is increasingly used to augment groundwater water supplies. In Orange County, Southern California, water from the Colorado and Santa Ana Rivers (SAR) is feed to a deep recharge basin for groundwater recharge. Water samples from the recharge basin and two wells that draw water supplied by the basin were analyzed to evaluate trace organics behavior. In autumn of 1996 and again in spring of 1997, the basin was fed with water imported from the Colorado River (COR), which is high in sulfate (263 mg/L) compared to the river 100 mg/L. Residence times were obtained by identifying pulses of high-sulfate water in the wells. The average concentration after 20 d and 170 d travel are indicated in Table.

Table 1. Concentration after 0, 20 and 170 d travel

Time [d]	DOC mg/L	DO mg/L	EDTA μg/L	APECs μg/L
Basin	5.00	7.3	5.9	1.9
20	2.5	0.45	3.9	0.19
170	1.5	0.94	0.85	0.16

SAR DOC was removed during transport to the wells (approximately 50% 31% after 20 and 170 days of transport, respectively) and DOC removal consumed nearly all dissolved oxygen (DO). The fraction of DOC not removed was retarded by a retardation factor 1.3. EDTA and alkylphenol polyethoxy carboxylic acids (APECs) were removed to a greater extent than DOC but persisted at trace levels. Data from shallow (5 m) wells indicate that most of the DOC removal (40%) occurs within the first day after infiltration. EDTA passes through the 5 m infiltration zone with little attenuation. APEC removals decreased to 25% after basin cleaning but increased to 100% after approximately 3 weeks of basin operation. Data indicate trace organics can pass through the biologically active infiltration zone consistent with results from biological laboratory columns.

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Nutrient retention ponds in agriculture – load and efficiency

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Introduction

The application of liquid manure to artificially drained grassland soils in the Central Swiss Plateau results in excessive nutrient fluxes through the drainage system into the receiving waters. In the catchment area of Lake Sempach several artificial ponds were constructed in order to collect the mobilized nutrients from the drainage system and to reduce their transport to the lake.

Study site and methods

In 2001 we determined the nutrient retention capacity of one selected pond (volume: 1200 m³; surface: 2000 m²; max. depth: 0.8 m) near the farm Sonnhof which receives drainage water from a catchment area of about 204 000 m². The combination of regular sampling and online analytical techniques with the registration of the hydrologic regime allows us to establish a detailed nutrient budget and to detect seasonal changes of the nutrient fluxes. The concentrations of the different phosphorus species and total nitrogen are determined with conventional chemical analysis, whereas nitrate and ammonia concentrations are recorded applying a flow-through cell with ion-selective electrodes (temporal resolution: 12 minutes).

Results and discussion

First results of our study show that most of the phosphorus and nitrogen load is transported during few heavy rainfall events throughout the year (Fig. 1). The retention of the nutrients and therefore the effectiveness of the pond increases with the water residence time. On an annual basis it is possible to retain about 40 % of the total phosphorus and 25 % of the nitrogen input corresponding to approximately 4 kg phosphorus and 88 kg nitrogen.

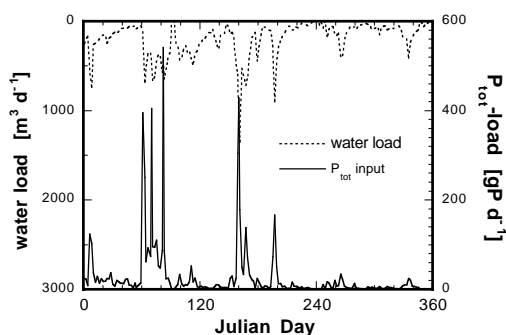


Fig. 1: Water and phosphorus load into pond Sonnhof

The effects of melt percolation on the Os isotopic systematics of the Sidamo peridotites, Ethiopia

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Os isotopes are among the most reliable tracers of ancient magmatic processes. However, there is increasing evidence that Os is more mobile in mantle rocks than originally thought. To investigate the mechanisms of Os mobility we have studied peridotite xenoliths from Sidamo, Ethiopia. These rocks record melt-rock reactions resulting from pervasive infiltration of melts at the base of the lithosphere, above a mantle plume (Bedini et al., 1997). Two textural/geochemical groups have been recognized. Granular peridotites were extensively re-equilibrated with basaltic melts in the lower, high porosity, region of the lithospheric mantle. In contrast, deformed peridotites record interaction with volatile-rich small melt fractions, highly evolved by reaction with peridotite, that infiltrated into the shallow, low porosity, mantle lithosphere.

As a group, all of the samples define a rough correlation between ¹⁸⁷Os/¹⁸⁸Os and Al₂O₃ content, suggestive of ancient (~ 2.7 Ga) melt extraction. Nevertheless, the granular lherzolites have Os isotopic ratios 1 to 4% higher than expected, suggesting that they were modified by interaction with the percolating basaltic melts. This mechanism is favored by the intergranular position and metasomatic character of the sulfides, which contain essentially all of the Os in these rocks. High melt/rock ratios are implied, given the contrasting Os concentrations of peridotites and typical mafic magmas. Both Os concentrations and Os isotopic ratios are quite reproducible in this group of samples. The deformed harzburgites also have higher than expected ¹⁸⁷Os/¹⁸⁸Os ratios, which can be highly heterogeneous within samples. These harzburgites contain no sulfides. Instead, the higher Os concentrations obtained after NiS fusion, compared to those determined after Carius tube dissolution, show that the Os is contained in highly refractory phases (e.g. Os-Ir alloys). The low porosities existing in the deformed region suggest that the Os compositions were modified by interaction with relatively small volumes of highly radiogenic fluids, perhaps derived from nearby ancient mafic layers.

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Timing of UHPM in metasediments from the Rhodope Massif, N Greece

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The Rhodope Massif in N Greece is part of the internal Hellenides that was subjected to severe alpine deformation and metamorphism. Since the discovery of UHPM rocks in N Greece (Kostopoulos et al., 2000), the relation between this UHPM event and the observable alpine orogenic processes is an open question. Such HP and UHPM rocks belong to the Upper Tectonic Unit and comprise gneisses and migmatites associated with marbles, amphibolites and variably retrogressed eclogites. In this study we concentrated on felsic metasediments near Xanthi that record UHPM in excess of 7 MPa. These metasediments are composed of garnet, white mica, kyanite, quartz, feldspar, and biotite as major constituents, and some rare accessory minerals such as zircon and monazite. The garnet porphyroblasts contain inclusions of diamonds, and exsolutions of rutile and silica forming after majoritic garnet as further witnesses of the UHP.

We analysed monazite by microprobe and calculated U-Th-Pb ages, which are grouped into two major populations at 185 Ma and 165 Ma, and two minor at 200 Ma and 146 Ma. The spatial age distribution within the individual grains form regular pattern with ages younging towards the rim. We also determined a Sm-Nd garnet - whole rock age of 140±4 Ma. The mica were dated with Rb-Sr yielding mineral whole-rock ages of 37 Ma for the white mica and 34 Ma for the biotite. We also analysed single zircons of a granitic gneiss from the same region by Pb-Pb evaporation yielding 140±3 Ma. It is noteworthy that the 140 Ma age coincides with the age of metamorphic rims of zircons from the same area (Liathi and Gebauer, 2001).

We suggest the following interpretation. The monazite age of 186 Ma is the closest approximation to the UHPM peak, since monazite has the highest closure temperature of the minerals analysed from the metasediment. The other Jurassic ages reflect later metamorphic overprint during uplift, especially the ca. 140 Ma age appears to be of regional importance and indicates a major upper Jurassic event. The Rb-Sr mica ages document the passage of these minerals through the relevant closure temperatures in response to the exhumation during the Eocene.

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Direct versus indirect determination of biogenic barium as a proxy for productivity

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The reliability of the determination of biogenic barium by an indirect/normative calculation was assessed by a comparison with directly/sequential extraction determined biogenic barium results. The comparison showed that the terrigenous Ba/Al ratio is the critical factor in the normative approach that may introduce significant errors. In general, the postulated crustal average Ba/Al ratio of 0.005 to 0.01 (Rösler and Lange, 1972) seems to be too high for all analysed samples, which would result in an underestimation of the biogenic barium and thus an underestimation of the primary productivity recalculated from the normatively calculated Ba record. A terrigenous Ba/Al factor of ~0.0037 would lead to calculated biogenic barium contents that are in good agreement with the biogenic barium contents measured by sequential extraction for most investigated samples of the Atlantic, Pacific (Fig. 1) and Indian ocean.

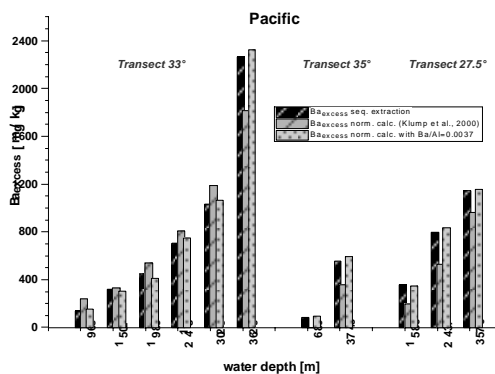


Fig. 1: Excess/biogenic barium in surface sediments of the Pacific Ocean.

However, the results from the Pacific Ocean (Fig. 1) show that the sequential extraction technique is required in sedimentary environments with a terrigenous fraction of >40%. Comparing samples from different deep-sea regions suggest that using an average crustal Ba/Al ratio in many cases will lead to erroneous results.

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Trace element behaviour during magma mingling: the case study of the gabbro-granite association of Ota (western Corsica)

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The gabbro-granite association of Ota developed during the post-collisional phase of the Variscan orogeny, at about 280 Ma [3]. Gabbros and granites display mingling relations indicating their coeval crystallization [1]. The gabbros are characterized by ophitic clinopyroxene with coronas of titanian pargasite. The granites are subsolvus and characterized by biotite as the only mafic phase. On the basis of Nd-Sr-O isotope compositions, the granites were related to partial melting of lower-crustal reservoirs (Poitrasson et al., 1995). Hybrid rocks develop along the contacts between gabbros and granites, and are mostly represented by clinopyroxene-free, hornblende-rich quartz-diorites to quartz-monzodiorites. Minor hornblende-bearing granodiorites to monzogranites are also locally present. The hybridization is shown by field relations, complex chemical zonings of plagioclase and hornblende, and by the common occurrence of acicular apatite, skeletal opaque phases and quartz ocelli rimmed by hornblende coronas. To decipher the chemical effects of the mingling between basic and acid magmas, trace element mineral analyses have been carried out by LA-ICP-MS. Clinopyroxene compositions indicate that the gabbros formed by fractional crystallization of tholeiitic melts, overall similar to transitional MORB. Plagioclase and amphibole exhibit a decrease of Ti, Zr, Hf, Eu, Sr and Ba from the gabbros to the hybrid rocks and to the biotite-bearing granites. Conversely, the abundances of Rb and Pb increase. These mineral variations parallel the whole-rock chemical compositions of gabbros and granites, which were interpreted to represent the original basic and acid melts, respectively [2]. The intermediate chemical feature of plagioclase and amphibole from the hybrid rocks thus indicates a process of chemical mixing between mantle and crustal liquids. The variations of LREE, U and Th abundances in plagioclase and amphibole do not display a simple correlation with whole-rock chemical variations, and are most likely controlled by the development of LREE-, U- and Th-rich accessory phases (i.e. allanite and zircon).

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Carbon isotopic composition of macrodiamonds from Yubileynaya pipe (Yakutia)

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Yubileynaya pipe is one of the largest diamond mine in Yakutia. The $\delta^{13}\text{C}$ values of 12 diamonds about 2 mm in average size are reported. All crystals contain mineral inclusions of U-type mantle paragenesis (olivines, chromite and pyropes). 100Mg/(Mg+Fe) ratio in olivines vary from 92.0 to 93.3 % ($\bar{x}=92.8$). NiO contents vary from 0.34 to 0.37 wt.%, Cr_2O_3 - 0.03-0.08 wt.% and CaO - to 0.02 wt.%. The garnets are presented by high-Mg subcalcic pyropes with Cr_2O_3 contents from 8.91 to 9.94 wt.%.

Obtained $\delta^{13}\text{C}$ values vary from -2.9 to -5.9 ‰ ($\delta^{13}\text{C}_{\text{mean}} = -4.4$ ‰; $\sigma=0.9$; $n=12$). According to Kinny et al (1999) $\delta^{13}\text{C}$ values for microdiamonds from the same pipe are from -1.7 to -5.7 ‰ ($\delta^{13}\text{C}_{\text{mean}} = -3.4$ ‰; $\sigma=1.3$; $n=10$). The same relations between micro- and macrodiamonds was noted for other localities (Reutsky, Zedgenizov, 2001).

The variations in composition of olivines correspond to the magmatic fractionation trend (fig.1). No relations between $\delta^{13}\text{C}$ of diamonds and petrogenetic fractionation are present.

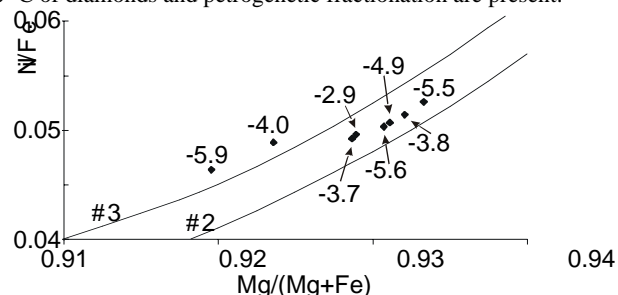


Fig.1. Ni/Fe, Mg/(Mg+Fe) ratio of olivine inclusions and the $\delta^{13}\text{C}$ of their hosts. Curves #2 and #3 are fractionation trends for different initial Ni/Fe ratios (from Deines et al., 1997).

