

Landscape preservation under ice sheets

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Some areas within ice sheet boundaries retain landforms that appear unmodified by glacial erosion. These relict areas have either remained ice-free islands (nunataks), or were preserved under ice. Differentiating between these alternatives has significant implications for palaeoenvironment, ice sheet surface elevation, and ice volume reconstructions.

We collected samples from what are mapped as glacially eroded and relict surfaces in the northern Swedish mountains and areas closer to the centre of maximum Fennoscandian ice sheet extent, to test whether or not the mapped relict areas have indeed been preserved. In situ cosmogenic ¹⁰Be and ²⁶Al concentrations from erratics on relict surfaces, and glacially eroded bedrock adjacent to these surfaces, provide consistent last deglaciation exposure ages (~8-13 kyr), confirming ice sheet overriding as opposed to ice free conditions. Exposure ages of 34 kyr to 61 kyr on bedrock surfaces in these same relict areas demonstrate that these areas were preserved through at least the last glacial cycle, probably as a result of frozen-bed conditions. Based on the relative decay of ²⁶Al and ¹⁰Be it can be inferred that these relict bedrock surfaces remained largely unmodified during multiple ice sheet growth and decay phases.

Subglacial preservation implies that source areas for glacial sediments in ocean cores are considerably smaller than the total area covered by ice sheets. Our results indicate that boundaries between glacially sculpted and preserved landscapes should not automatically be interpreted as former ice limits in palaeoclimatic and palaeoglaciological reconstructions. Relict areas need to be accounted for as frozen bed patches in basal boundary conditions for ice sheet models, and in landscape development models.

Biogeochemical cycling of various metals in Baldeggersee, Switzerland

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This study focuses on the biogeochemical cycling of Ca, Mg, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sb, Mo, and Pb in Baldeggersee, a eutrophic lake in Switzerland. Sedimentation was recorded at the deepest site of Baldeggersee (65 m) during 1994 using sediment traps. A sediment core was taken at the same site with a freeze corer five years later (1999). The sediment layer deposited in 1994 was sampled and the metal accumulation in this layer was determined. Based on this data, we established the balance of sedimentation and remobilisation (Table 1).

Table 1: Annual (1994) sedimentation found in sediment traps and accumulation in the sediment (in mg m⁻²).

	Sedimentation	Accumulation	Remobilisation
Ca	390'000	260'000	34%
Fe	32'000	27'000	16%
Mn	30'000	9'000	70%
Mg	15'000	10'000	31%
Zn	240	180	23%
Ni	150	150	0%
V	78	69	11%
Cr	64	42	34%
Cu	62	54	13%
As	52	40	22%
Pb	21	17	19%
Mo	6.1	1.7	72%
Sb	2.1	1.2	47%

The results show that the lake sediment acts as a sink for most of the metals studied. Less than 25% of the settling Fe, Cu, Ni, Zn, V, Pb, and As are remobilised. For Ca, Mg, and Cr, remobilisation accounts for one third. On the other side, the major fraction of Mn, Mo, and Sb are remobilised upon sedimentation.

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Combined modelling of hydrological and hydrochemical dripwater data to deduce karstic plumbing

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Two of the incentives for improving our understanding of the vadose zone of karstic aquifers are the need to model the behaviour of pollutants and the drive to find proxy indicators for palaeoclimate in speleothems formed from dripwaters. Specifically, quantitative knowledge of karstic plumbing could generate a predictive capability. Models of karstic plumbing can be approached by combining hydrological and hydrochemical data.

Here we report on a study on data from the disused limestone mines under Browns Folly, Bathford, near Bath (UK) which contain a number of dripwater sites, associated particularly with major open joint systems. The drip sites offer a range of hydrological behaviours that fall within the seepage flow and seasonal drip categories of previous authors, and there is an overall correlation between variation in drip rate and mean drip rate. A sub-set of sites exhibit hydrological behaviour that is clearly tied to major rainfall input events. Such sites also display distinctive variations in geochemistry with drip rate. At low drip rates there is either an evidence for increased prior calcite precipitation in the aquifer above the drip (decrease in Ca), or an increase in Sr/Ca or Mg/Ca from inferred low discharge sub-sections of the aquifer, or both.

Quantitative modelling of three sites representing the full range of mean drip rates has been approached by a box modelling approach with finite time steps, initially calibrated by hydrological response to rainfall events, but tuned by the geochemical data. The results allow different conceptual models of karstic plumbing to be evaluated. In particular the relative importance of macropore flow routes through soils and fissure flow in relation to seepage flow can be determined and possible geometries of coupling of different flow routes can be assessed.

Significance of oxygen isotopic signature in magnetite [Fe^{III}₂Fe^{II}O₄] under Earth surface conditions: preliminary results

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Under present surface Earth conditions, nanoparticles of biotic magnetite are intracellularly formed in the magnetosomes of magnetotactic bacteria. Thus, magnetite nanoparticles found in carbonate globules of Martian meteorites have been related to a possible extraterrestrial life. In order to determine if oxygen isotopes can be used as a proxy of bacterial signature, inorganic magnetite has been synthesized under controlled chemical affinity conditions at temperature of 298 K, oxygen fugacity close to 0, ionic strength of 0.2 M and high solution saturation state (> 100). Total dissolved iron of stoichiometric ratio (i.e. Fe^{II} / Fe^{III} = 0.5) was varied to identify the role of this variable on the kinetic rate and on the oxygen isotope fractionation.

Under our experimental conditions, magnetite particles of an average dimension of 8 nm are formed only when [Fe_{tot}] is higher than 9 mM while in lower dissolved iron concentration, only goethite [Fe^{III}O(OH)] particles are formed. Oxygen isotopes fractionation, 10³ln α_{m-e}, decreases by 6 times when the iron concentration increases more than one order of magnitude.

Since biotic magnetites have similar oxygen isotope signature (Mandernack et al., 1999) to our abiotic magnetite particles, we propose that bacteria may simply produce an increase of solution saturation state in the magnetosomes that, in turn, control the precipitation of magnetite nanoparticles in surface conditions.

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Carbon isotopic composition of fatty acids in the marine aerosols from the western North Pacific: Implication for the source and atmospheric transport

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Abstract – A combined molecular and isotopic approach was used in this study to reveal the source and transport of aerosols at a remote oceanic site. Fatty acid distributions and stable carbon isotopic compositions of individual fatty acids were determined in the aerosol samples collected at Chichijima in the western North Pacific over a period of forty-one months. Fatty acid concentration and isotopic composition $\delta^{13}\text{C}$ (vs. PDB) exhibited temporal variations. Concentrations of fatty acids (C_{12} to C_{34}) ranged from 7.6 to 20.7 ng/m³. The concentrations of lower molecular weight (LMW) fatty acids (C_{12} - C_{19}) tend to decrease in winter and increase in summer, whereas the higher molecular weight (HMW) C_{20-34} fatty acids exhibited a reversed trend. Compound specific isotopic analysis revealed that the LMW fatty acids exhibited consistently less negative $\delta^{13}\text{C}$ values than the HMW fatty acids. However, both the LMW and HMW fatty acids displayed similar trend of temporal variations in $\delta^{13}\text{C}$, suggesting that the fatty acids experienced similar atmospheric pathways and transport processes to the remote marine atmosphere, whereas the difference in absolute $\delta^{13}\text{C}$ reflects the different sources of the fatty acids.

Modelling the sorption of metal cations on metal hydroxides: experiment vs. model.

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Modelling of the local structure around metal cations in Earth materials of environmental importance is based on thorough analyses of available spectroscopic and scattering information for these samples. However, construction of atomistic models of metal ion sorption on mineral surfaces from experimental data is not straightforward. In order to refine our understanding of sorption processes, we have developed a procedure for refining EXAFS spectroscopic data based on wavelets and Monte-Carlo modelling of the local structure around the sorbate ion. Then, electrostatic potential and bond valence considerations are used to validate and constraint the model. Finally, this model is compared with predictions from the CD-MUSIC model and with macroscopic information obtained from potentiometric titrations.

To illustrate this approach, the sorption of gold on the surface of goethite will be examined (based on the EXAFS data of Berrodier et al., 1999). Medium-range inter-polyhedral relationships were obtained from a wavelet analysis of the EXAFS spectra, which excludes spurious artefacts such as multi-electronic transitions and multiple-scattering features, and provides a correct estimate of the k -range needed to derive robust structural information from the EXAFS spectra. Then, bond valence models were constructed in 3-D and refined using Monte-Carlo-type methods to match the experimental results. Several unique models were tested by calculating effective charges on each atom using self-consistent potentials (which also include protons) with the FEF8 code (Ankudinov et al., 1998). These bond-valence models were then refined using the CD-MUSIC package (Hiemstra and van Riemsdijk, 1996), which predicts the speciation of gold at the goethite/solution interface (110 and 021 faces). The results of this approach are in excellent agreement with potentiometric titrations up to pH 12.