Conclusions

Mean $\delta^{13}\text{C}$ values of diamonds from Yubileynaya pipe is -4.0 ‰ ($\sigma=1.2$; $n=22$). Preliminary, the macrodiamonds are depleted by ^{13}C relatively to microdiamonds to 1‰.

The composition of olivine inclusions are linked to partial melting process but $\delta^{13}\text{C}$ of their host diamonds are not linked with petrogenetic processes.

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Nontronite formation in rhyolitic ignimbrite

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The voluminous (>300 km³) rhyolitic Ongatiti Ignimbrite (OI, 1.25 ± 0.12 Ma) in the Taupo Volcanic Zone of New Zealand (Wilson et al., 1995; Black et al, 1996) contains sporadic occurrences of <10 to 100 mm-wide nontronite seams. Nontronite was initially deposited in OI fissures as a colloidal gel, and developed into larger and more ordered crystals with time. However, before precipitation of nontronite in fissures, solutions reacted with the OI. This resulted in leached selvages and replacement by nontronite of OI components, <10 mm thick, along the sides of fissures. The rest of the OI remains fresh. From Fe contents in the OI (2.4 wt.%) and nontronite (16.2 wt.%) about 300 m³ of fresh rhyolite needs to be dissolved to produce 50 m³ of nontronite, using the equation below (Reyes and Vickridge, 1996):

$$\log(C_A/C_F) = \log M_F - \log M_A$$

(C= concentration, M= mass, A= altered rock, F= fresh rock;
_(OI) = 2.5 g/cm³, _(nontronite) = 2.25 g/cm³)

Leaching and dissolution of ignimbrite can occur around rootless fumaroles (e.g., Keith, 1991), where interaction of volatiles from cooling ash flows with groundwater result to acid waters. Nontronite only started to deposit (Fig. 1) once the OI has partly cooled while still having the capacity to release volatiles.

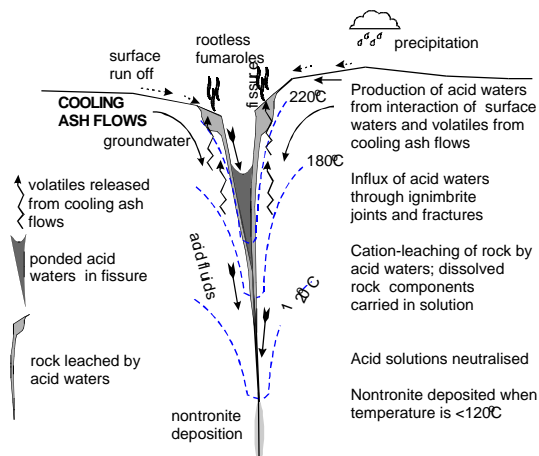


Fig.1. Nontronite formation in the Ongatiti Ignimbrite.

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Selective mobilization of metals from granitic melt into exsolved fluid and their separate deposition during formation of the F-Be deposit

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An aegirine granite intrusion associated with the Yermakovka F-Be deposit (Transbaikalia, Russia) hosts pegmatites which, to a first approximation, are considered as a geochemical model of a deep-seated reservoir of rest magma, possible source of ore-forming fluids (Reyf & Ishkov, 2001). Melt (MI) and fluid (FI) inclusions in magmatic quartz and fluorite have been studied using micro-thermometry, EPMA, and AES of laser-opened FI (Reyf, 1997). The data obtained suggest that initial granitic melt was enriched in F (2.6 wt%) and H₂O (4.5wt%) and had become fluid-saturated at ~700°C, prior to segregation of the intergranular residual melt into cracks within crystalline carapace. Exsolved fluid is found to be a mixture of immiscible alkaline-fluoride-sulphate brine (L1) and a low-salinity CO₂-bearing solution (L2). This is evident from the confinement of the L1 and L2 inclusions to the same growth-zones of host minerals. The immiscible phases have different salinity, density (1.7-2.1 and 0.75-0.85 g/ml), and metal content (see Table).

	Concentration, wt%					Max. concentr., g/kg				
	(Na,K) ₂ O	SO ₃	F	NaCl	CO ₂	Be	Mo	Mn	Fe	Ce
L1	20-23	12-15	8-9	+	-	0.3	17.8	9.6	4.3	+
L2		-	+	2-6	8-14	0.7	<0.7	<1	0.6	-

The evidence for both joint and separate migration of the immiscible fluid phases are revealed, and the activity of autonomous brine flows is studied more carefully since it is enriched in many metals. Zones of albitization within granite intrusion are found to be formed by the fluid mixture at T=650-580°C. Only pyrite and minor molybdenite were deposited in the course of albitization. More abundant molybdenite along with monazite precipitated from autonomous brine flow during formation of quartz veinlets in endocontact part of the intrusion at T=650-600°C, and molybdenite-rich dolomite-garnet-oligoclase veinlets in biotite schists were formed by the brine flow at 600-550°C. At the level studied, no beryllium minerals were precipitated from the Be-bearing brine at T>500°C, however, they could precipitate within cooler area. The high-grade phenakite-fluorite ores precipitated at 400-150°C, predominantly from autonomous flow of L2.

The separation of Mo and Be is likely to result from different stability of the complexes NaHMoO₄⁰ and BeFCO₃⁻ in the immiscible magmatic fluids and from different dependence of their solubilities under subsolidus conditions

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Effect of feeding on the carbon isotopic composition of the zooxanthellate coral *Stylophora pistillata*

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Abstract

The effect of feeding on the carbon isotopic composition of zooxanthellae, animal tissue and skeleton was investigated in the scleractinian coral *Stylophora pistillata*. Two sets of corals were grown with filtered seawater under controlled conditions. One group of colonies was fed with *Artemia* nauplii and compared to a control group that was starved. Fed corals exhibited higher concentrations of calcification rates than starved colonies. The average $\delta^{13}\text{C}$ value of *Artemia* nauplii used for feeding was -12‰. $\delta^{13}\text{C}$ was significantly heavier in zooxanthellae than in animal tissues, for both fed (-10.1 vs. -11.7‰) and starved colonies (-10.9 vs. -13.2‰). Isotopic data reflected the incorporation of *Artemia* carbon into the coral tissue in that the $\delta^{13}\text{C}$ was significantly heavier in fed than in starved colonies (-11.7 to -13.2‰ respectively), although there was no difference in the $\delta^{13}\text{C}$ of the zooxanthellae fraction. Skeletal $\delta^{13}\text{C}$ was similar in fed and starved colonies (mean = -4.6‰).

These data are used to establish a conceptual model of the carbon flow between the various compartments of a symbiotic coral.

Groundwater weathering rates from U- and Th- series nuclides

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The transport of U, Th, Ra and Rn nuclides of the ²³⁸U- and ²³²Th- decay series has been investigated in a large sandy confined aquifer in New Mexico. Groundwater data are compared with a model of weathering of aquifer grains and interaction with surface coatings, to constrain important physico-chemical parameters that occur within the aquifer, principally weathering rates, α -recoil effects, adsorption-desorption characteristics, and irreversible precipitation (Tricca *et al* 2001). The model can explain the observed nuclide activities measured in the groundwater. The relative importance of α -recoil effects compared to bulk weathering of mineral grains can be estimated from the $\delta^{234}\text{U}$ values in the groundwater.

Thorium concentrations are at their saturation limit throughout the aquifer. The total Th activity in the surface coating increases linearly with the age of the aquifer for ²³²Th, but reaches a steady-state activity for ²³⁰Th. In order to explain the Rn concentration, it appears that between 2 and 7 % of the host rock has been chemically weathered in the aquifer over the past 10 yr in an early stage of weathering, which has left behind a surface coating enriched in ²³²Th and ²³⁰Th. This provides the high Rn in the waters. Radium is strongly adsorbed onto the surface of the host aquifer rocks, roughly 1000 times more than is in solution. The $\delta^{234}\text{U}$ found in the aquifer is ~8000. It was found that water in the aquifer could not be derived from the present vadose zone waters which have high ²³⁸U concentrations and $\delta^{234}\text{U}$ ~500.

From the U-decay series it is found that the average α -recoil fraction is ~0.007, and the average weathering rate in the aquifer is $\sim 6 \times 10^{-17} \text{ s}^{-1}$, that equates to a chemical exhumation rate of the aquifer rock of 0.1 mm/kyr, or 0.25 ton/km²/yr. Simply from their relative $\delta^{234}\text{U}$ values, the weathering in the vadose zone must be over 20 times the weathering rate inside the aquifer, around $1 \times 10^{-15} \text{ s}^{-1}$, or 4.5 ton/km²/yr for a 55 m thick vadose zone. Despite low weathering rates estimated for this region, the overall chemical exhumation rates are still relatively large. The results demonstrate that the U- and Th-decay series provide a powerful tool to investigate the long-term evolution of groundwater-systems and can constrain the physico-chemical reactions that affect the transport of actinides in groundwater systems.

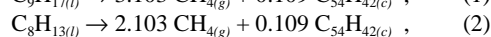
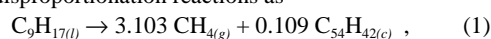
Reference: Tricca A., Wasserburg G. J., Porcelli D. and Baskaran M. (2001) *Geochim.Cosmochim.Acta.* 65. 1187-1210. Caltech Contribution 8782(1093) Research supported by DOE DE-FG03-88ER13851.

Thermodynamic analysis of pyrobitumen formation during thermal alteration of crude oil in deep hot reservoir and source rocks

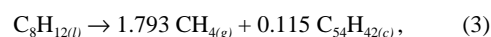
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Gibbs free energy minimization computer experiments indicate that the oil generated in hydrocarbon source rocks during the incongruent melting of kerogen with increasing depth becomes progressively dominated to an increasing degree by low-molecular weight aromatic species such as toluene and ethylbenzene as temperature increases above ~ 175°C. This increase favors the irreversible disproportionation of crude oil to form natural gas and pyrobitumen in both hydrocarbon reservoirs and source rocks. For example, if we represent the crude oils produced in the computer experiments with average compositions corresponding to C_9H_{17} , C_8H_{13} , and C_8H_{12} at 150°C, 200°C and, 250°C, respectively, we can write the overall disproportionation reactions as



and



where $C_{54}H_{42(c)}$ stands for a representative pyrobitumen of anthraxolitic composition. It can be deduced from the stoichiometries of these reactions that the formation of pyrobitumen relative to methane is favored to an increasing degree by the concomitant increase in both the temperature and aromaticity of the oil. In fact, for each mole of $CH_{4(g)}$ produced, 0.035, 0.052, and 0.064 moles of pyrobitumen are formed, respectively, with increasing temperature from 150°C to 250°C.

Development of a micro-cavity ion source for enhanced efficiency in thermal ionisation mass spectrometry

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The need to precisely and accurately measure isotope ratios on very small amounts of sample (nanograms to sub-picogram) is of increasing importance in a variety of applications. To improve sample utilization for isotope ratio measurements, we have adapted a micro-cavity source to two sector thermal ionization mass spectrometers (TIMS), a home-built double-focusing instrument equipped with a single pulse-counting detector, and a commercial Finnigan MAT 262 instrument. Unlike traditional TIMS sources which employ a filament design, the sample is loaded into a narrow (0.2-0.5 mm diameter) micro-cavity bored in a tungsten or rhenium rod, which is then heated by electron impact. The source's confined geometry and ability to operate at much higher temperatures (>3000C) provide the potential for enhanced ionization efficiency compared to traditional TIMS sources.

Thus far, our work has focused on uranium and plutonium. On both instruments, efficiencies (ions detected/atoms loaded) measured using the cavity source are an order of magnitude or more higher compared to those measured using filaments. Using single resin beads loaded with ~10ng of U, W cavities on the 262 instrument yielded efficiencies of 0.02 to 0.04%; similar tests on the ORNL instrument using 1ng beads indicated efficiencies of up to 0.4%. Adding a Re/C slurry to W cavities increased efficiencies to 0.1 to 0.2% on the 262. Efficiencies of up to 0.6% were measured on the 262 using Re cavities. In comparison, efficiencies of 0.01 and 0.04% were measured using single Re filaments on the 262 and ORNL instruments, respectively. More limited data has been obtained utilizing resin beads loaded with 30pg of Pu. Efficiencies exceed 0.08% for W filaments, and 0.4 to 1.2% for Re cavities on the 262. Various observations indicate that transmission from the source into the mass spectrometers is far from optimised, suggesting that actual ionization efficiency is significantly higher than the effective efficiency measured in these tests. In spite of this, these results match or exceed many of the best reported TIMS efficiencies. The measurements reported here were not optimised for precision and accuracy of isotope ratio measurements. However, U measurements on the ORNL instrument suggest that accuracy is 0.5% or better, and precision is similar to that obtained using filament measurements.

Coccolith chemistry considered

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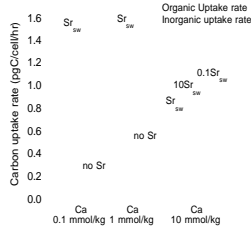
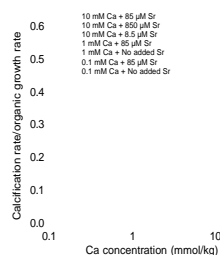
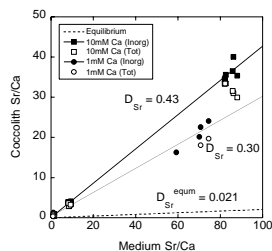
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Abstract

The isotopic and trace metal chemistry of marine biogenic calcites has the potential to act as a tool to probe past ocean conditions and related climate change. The composition of biogenic carbonates depend on ocean chemistry, and also on the partitioning associated with mineral formation. We challenge the view that the partitioning occurs according to predictions for inorganic calcite precipitation. Instead we propose that the chemistry of the biogenic calcite is controlled by biological discrimination during the calcification process.

We investigate the chemistry of calcite produced by coccolithophores cultured in various Ca and Sr media. Coccolithophores assemble their liths in an intracellular vesicle and therefore provide the biological end member of the spectrum between equilibrium precipitation of calcite and biologically mediated precipitation (Fig 1). Altered concentrations of Ca and Sr also affect the biological processes and growth of coccoliths (Fig 2, 3). We suggest that the biological discrimination between similarly sized ions by Ca²⁺-selective channels and pumps, or the organic template, is the dominant control on the chemistry of the calcite. Similarly we investigate the role of Sr and Ca in calcification and other biological mechanisms.



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Does the ocean iron cycle destabilize the glacial climate system?

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Recognition of the role of feedbacks is a long established element in the analysis of system behaviour in disciplines such as electrical engineering. However, as the environmental sciences move towards a more holistic approach to understanding climate change on a range of time scales (so-called “Earth system science”) it is becoming increasingly clear that feedbacks are also integral to the operation of the Earth system. For instance, climate models suggest that positive feedbacks between vegetation and rainfall can give rise to the existence of two distinct states for the Sahel region, one relatively moist and vegetated, and the other, arid. Here, a climatic sub-system having the necessary properties for positive feedback is identified, with the iron-sensitive regime of the Southern Ocean as its central component.

Results of recent open ocean iron enrichment experiments, together with numerical models of the ocean-atmosphere carbon cycle all appear to be consistent with the “iron hypothesis” – increased dust supply to the Southern Ocean during glacial periods driving a lower mixing ratio of CO₂ (xCO₂) in the atmosphere. However, dust may play a far more integral role in determining climatic behaviour than simply as a passive ‘communicator’ of events between different components of the Earth system. If changes in dust flux affect atmospheric xCO₂, and with it climate (though radiative forcing by greenhouse gases), and dust fluxes are in turn responsive to global climate (such as through changes in sea level and the strength of the hydrological cycle), a positive feedback is formed. During glacial periods, operation of this feedback might give rise to two distinct states in the Earth system, one of ‘high-xCO₂ low-dust’, and the other ‘low-xCO₂ high-dust’. This is broadly consistent with data from the Vostok ice core, and with developing views of the Earth system as being characterized by the presence of different quasi steady states with abrupt transitions between them. By enabling an inherently unstable ‘super-glacial’ state to be periodically attained, the dust-sensitive carbon cycle of the Southern Ocean may also help set the pre-conditions necessary for precipitating the collapse of the Northern Hemisphere ice sheets, thus terminating the glacial state.

Diffusion in metal: application to zoned metal grains in chondrites

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Zoned metal grains in metal-rich chondrites [1-3] have been interpreted as condensates from a gas of solar nebular composition [e.g., 1]. However, deviations from solar Ni/Co values indicate operation of an additional process, such as diffusional re-equilibration or fractional condensation [3].

To evaluate the role of diffusion in generating zoned metal grains, we have measured diffusion coefficients for Ni, Co, Ga, Ge, Ru, Pd, Ir and Au in Fe metal from 1200 to 1400 °C and 1.0 GPa. Diffusion couples were prepared from high purity Fe metal and metal from the IIA iron meteorite Coahuila or the pallasite Springwater, encapsulated with MgO, and held at run conditions between 18 and 76 hrs. Although the meteoritic starting metal was kamacite, at run conditions both coupled metals are taenite. Diffusion profiles were measured using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [3], or electron microprobe (Ni, Co, P). Low concentrations of siderophile elements in the meteoritic metal allow determination of diffusion coefficients at concentration levels appropriate for natural systems.

Our new diffusion coefficients for Ni and Co are as much as 5x lower than some published values, perhaps due to several effects. The degree of crystallinity in our taenite could be different (perhaps even single crystal) from that of previous studies and this could affect the role of grain boundary diffusion. Also, Ni contents of the metals are slightly different from previous work, and diffusion of tracers in metal is known to be a function of Fe/Ni ratio. Our new data for Ni indicate that diffusion lengthscales could be 2-3x shorter than previous estimates [1], and that the lengthscales for Ni and Co should be similar (e.g., D_{Ni} and $D_{Co} \sim 1.1 \times 10^{-14} \text{ m}^2/\text{s}$ at 1300 °C). Diffusion of Ni and Co in taenite should not significantly fractionate the Ni/Co ratio. On the other hand, the large difference in D_{Ni} and D_{Ir} (D_{Ir} is ~5x lower) and the similarity of D_{Ni} and D_{Ru} at all temperatures investigated indicates that Ni/Ir and Ni/Ru ratios in zoned metal grains will be useful discriminators. These new data on refractory and volatile siderophile elements will be used to determine the relative roles of fractional condensation from a supersaturated solar nebula and diffusive re-equilibration [3].

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Preliminary ¹⁰Be chronology for the last deglaciation of the southern Scandinavian Ice Sheet

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Prominent moraines crossing the Baltic region mark the late Pleistocene maximum extent and recessional phases of the southern margin of the Scandinavian Ice Sheet (SIS). Five moraines present between the advance during the Last Glacial Maximum (LGM) and the Younger-Dryas Salpausselkä Moraines in Finland dated at 11.6 ± 0.5 ¹⁰Be ka (Tschudi et al., 2000) suggest a millennial-scale signal for this sector of the ice sheet. However, dating control constraining the age of the LGM and retreat phases of the southern SIS margin in the region is all but lacking. We have sampled boulders for surface exposure dating with the cosmogenic nuclide ¹⁰Be from moraines along a broad south-to-north transect spanning Poland, Lithuania, Latvia, Belarus, Estonia, and Finland. Here we report ¹⁰Be concentrations on 54 boulders measured by accelerator mass spectrometry at the Tandemron facility, Gif-sur-Yvette, France. We used a production rate of 5.1 ± 0.3 atoms $\text{g}^{-1} \text{yr}^{-1}$ scaled for latitude and altitude according to Stone's factors. No corrections for snow cover or erosion have been applied. Four boulders from the LGM have a weighted mean age of 18.7 ± 0.7 ¹⁰Be ka. Twenty three samples from the Pomeranian Moraine have a weighted mean age of 14.8 ± 0.3 ¹⁰Be ka. Eight samples from the Middle Lithuanian Moraine have a weighted mean age of 13.5 ± 0.6 ¹⁰Be ka. Nine samples from the North Lithuanian Moraine have a weighted mean age of 13.0 ± 0.4 ¹⁰Be ka. A single boulder on the Pandivere Moraine was dated at 14.4 ± 1.3 ¹⁰Be ka. These results define a preliminary time frame for the deglaciation of SIS southern margin in this region. The chronology will be further refined based on ¹⁰Be results from an additional 106 samples.

The oldest zircons from the South America Continent

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The Quijingue granite (2,16 Ga), located in the central-north part of the Serrinha Nucleus (SerN), northeast of Bahia, Brazil, is a small ($\pm 21 \text{ km}^2$) north-south elongated intrusion bounded by faults. It is emplaced as a dome, cross-cutting the Paleoproterozoic Itapicuru volcano-sedimentary belt and the Archaean gneissic-migmatitic basement of the SerN. The Quijingue granite shows chemical patterns very similar to those of TTG rocks. It has a calc-alkaline signature, with narrow variations of silica and alumina contents. Strong LILE enrichment combined with a high initial Sr ratio (0.705), archaean model age ($T_{2DM} = 3,27 \text{ Ga}$) and negative epsilon Nd_T values (-12), indicate contributions from partial melting of an older Archaean continental crust. Zircon crystals as old as 3.6 Ga have now been found in this pluton. Single zircon crystals recovered from the least magnetic fraction from the Quijingue pluton were analyzed by isotope dilution using thermal ionization mass spectrometry at the Royal Ontario Museum, Toronto, Canada. These zircons are typically small, elongate or oval shaped crystals, with rounded edges, mostly without zones. Due to pervasive alteration, only a few grains were suitable for analyses. Based on zircon colour, two distinct populations were isolated: Population one (P1) is a uniform group of generally clear and colourless well-faceted crystals, and predominates in this sample. Population two (P2) consists of rare pink or light brown grains. U-Pb data on P2 zircons yield ages ranging from $3614 \pm 2 \text{ Ma}$ to $3620 \pm 3 \text{ Ma}$ (pink) and $2892 \pm 2 \text{ Ma}$ (pale brown) and have been interpreted as xenocrysts from underlying crust. No evidence was found that they form cores in the younger grains. Another 3.6 Ga old zircon xenocryst was found in the Euclides Granite ($3654 \pm 125 \text{ Ma}$), located a few kilometres east of Quijingue. Data from these older inherited xenocrysts are almost concordant. They suggest that a crustal growth event occurred at ca 3.6 Ga in the SerN. The colourless crystals (P1) are near-concordant, and give an age of $2155 \pm 3 \text{ Ma}$. This is interpreted as the crystallization age of the Quijingue pluton. It agrees with the age of other calc-alkaline Paleoproterozoic plutons from the SerN and probably reflects the beginning of Paleoproterozoic intrusive activity in the SerN area. These are the oldest zircon crystals ever reported from the South American continent. These new data indicate that crust formation in the area began during the early Archaean (~3.6 Ga) and continued episodically until ca 2.1 Ga. *Acknowledgments: This work was supported by CAPES (Process: 1332/98-8) and Companhia Baiana de Pesquisa Mineral. This is the contribution number 123 of GPA-CPGG-UFBA.*

Groundwater contribution to ($^{234}\text{U}/^{238}\text{U}$) a.r. of surface waters : Mount Cameroon case.

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^{234}U - ^{238}U isotope ratios in river waters may represent an appropriate tool to estimate and quantify the nature and the origin of the chemical weathering fluxes carried by rivers (e.g. Vigier et al., 2002). Along with surface weathering fractionation of ^{234}U and ^{238}U , riverine U could be influenced by deep U fluxes which are different from those occurring close to the surface (Riotte et Chabaux, 1999, Durand et Chabaux, this issue). The purpose of this study is to focus on the parameters, others than lithology, controlling the ^{234}U - ^{238}U fractionation in the hydrological system of Mount Cameroon, by analyses of streams, springs and wells all around this volcano.

At the scale of Mount Cameroon volcano, the ranges of U concentrations and ($^{234}\text{U}/^{238}\text{U}$) activity ratios in surface waters are wide, from 0.01 to 0.3 $\mu\text{g/L}$ and from 1.038 to 1.397, respectively. On the basis of major and trace (Sr, Rb, Ba) elements, three groups of water samples were defined, depending on their topographical and geographical locations. Comparison of these data with ($^{234}\text{U}/^{238}\text{U}$) activity ratios demonstrates that only two processes control ^{234}U - ^{238}U fractionation in Mount Cameroon waters. Small ^{234}U - ^{238}U fractionations, between 1.038 and about 1.10, are related to a surface and meteoric weathering of the bedrock, whatever the nature of secondary mineral phases occurring in the weathering profiles. By contrast, the largest ^{234}U - ^{238}U fractionations a deep water U input into surface waters. This interpretation is confirmed by independent hydrological studies of Mount Cameroon, indicating that two kinds of water circulation coexist in the volcano. One consists in small aquifers close to the surface, which leads to low ^{234}U - ^{238}U fractionations in surface waters whatever rainfall and altitude of the sampling location. The other corresponds to deeper circulation percolating through Mount Cameroon : these deep waters outflow around the volcano, at low altitude, where they mix with surface waters.

Therefore, variations of ($^{234}\text{U}/^{238}\text{U}$) activity ratios in the surface waters of Mount Cameroon would mainly trace the importance of deep waters supplies into surface waters rather than the intensity and/or on the nature of the surface weathering processes. This study illustrates the potential of ^{234}U - ^{238}U disequilibrium to characterise the different water-rock interaction levels which contribute to the chemical fluxes carried by rivers.

Water and Organic matter D/H ratios in the solar system : a record of an irradiation of the nebula ?

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Water and organic molecules are intimately mixed in the primitive planetary objects of the solar system such as Meteorites, Comets, IDPs. In few rare examples, the D/H ratios of both water and organic matter (OM) have been measured independently in these objects. A critical review of these data is presented.

No systematic relations exist between the D/H ratio of water and OM as shown by the scattering of the data points in a diagram with (D/H)_{water} vs. (D/H)_{OM}. Several conclusions can be withdrawn from this observation : (1) the bulk D/H ratio of solar system objects are not governed by the relative proportion of water and OM (2) the relative intensity of a unique isotopic fractionation process cannot explained the solar system data (3) the "canonical" turbulent model developed for the protosolar nebula cannot account for this distribution.