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New concepts in XAFS analysis

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The extraction of robust structural information from the x-ray absorption fine structure (XAFS, including XANES and EXAFS regions) spectra is highly dependent on the methods used to extract the desired information. We present here a variety of new methods to further reduce the XANES and EXAFS spectra.

Deconvolutions

Pre-edge, XANES and EXAFS deconvolutions (see Filipponi, 2000) are used to enhance spectral features such as electronic transitions in the pre-edge region. Application to the case of Fe in glasses suggests that Fe(II) do not form any 6-coordinated environment, but a mixture of 4-, and 5-coordinated Fe(II). Using deconvolutions, one can also show that the enhanced pre-edge (Fe-K) for ferrihydrite is related to some extra transition, which is not related to crystal-field splitting (probably a Fe-Fe transition, as in epidote: Farges, 2002). Finally, deconvolutions of the EXAFS region help to evidence multi-electronic transitions, as it will be shown for Th in zircon.

Fourier modelling of the XANES

Analysis of the XANES can now be performed using FT methods, considering single-, and multiple scattering paths of the photo-electron (Bugaev et al., 2002) to get speciation information such as for Ti in radiation damaged titanites or in silicate glasses. Despite of the intrinsic limitations, the obtained information is consistent with that obtained from pre-edge or EXAFS analysis and other methods such as scattering methods (Bugaev et al., 2002).

Principal Component Analysis

In order to get the components composing the XAFS spectra of a mixture, principal component analysis provides some statistics on the number of end members to model. By inversion, the spectra for the end members can then be derived. An application to the photo-reduction of Au on ferrihydrite will be presented as well as for Fe in glasses synthesized under variable redox conditions.

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Using proton-induced ³He to study He diffusion kinetics and rock thermal histories

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We have investigated He release kinetics by step-heating of minerals in which we introduced artificial ³He with a beam of ~150 MeV protons in a particle accelerator used primarily for cancer therapy. This process mimics cosmic-ray spallation, and produces He with a ³He/⁴He ratio of about unity. The induced helium is homogeneously distributed within the target crystals, and because it is emitted with few MeV energies, the ³He should reside in sites indistinguishable from those of radiogenic ⁴He. As a consequence it is reasonable to use ³He as a proxy for radiogenic ⁴He during step heating. The advantage of this procedure is that we can measure He diffusion coefficients from essentially any mineral, even those for which there is little or no natural He or He retention. In addition, diffusion coefficients computed using standard step-heat procedures would be erroneous if the He is not uniformly distributed within the diffusion domain. For example a slowly cooled apatite sample will have a highly rounded ⁴He concentration profile which would retard the early He release in a step heating experiment, thus yielding erroneously low apparent diffusion coefficients. By using the artificial ³He we can invert for the ⁴He concentration profile *and* helium diffusivity simultaneously (e.g., see Albarede, 1978). This may prove useful as a technique for narrowing down permitted rock thermal histories.

Experiments on Durango apatite reveal excellent agreement between induced ³He and radiogenic ⁴He diffusion, supporting our approach. In contrast, probable slowly cooled apatites yield ⁴He/³He ratios that rise as the step heat proceeds, consistent with rounded ⁴He concentration profiles. However in the first few steps the ³He diffusion is anomalously high; we do not yet understand the origin or implications of this phenomenon.

Insight into crust-mantle coupling from anomalous $\Delta^{33}\text{S}$ of sulfide inclusions in diamonds

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Sulfur isotope compositions of 26 sulfide inclusions from diamonds have been measured with the Cameca IMS 1270 ion microprobe at UCLA. Inclusions were extracted from 12 diamonds from the Orapa kimberlite pipe, Kaapvaal-Zimbabwe craton, Botswana. In-house reference standards were analyzed between every 3 analyses, and estimated (2σ) uncertainty for $\Delta^{33}\text{S}$ is $\pm 0.14\%$ - adequate to document that inclusion populations from 4 diamonds have anomalous $\Delta^{33}\text{S}$ (0.55‰, 0.24‰, 0.41‰, 0.62‰). Inclusions from the other 8 diamonds yielded $\Delta^{33}\text{S} = 0.04 \pm 0.10\%$ (2σ). Preliminary EPMA analyses indicate these have an eclogite affinity.

$\Delta^{33}\text{S}$ is an excellent geochemical tracer of Archean crust-mantle interactions because it is invariant during geological processes and in bulk meteorites (Farquhar et al. 2000a). Observation of anomalous $\Delta^{33}\text{S}$ of inclusions in diamond confirms earlier assertions that some diamond sulfur derives from the surface (Chaussidon et al., 1987; Eldridge et al., 1991) and also provides new ways to study coupling between Archean mantle, crust and atmosphere. Our measurements of peridotite xenolith sulfur yield near zero $\Delta^{33}\text{S}$ ($0.03 \pm 0.06\%$ (2σ)). Mean and median of whole rock $\Delta^{33}\text{S}$ measurements for Archean sulfide (Farquhar et al. 2000b) are 0.6 and 0.3‰, respectively. Regardless of whether these $\Delta^{33}\text{S}$ values reflect average Archean crust and mantle compositions, they form a framework that can be used in combination with $\Delta^{33}\text{S}$ for sulfide from diamonds to place limits on the proportions of mantle and crustal sulfur prior to trapping in diamond. This approach can be extended to the atmospheric subcycle since we attribute $\Delta^{33}\text{S}$ variations in Archean samples to 193 nm SO_2 photolysis which produces S^0 with $\Delta^{33}\text{S} = 65 \pm 4\%$ (Farquhar et al., 2001). In this context, our data indicate that all of the sulfur in these inclusions may represent subducted, but undiluted crustal sulfur and that up to 1% of the sulfur for sulfide inclusions was processed through the Archean atmosphere.

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Crystallisation of plate spinifex texture at 1 atm. pressure in a thermal gradient

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The spinifex zone in a komatiite flow consists of a thin upper layer of fine, randomly oriented olivine grains underlain by a thicker layer (30 cm to several metres) made up large plates of olivine oriented perpendicular to the flow top. Random spinifex is readily synthesized in dynamic cooling experiments that reproduce conditions during rapid cooling at the flow top. The coarse-grained spinifex is more problematic because the morphology of the olivine plates resembles those of dendritic crystals that grow experimentally only at high cooling rates, 50 to 100°C/hr. Cooling rates 1-3 m beneath the komatiite flow top, in contrast, are calculated to be <5°C/hr. This paradox has led to the suggestion that komatiites are hydrous magmas that crystallized in mid-crustal intrusions; a suggestion refuted by field studies that demonstrate clearly that most komatiites are extrusive.

To help resolve the problem we undertook a series of experiments in which synthetic Fe-free charges (51.9 wt. % SiO_2 , 17.4 wt. % MgO , 13.2 wt. % Al_2O_3 , 17.3 wt. % CaO) were slowly crystallized in a temperature gradient, such as exists at the top of a komatiite flow. The charges were confined in 5-cm-long graphite capsules in the upper part of a 1-atm vertical furnace (argon atmosphere) where the gradient is ~20°C/cm, like that during cooling of a komatiite flow top. At cooling rates between 2 and 5°C/hr, we grew long parallel dendritic olivines whose morphologies resemble those of crystals that grow only at cooling rates >50°C/hr in experiments on the same starting material but without a thermal gradient. Plumose spinifex-like pyroxenes grow between the olivine crystals. These experiments demonstrate that plate spinifex texture forms naturally during cooling of ultramafic lava flows. The presence of water is not required to explain the texture.

Short scale changes in soil properties due to structural iron reduction.

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Introduction

Cation exchange capacity (CEC) is one of the most important soil parameter, determining major retention and physical soil properties. CEC is due to cation heterovalent substitutions in the clay crystal and is therefore considered as a constant. As reviewed in Stucki (1997), structural iron (Fe_s) in the clay lattice of pure clay can be reduced, resulting in sharp changes in clay layer charge and CEC. Favre et al. (2002) reported simultaneous structural iron reduction and CEC increase in field and incubated bulk soil. Induced by bacteria, soil reduction may occur on short time and space scale. The redox-induced changes in CEC, exchangeable cations and clay particle organization in a rice-cropped vertisol with 40% of iron-bearing smectite are presented here.

Methods

Eh and pH were monitored in the field and in laboratory incubated bulk soil samples with native bacteria. Soil samples were collected in incubators at different Eh values. Structural iron reduction was assessed using chemical analysis and Mössbauer spectroscopy. Changes in clay texture and organization were observed using TEM images. Experiments were performed under N₂ atmosphere to avoid re-oxidation.