A new interpretation for the origin of the deuterium enrichment in water and OM is proposed : the variation in the temperature at which the deuterium is concentrated in water and in OM via ion-molecule reactions may yield such an apparent scatter of the data. If correct, the origin of the deuterium enrichment in the solar system is linked to an early X-ray irradiation of the protosolar nebula, where ion-molecule reactions took place at the very surface of the disk.

The difficulty raised above by the point (3) needs to be quantitatively evaluated via new models of the protosolar nebula where ion-molecule reactions take place at the very surface of the disk.

Using the D/H ratio to trace the terrestrial water contamination in chondritic meteorites

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Issues : Several recent ion microprobe studies have reported the distribution of D/H ratios in extraterrestrial samples (SNC, Chondrites, IDPs). All these studies are subject to controversies because the effect of the terrestrial contamination on the D/H ratio has never been precisely quantified. Judging from literature discussions, two issues can be distinguished : (1) When an extraterrestrial sample exhibits a D/H ratio clearly out of the terrestrial range, what is the exact contribution of the terrestrial contamination on this D/H ratio ? (2) When in the terrestrial range, can we firmly assert that the initial indigenous water (or -OH) has a terrestrial-like D/H ratio or result exclusively from terrestrial contamination ? Here we report a detailed study of these problems (more than 650 individual determinations of D/H ratios were performed). The Semarkona meteorite has been analyzed with the CRPG 3f ion-microprobe. Samples were prepared using terrestrial and deuterium-rich water. All possible sources of contamination were considered and quantified.

Conclusions : In light of the large D/H variations observed in Semarkona (up to +5500‰), the problem of the terrestrial contamination can be ignored. To be precise, the sample preparation procedures involving liquid water (thick section, polishing, etc.) cause a water contamination of the sample ≈7% on average and a correction of - at maximum - 15% can be propagated on the measured D/H ratios.

Another contamination process may nevertheless take place and not being detected by our experiments : some clay minerals, whose isotopic composition cannot be changed after their formation (irreversible alteration reactions with atmospheric water vapour ?), have grown inside the rock during its stay in the Museum... This seems highly unlikely.

Th, Pa and U isotopes in Bahamas seawater by MC-ICP-MS

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Thorium and protactinium isotopes in water are becoming widely used as oceanographic tracers in the open ocean. Their short residence time means that they can respond to processes on short timescales (annual to decadal). In this study we build upon recent attempts (e.g. Choi et al. 2002, Moran et al. 2001) to make precise and rapid measurements of small (4-5 litres) water samples. We use a Nu Instrument ICP-MS equipped with multiple ion counters. This set up enables synchronous analysis of Th and Pa isotopes thereby increasing ion yields and removing the necessity of separating Th from Pa chemically.

We present Th isotope data from the Bahamas, a near-shore environment in which oceanic chemical tracers are not overwhelmed by terrestrial inputs, and where there is a complex topography and water flow system. The Tongue of the Ocean, which separates the Great and Little Bahama Banks, exhibits a ²³²Th/²³⁰Th (atom ratio) minimum at ~400m. ²³²Th/²³⁰Th decreases from >20,000 in surface waters down to ~10,000 at 400m. This change is interpreted as ingrowth of ²³⁰Th in the water column and suggests a residence time of ~8 years in the Atlantic thermocline. Below this depth ²³²Th/²³⁰Th increases to reach values close to surface water, suggesting either downward flow of dense surface waters, advection of water from the Florida Straits or exchange with settling particles. Similar U concentrations in surface and deep water favour the former explanation. U isotopes were also analysed and indicate that seawater $\delta^{234}\text{U}$ does not vary by more than 2 ‰.

Surface waters from the bank top and from Exuma Sound, taken at high tide, have ²³²Th/²³⁰Th that vary by a factor of two. This difference between waters in close proximity shows that the ²³²Th/²³⁰Th can evolve very rapidly. Measurements on modern carbonates from the Bank Top have the same ²³²Th/²³⁰Th as bank-top waters. This result supports the assumptions inherent in U-Th dating of Bahamas carbonates.

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Weathering reactions within a basaltic glacial outwash plain

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Glacial environments are important contributors to global geochemical fluxes. Significant solute fluxes can be produced from glacial outwash plains in volcanic regions, due to a combination of highly reactive basaltic material, high precipitation, large volumes of glacial melt, and highly permeable unconfined aquifers formed from the outwash material. This study is based at Skei_arársandur in south-east Iceland, reputedly the world's largest active outwash plain with an area of c.1000 km².

Weathering reactions and solute sources within the groundwater system have been studied using chemical and isotopic techniques. Initial results of $\delta^{34}\text{S}$ suggest several different sources of solute. High conductivity groundwater from the sandur mirrors the $\delta^{34}\text{S}$ and 1/SO₄ signatures of water collected from a localised hydrothermal area, while higher $\delta^{34}\text{S}$ values were measured in the Skei_ará river during a drainage event from the Grímsvötn caldera. Thus additional to low temperature weathering within this glacial and proglacial environment, localised and more regional hydrothermal areas add significantly to the solute input from the sandur.

A series of water and weak acid leaches have been carried out on a range of materials from the sandur environment in order to determine the sources of strontium in the groundwater. Initial ⁸⁷Sr/⁸⁶Sr ratios from groundwater have shown significantly more radiogenic values (0.7035 to 0.7038) than ⁸⁷Sr/⁸⁶Sr ratios of products from the active volcanic centres beneath the Vatnajökull ice cap (0.7030 to 0.7032 from Sigmarsson *et al.*, 2000) which produce the majority of the sandur surficial deposits during recent jökulhlaups. The ⁸⁷Sr/⁸⁶Sr ratios in the groundwater closely correspond to values from the young rocks from the Örafajökull volcanic centre (0.7035 to 0.7038 from Prestvik *et al.*, 2001) to the east of the sandur, which erupted in 1362. This suggests that the stratigraphy of the sandur from large historical eruptions may play an important role on the solute fluxes from the sandur.

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Iron: Potential Fuel of the Deep Biosphere?

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It is usually assumed that iron weathered at the Earth's surface and deposited into sedimentary environments occurs as Fe(III), mainly as oxides and silicates. Here, we are interested in the extent to which Fe(III) survives early diagenesis and remains available as a terminal electron acceptor for use by microbes inhabiting deeply buried sediments. We have studied the distribution and valence of iron within rapidly deposited upper slope mudstones (0.5-1% TOC) from the foot of the Mississippi Delta. Sample well depths range from 1500-6900 metres, corresponding to a temperature range of 33–145°C. Wet chemical, XRD and electron beam approaches have been integrated to determine the location of iron and the stability of its valency during diagenesis.

Total Fe concentrations average $4.2 \pm 1\%$, the majority of which is Fe(III), with only a small fraction present as pyrite and carbonate. Iron oxides persist throughout the section and comprise around 10% of the total Fe. Around 90% of the total Fe is bound within silicates. Wet chemical analysis of the silicate fraction shows that at temperatures below ~115°C, most silicate Fe occurs as Fe(III), mainly within smectite and partly within detrital chlorite and mica. XRD and AEM data indicate that the conversion of smectite to illite (temperatures between 115-130°C) results in the loss of Fe from the illite-smectite phase and its partial relocation into Fe-rich chlorite. The bulk silicate data are supported by data from EELS, here used for the first time to track changes in the valence of silicate Fe during burial diagenesis.

What are the implications of these data for the deep biosphere? Firstly, they show that sufficient Fe(III) is buried into deep mudstones to convert every atom of organic carbon to carbonate. However, the extent to which this potential energy source is actually tapped remains uncertain. Most Fe-reduction in these sediments occurs during the recrystallisation of smectite, at temperatures in excess of those normally associated with the base of the biosphere. Furthermore, iron oxide, the most reactive Fe phase buried below the early diagenetic zone, is present in similar amounts throughout the sediment pile. If Fe(III) is acting as a terminal electron acceptor in these deeply buried muds, either its influence is small and/or the rates of metabolism are extremely low.

Carbon isotope composition of bioturbation infills as indication of the macrobenthic-colonization timing across the Cretaceous-Tertiary boundary (Agost section, SE Spain)

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The Cretaceous-Tertiary (K-T) boundary section of Agost (SE Spain) is one of the most complete K-T boundary sections. Here, the K-T boundary is marked by a 2 mm-thick rust-red layer containing the impact evidence and representing the distal ejecta of the Chicxulub impact. A relatively abundant trace-fossil assemblage is observed in the *Plummerita hantkeninoides* Biozone (Late Maastrichtian). The trace-fossil assemblage is mainly composed of traces filled by dark-colored sediment (*Chondrites*, *Zoophycos*, *Thalassinoides* and *Planolites*), and secondarily structures filled by light sediment (*Chondrites*, *Zoophycos*, *Planolites*, and some unidentified structures). Difficulties in recognizing trace fossils affecting the K-T boundary layer, as well as obtaining a biostratigraphic characterization of these traces avoided a conclusive interpretation on the timing of this macro-benthic colonization at the Agost section. Since the carbon isotope composition of uppermost cretaceous and lowermost tertiary sediments is clearly different as consequence of the sudden decrease in ocean productivity, we determined the $\delta^{13}\text{C}$ of the carbonate fraction of dark and light filling materials from passively filled bioturbations to discriminate between traces fossils generated at different moments during the K-T boundary transition. The data obtained revealed a clear differentiation related to the type of analyzed material: (a) Most of the $\delta^{13}\text{C}$ values are in a range between 0.21 to 1.22‰; all of them corresponding to samples from dark filling material. (b) Few samples show a $\delta^{13}\text{C}$ higher than 1.6‰, corresponding to light colored sediment filling bioturbation. These data evidence a significant discrimination between light-filled traces, with $\delta^{13}\text{C}$ values higher than 1.6‰ PDB, coherent with those obtained from uppermost cretaceous sediments, and dark-filled bioturbations with $\delta^{13}\text{C}$ values between 0.21 and 1.2‰ PDB, in accordance with those obtained from lowermost tertiary materials. Thus, the obtained data evidence that the macrobenthic colonization occurred at different phases across the K-T boundary interval, pre- and post- impact event corresponding to light and dark-colored traces, respectively.

Dynamics of DOM and its influence on CO₂ and CH₄ production potentials in a northern peatland.

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Peatlands are sinks for CO₂ and source of CH₄ and store approximately 455 Gt of carbon equivalent to 1/3 of the global soil organic carbon. Carbon accumulates due to the saturated conditions, which slow the decomposition rate. Dissolved organic matter plays a key role in the decomposition process since only a fraction of this is available for microbial utilisation. The fermentation of complex polysaccharides provides the substrate available for the metabolic pathway of most organisms. In anaerobic environments fermentors are the sole organisms that can hydrolyse and utilise polymers and promote their breakdown into low molecular weight compounds. Extracellular enzymatic hydrolysis is often the rate limiting step. Water soluble carbohydrates are the most available substrate for microbial utilisation but are often overlooked in current studies.

Our study has shown that water soluble carbohydrates can play a potential role in the production of CO₂ and CH₄ in peatlands systems. Temperature has also been postulated to play a large role in controlling the balance between production and consumption of these substrates. The dynamics of both water soluble carbohydrates and DOM release are tightly coupled. The release dynamics may provide the link explaining the decoupling between DOM production following water table fluctuation events. Further, our results of incubation amendments have shown that the substrate limitation imposed on the production of CO₂ and CH₄ is spatially highly variable across a peatland gradient and that each of these settings is limited at different stages of decomposition.

Ecology and shell chemistry: a whole-fauna stable isotope study of Eemian sapropel S5

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Results are presented for a case study on planktonic foraminiferal (palaeo-)habitat preferences during the deposition of Eemian Mediterranean sapropel S5 (project with Sprovieri, M., Cane, T., Casford, J., Cooke, S., Hayes, A., Bouloubassi, I., Emeis, K., Jorissen, F., Schiebel, R. and Kroon, D.). Today, the study area is oligotrophic with well-ventilated deep water, in stark contrast with conditions during the formation of S5. We obtained very-high resolution (0.5 cm) foraminiferal abundance distributions, planktonic foraminiferal stable isotope ratios on all relatively continuous species, and Uk'37 SST values through S5 in NW Ionian core KS205, comparing results with similar data from ODP Holes 971A and 967C. The data are used to assess the interaction between hydrographic developments and foraminiferal habitats during S5. Affinity of the various species is considered to five potential water masses: (1) intermediate water; (2) winter mixed layer; (3) summer subthermocline (Ssth); (4) summer mixed layer; (5) fresh-water diluted toplayer/lenses. Reconstructions are validated with a ¹⁸O box-model that represents a seasonal mixed-layer distinction within the model of Rohling (1999). Excellent agreement is found between model results and the analytical series. Below, we summarise our S5 palaeo-habitat conclusions for the species analysed, in comparison with their modern habitats. The presentation will also discuss palaeosalinity implications.

	Present-day Mediterranean Habitat ⁽¹⁾	Reconstructed S5 Habitat
<i>G. ruber</i> (white)	Upper 50 m (summer), to upper 100 m (winter)	Summer ml + lenses
<i>G. ruber</i> (pink)	Very shallow (~20 m), peaks above summer thermocline	Spring ?
<i>G. sacculifer</i>	Together with trilobus types	Summer ml
<i>G. sacc</i> (<i>tril.</i>)	Summer ml (20-50 m)	Summer ml
<i>O. universa</i>	Summer mixed layer	Summer ml
<i>G. glutinata</i>	Rare. Winter, to 200 m	Spring
<i>G. bulloides</i>	Winter and early spring	Spring
<i>G. siphonifera</i>	Winter ml, peak 100-200 m	Winter ml
<i>N. pachyd.</i> (dextral)	Year-round, 50-200 m; link with density gradients ⁽²⁾	Ssth / Intermed.
<i>G. scitula</i>	Mesopelagic, at ~ 100 m	Ssth / Intermed
<i>G. inflata</i>	Winter. Annual at fronts ⁽²⁾	Winter ml ⁽³⁾

(1). Pujol and Vergnaud-Grazzini (1995); (2) see also Rohling et al. (1995); (3) Derived in ways similar to those described here from the post-glacial record in SE Aegean core LC21.

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The geodynamic evolution of hydrothermal vein deposits in the Madan metamorphic core complex, Bulgaria

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Carbonate replacement and vein-type lead-zinc deposits and silicic dyke swarms are associated with the Madan Dome in the Central Rhodope region, South Bulgaria. Interpreted as a large metamorphic core complex, the Madan Dome is well suited for a study of the geodynamic relationships between extension, magmatism and hydrothermal ore formation. High-precision geochronology in conjunction with detailed field observation is used to date the thermal to hydrothermal history of the complex.

In the Late Cretaceous, a compressional stage led to large-scale thrusting and amphibolite facies metamorphism in the Rhodope region. This was followed by a widespread extensional collapse during the Oligocene, marked by a detachment system, leading to exhumation of highly metamorphosed rocks, including migmatites in the footwall. The detachment fault is crosscut by undeformed silicic dykes, which are in turn crosscut by the ore veins and overprinted by associated sericite ± carbonate alteration. Magmatism thus postdates the extensional movement, and hydrothermal mineralization occurred during or after silicic magmatism.

Rb-Sr-isochrons of biotite and feldspar and Ar-Ar- dating on biotite yielded cooling ages of gneisses of both hanging- and footwall of about 35.5 Ma. Ar-Ar ages of white mica in skarn mineralization preceding the main Pb-Zn mineralization event yield very similar ages of 35.5 Ma. U-Pb dating on zircons of the silicic dykes dates their emplacement at 32 - 30 Ma ago. New Ar-Ar measurements of sericite associated intimately with the main vein-hosted Pb-Zn mineralization reveal mica crystallization ages of 30.5 - 29 Ma.

The Rb-Sr data indicate that cooling of footwall and hanging wall occurred at the same time, shedding doubt on a major extensional detachment as the cause for exhumation the Madan Dome. Magmatism and hydrothermal ore formation are coeval, but postdate uplift by about 3 - 6 Ma. Isotopic tracing work will be used next, to clarify whether the temporal relation reflects a direct genetic link between magmatism and hydrothermal ore formation.

Fluid flow and element mobility in middle-crust shear zones of collisional orogens: insights from the Mont Blanc Massif shear zone network

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Networks of kinematically-related shear zones in late Hercynian granitoids in the Mont Blanc massif have localised fluid flow, hydrothermal alteration and associated vein formation during their formation at mid-crustal depths during Alpine collision. The shear zones are mylonitic in the core of the massif, and become cataclastic near its SE rim. They have developed in response to NW-SE shortening and vertical extension. Calcite-quartz $\delta^{18}\text{O}$ thermometry on shear-hosted veins in the massif and in the adjacent Helvetic nappes indicates temperatures around 400°C during shear zone formation. Mineral assemblages in the shear zones reflect similar temperatures and relatively high pressures (6-7 kbar). Geochemical changes due to fluid-driven alteration, while the shear zones were active, are compatible with generally small volume changes. Three main reaction types are recognised from the margin to the core of the shear zones: (1) in the NW part of the massif, biotite-plagioclase are replaced by epidote-muscovite; (2) in the SW part of the massif, biotite is replaced by muscovite and epidote is absent; (3) chlorite is a major phase in the cores of various shear zones. Very variable depletion/enrichment patterns of major, trace and Rare Earth Elements (REE) are interpreted to reflect major differences in (1) fluid chemistry, (2) fluid flow directions relative to P/T gradients, and (3) connectivity between elements of the shear network and fluid reservoirs, in different parts of the shear network. REE, in particular, can be very mobile and locally exhibit both enrichments and depletions, which are controlled by the stability /instability of REE-bearing phases including allanite, aeschynite, bastnäsite and monazite. C, O and H stable isotope signatures of vein assemblages associated with the shear zones indicate that fluid chemistries have been influenced by two reservoirs. In the core of the massif, the shear networks have facilitated escape of reduced fluids from deeper crustal fluid reservoirs, whereas near the SE margin of the massif there is evidence for mixing with fluids originating from the Helvetic nappes cover sequence.

Arsenic removal by gypsum and calcite: the continuum between sorption and solid-solution phenomenon

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Results and Discussion

The reactions developed during As (III or V) uptake by calcite and gypsum from aqueous solution were characterised by solubility and X-Ray and Neutron Diffraction structural studies. As-containing solids (calcite and gypsum) were grown from room-temperature supersaturated aqueous solutions doped with As(III) and As(V), respectively.

Solubility data (Fig 1 a, b) shows a continuum between sorption and formation of solid-solutions ($\text{Ca}(\text{SO}_4, \text{HAsO}_4)$ and $\text{Ca}(\text{CO}_3, \text{HAsO}_3)$).

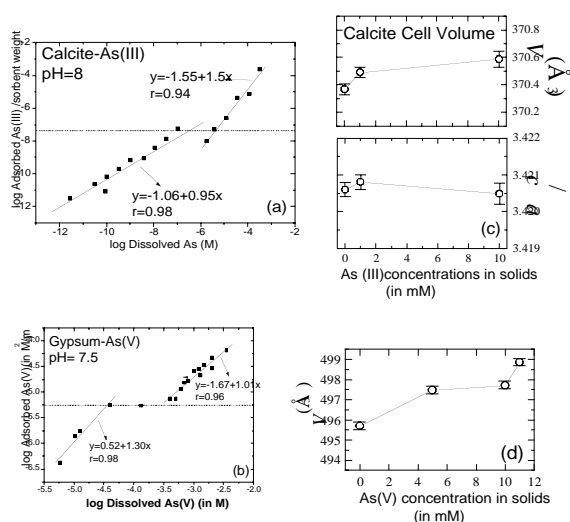


Fig. 1: a, b) Adsorption isotherms; c, d) cell volume vs. As contents

By means of Rietveld refinement of X-Ray and Neutron diffraction spectra, we have obtained unit cell volumes of these solid-solutions to vary with arsenic contents. This dependence is weak for As(III) incorporation in calcite (Fig. 1c) but strong for As(V) incorporation into gypsum (Fig. 1 d). Calcite and gypsum are therefore adequate sinks for arsenic in calcium rich sites under alkaline and acid conditions, respectively. The long-term stability of these solids solutions needs further studies.

Effect of metamorphic reaction history on isotopic dating of minerals

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Metamorphism of the Saxon Granulite Massif (SGM) culminated in P-T conditions in the range of 22 kbar and 1050°C and ceased under rapid exhumation to the middle crust and subsequent cooling within a few million years after the metamorphic peak (Romer and Rötzler, 2001). The fast exhumation and cooling should reduce the possibility of post-crystallization diffusional loss of in situ formed radiogenic isotopes. Ultrahigh-temperature (UHT) metamorphism should favor isotopic homogenization among both reactant and product minerals of the metamorphic reactions. Initial isotopic heterogeneity among metamorphic product minerals would indicate that even at UHT isotopic homogenization is not reached and that sequential metamorphic reaction is a poor process to homogenize the isotopic composition. Consequently, it is even less likely that isotopic homogenization is reached at lower metamorphic grade.

The closely spaced samples from the SGM passed together the same P-T conditions, but developed contrasting mineral assemblages due to different bulk rock composition. Dating the same metamorphic minerals in the various samples should yield for one mineral the same age in all samples. If the corresponding mineral ages among the various samples differ by an amount larger than the duration of the entire metamorphic cycle, this difference could arise only from the reaction history of these rocks. The geochronologically relevant elements are redistributed among remaining reactants and reaction products during metamorphism. Subsequent reactions involve different reactants, i.e., a different subvolume of the rock, and the isotopic composition of the reaction products is likely to be different from earlier formed product minerals. Thus, the sequence of metamorphic reactions does not result in isotopic homogenization.

Our analytical results imply that contrasting ages obtained by different geochronological systems (U-Pb, Sm-Nd, Rb-Sr) or on different metamorphic minerals not necessarily reflect (1) contrasting closure behavior of these minerals or (2) highly contrasting diffusion rates among the elements used for dating, but rather represent the effect of heterogeneous initial isotopic composition of Pb, Nd, and Sr due to the reaction history.

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Geochronology of the South Bahia Alkaline Province (NE Brazil)

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The South Bahia Alkaline Province (SBAP) covers an area of about 6,500 km² and is formed by an association of twenty alkaline massifs, elongated in NE-SW direction and predominately composed of silica subsaturated rocks. The SBAP hosts blue sodalite syenite, which represents the most important ornamental stone of Brazil. These alkaline massifs are emplaced in Archaean to Paleoproterozoic granulite, migmatite and anorthosite terrains forming the interface between the São Francisco Craton (east) and Araçuá mobile belt (west).

The four most important syenitic intrusions are: Itabuna Massif (north, 430 km²), Floresta Azul Complex (northeast, 180 km²), Serra das Araras Massif (southwest, 220 km²), and Itarantim Massif (south, 150 km²). Previous geochronological studies link the SBAP to Neoproterozoic magmatism. The age data (Rb-Sr, K-Ar) are very heterogeneous and range from 500 Ma to 740 Ma. A baddeleyite from the Itabuna Massif gives a relatively precise U-Pb age of 676 ± 5 Ma.

In this paper, we will present preliminary results of a systematic geochronological investigation of the other three massifs by ²⁰⁷Pb/²⁰⁶Pb zircon evaporation and Rb-Sr whole rock techniques. The data were obtained at the Laboratory of Isotope Geology of the Federal University of Pará (Pará-Iso). The Floresta Azul Complex is composed of rocks associated with four distinct magmatic pulses. Single zircon ²⁰⁷Pb/²⁰⁶Pb evaporation data give 699 ± 11 Ma for a granite and 688 ± 2 Ma for a diorite. A quartz syenite rock from the Serra das Araras Massif shows a ²⁰⁷Pb/²⁰⁶Pb age of 739 ± 2 Ma. The nepheline and sodalite syenite rocks from Itarantim Massif yields a Rb-Sr isochron age of 727 ± 30 Ma (MSWD = 1.5).

The results indicate that the SBAP was probably formed between 690 and 730 Ma and thus can be linked to the Rio Pardo rift. The alkaline intrusions become successively younger towards the São Francisco Craton, which implies that the isotopic system (Pb/Pb) was not disturbed during the Araçuá belt collision.

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Modeling the effects of reaction kinetics, diffusion-dispersion, and fluid infiltration on mixed-volatile (CO₂-H₂O) metamorphic reactions

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We evaluate the effects of reaction kinetics, diffusion-dispersion coefficient, and fluid infiltration rate on infiltration-driven decarbonation reactions with a 1-D model of coupled heat and mass (CO₂) transport. Our modeling results show that the positions of reaction fronts (isograds) and the thickness of reaction zones--observable features in natural systems--are functions not only of the fluid infiltration rate (v); reaction rate constant (k_0); and diffusion-dispersion coefficient (D), but of the direction of fluid flow with respect to temperature gradient and the bulk composition (that is, the abundance of reactant minerals), in addition to the time-integrated fluid flux. None of these parameters will exert exclusive control on the observed positions of isograds and widths of reaction zones in contact metamorphic aureoles.

At fluid infiltration rates sufficient for the advection-controlled transport of CO₂ ($> 10^{-10}$ m³/m² sec), the modeling results show that reaction fronts will advance into the wallrocks at significantly higher rates (factor of ≥ 2) for up-temperature flow compared to down-temperature flow, for the same conditions of reaction rate and transport. These differences arise from the very different spatial profiles of $X(\text{CO}_2)$ along the flowpath. Bulk composition has significant impact on the rate of advance of a reaction front (isograd) in down-temperature flow but not in up-temperature flow. As fluid infiltration rate decreases below 10^{-10} m³/m² sec where the transport of CO₂ becomes diffusion-controlled, the rate of advance of the reaction front in down-temperature flow increases to rates, for equivalent kinetic conditions, equal to those for up-temperature flow. This change occurs because the $X(\text{CO}_2)$ profiles become progressively more similar as advective transport of CO₂ decreases. At these low values of infiltration rate, the maximum rate of advance of the reaction front--at a given kinetic rate constant-- is limited by the rate of diffusive transport for CO₂ in the pore fluid.

For the same bulk composition and the same conditions of transport and reaction kinetics, the reaction zone developed in up-temperature flow will be considerably wider than that developed during down-temperature flow. Despite these inherent differences, reaction zones well beyond 100 m in thickness can be developed during down-temperature flow at conditions of sufficiently low reaction rates ($k_0 \leq 10^{-13}$ mole cm⁻² s⁻¹) or with fluid infiltration rates at or below $v = 10^{-8}$ m s⁻¹. If such conditions are obtained in natural contact aureoles, occurrences of reaction zones of significant width are not unambiguous indicators of up-temperature fluid flow.