Results and discussion

CEC increased two times upon reduction. The increase was related to structural iron reduction. The CEC increase was almost balanced by Fe²⁺ and NH₄⁺ adsorption without release of other cations (see table below). Reductive dissolution of iron oxides was simultaneously observed. TEM images showed sharp changes in clay organisation, namely increase in particle thickness, elongation and stacking order.

E _H	Fe _s ^{II}	CEC	Ca _x	Mg _x	Na _x	K _x	Fe _x ²⁺	NH ₄ _x ⁺
[V]	[%]	[cmol _c ⁺ kg ⁻¹]						
0.4	0.1	22.6	15.1	10.2	0.5	0.5	0.0	0.2
0.0	0.8	55.0	10.8	6.8	0.1	0.4	18.3	7.1

Conclusions

These results show that structural iron reduction actually occurs in field conditions and changes major soil physical and retention properties. Structural iron and iron oxides seem to be reduced at similar redox potentials. This process is likely to occur either on large or short time and space scales in soils and sediments.

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A new method for U-Pb isotopic analyses of uranium oxide minerals by SIMS

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We present a new SIMS method that combines the advantages of conventional U-Pb dating (*i.e.*, use of concordia) and *in situ* analysis, and therefore is ideally suited for the study of chemically complex and fine-grained uranium-oxides associated with uranium deposits. During SIMS analysis, differences in the chemical composition of the target phase can affect both relative ion-yields among the isotopes of a given element, and between different elements (e.g., U⁺ and Pb⁺). These matrix effects can lead to erroneous elemental and isotopic ratios determinations if not corrected (e.g., Holliger, 1991). Therefore, an ion-yield normalizing coefficient (α SIMS) that accounts for variation in relative ion-yields with chemical composition for the mineral of interest is necessary. We assembled a suite of uraninite standards that cover a range of U and Pb compositions to develop an appropriate empirical mass bias model. The ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U ratios measured for each standard by TIMS were compared to the ²⁰⁶Pb⁺/²³⁸U⁺ and ²⁰⁷Pb⁺/²³⁵U⁺ ratios obtained by SIMS. α SIMS varies as a function of wt% PbO, requiring two working curves to define the relationship between the ²⁰⁶Pb⁺/²³⁸U⁺ and ²⁰⁷Pb⁺/²³⁵U⁺ ratios measured by SIMS vs. the "True" ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U:

$$y_1 = 0.8277 x_1^{0.65}$$

$$y_2 = 0.3185 x_2^{0.58}$$

where y_1 and y_2 are "True" values and x_1 and x_2 are the ratios ²⁰⁷Pb⁺/²³⁵U⁺ and ²⁰⁶Pb/²³⁸U, respectively, measured by SIMS.

The application of this technique to unconformity-type uranium deposits in Canada, demonstrates that at the microscale these deposits preserve a temporal record of accretion and break up of supercontinents. Prior to *in situ* analyses, this detailed chronological record was obscured by the wide variability in U-Pb data obtained by micro-drilling and conventional isotopic analyses due to mixing of different generations of minerals. Only in studies that integrated a variety of crystal chemical techniques were these records less obscure. *In situ* U-Pb data demonstrate that uranium deposits can record the timing at which various continent-sized blocks came into existence and their histories of growth.

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Tellurium isotopes and the origin of the solar system

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¹²⁶Sn decays to ¹²⁶Te with a half-life of 0.235 Myrs. ¹²⁶Sn cannot be produced in significant amounts by the s-process; it is an r-process nuclide that is probably formed in a supernova environment. The discovery of ¹²⁶Te excesses that correlate with Sn/Te in meteorites would thus provide powerful confirmation of the theory that a supernova injected freshly synthesised nuclides into the molecular cloud from which our solar system formed, providing evidence of a trigger.

Tellurium is of additional interest because it has eight stable nuclides that are well suited for the study of nucleosynthetic isotope anomalies. The nuclides ¹²²⁻¹²⁴Te are produced only by the s-process, ^{128, 130}Te only by the r-process, ¹²⁰Te only by the p-process, whereas ^{125, 126}Te are produced by the r- and s-process. Recently, ε-level Mo isotope anomalies have been reported in bulk meteorites (Dauphas et al., 2002; Yin et al., 2002). These anomalies were inferred to be of nucleosynthetic origin because they mirrored the s- and r-process anomalies that were identified in presolar grains. Previous studies have also reported large (100%-level) Te isotope anomalies in acid-etched residues of Allende (Richter et al., 1998; Maas et al., 2001). Thus bulk carbonaceous chondrites may also display nucleosynthetic Te isotope anomalies.

In the present study, we analyzed bulk samples of the carbonaceous chondrites Orgueil (CI), Murchison (CM), ALH3100 (CM), Allende (CV) and ALH84028 (CV) for their Te isotope composition. All measurements were conducted by MC-ICPMS. The data are normalized to ¹²⁵Te/¹²⁸Te=0.22204 with the exponential law. Results are expressed in ε-units relative to a JMC Te solution. The reproducibility (2s) of the isotopic measurements for 100 ng samples of Te is typically ±4500 ppm for ¹²⁰Te/¹²⁸Te, ±140 ppm for ¹²²Te/¹²⁸Te, ±100 ppm for ¹²⁴Te/¹²⁸Te, ±30 ppm for ¹²⁶Te/¹²⁸Te and ±60 ppm for ¹³⁰Te/¹²⁸Te.

The Te isotopic compositions of all chondrites were within error identical to the JMC standard. Bulk chondrites thus preserve no resolvable evidence of the nucleosynthetic isotope anomalies found in presolar grains. Any ¹²⁶Te anomalies due to decay of ¹²⁶Sn are furthermore either too small to be resolvable or absent. This indicates that the initial abundance of ¹²⁶Sn was either very small or that Sn/Te fractionation occurred too late. The Te isotopic composition of the silicate Earth is probably dominated by the late veneer (Yi et al., 2000) and is therefore unrelated to the bulk earth Sn/Te. However, assuming the bulk Sn/Te ratios of carbonaceous chondrites reflect variable early volatile element depletions during condensation in the nebular that represent their parent bodies, we can calculate a maximum initial ¹²⁶Sn/¹¹⁸Sn of 1×10^{-4} .

Low pH protonation of bacterial cell walls: New data for *Bacillus subtilis*

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Previous potentiometric studies of the charging behavior of bacterial cell walls have focussed primarily on pH conditions higher than approximately 3.5. However, recent bulk metal adsorption and X-ray absorption spectroscopy data suggest that cell wall functional groups can be proton active below pH 3.5, and that surface complexes involving these functional groups can remain important under higher pH conditions. To provide constraints on the speciation of the bacterial cell wall under low pH conditions, we have conducted potentiometric titrations using the Gram-positive aerobic species *Bacillus subtilis*, covering the pH range 1.5 to 10.5.

Titration experiments were conducted using an auto-titrator assembly, with the bacteria suspended in 0.1 M NaClO₄. A thorough wash procedure was used to ensure that the cell walls were free of growth media components, and the electrolyte used was purged of dissolved CO₂ by bubbling N₂ gas through it for 60 minutes prior to the titration. The titrations were conducted in a N₂ atmosphere. Both down-pH and up-pH titrations were conducted, and full reversibility of the protonation reactions was observed over the entire pH range of the experiments.

The titration curves above pH 3.5 are consistent with those from previous studies over this pH range. However, we observed significant adsorption of protons under low pH conditions. In fact, this proton adsorption continued to the lowest pH values examined, indicating that proton saturation did not occur under any of the conditions of the experiments. Zeta potential measurements indicate that the cell wall remains negatively charged, even under the lowest pH conditions studied, and EXAFS data suggest that the low pH-active functional group is a phosphoryl site. We model our titration data using a range of electrostatic models, solving for the acidity constant and site concentration of the functional group that is active under low pH conditions. This study indicates that the cell wall of *B. subtilis* can interact with protons and metals under extremely low pH conditions, and that the nature of the surface phosphoryl sites is likely more complex than has been previously envisioned.

Steady-state $^{226}\text{Ra}/^{230}\text{Th}$ disequilibrium in hydrous mantle minerals

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The short half-life of ^{226}Ra (~1.6 ka) makes it an ideal isotope for studying magmatic processes. However, observed excesses of ^{226}Ra are often larger than expected based on other U series nuclides and difficult to explain. The ^{226}Ra excesses in primitive IAB ($^{226}\text{Ra}/^{230}\text{Th} \leq 7$) are particularly large in comparison to MORB ($^{226}\text{Ra}/^{230}\text{Th} \leq 3$) and OIB ($^{226}\text{Ra}/^{230}\text{Th} \leq 1.5$) (Turner et al., 2001). The IAB super-excesses of ^{226}Ra may be a consequence of strong Ra/Th fractionation by the hydrous mantle minerals amphibole and phlogopite, coupled with a high diffusivity of Ra at mantle temperatures (calculated using the model of Van Orman et al., 2001). Partition coefficients (calculated and/or experimentally determined) suggest that equilibrium Ra/Th ratios in phlogopite (amphibole) are ca. 10000 (100) times higher than in clinopyroxene. Radium diffusion is predicted to be several orders of magnitude faster than Th in cpx. Consequently, as ^{230}Th decays to ^{226}Ra , the latter can diffuse out of cpx and into neighboring phlogopite or amphibole. The efficiency of the diffusional fractionation effect is related to the ratio of the cpx grain radius to $(D_{\text{Ra}}/\lambda)^{1/2}$. At temperatures >1000°C, the effect is significant for radii up to 1cm. Hydrous minerals present in low modal abundance can maintain large steady state $^{226}\text{Ra}/^{230}\text{Th}$ excesses (>10x equilibrium). Clinopyroxene will have complementary steady state depletions. Incipient melts may inherit the strong Ra excesses in the hydrous minerals by preferential incorporation of these early-melting phases, and hence could have Ra excesses larger than would be predicted by the ratio of Ra and Th distribution coefficients in major mantle minerals. The degree of ^{226}Ra excess in derived melts increases with ambient mantle temperature, and decreases with clinopyroxene grain size, degree of partial melting, and the time required for melt extraction. Further Ra enrichment during melt transport could contribute to the large observed ^{226}Ra excesses and hence relax the requirements for super-fast magma transport.

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On-line separation of PGE

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The increase in applications for the Re-Os and Pt-Os isotope systems raised the interest of determining the other platinum group elements (PGE). In the past few years, various analytical procedures have been developed to meet the demand on analyzing platinum group elements at the sub 10 ng/g level. The well known nugget effect tends to mislead the analytical geochemist making him believe that irreproducible results are caused or dominated by this effect. The complexity of separating uncertainties due to sample inhomogeneity from deficiencies of the methods (e.g. digestion, measurements) especially close to the limit of quantification make it difficult to validate the procedure. Validations of procedures with reference materials (RM) are currently not possible since these are not adequately certified. But being able to analyze RM accurately not necessarily allows to infer that every determination of unknown samples will be correct.

Preconcentration techniques are essential for PGE determinations. Thus not only complete digestions but also an effective analyte-matrix separation is required. The use of ICP-MS is very demanding, since problems of molecular interference are often uncontrolled. Separations via ion-chromatography with anion or cation exchange resins rely on the reproducible behavior of PGE (mostly as chloro-complexes) and the interfering species on the column.

Here complete liberation of the PGEs is achieved with a high pressure asher (HPA-S). But only through the on-line coupling of a cation-exchange column to an ICP-MS it is possible to monitor molecular interferences and the completeness of the species separation. Through this procedure (HPA-S and online separation) we are now able to gain confidence on the "trueness" of analytical results of every sample analyzed. As a consequence we can now identify uncertainties due to true sample heterogeneity since reproducibilities (1s) are 2-3%rel. for Pd, Pt and Re, 6-7%rel. for Ru, Os and Ir in UB-N, a peridotite RM. The differences between the two PGE subgroups is explained by the different affinities to mineral phases e.g. homogeneous distributed interstitial base metal sulfides and PGM nuggets e.g. laurites (Ru(Os,Ir)S₂).

Biogenic evolution of microscale heterogeneity: Impact on contaminant dynamics

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Soils and sediments are complex assemblages of organic and inorganic material which are seldom at sustained equilibrium. Coupled biological, chemical, and physical factors dictate the evolutionary pathways of the system and result, generally, in (extreme) heterogeneity from macro- to micro-scale. Here we demonstrate the complexity that develops within simple systems composed of one reactive solid-phase and a single bacterial strain. Reductive dissolution of ferrihydrite by dissimilatory iron reducing bacteria under hydrodynamic conditions results in a complex mineral assemblage dominated by the production of goethite and magnetite—only minor quantities of green rust were noted. The principal bacterial role is in supplying an Fe(II) source: Fe(II) concentration is the dominant factor controlling the biomineralization pathway. At low Fe(II) concentration (less than 0.4 mM at pH 7), goethite is the dominant product, with magnetite being the major product at higher ferrous iron concentrations. Abiotic experiments confirm the role of Fe(II) in the mineralization process.

While similar minerals are produced in biologically active and inactive experiments, their distribution and crystal properties differ appreciably. Biogenic solids are constrained in morphology and crystal size, generally being mono-domainic and less than one-tenth the size of minerals formed under comparable abiotic conditions. Moreover, under biologically active conditions, both magnetite and goethite nucleate on ferrihydrite, leading to mixed-mineralogical assemblages. Further additives of the biological systems are exopolysaccharides (EPS) that coat and bridge minerals.

The fate of contaminants such as chromium and uranium will be impacted dramatically as a consequence of reductive biomineralization. Adsorption properties will be modified appreciably with the shift in mineralogy and the development of reactive ferrous iron bearing phases (solution, surface, and solid) will have important ramifications on reductive stabilization. For example, owing to the formation of dissolved, surface associated, and green rust bearing Fe(II), chromate reduction proceeds at a rapid rate and leads to the formation of a sparingly soluble phase. Uranium, in contrast, is controlled by competing processes, retention within magnetite zones and enzymatic reduction to U(IV).

Total Gaseous Mercury Exchange Between Air and Water Surface over Baihua Reservoir in Guiyang, China

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The exchanges of mercury between surface and air are of significance in the biogeochemical cycling of Hg in the environment, but there are still few reliable data on air/surface exchange in aquatic systems. Field measurement campaigns over lake water surface at Baihua reservoir in Guiyang, Southwestern China were conducted to measure mercury flux using a dynamic flux chamber technique coupled with automatic mercury vapor-phase analyzer from October 30 to November 4, 2001. The dynamic flux chamber is made of quartz glass, and has low blanks. Water samples were collected, and dissolved gaseous mercury (DGM), reactive and total mercury concentrations in water were measured using gold trap pre-concentration and AFS detection method. Meanwhile meteorological parameters, such as wind speed, wind direction, intensity of solar radiation, air and water temperature, and relative humidity, were monitored using a portable weather station.

Water surface is a net atmospheric mercury emission source even at cold season (autumn), and the average mercury emission rate is $3.0 \text{ ng m}^{-2} \text{ h}^{-1}$. It is shown that lake water is super-saturated in terms of dissolved gaseous mercury, which is the driving force of mercury emission from water to the air. The DGM, which is mainly in form of Hg^0 , could be formed in many processes in the water system. Demethylation, bacterial reduction from water and sediment, reduction by humic and fulvic acid in water, and photo-induced reduction in water are so far the possible processes suggested to be responsible for the formation of DGM in aquatic system. We observed a strong positive correlation between wind speed and mercury emission rate, suggesting that strong wind facilitate mercury evaporation process from the water system.

XRD-Rietveld and RMC analysis of the aging process in glauconites

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Glauconites work as open systems at seawater-sediment interface leading to simultaneous chemical and structural rearrangements on aging. A precise knowledge of this process, usually termed as *glauconite maturity*, is of interest for oceanographers and sedimentologists in order to characterize paleoenvironmental changes and to stimate sedimentary conditions for sequence stratigraphic studies.

Usual models are based on empirical markers as are the colour, K⁺ contents, distance between the 001, 020 reflections from XRD patterns, magnetic susceptibility, etc. Nevertheless, a complete characterization of evolutionary stages of glauconite must able to relate the chemical changes taking place during the growth process with the structural variability, from a nearly amorphous initial stage to a highly evolved glauconite, as function of both the variation on stoichiometry and the structural disorder.

In this work, the aging process in glauconites has been examined using the XRD-Rietveld analysis to characterize the average structural disorder associated with several compositional variations in the glauconite formula. This was done by simultaneous constrained refinement of both the occupancy factors and the crystallite-size domains, as a measure of the cristallinity degree. The celadonite atomic coordinates were used as starting structural model. Fifty glauconite samples located at the NW of Spain continental shelf, with several maturity degrees were employed in the refinements and to perform geochemical mapping relating the space distribution of the glauconite maturity to the chemical variability.

The results show that although the rise in K⁺ in the structure is the driving variable in the ordering process this is coupled with simultaneous loss in Fe, given a progressive tendence towards the enrichment of Al³⁺ and Mg²⁺.