Planktonic foraminiferal Mg/Ca paleothermometry and its application for reconstructing sea surface temperatures

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Mg/Ca measurements on mixed-layer planktonic foraminifera offer the ability to independently estimate past changes in sea surface temperatures (SST). Paired with isotopic measurements the method allows for reconstructing seawater $\delta^{18}\text{O}$ and by inference sea surface salinity as well as assessing the temporal relationship between SST changes and the growth and decay of continental ice-sheets. The accuracy of this method is confounded, however, by the need to correct Mg/Ca records for alteration by post-depositional dissolution. We have examined the possibility of using changes in the size-normalized weight of planktonic foraminiferal tests for correcting Mg/Ca-based SST reconstructions for varying degrees of shell preservation/dissolution. The method is based on the observation of a strong linear correlation between changes in shell weight, bulk shell Mg/Ca and the degree of calcite saturation of the bottom water. The concomitant decrease in shell weight and Mg/Ca reflects the preferential removal of Mg-rich foraminiferal shell calcite during post-depositional dissolution. Based on this observation we suggest that extrapolating the observed trends back to the initial size-normalized shell weight, which is the weight the shell presumably had when it sank to the seafloor, may provide the means for correcting SST reconstructions for alteration by dissolution. New observations suggest, however, that the initial shell's weight/size ratio may vary, possibly as a function of the CO_3 ion content of the surface water. In this talk we will discuss the implications of these effects on the accuracy Mg/Ca paleothermometry. Reconstructions of LGM SST in the equatorial Pacific from cores in different preservational environments suggest that the inaccuracy associated with these effects is typically less than 1°C . The uncertainty may be, however, greater when applied to older time intervals.

The amplitude and phasing of climate change during the last deglaciation in the Sulu Sea, western equatorial Pacific

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Records of climate change from different tropical regions produced apparently contrasting results. Particularly controversial are records from the equatorial Pacific. We present a high-resolution $\delta^{18}\text{O}$ and Mg/Ca records in the planktonic foraminifera *G. ruber* from the Sulu Sea, suggesting that SST in this site was $3.4 \pm 0.5^\circ\text{C}$ colder than present during the LGM, similar with inferred cooling in other equatorial Pacific sites. The most conspicuous features of the record are: (1) the LGM-Holocene $\Delta\delta^{18}\text{O}$ amplitude in the Sulu Sea is comparable with the global ice effect ($\sim 1\text{‰}$), similar with that observed in the western equatorial Pacific (WEP) (Lea et al., 2000), but significantly lower than observed in the South China Sea (SCS; $\sim 1.7\text{‰}$) (Kienast et al., 2001); (2) SST in the Sulu Sea increases gradually throughout the deglaciation and early Holocene showing no discernible evidence for abrupt warming at the Bølling-Allerød transition or YD cooling. The warming trend in the Sulu Sea appears more similar to the warming pattern observed in Antarctica than Greenland; (3) SST warming in the Sulu Sea leads foraminiferal $\delta^{18}\text{O}$ largely because during the early phase of deglaciation (between 20 and 14.8 ky B.P.), Sulu Sea's surface water $\delta^{18}\text{O}_{\text{seawater}}$ became heavier by $\sim 0.3\text{‰}$ before starting to decrease to Holocene levels; (4) sub-orbital events seen in the Sulu Sea $\delta^{18}\text{O}$ record are coherent and coincide with events observed in the foraminiferal $\delta^{18}\text{O}$ records from the SCS, Hulu Cave (Wang et al., 2001) and Greenland $\delta^{18}\text{O}$ records.

Comparison between the WEP, Sulu Sea and SCS records supports the idea of different climate controls on the open-ocean equatorial regions vs. marginal seas. Because of its proximity to the continent and restricted circulation, the climate variability in the SCS is dominated by the mean state of the East Asian Monsoon (EAM) and thus tightly coupled with Northern Hemisphere climate. The Sulu Sea and open-ocean WEP show, however, a more complex climate response: its thermal evolution appears to be linked with the Southern Hemisphere whereas its hydrology is strongly influenced by the interactions between ENSO and EAM systems as well as its location between the SCS and the western Pacific warm pool.

>3700 Ma oxidized ocean water, Pb isotopic evidence from Isua, West Greenland.

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The >3700 Ma Isua supracrustal belt, West Greenland, comprises water lain sediments which preserve information about early Archaean ocean chemistry. The REE chemistry of Isua banded iron formation show marked negative Ce anomalies consistent with scavenging of tetravalent Ce from the ocean water in local oxidized environment [1]. We have analyzed the Pb isotopic compositions of metamorphosed pelagic sediments rich in ^{13}C depleted reduced carbon in an effort to establish the U/Th of the original sediment. These sediments are interpreted as originally deposited with high contents of biogenic organic debris [2]. The metasediments have extremely radiogenic Pb compositions, which plot above the Stacey & Kramer growth curve for uranogenic Pb and to the right of the growth curve in the thorogenic-uranogenic system. This indicates that the sediments evolved with high U/Pb ratios ($\mu = 22$) while there was only insignificant production of thorogenic Pb due to extremely low Th/Pb values during the early Archaean. The strong fractionation of U from Th observed in the Isua metasediments is similar to the situation in modern black shales, and can best be explained by solute transport of U by oxidized water followed by precipitation by organic debris at the site of sedimentation. The strong U/Th fractionation indicates the existence of relatively oxidized compartments in the >3700 Ma oceans, probably maintained by biologic activity.

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Isotopic crustal and slab fingerprints in arc volcanic rocks from the Central Volcanic Zone of the Andes

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The continent-ocean collision system of the Central Andes is characterised by a thick continental lithosphere and is therefore suited to study the interaction of mantle wedge-derived magmas with different source reservoirs, especially the subducted slab and the continental crust. We present Sr, Nd, Pb and B isotope data from Pliocene to Quaternary volcanic rocks of the Central Volcanic Zone (CVZ) between 22° and 27° S and discuss them in light of new Andean basement data from Lucassen et al., (2001).

Radiogenic isotope ratios fall in the same range as those reported from Trumbull et al., (1999) and Kay et al., (1994) for other volcanic centers in the study region. The $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios vary between 0.70603 and 0.70811 and between 0.512249 and 0.512481, respectively. The Pb isotope compositions are very homogeneous, with $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of 18.722 to 18.887. The Pb isotope ratios plot near the Andean Pb-line (post Archean $\mu=10$), which has been defined from basement lead data (e.g. Lucassen et al., 2001). The $\delta^{11}\text{B}$ values of samples from the volcanic front are positive and range from +4 to +2‰.

The radiogenic isotope ratios indicate a crustal component in all investigated rocks. Because the continental crust is highly enriched in Pb relative to the mantle and the oceanic crust, only a small degree of crustal contamination is sufficient to overprint a mantle derived Pb signal. In contrast, Sr and Nd isotope ratios are not fully overprinted by crustal contamination. Compared with the Sr and Nd isotope ratios from island-arc basalts, Andean $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are much more radiogenic and $^{143}\text{Nd}/^{144}\text{Nd}$ are less radiogenic. ϵNd and $^{87}\text{Sr}/^{86}\text{Sr}$ data form a negative correlation, consistent with mixing between a mantle endmember and continental crust. Using the average Andean basement values for Sr and Nd from Lucassen et al., (2001), mixing models indicate an addition of 20 to 45% crust to the arc-magmas. However, the positive $\delta^{11}\text{B}$ values rule out a pure crust-mantle mixing origin for the arc magmas and indicate involvement of ^{11}B -rich fluids from the subducted slab.

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Theoretical Evaluation of Electron Transfer Kinetics at Fe(III)-Oxide Surfaces with Implications for Microbial Respiration

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The respiration of dissimilatory Fe(III)-reducing bacteria involves a poorly understood heterogeneous electron transfer (ET) step to terminal acceptor sites at Fe(III)-oxide surfaces. Recent discussion centers around the relative efficacy of Fe(III) reduction by ET from outer membrane cytochromes versus exogenous electron shuttle species. Because the kinetics of elementary ET reactions at surfaces are difficult to access experimentally, theoretical treatments could be of great utility for developing a mechanistic understanding of macroscopically observable kinetics.

For the purposes of building atomistic kinetic models to evaluate hypothetical ET reactions at various Fe(III)-oxide surfaces, we utilize a combination of Marcus theory and ab initio calculations. This approach has allowed us to compute the physical quantities controlling rates of ET involving surface and near-surface Fe(III) sites at hematite (001) and (012), and magnetite (100) and (111) surfaces. Marcus principles relate the activation free energy (ΔG^*) to the driving force (ΔG°) and the energy to reorganize bonds in the inner spheres of the reactants (λ_{is}) and the surrounding dielectric media in the outer sphere of the encounter complex (λ_{os}). Using known possibilities for the surface structures and including sorbed water species, we utilize a molecular orbital cluster-based strategy to calculate the λ_{is} explicitly for all Fe(III) site possibilities at the density functional level of theory. The cluster calculations also provide estimates of the relative redox potentials for each site leading to estimates of ΔG° . λ_{os} is calculated using Marcus continuum equations.

We have applied these methods to estimate rates of heterogeneous ET reactions from anthraquinone 2,6 disulfonate (AQDS), a model electron shuttle compound, and from model outer membrane cytochromes (OmcA) to acceptor sites on the different of Fe(III)-oxide surfaces. Primary factors which differentiate the ET rate are the reorganization energy terms and the density of Fe(III) sites in the near-surface region. For the different possible sites at the various surfaces, λ_{is} may be generally ranked according to $Fe_{surface} > Fe_{bulk}$ because of increased degrees of freedom at the surface to accommodate conformational changes in Fe-O bonding through the $Fe^{2+/3+}$ transformation. The ET distance is a primary factor in differentiating the ET rate between AQDS to surface sites from OmcA to surface sites. The model results are in qualitative agreement with recent experimental observations of bacterial growth on these surfaces being used as the sole electron acceptor.

Geochronology of the Peloritani Mountains (Sicily): Hercynian, pre-Hercynian, but not Alpine

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The Peloritani Mountains are a fragment of the Hercynian belt whose metamorphic units show different metamorphic paths. The Ar-Ar, U-Pb stepwise leaching and Rb-Sr data reported here demonstrate that the medium-high grade units (Aspromonte and Mela Units) also differ in their geochronological evolution.

The main thrusting of the Aspromonte Unit over the lower grade units (Mandanici Unit) took place at 301 ± 2 Ma. Brittle Tertiary reactivation of Hercynian thrust planes did not produce any rejuvenation of white micas.

The Aspromonte Unit is geochronologically heterogeneous. Proterozoic ages are preserved both in amphibole relics and in titanite from the Cumia sub-unit; Devonian amphibole and apatite ages are found in the Saponara sub-unit; Carboniferous amphiboles occur in other sub-units; no Tertiary amphiboles were formed. We propose to consider the chronologically heterogeneous sub-units as accreted pre-Hercynian terranes (microplates) amalgamated late during the Hercynian orogeny.

The Mela Unit amphiboles are Carboniferous, younger than those of the Aspromonte Unit, in parallel with the different P-T path which is characterized by pervasive retrogression of peak assemblages.

Micas in both units give scattered Mesozoic Ar-Ar and Rb-Sr ages, with evidence for heterochemical mica generations. We interpret them as a result of widespread hydrothermal circulation event(s).

Tertiary metamorphic minerals are generally absent, with the exception of a small area near Messina where biotite and muscovite underwent a complex recrystallization history in the interval 48-61 Ma.

Acid-leaching of clay mineral: a new dating method of fluid-flows?

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Clay minerals were often used as indicator during diagenetic evolution of a sedimentary succession since they could date diagenetic or hydrothermal activities. However, frequent occurrence of detrital material as well as of authigenic soluble mineral phases in the finest separated size fractions modify the K-Ar and Rb-Sr dates which prompted the use of leaching techniques. They are commonly used now to improve the fit of clay fraction data points in isochron diagrams by concentrating adsorbed elements and soluble mineral phases in the leachates. Chemical analysis of the leachates also provides information about the type of the crystalline phases intimately mixed with the clay particles (e.g. carbonates or phosphates).

In this study, the HCl-leaching method was applied to a smectite-rich bentonite layer occurring in a sedimentary claystone succession. Bentonite was known to be detrital material free. A Rb-Sr isochron age based on the leachate and residue data points of the finest size fraction was identical to the K-Ar value of the same fraction (140 Ma), suggesting that: (1) this age corresponds to the crystallization time of the smectite, and (2) the HCl-soluble phase and the smectitic material are contemporaneous. This result allows to constrain an evolution model for the clay minerals of the claystones, despite low burial temperature and systematic occurrence of detrital material in the clay fractions.

The same leaching method was also applied to the <0.2 μ m clay fractions of the claystones and the REE patterns suggest the occurrence of apatite-like minerals in the leachates. Use of the Rb-Sr isochron method outlined two types of leachates: those of the smectite-rich illite/smectite mixed-layers (I/S) giving meaningless Rb-Sr dates suggesting a mixture of non-contemporaneous soluble mineral phases, and those of the illite-rich I/S providing a value of 100 Ma, which indicates the crystallisation of authigenic phosphates during late fluid-flows without interactions with the clay particles.

In addition, chemical compositions of Na-saturated fundamental particles from the same samples suggested that the smectite interlayers contributed to the chemical and isotopic characteristics of the leachates. This behaviour might explain the deviation of the <0.2 μ m smectite-rich clays from the 100 Ma-isochron line. To validate the 100-Ma age, it is needed to estimate the contribution of the smectite interlayers, in saturating <0.2 μ m fractions with a Na-rich solution containing Sr with a known isotopic signature.