The previous study leads an average characterization de ordering process. Nevertheless several local mechanisms, like layer interstratification or stacking faults dues to layer rotation (Drits and Tchoubar, 1990) have been proposed. Then, to analyse detailed aspects of the local structural disorder, additional Reverse Montecarlo (RMC) calculations based on the average structure previously obtained from Rietveld analysis have been performed.

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Sorption of Pb²⁺ on barite and crystallisation of (Ba,Pb)SO₄ in aqueous environments

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Sorption of lead ions on barite surface by precipitation of (Ba,Pb)SO₄ solid solutions represents a potential removal process of this contaminant in aqueous environments.

Thermodynamics models for the (Ba,Pb)SO₄-H₂O system reveal that this solid solution presents a wide miscibility gap (Kornicker et al., 1991). Moreover, the low solubility of barite compared to lead sulphate involves a strong preferential partitioning of Ba to the solid phase. However, under non-equilibrium conditions the complete solid solution series can be crystallised (Takiyama and Kozuki, 1969) and the preferential partitioning of Ba to the solid becomes less important.

We present experimental work on (i) crystallisation of (Ba,Pb)SO₄ solid solutions, and (ii) sorption of lead on barite in aqueous environments.

Crystallization experiments have been carried out by counter-diffusion of (Pb²⁺,Ba²⁺) and SO₄²⁻ in a silica hydrogel column. The gel reduces the nucleation density and favours the development of relatively large crystals. Representative single crystals of the complete solution series were obtained and the evolution of both morphology and composition during the growth process was studied.

In addition, two different kinds of sorption experiments have been performed. In a first set, Pb-containing aqueous solutions were placed in contact with barite grains in a stirred reactor to study the decrease in (Pb²⁺)_{aq} concentration as a function of time. Moreover, assuming that sorption occurs by surface precipitation of Pb-bearing solids, a second set of experiments were carried out in a gel medium. This procedure increases the size of the sorbed entities, that were then characterized as nearly two-dimensional (Ba,Pb)SO₄ crystallites that grow epytaxially onto the {001} barite cleavage surfaces.

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Simulating partial melting and chemical fractionation in mantle dynamics models

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Neither geophysical observations on mantle dynamics, nor geochemical measurements on basalt are able to constrain by themselves the long-term evolution of the Earth's mantle. However, combining both approaches is promising to restrain the set of possible mantle dynamics models, and to get a better understanding of mantle mixing. Here, we present the results of numerical mantle convection studies incorporating partial melting and chemical fractionation at ridges. We use the 2D-cartesian convective code ConMan (King et al 90) to carry out the calculations. We advect passive tracers with assigned chemical concentrations in U, Th, He, Pb and K. Partial melting at ridges is controlled by the local temperature and the mean previous degree of partial melting encountered by matter at a local scale (with a resolution of about 25 km). Reversely, latent heat consumption due to partial melting has a feedback on the temperature and velocity fields. The subsequent chemical fractionation yields a thin, highly degassed and enriched in incompatible elements oceanic crust, and a thicker residual lithospheric mantle. This process has a non-negligible impact on the global mixing properties in the system, since it generates an heterogeneous chemical distribution between crust and lithosphere, while smoothing the melt product relative to the source. In this presentation, we will focus on the effects of the petrologic parameters (such as the bulk partition coefficients) on the resulting long-term chemical evolution of the system. What are the chemical implications of some candidate models for the Earth's mantle dynamics (Hot Abyssal Layer (Kellogg et al 99), D" crust trapping (Christensen and Hofmann 94))?

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Melt/Biotite ¹¹B/¹⁰B Isotopic Fractionation And The Boron Local Environment In The Structure Of Volcanic Glasses

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¹¹B/¹⁰B isotopic compositions were determined on biotite and glass from three evolved volcanic rocks belonging to the Neogene-Quaternary magmatism of Central Italy. ¹¹B MAS NMR spectra were also performed on the same glasses. In these samples the measured boron biotite-glass partition coefficient ranges between 0.004 and 0.011 indicating that boron behaves as an incompatible element during biotite crystallization. The ¹¹B MAS NMR spectra reveal the presence of trigonal BO_{3/2} units, tetrahedral BO_{4/2}⁻ sites and three-coordinated BO_{2/2}O⁻ species containing one non-bridging oxygen. The ¹¹B/¹⁰B isotopic fractionation between biotite and melt/glass was observed to be large even at magmatic temperatures and was found to be between 1.0066 and 1.00279. The measured α values are significantly higher than those calculated using the Reduced Partition Function Ratio (RPFRR) values for B(OH)₃ and B(OH)₄⁻ as well as the abundance of trigonal and tetrahedral boron obtained by ¹¹B NMR spectra. Furthermore, a non-linear relationship is observed between the %BO₄ in the glass structure and the measured 1000ln α suggesting that the approximation of monomeric B(OH)₃ and B(OH)₄⁻ species contribution through ideal mixing in calculating the RPFRR in polyanions probably does not apply to silicate glasses.

Barite dissolution rates measured with different methods

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Barite (BaSO_4) is a model substance for study of crystal dissolution. Cleavage on barite's {001} surface is perfect and can yield an atomically flat surface, making it ideal for atomic force microscopy (AFM) studies. Barite crystals are easily grown in the laboratory, eliminating the need for mechanical grinding, and making them ideal for powder experiments. The chemical structure of barite is a simple two-component system consisting of Ba^{2+} and SO_4^{2-} ions. Dissolution of this [AB] structure is significantly easier to conceptualize than other mineral systems. Barite is thus well suited for computer simulations, and lacks much of the complexity with which similar two component systems, e.g., carbonates, must contend. Therefore, barite is a perfect mineral for comparison of different experimental and analytical techniques.

Overall bulk dissolution rates are composed of various components, e.g., development of deep and shallow etch pits, as well as lateral step movement. These processes contribute to the overall rate, and must be measured using different techniques at different scales to understand their respective contributions. For example, Figure 1 shows the overall removal of material from stepwaves (29 nm) as well as localized development of deep etch pits (40 nm), and shallow, linearly coalescing etch pits (trenches, 7 nm). These processes contribute to the overall ("bulk") dissolution of 1.86×10^{-8} moles $\text{m}^{-2} \text{sec}^{-1}$.

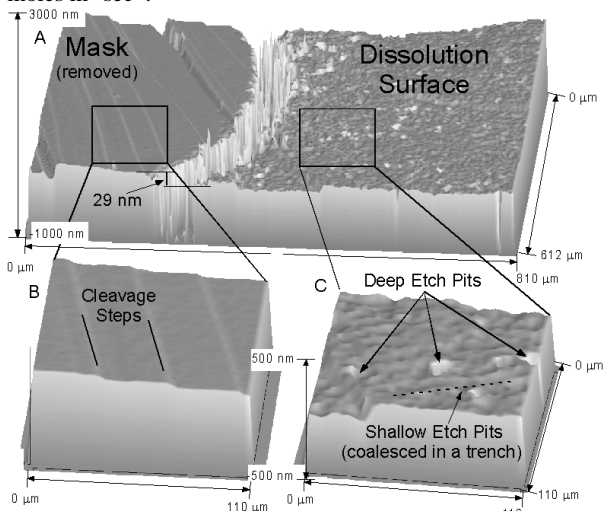


Figure 1. Barite {001} vertical scanning interferometry (VSI) data, 4 hours, 0.05 M EDTA, pH~12, 25°C

We present rate data measured using VSI and provide comparisons to published rates from AFM and powder experiments. Our goal is to identify the causes of discrepancies between rates measured by various techniques.

Effect of agricultural activities on the mineralogy of soil clays

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Soils from different locations in Texas were studied by Potter *et al.* (1999) for their soil organic carbon (SOC) content and its relation to agricultural practices. More than 100 years of continuous agricultural activity has reduced SOC by more than 50% compared with untilled prairie soils. Although return to grass reverses this effect, the carbon sequestration rate is then very slow. Agricultural practices may also modify the soil clay mineralogy, and these "modified" clays could play an important role during SOC mineralization or sequestration. Our objective was to study the effects of agricultural practices on soil clays.

The cultivated (AGRI) and prairie (PRAI) soils selected for the present study are vertisols, previously studied for SOC by Potter *et al.* (1999). These soils, located near Temple (Texas), are classified as Houston Black clay (Udic Haplusterts), with large dioctahedral clay contents. Selected cores of AGRI and PRAI were split into depth segments, air dried, crushed to pass a 2-mm sieve, and suspended in water. The SOC was decomposed with H_2O_2 (30%) in the presence of a NaOAc buffer (pH5). The 0.1-0.25 μm fractions were studied by X-ray diffraction (XRD; mineralogy, charge, swelling) and Fourier transform infrared spectroscopy (FTIR; OH stretching and bending modes) after various treatments.

FTIR and XRD results indicate that dioctahedral smectites dominate the clay mineralogy of both AGRI and PRAI. NEWMOD simulations of the XRD patterns after Ca-exchange and glycolation suggest that the smectites are randomly interstratified illite/smectite with ~50% expandable layers. FTIR data established the aluminous character of the clays (intense Al_2OH bending band), and substitution of Fe^{3+} and Mg for Al was also observed (low-intensity Fe_2OH and AlMgOH bending modes). Low amounts of kaolinite and micaceous phases are present in both AGRI and PRAI, with a slightly greater micaceous component in AGRI. XRD data after K-exchange and treatment at 110°C overnight show slightly more high-charge smectite layers in AGRI than in PRAI (more irreversibly collapsed layers). Results after Li-exchange and treatment at 300°C (Greene-Kelly test) indicate that the smectite layers are predominantly beidellitic in both AGRI and PRAI, although there are slightly more montmorillonitic layers in PRAI. It is clear that agricultural practices induced only minor modifications of the clays, probably due to the low charge of the smectite layers and the short period of time involved.

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Origin of methane within a subduction related high-temperature hydrothermal system and its role in risk evaluation

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Introduction

The origin of methane within subduction related high-temperature hydrothermal systems (abiogenic vs thermogenic) and its role in risk evaluation is still a matter of debate. In order to address these questions we present a combined approach where fumarolic gas discharges from Nisyros volcano, Greece, are both investigated for their chemical and isotopic composition.

Discussion of results

With varying relative amounts of CH₄ and CO₂ carbon isotopic composition of both gases stays constant implying an origin from a single source. Apparent temperatures derived from carbon isotope partitioning between CH₄ and CO₂ are around 350°C and correlate well with temperatures measured directly for a deep aquifer (330-340°C, as known from two geothermal drillings). Apparent temperatures inferred from compositional data using the H₂O - H₂-CO₂-CO-CH₄-geothermometer (Chiodini & Marini, 1998) show a much larger spread, but highest temperatures again coincide with measured deep aquifer temperatures. Molar ratios of CO₂, CH₄, H₂ and H₂O at fumarolic outlet are in agreement with formation after Fischer-Tropsch CO₂ + 4H₂ = CH₄ + 2H₂O in the liquid phase, followed by adiabatic boiling and local quenching of the liquid into the vapor phase.

Conclusions

A pure inorganic reaction seems to be responsible for CH₄-formation within the high-temperature hydrothermal system of Nisyros. CO₂ and CH₄ within the deep aquifer are initially in chemical and isotopic equilibrium. Local discrepancies between the chemical and isotopic composition observed at fumarolic outlet are caused by secondary re-equilibration phenomena, such as reaction of CO to CO₂ during the ascent of the gases. These do not affect carbon isotope partitioning between CO₂ and CH₄. Since rates of isotopic exchange between dissolved CO₂ and CH₄ are unknown, the role of the carbon isotope geothermometer in monitoring volcanic-hydrothermal activity remains speculative.

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Distribution of ²³⁰Th and ²³¹Pa off SW-Africa

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The North Atlantic is one of the key areas for the formation of newly formed deep water masses (e.g. North Atlantic Deep Water (NADW)) which ventilate the world ocean basins. Changes of the formation rates are believed to influence the world climate significantly. Therefore one of the key issues in paleoceanography is the investigation of changes in the production rate of NADW in the geological past. Based on ratios of the natural radioisotopes ²³⁰Th (T_{1/2} = 75.2 ky) and ²³¹Pa (T_{1/2} = 32.2 ky) preserved in the sediments it was proposed that NADW formation rates did not change during the last glacial maximum compared to recent times. This suggestion was based on a mass balance of ²³⁰Th and ²³¹Pa for the Atlantic Ocean. Since these radioisotopes are particle reactive, areas with high particle flux, e. g. the upwelling area off SW Africa, may have an important effect on this balance.

During Meteor cruises M48/4 (2000) we investigated the distribution of ²³⁰Th and ²³¹Pa in the water column and surface sediments in the Angola and Kap basins. At 11 locations covering near shore sites as well as the open ocean, surface sediments as well as water samples (total and particulate) were obtained in up to 10 depth levels. In the Angola basin a gradual increase of ²³⁰Th concentrations with depth was observed comparable to the ²³⁰Th water-column distribution in most ocean basins. In general, concentration-depth gradients are similar in the Angola and in the Kap basins; but at the near-shore sites in the Kap basin ²³⁰Th concentrations were reduced indicating a boundary scavenging effect which is probably related to high particle flux caused by the upwelling environment off the Namibian coast. In the western Kap basin a drastic increase in ²³⁰Th concentrations of up to a factor 3 was observed in the Antarctic Bottom Water which fills the Kap basin in > 4000m water depth. It is proposed that these ²³⁰Th enriched water masses were advected from areas like the Weddell Sea where export of ²³⁰Th enriched water masses was previously observed. Both water masses and boundary scavenging control ²³⁰Th/²³¹Pa ratios preserved in the surface sediments in the area investigated. The upwelling area off Namibia seems to be an unimportant sink for ²³⁰Th and ²³¹Pa.

Calibration of the production rate of ^{36}Cl from potassium

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Production of ^{36}Cl by cosmic ray bombardment of potassium at the earth's surface is higher than from any other target element. Since many rock types contain abundant potassium, an accurate value for the rate of this production is crucial for exposure-age and erosion studies that exploit the *in situ* production of ^{36}Cl in surface rocks. Here, we report a calibration of this rate, or rather rates, because there are separate contributions from spallation, muon capture, and neutron capture.

The calibration strategy was as follows:

- Select surfaces of well-known age.* Samples were collected from rock surfaces exposed by the end of the Loch Lomond Readvance glaciation in Scotland 11,600 (± 500) years ago.
- Select a potassium-rich mineral.* Mineral separates of K-feldspar were extracted from the sandstone or granite samples.
- Independently calibrate the production due to neutron capture by chloride.* Chlorine-36 was measured in quartz separates from the same rocks.
- Determine separately the production due to muon capture.* A 6m-long depth profile of ^{36}Cl in K-feldspar separates from a granite quarry at Wyangala in SE Australia was measured in order to disentangle the relative contributions from spallation and muon capture.

Samples were prepared as AgCl using standard techniques. Chlorine-36 concentrations were measured by accelerator mass spectrometry using the 14UD accelerator at the Australian National University. From these data, we deduce the following ^{36}Cl production rates from potassium at sea level and high latitude:

Spallation by fast nucleons $161 \pm 9 \text{ atom (gK)}^{-1} \text{ yr}^{-1}$
Capture of negative muons $10.2 \pm 1.3 \text{ atom (gK)}^{-1} \text{ yr}^{-1}$

Characterisation of Sr in coral aragonite by EXAFS

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We have analyzed the aragonite from *Porites lobata*, *Pavona gigantea*, *Pavona clavus* and *Montastrea annularis* corals using Sr K-edge Extended Absorption X-ray Fine Structure (EXAFS) and compared these with aragonite, strontianite and mechanically mixed standards. We seek to know the structural state of Sr in coral aragonite, specifically whether it is entirely substituted for Ca within the aragonite (single-phase), or whether submicroscopic crystals of strontianite are also present in the structure (dual phase), as suggested previously. We performed bulk analyses and compared the data with equivalent μEXAFS analyses on small ($\sim 400 \mu\text{m}^3$) analytical volumes using a microfocussed x-ray beam. As a result of the architecture of the coral skeleton, the crystals within the microanalytical volume are not randomly oriented, and the microanalytical x-ray absorption spectra show orientational dependence. However, refinement of bulk and microanalytical data provided indistinguishable interatomic distances and thermal vibration parameters in the third shell (indicative of Sr speciation). Analysis in μEXAFS mode allows the structural state of individual parts of the coral skeletal architecture to be ascertained, and the data quality is comparable with bulk analysis. The Sr K-edge EXAFS of all the coral samples refine, within error, to Sr ideally substituted in aragonite, in contrast to previous studies, in which strontianite was reported. Some samples from that study were also analyzed here. Strontianite may be less widely distributed in corals than previously thought. Coral aragonite is a Sr-supersaturated, metastable, single-phase aragonite. These observations have implications for the long-term stability of coral aragonite and the use of Sr in corals to reconstruct past seawater temperatures.

A Subduction Zone Barrier for Sediment-Derived Nitrogen

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The distinct isotopic compositions of the noble gases in various terrestrial reservoirs makes them ideal for exploring deep Earth processes. Helium in particular is a powerful tracer of mantle versus crustal contributions to volatile degassing at the surface. Here we use He in combination with N-isotope systematics to trace the sources of nitrogen in subduction zones, and to address the mass balance between the input of nitrogen into the subduction zone and the output via arc volcanism. We show that nitrogen stored in sediments of the oceanic crust is efficiently recycled back to the atmosphere and is not transported into the deeper mantle. To subduct nitrogen past the zone of arc magma generation transport of nitrogen in the oceanic basement is necessary.