This new method may ultimately be used as a tool to date fluid-flow epochs in sedimentary sequences, and contribute to knowledge of fluid circulations leading to permeability decreases in these rocks.

Abiotic or biotic iron isotope fractionation during oceanic crust alteration ?

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In this study we explore the potential of using Fe isotope signatures to unravel the presence of the deep biosphere associated with the alteration of the oceanic crust. We carried out this investigation using samples from ODP site 801C drilled during Leg 129 and 185 in Jurassic Pacific oceanic crust seaward of the Mariana Trench [1]. The site comprises approximately 450m of sediment overlying a section of 500m of basalt which includes intercalated pelagic and chemical sediments in the upper basaltic units and two low-temperature (10-30°C) ocherous Si-Fe hydrothermal deposits. Thread-like filaments of orange Fe-oxyhydroxide are locally present in the hydrothermal deposits and are similar to those produce by Fe-oxidizing bacteria.

Fe was chemically separated from 70 selected samples and ⁵⁷Fe/⁵⁴Fe ratios were measured by MC-ICP-MS *Isoprobe*. The results are reported relative to IRMM-14 with an external precision of 0.2‰ (2 σ). A detailed investigation of the $\delta^{57}\text{Fe}$ values and Fe redox state of Fe-bearing phases indicates that the deep-sea sediment section has a restricted range of $\delta^{57}\text{Fe}$ which is close to the Bulk Earth value. In contrast, large variations are observed in the basaltic section with positive $\delta^{57}\text{Fe}$ values (up to 1.95‰) for highly altered basalts and negative values (down to -2.47‰) for the associated alteration products. Secondary Fe-minerals, such as Fe-oxyhydroxides or Fe-bearing clays have $\delta^{57}\text{Fe}$ values highly variable which have been interpreted as resulting from the partial oxidation of Fe²⁺ leached during basalts alteration. In contrast, altered basalts display an increase in $\delta^{57}\text{Fe}$ values relative to fresh values due to the preferential leaching of light iron. The apparent fractionation factor between dissolved Fe²⁺ and Fe remaining in the mineral is between 0.5‰ to 1.3‰ and may be consistent with an biotic scenario where Fe isotope fractionation is the result of chelating ligands stripping Fe from the minerals [2].

The Fe-isotope systematics presented in this study suggest that, despite iron behavior during seafloor weathering may be mediated by microbes, such as iron-oxidizers, $\delta^{57}\text{Fe}$ variations of more than 4‰ may also be explained by abiotic processes. Further laboratory experiments are now required to distinguish between biotic and abiotic Fe isotope fractionation during seafloor weathering.

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Sulfate respiration in extreme environments: A kinetic study

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Measured sulfate reduction rates from hydrothermal springs at Yellowstone National Park, USA, varied between 2 and 600 nmol cm⁻³ d⁻¹ with the majority of the rates remaining below 100 nmol cm⁻³ d⁻¹. Higher rates were associated with microbial mats. In general, the measured rates are comparable to modern environments where activity of sulfate reducers is limited due to substrate availability or competition from other microbes.

Results from incubation experiments performed at two sites (Obsidian Pool and Black Sediment Pool) suggest that the microbes were capable of utilizing only very simple organic molecules as electron donors. Their efficiency to respire decreased when the electron donor was changed from formate to acetate or lactate. Activation energy for sulfate reduction at the same two sites was 16 and 38 kJ mol⁻¹ respectively. These values for activation energy are consistent with other microbially mediated processes. At another site (Mushroom Spring), the activation energy was found to be 131 kJ mol⁻¹. Surprisingly, however, this is the same site where comparably higher sulfate reduction rates were measured and the microbes preferred lactate to acetate or formate as electron donor.

K_s (half saturation constant), for sulfate reduction was determined at two sites (Black Sediment Pool and Mushroom Spring). Again Mushroom Spring provided the highest value for K_s (3.17 mM). At Black Sediment Pool the value of K_s (1.24 mM) was close to the one known for modern deep-sea sediment and was much higher than those determined in laboratory cultures or in sediments from other aquatic environments.

Their preference towards simple organic molecules suggests that microbes in some of these hydrothermal springs may be more primitive than other sulfate reducing bacteria, i.e., they may be archaea and not bacteria. However, a detailed phylogenetic classification of microbes present in the springs is required to confirm these claims.

It is clear that sulfate reduction is limited in these hydrothermal springs. Addition of organic acids did not increase the sulfate reduction rate, implying that organic carbon may not be the limiting factor. Rather, low sulfate concentration in the porewaters is the reason for the limitation. Measured porewater sulfate concentrations in these springs are much lower than the K_s values retrieved during these experiments.

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A critical review of CO₂ proxies and models

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In order to understand the operation of the carbon cycle in the geologic past, various proxies and geochemical models have been developed to reconstruct pre-Quaternary levels of atmospheric CO₂. The generation and use of these techniques have resulted in a recent proliferation of CO₂ data. Here, I evaluate the strengths and limitations of the major techniques.

Atmospheric CO₂ can be predicted from mass balance expressions that quantify carbon fluxes to and from the atmosphere. Some of the fluxes are poorly constrained, and so errors can be larger than ±1500 ppm for the early Paleozoic and other times of high CO₂. These models are powerful predictors of general Phanerozoic CO₂ patterns, however because of their typically coarse time resolutions (~10 m.y.) they cannot resolve short-term anomalies.

The δ¹³C of pedogenic carbonates reflects the mixing of atmospheric and plant-derived soil carbon. Atmospheric CO₂ estimates are dependent on the δ¹³C of co-existing organic matter, and so should be measured directly, not inferred from the marine carbonate record. Errors are moderately large (±500 to 1000 ppm), particularly in comparison to other methods for the Tertiary, but is applicable back to the Devonian.

The δ¹³C of photosynthate in phytoplankton is partially dependent upon [CO₂]. Marine sediments therefore offer the potential for high resolution CO₂ reconstructions. Errors are reasonably well constrained (±25 to 100 ppm), however the effects of growth rate and O₂ concentrations are not fully understood. This proxy saturates at CO₂ levels >1000 ppm, and so is not appropriate for times of high CO₂.

The stomatal indices and stomatal ratios in the leaves of most vascular plants inversely respond to atmospheric CO₂. High resolution reconstructions (10¹-10² years) are possible. Errors are low with the stomatal index method (< ±50 ppm), however it saturates at CO₂ levels >500 ppm, and is species-specific, and so is not appropriate for pre-Cretaceous sediments. The stomatal ratio method is less quantitative, but can be applied back to the Devonian.

The δ¹¹B in marine carbonate shells is sensitive to seawater pH, which in turn reflects CO₂. It is the least constrained method discussed here, principally because it assumes that the δ¹¹B of the ocean has remained nearly constant. Some Quaternary studies do not support its use in the pre-Quaternary record.

With few exceptions, there is good agreement among the proxies and models for the Phanerozoic. Furthermore, periods of low inferred CO₂ correspond well with evidence for continental glaciations, while little such evidence exists for periods of high CO₂. CO₂ and global temperatures have been coupled for much of the Phanerozoic.

The link between U-Pb ages of accessory minerals and metamorphic conditions

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U-Pb geochronology has long suffered the difficulty of relating ages to metamorphic conditions and deformation. In fact, the U-Pb method mainly relies on accessory mineral (e.g. zircon and monazite), which behaviour and stability in metamorphic environments is not well known. Moreover, textural analysis of accessory minerals is generally of little significance.

The most direct way to relate U-Pb ages to metamorphic conditions are inclusions found in the dated mineral zone. Multiple generations of inclusions in zircon from the diamond facies gneisses of the Kokchetav massif combined with cathodoluminescence allowed the distinction of four zircon domains. Inclusions of key minerals such as coesite, diamond, garnet, feldspar and micas of variable composition, allowed relating the formation of the different domains to the evolving rock paragenesis and thus to specific metamorphic conditions.

Titanite is one of the few minerals datable by U-Pb whose thermodynamic properties, stability and role in metamorphic reactions are reasonably well known. Titanite from the Dora Maira ultra-high pressure unit retains four growth zones with different chemical (major and trace elements) and isotopic compositions. With the help of mineral inclusions and the modelling of mineral equilibria involving titanite, the ages obtained for the Alpine titanites were linked to three stages in the tectono-metamorphic evolution of the unit.

An additional and more general method to link U-Pb ages and petrology is based on the trace element composition of the dated mineral. The trace element composition of zircon varies according to the composition of coexisting minerals that incorporate the same trace elements found in zircon. The coexistence of zircon and feldspars is reflected in a negative Eu anomaly in the zircon REE pattern. The coexistence of garnet with zircon produces a systematic depletion of Y and HREE in the zircon. Through the experimentally determined equilibrium partitioning of trace elements between these two minerals, the formation of metamorphic zircon can be related to a specific garnet zone. Zircon ages can thus be linked to pressure and temperature conditions obtained from the garnet. Similar variations in trace element composition are under investigation in other U-bearing minerals such as titanite and monazite.

The combination of these techniques leads to the definition of detailed pressure-temperature-time paths that are the base for crucial geological and tectonic data, such as exhumation and subduction rates.

Mechanisms of metal-silicate equilibration in the terrestrial magma ocean

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It has been proposed that the high concentrations of moderately siderophile elements (e.g. Ni and Co) in the Earth's mantle are the result of metal-silicate equilibration at the base of a deep magma ocean that formed during Earth's accretion. According to this model, liquid metal ponds at the base of the magma ocean and, after equilibrating chemically with the overlying silicate liquid at 25-30 GPa, descends further as large diapirs to form the core. Here we investigate the kinetics of metal-silicate equilibration in order to test this model and place new constraints on processes of core formation. We investigate two models: (1) Reaction between a layer of segregated liquid metal and overlying silicate liquid at the base of a convecting magma ocean, as described above. (2) Reaction between dispersed metal droplets and silicate melt in a magma ocean. In the liquid-metal layer model, the convection velocity of the magma ocean controls both the equilibration rate and the rate at which the magma ocean cools. Results indicate that time scales of chemical equilibration are about 3 orders of magnitude longer than the time scales of cooling and crystallization of the magma ocean. In the falling metal droplet model, the droplet size and settling velocity are critical parameters that we determine from fluid dynamics. For likely silicate liquid viscosities, the stable droplet diameter is estimated to be about 1 cm with a settling velocity of about 0.5 m/s. Using such parameters, liquid metal droplets are predicted to equilibrate chemically after settling a distance of a few hundred meters. These models show that the concentrations of moderately siderophile elements in the mantle could be the result of chemical interaction between settling metal droplets and silicate liquid in a magma ocean but not between a segregated layer of liquid metal and overlying silicate liquid at the base of the magma ocean. Consequently, the depth of the magma ocean is unlikely to have corresponded to the apparent equilibration pressure of 25-30 GPa. Preliminary results of polybaric metal-silicate fractionation models show that the dynamics of silicate mixing during metal droplet fallout has a large effect on the apparent equilibration pressure.

Controls of Copper Isotope Fractionation

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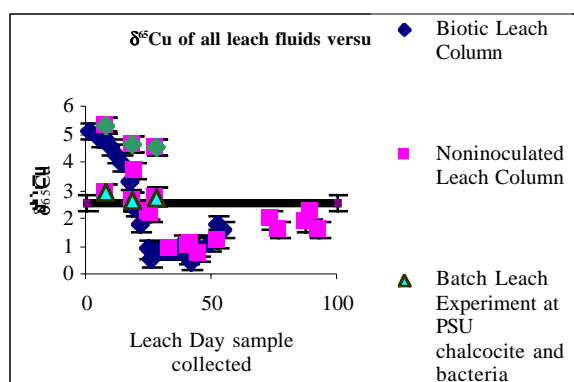
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Studies of copper isotope variations show that naturally occurring copper sulfides have variations of up to seven permil, which is a much larger variation than that shown for iron isotopes in natural systems. As with most, if not all, stable isotope systems in nature, the variations in isotope ratios are probably caused by inorganic processes as well as

biologically aided reactions. In order to determine the magnitude of isotope fractionation caused by organic versus inorganic processes, we have measured the isotope fractionation in experiments with and without bacteria and in benchtop to leach-pad scale. Our results indicate that inorganic process produce large positive shifts in copper isotopes. These reactions are controlled by the copper phase that is in equilibrium with the fluid. These large shifts are not observed in iron isotopes because there are fewer iron phases than copper phases in natural systems. To heavier copper in the eluted fluids. Biologically aided fractionation produces negative shifts in the copper isotopes during dissolution of sulfides.



Adsorption of ⁹⁰Sr and ¹³⁷Cs under elevated temperature and pressure conditions

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Introduction

Sorption and desorption kinetics have been studied in batch experiments conducted with radioactive acid (pH ≈ 3) solutions (containing ⁹⁰Sr and ¹³⁷Cs) under different temperature (T)/pressure (P) conditions (T=20 and 70 °C, and P=Patm and 3 MPa). Rock-samples were selected from a radioactively contaminated site associated with deep-well injection of the radioactive waste.