Investigation of the He-N₂ systematics of volcanic and geothermal gases discharging from the Costa Rican and Guatemalan segments of the Central American arc shows that 1) The majority of samples have ³He/⁴He ratios in the range 5-8 R_A indicating that both arc segments sample He primarily of mantle wedge origin; 2) nitrogen isotope systematics (and N₂/He ratios) vary considerably between Guatemala and Costa Rica. Guatemala volatiles have δ¹⁵N values in the range -0.5 to 6.3 ‰ and N₂/He ratios fall between 1,400 and 25,000 (typical range of other arc-volcanoes). Volatiles from Costa Rica, have significantly lower N₂/He values (73- 333) and mostly negative δ¹⁵N (-3.0 to 1.7 ‰). With the effects of air contamination removed, the data is interpreted as a binary mixing between mantle-derived nitrogen (³He/⁴He = 8 R_A, δ¹⁵N = -5‰) and subducted sedimentary nitrogen (³He/⁴He = 0.05 R_A and δ¹⁵N = +7 ‰). Volatiles from Costa Rica are characterised by mantle-derived nitrogen, whereas in Guatemala the subducted sedimentary contribution dominates.

To evaluate nitrogen mass balance, we determine the volatile input flux via the Central American trench by combining estimates of the volatile characteristics of localized sediments and oceanic basement with extrinsic properties such as subduction rate, arc length, sediment thickness and porosity. The flux of sediment-hosted N is 2.3 x 10⁸ mol N/yr for the Central American margin. The output is determined by combining the chemistry of the gas emissions (CO₂, SO₂, N₂) with the time-averaged SO₂ flux from the arc. This approach yields a non-air N₂ flux of 2.9 x 10⁸ mol/yr, which balances almost exactly the input flux of nitrogen via the trench. This implies that nitrogen is efficiently released from the slab and transported through the mantle wedge to the atmosphere via arc volcanism. We argue that this observation holds for arcs globally suggesting that subduction zones act as a barrier to the deeper mantle for sedimentary nitrogen.

Constraining landscape evolution of the West Antarctic rift flank of southern Victoria Land

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The Transantarctic Mountains (TAM) define the western flank of the intracontinental West Antarctic rift system (WARS). Cretaceous extension is distributed across the WARS, whereas extension since the early Cenozoic was concentrated along the western side of the WARS adjacent to the front of the TAM. Cenozoic geomorphic evolution of the TAM in this area has previously been summarised as escarpment retreat, formation of planation surfaces and down-cutting by fluvial processes until about the mid-Miocene. Subsequent modification of the landscape by glacial processes has been minor due to the hyper-arid polar climate. Erosion rates since rift flank formation are constrained using apatite fission track thermochronology (AFTT), (U-Th)/He dating of apatite, information from offshore drill-holes, preservation of volcanic ash, and cosmogenic surface exposure age dating. In general, AFTT constrained denudation rates in the Late Cretaceous are low but reach ~65 m/my on the inland flank of the Kukri Hills. Near the coast at Mt Barnes AFTT data indicate the onset of Cenozoic denudation at 55 Ma. Average denudation since then is ~85 m/my but at a rate of 115 m/my from 55-40 Ma. At Peak 1880 20 km inland, AFTT data suggest denudation started later at ~40 Ma, with a similar average rate. (U-Th)/He data from Peak 1880, while exhibiting considerable scatter in single grain ages due to the effects of slow cooling on zoned apatites, also suggest the onset of more rapid cooling at ~40 Ma. This younging-inland trend for the onset of early Cenozoic denudation is interpreted as escarpment retreat at a rate of ~1.5 km/my. Existing information from nearby offshore drill-holes in the WARS agree well with estimates on the amount and timing of denudation and continued slow erosion from the end of the Eocene through the Oligocene. Previously reported exposure age data indicate Miocene to present erosion rates of 0.1-1 m/my. Thus, a combination of different techniques document the history of this rift flank, its initial formation, the style and rate of geomorphic development, the overall slow and decreasing erosion rates, deposition of eroded sediment offshore, and preservation of the landscape since the mid-Miocene.

Deducing marginal marine seawater composition from biogenic carbonate and evaporites

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Knowledge of the natural variability of ocean water composition has grown with the number of chemical studies published. While disentangling the controls on chemical composition of biogenic minerals remains poorly constrained, an appreciation of the range of trace element, stable and some radiogenic isotope values typical of ocean water has developed. Values outside these established ranges are commonly discarded on the pretext that they represent diagenetically altered rather than primary signals. Marginal marine settings such as semi-enclosed seas, lagoons and estuaries are subject to much more extreme chemical changes than the open ocean. Discriminating between primary and altered material from marginal marine systems is therefore difficult and controversial.

We present data from a multi-proxy study of the Late Miocene evaporite succession preserved at Eraclea Minoa, Sicily. The succession of alternating foram-bearing marls and gypsum illustrates the strong variability of the water chemistry at the time where salinity fluctuated abruptly between levels able to support a foraminiferal assemblage to those required for gypsum precipitation (130-160 g/L). Careful visual, chemical and LA-ICP-OES screening of samples permits discrimination between primary and secondary mineralisation and allows interpretation of the composition of this anomalous Late Miocene seawater around Sicily. It also reveals chemical characteristics of fluids circulating either during or after deposition. Combined chemical, faunal and sedimentological interpretation of this succession allows a better understanding of the impact of climate and the relative dominance of ocean versus freshwater influx on marginal marine systems.

Carbonate apatite at high pressure

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There is an increasing awareness of the contribution of carbonated apatite (C-OHAp, C-FAp) to bone and dental enamel, as well as in the *in vivo* remodelling of bone material. However, the structural roles of the carbonate group in apatite remain unclear. In this study, carbonate apatite (CAp) and C-OHAp and C-FAp have been synthesized in an end-loaded piston cylinder apparatus at 2-3 GPa and 1400°C, and investigated by EPMA, FTIR and C *K*-edge XANES spectroscopy and single-crystal structure analysis, to follow structural change with progressive substitution of carbonate. The composition series investigated was $(9-y)\text{Ca}(\text{PO}_4)_{2/3} + (x+y)\text{CaCO}_3 \pm [\text{CaF}_2, \text{Ca}(\text{OH})_2]$, where $x = 1$ for CAp and $x < 1$ for C-OHAp and C-FAp. Our apatites saturated in the calcite stability field at $(x + y) \approx 2.0-2.5$.

In FTIR spectra, asymmetric stretch (ν_3) bands of the carbonate group are present at about 1459 and 1539 cm^{-1} in A-type CAp ($x = 1, y = 0$); about 1409, 1453, 1504, 1539, and 1563 cm^{-1} in A,B-type CAp; about 1408, 1455, 1471, and 1546 cm^{-1} in A,B-type CAp annealed in air at 1000°C; and about 1428, 1456, 1511, 1550, and 1574 cm^{-1} in B-type C-FAp. C *K*-edge XANES spectra are characterized by a sharp absorption peak at ~ 290.2 eV and a broad peak at ~ 301.3 eV due to transition of C *1s* electrons to unoccupied states of π^* and σ^* character, respectively. The area of the π^* peak increases in proportion to the amount of carbonate present.

Different from previous studies, X-ray structures of A,B-type CAp (space group $P6_3/m$) show that the channel (A) carbonate groups are deflected from the vertical plane to avoid a prohibitively short Ca2-O distance (1.74Å in the ideal structure). Also, high-pressure CAp can accommodate more than one channel (A) carbonate group per unit cell. This is possible because one of the oxygens in each group is located at the position of O(H) in OHAp but, even so, minimization of unfavourable O-O interactions results in considerable disruption in the decompressed structure. Partial decarbonation of the excess channel carbonate occurs on annealing A,B-type CAp in air at 1000°C. The B-type carbonate group is oriented close to one of the sloping faces of the vacant PO_4 tetrahedron, but tilted closer to the horizontal plane. For the full complement of Ca atoms (10 pfu), the ideal partitioning of the carbonate group between A- and B-type sites appears to be $A = [x + (y/3)]$, $B = [6 - (2/3)(9 - y)]$. However, the X-ray structures reveal that the amount of channel (A) carbonate is typically in excess of this ideal ratio in CAp because, under high pressure, carbonate is stuffed into the channel (A) sites in preference to available B sites.