Results and discussion

The results showed a kinetic effect in the dissolution of carbonate minerals which influenced the radionuclide adsorption/desorption. A mathematical model was developed which explains the anomalous or unexpected character of the kinetic breakthrough (Figure 1). A possible reason for the presence of a concentration minimum is the competition of two reactions. During the first stage of the experiment, the rock adsorbs radionuclides actively, and hence a drop in the concentration function $C(t)$ is observed. Later, the dissolution of the minerals leads to a saturation of the solution by the competing cation (e.g. Ca²⁺), which begins to displace the previously adsorbed radionuclide from the rock: its concentration in the solution begins to increase.

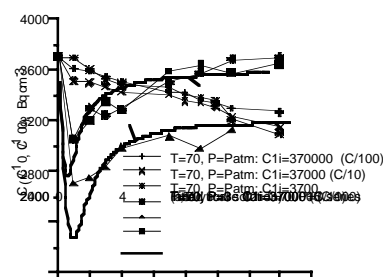


Figure 1: Adsorption of radiostrontium.

Conclusions

The studied problem deals with one of the most acute problems of environmental hydrogeology, namely a problem of a preferential flow through macropores of the subsurface, combined with a “fast transport” of radiostrontium.

Mass-independent and mass-dependent sulfur processing throughout the Archean

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Measurements of the ratios of the four stable isotopes of sulfur (³²S, ³³S, ³⁴S, ³⁶S) using a combination of multi-collector and mono-collector methods on a Cameca ims 1270 ion microprobe have confirmed Farquhar et al.'s (2000) discovery that both sulfides (pyrites) and sulfates (barites) display large anomalous or "mass-independent" effects throughout the Archean (3.9-2.5 Ga ago). Pyrites that are intimately associated with stratiform and cross-cutting barites have the same negative $\Delta^{33}\text{S}$ (and positive $\Delta^{36}\text{S}$) as the barites but are lighter in $\delta^{34}\text{S}$ by as much as 20‰ (six examples from three continents). This isotopic difference between co-existing sulfate and sulfide is attributed to equilibrium fractionation in low-temperature, hydrothermal environments. In this case, the pyrites retained the anomalous negative (positive) $\Delta^{33}\text{S}$ ($\Delta^{36}\text{S}$) which the sulfates apparently acquired from UV-induced photochemical oxidation of SO_2 in the anoxic Archean atmosphere (Farquhar et al., 2001). Alternatively, pyrites in black cherts and shales and banded iron formations are anomalously enriched in ³³S by as much as 7‰ ($\Delta^{33}\text{S} > 0$, $\Delta^{36}\text{S} < 0$) and, typically, have $\delta^{34}\text{S} > 0$. In this case, the pyrite is thought to be derived from elemental sulfur that obtained its anomalous $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ signatures as a result of UV-induced reduction of SO_2 , ultimately to S^0 (Farquhar et al., 2001; Pavlov and Kasting, 2002). Subsequent mixing of these two sulfide reservoirs in various geological environments has created pyrites in which $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are, respectively, approximately proportional and inversely proportional to $\delta^{34}\text{S}$.

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Does slab serpentization and deserpentinization create the primary HIMU mantle component?

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Hydration and dehydration of oceanic lithosphere play an important role in element recycling at convergent margins. Most studies agree that subduction related recycling is necessary to explain some aspects of the mantle's chemical evolution. However, these recycling processes are not yet well understood: OIB type lavas sometimes show a radiogenic ²⁰⁶Pb/²⁰⁴Pb component commonly termed HIMU whose origin is yet to be exactly determined. The MORB source appears to be even more influenced by this mantle component, with these depleted basalts having relatively high ²⁰⁶Pb/²⁰⁴Pb ratios (an expression of the so called lead paradox). This indicates that the mantle's U/Pb ratio has increased over time, although MORB/OIB related melting would preferentially remove U over Pb. Thus it seems that a non-melting subduction related fractionation process leads to the recycling of a high U/Pb component.

Earlier studies attribute this increase in U to the recycling of oceanic crust and sediments. However, here we show that serpentized mantle is maybe the more likely slab lithology to recycle a high U/Pb component. The transport mechanism is aqueous fluid flow; preferential U-pumping occurs because U is easily transported into serpentizing lithosphere by oxidized seawater, while Pb is more easily removed from deserpentinizing lithosphere during reduced high-T fluid escape. Plate bending induced normal faulting at the outer rise can potentially create the conduits for seawater to reach and react with cold lithospheric mantle to serpentize it, leading thus to seawater transported U enrichment. Subsequent partial high P-T dewatering further increases the host serpentinite's ratio of U/Pb. Recycled serpentized mantle therefore shows high U/Pb ratios along with depleted, low abundance, Nd and seawater Sr isotopic ratios with low Rb/Sr. Evolving this lithologic composition can produce the signature of the proposed HIMU mantle component.

We model fluid release beneath differing subduction zones, to further explore these recycling processes which we find to vary significantly among differing subduction zones. For example, varying the incoming plate age for a given slab petrology shows that for a 30my old plate 55% of the serpentinite-hosted water is released - for a 100my old plate only 10%. Differing subducting slabs therefore recycle differing amounts of water and U into the deeper mantle which helps to produce the chemical heterogeneity of the earth's mantle evident in both ocean island basalts and MORB.

Siderophile elements in dynamically segregated metallic liquids

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Introduction

The physical segregation of Fe-rich metallic liquids from silicate during the partial melting of chondrites imparts a geochemical signature on the composition of the resulting metallic liquids, as evidenced by the diverse compositions of iron meteorites. These chemical signatures vary according to parent body composition, segregation mechanisms and the degree to which early core-forming liquids (S-rich, and possibly O-rich) were extracted. We present new results on siderophile concentrations in metal dynamically segregated during partial melting and deformation of an ordinary chondrite.

Results

Metal quench in KM-17 (run conditions: P= 1.2 GPa, T= 940°C, strain rate=10⁻⁶/s) and Kernouve H6 starting material were microanalyzed by LA-ICP-MS using the methods of [1]. Figure 1 shows selected siderophile element abundances in KM-17 metal on a Fe, H-chondrite normalized plot. Bulk H4-6 metal abundances [2] are plotted as the solid gray line. Kernouve (H6) kamacites determined by LA-ICP-MS are shown as dashed gray lines. Two main metal types were recognized in KM-17 run products. The solid black line resembles kamacite compositions and represents residual solid. The thin black lines represent liquid compositions, which are depleted in compatible siderophiles (Re, Os, Ir, W, Co, Ru), and enriched in Ni and Pd, with weak Ga, Ge fractionation.

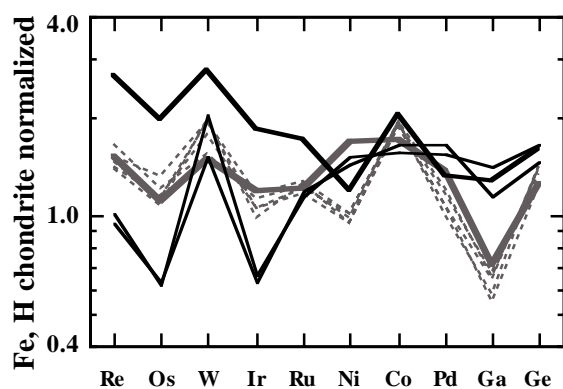


Figure 1: Siderophile concentrations of quench and residual metal in deformation experiment KM-17.

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Biomarkers and Climate Proxies, Lake Baikal, Siberia

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Compared with the evidence from the deep cores of the oceans most Quaternary continental palaeoclimate records are very fragmented (in space and time), primarily because of the effects of the advance and retreat of the great Northern Hemisphere ice sheets. Of the available continental archives lake sediments have the potential to provide long records of palaeoclimate change which might be comparable to the marine record. Lake Baikal in Siberia, the deepest continental depression on earth, is essentially unique as a natural laboratory for the study of continental palaeoenvironments. With over 7500m of accumulated sediments it contains a potentially uninterrupted record of past environmental conditions which would be comparable to that of the marine record.

Biomarkers have a proven record as proxies for palaeoclimate/palaeoenvironment studies in marine sediments, e.g. long chain alkenones and the calculation of sea surface temperatures (e.g. see review by Sachs *et al.*, 2000), therefore their application to continental sedimentation is considered to be a realistic approach to determining past environmental and climatic states. We are studying the record of palaeoclimate changes in Lake Baikal by characterising and quantifying biomarker lipids in sediment trap material, water particulates and sediments at several sites in the lake. The lipids of the water filters (at 5, 10 & 30m depth) show compositional differences between the north and south basins of the lake and also a decrease in abundance with depth, more marked in the central basin. The sediment lipids are significantly different to the water column lipids, containing ketones and hopanoids and with more abundant *n*-alkanes.

This study is in the early stages but it is expected that as well as providing biomarker proxies for climate change in Lake Baikal that an insight into the similarities/differences between continental and marine records of climate change will be gained. In addition, it is hoped that a calibration of the continental record with the marine record will be achieved.

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REEs in Al-rich chondrules: Clues to their origin

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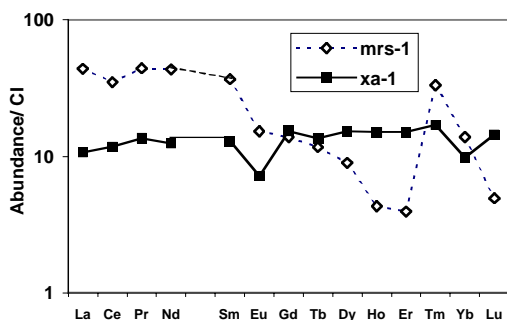
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Introduction: CAIs are now widely thought to have a single source followed by distribution throughout the chondrite groups; these data are compatible with formation near an active Sun and subsequent transport to the asteroidal regions in an x-wind [1,2]. However, it is not clear whether chondrules have a similar remote origin. We are undertaking a project to measure REEs in Al-rich chondrules to investigate their origins. These objects are in some respects intermediate in properties between CAIs and ferromagnesian chondrules. Samples, from the CV3 Allende, were measured using LA-ICP-MS.

Results: MRS-1 is composed of anorthite laths with interstitial diopside and abundant Mg-spinel phenocrysts. XA-1 has a core remarkably similar to MRS-1; however it exhibits a mantle of finer-grained pyroxene and anorthite.

MRS-1 contains bulk REEs at 4-40xCI, and exhibits a fractionation pattern similar to CAIs' Group II patterns. XA-1 has bulk REE abundances approximately ~10xCI and exhibits a pattern similar to the Group III patterns in CAIs. For both chondrules, anorthite is poorer in REEs than diopside, and exhibits a complementary Eu anomaly.



Conclusions: These results suggest that this type of object formed from similar materials to CAIs, although their bulk composition is less refractory than Type B CAIs suggesting they were removed from their formation region at a lower temperature. Typically, chondrules of this type have lower initial ²⁶Al contents than Type B CAIs. These objects may have formed close to the Sun, but further out than CAIs, in a region that experienced less irradiation than the CAI-forming region.

[1] Shu et al. (1996) *Science* **271** 1545. [2] McKeegan et al. (2000) *Science* **289** 842.

Agulhas Leakage variability from Sr isotopes in South Atlantic detritus

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Thermohaline ocean circulation is an important mechanism for the transport of heat around the Earth. Here we show that the terrigenous clastic contributions from the Agulhas Leakage to the Cape Basin waxed and waned over the last glacial cycle in concert with changes in deep ocean $\delta^{13}\text{C}$ and ϵ_{Nd} , tracers of North Atlantic Deep Water (NADW) flux. Thus the detrital Sr isotopes provide a means to link changes in the contribution of Agulhas water to the Atlantic Ocean during cold stages with NADW flux and northern hemisphere glaciation.

Detrital ⁸⁷Sr/⁸⁶Sr ratios in cores TNO57-21 (41°8'S, 8°34'E, 4,981m) and RC11-83 (40°36'S, 9°34'E, 4,718m) from the Cape Basin, South Atlantic, vary between cold stage lows and warm stage highs. The source of the high ⁸⁷Sr/⁸⁶Sr detritus is particulates from the SW Indian Ocean carried to the South Atlantic by the Agulhas Leakage.

Possible explanations for lower ⁸⁷Sr/⁸⁶Sr ratios during cold stages include a decreased Agulhas flux, or enhanced input of the low ⁸⁷Sr/⁸⁶Sr endmember through high glacial fluxes of Patagonian dust. In order to address this issue we have compared the <2 μm fraction of TNO57-21 samples with the <63 μm fraction. ⁸⁷Sr/⁸⁶Sr ratios show a strong correlation, indicating binary mixing, with the <2 μm fraction consistently higher than the <63 μm fraction. The data show that lower bulk sediment ⁸⁷Sr/⁸⁶Sr ratios during cold stages reflect a decrease in the contribution from the fine particulate fraction.

Eolian dust from Patagonia dust is characterized by fine grain size and low ⁸⁷Sr/⁸⁶Sr ratios, thus it can be ruled out as driving the isotopic variability during cold stages. Rather, the lower cold stage values reflect a reduced input of the Agulhas end-member. Thus the climatically coherent changes in the terrigenous clastic ⁸⁷Sr/⁸⁶Sr ratios in the Cape Basin are best explained by variability of the Agulhas Leakage. This means that Sr isotopic variations in SE Atlantic sediment can be a sensitive indicator of the return flow of the conveyor. The results have implications for future studies of climate forcing. Through comparison with proxies of NADW strength in the same cores, the timing changes in tropical (Agulhas) inputs to the South Atlantic and global deep ocean circulation can be assessed.