Stable Equatorial Pacific Productivity over the last 1Ma

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The large glacial to interglacial fluctuations in the atmospheric CO₂ concentration during the Pleistocene have been attributed to changes in the oceanic carbon system, i.e. ocean productivity. The Equatorial Pacific represents an important component of global oceanic productivity and, thus, is speculated to have a major influence on global climate.

Conventional wisdom has held that Equatorial productivity was substantially greater during glacials than during interglacials. Support for this hypothesis comes for example from Paytan et al. (1996) reporting that the burial rate of barite varied by a factor of 5-6 between interglacials and glacials throughout the Pleistocene climate cycles.

To test this hypothesis we present ²³⁰Th and ³He data for two cores from the central equatorial Pacific at 140W (PC 72, PC114). Both tracers represent constant flux proxies (CFP), i.e. tracers of constant supply through time, which allow us to reconstruct accumulation rates that are not biased by sediment redistribution or errors in the stratigraphy. Consequently, we use these tracers to re-evaluate the sedimentation record of paleoproductivity proxies. Normalizing the excess Ba record of the past 1Ma to CFPs eliminates the large variability in the conventional ¹⁸O-derived accumulation rates. We show that the fluctuations reported by Paytan et al. (1996) are an effect of the use of stratigraphy-derived sedimentation rates. This holds also true for the period of the Mid-Pleistocene Climate Transition (MPT, 800-560ka) for which Murray et al. (2000) inferred a major productivity increase from Ti-normalized Ba, Al and P data. Using normalization to ³He we show that the apparent maxima in the profiles during the MPT are due to a decrease in Ti, i.e. dust, and that there was no significant productivity increase during the MPT.

Re-evaluation of the Ba records with CFPs implies that the export productivity in the Equatorial Pacific was constant during the past 1Ma. The variability in the carbonate pattern in the Pacific Ocean can be exclusively attributed to variable CaCO₃ dissolution driven by changes in the paleochemistry of the deep ocean. Our study proves the unequivocal need to apply constant flux proxies (instead of stratigraphy-based sedimentation rates) to reconstruct sedimentary fluxes in the past.

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The Origin of Solar System Organic Matter: Evidence from IDPs

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Some extraterrestrial material contains organic matter, but the origin of the organic compounds has not been established. A variety of mechanisms have been proposed, with a Miller-Urey type process, producing organic matter in an aqueous process, and a Fisher-Tropsch type process operating in the Solar Nebula as two extreme cases. If the organic matter were produced by a Miller-Urey type process we would expect to see organic matter predominately in extraterrestrial samples that exhibit other evidence of aqueous processing (e.g., abundant clay minerals) while a Fisher-Tropsch type process should result in comparable amounts of organic matter in either hydrated or anhydrous samples.

The hydrated carbonaceous meteorites have %-level concentrations of organic matter, but anhydrous carbonaceous chondrites have much lower concentrations, with most of the carbon in elemental form. This observation favors a Miller-Urey type mechanism. But all anhydrous carbonaceous chondrites are depleted in volatile elements. These depletions are believed to result from either incomplete condensation or subsequent vaporization of elements more volatile than Mn. Such a process requires temperatures in excess of 1200° C, and is incompatible with the survival of organic matter.

We determined the abundance and types of carbon in anhydrous and hydrated interplanetary dust particles (IDPs) collected from the Earth's stratosphere. Many anhydrous IDPs have contents of the moderately volatile elements \geq C₁, unequilibrated minerals, and D anomalies within a few μ m of D-normal material. These features indicate many anhydrous IDPs have never been significantly heated, making them better candidates to test the origin of Solar System organics.

Scanning Transmission X-ray Microscope (STXM) carbon maps show carbon contents ranging from a few vol-% to over 90 vol-%, with comparable amounts of carbon in anhydrous and hydrated IDPs. Carbon X-ray Absorption Near Edge Structure (XANES) spectra of both anhydrous and hydrated IDPs show similar pre-edge spectra: with a strong C-ring absorption at ~285 eV and a carbonyl (C=O) absorption at ~288.5 eV. We confirmed the presence of percent-level carbonyl by oxygen XANES.

FTIR spectroscopy detected C-H stretching absorptions from aliphatic hydrocarbon at about the same strength in both hydrated and anhydrous IDPs. We compared the relative strength of C-H stretching and silicate absorptions in IDPs to mixtures of aliphatic hydrocarbon and glass, and conclude aliphatic hydrocarbon is present at the %-level in most IDPs.

Since we found organic matter of similar types and abundances in both anhydrous and hydrated IDPs, it appears that the bulk of Solar System organic matter was produced early in Solar Nebular history, possibly by a Fisher-Tropsch type process or by irradiation of carbon-rich ices.

Sangeang Api: upper plate magma chamber processes and the origin of alkaline arc lavas.

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Sangeang Api is an active alkaline volcano in the Indonesian Sunda Arc. It is composed of oxidised, potassic, Cl- and volatile-enriched, undersaturated lavas with abundant clinopyroxene-rich mafic and ultramafic xenoliths. There is strong evidence that suites of lavas and xenoliths are co-magmatic and that the xenoliths are accumulative rocks in equilibrium with the Sangeang Api melts. U-Th-Ra isotope data (Turner & Foden, 2001) indicate that the melts have limited ²³⁸U/²³⁰Th disequilibrium, from slight Th- to slight U-excess, but show extreme enrichment of ²²⁶Ra relative to ²³⁰Th. Excess ²²⁶Ra might result from fractionation during dehydration and partial melting of the slab, implying very fast magmatic ascent rates. However the limited U-Th disequilibrium tends to discount this. Excess ²²⁶Ra might otherwise record very efficient fractionation in the shallow sub-arc regime, implying that melts have "seen" very large volumes of crystals.

Conclusions

Evidence for equilibrium crystallisation and for successive stages of growth and resorption of secondary amphibole and phlogopite in the xenoliths supports a model of percolation flow during waxing and waning thermal conditions. Flow varied from sluggish infiltrative grain-boundary flow to more rapid conduit flow, with periodic stagnation in interconnected small magma chambers. Periodic eruptions may then be associated with the influx of new more rapidly flowing pulses of melt migration in temporary dilatational conduits. The xenolithic clinopyroxenes invariably have relative Th-excess consistent with the D_{Th}/D_U conditions resulting when $P < 1.5$ GPa. (Wood et al., 1999). Partial melting of these clinopyroxene-rich crystal residues may periodically occur and will yield Ca-rich ankaramite liquids (Schiano et al, 2000), which at the time will show Th-excess.

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Trace element partitioning evidence for growth of early continental crust from amphibolites, not eclogites

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It is generally accepted that the first continental crust formed by melting of either eclogite or amphibolite, either at subduction zones or on the underside of thick oceanic crust. The compositions of early crustal gneisses and experimental studies support these interpretations, but our understanding of trace element partitioning could not distinguish between them up to now. We have investigated the trace element consequences of melting amphibolites and eclogites in various tectonic settings realistic for the Archean on the basis of new experimental trace element partitioning data sets¹⁻³. The critical tests are given by the element ratios Nb/Ta and Zr/Sm: early continental crustal gneisses (TTG gneisses) fall in the lower right quadrant with low Nb/Ta and high Zr/Sm relative to primitive mantle and modern oceanic basalts. Melting of eclogite cannot cause a decrease in Nb/Ta of melts under any circumstances (batch or pure fractional melting); Nb/Ta is *increased* substantially in melts if rutile remains in the residue. In contrast, the Nb/Ta ratios of partial melts of amphibolites depends on the Mg# [Mg/(Mg+Fe)] and titanium content of the amphiboles. Those with high Mg# (0.8-0.9) such as in mafic-ultramafic cumulates from primitive basaltic-picritic melts cannot fractionate Nb from Ta, whereas amphiboles with lower Mg# (30-60) can cause a dramatic *decrease* in Nb/Ta of melts.

We conclude that early continental crustal gneisses with low Nb/Ta could be produced by melting of amphibolites in a subduction zone in which fractionated basalts lead to low Mg# amphiboles during subduction. Melting of the underside of thick oceanic crust is unsuitable because of the high Mg# to be expected in the cumulate pile. Furthermore, water contents are probably very low in this environment, so that dry transition to eclogites and pyroxenites is more likely than the formation of amphibolites during metamorphism. The relative scarcity of crustal gneisses in the early Archean must reflect the rarity of conditions in which fractionated basalts could melt as amphibolites at that time.

These conclusions from trace element partitioning are consistent with those derived from experimental investigations of metamorphic reactions in picritic to komatiitic rocks which may have been common in the early Archean ocean crust⁴.

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The phosphorus burial curve revisited

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Phosphorus (P) serves as an element essential to life, and is closely linked to carbon (C) through photosynthesis and biogeochemical weathering. A proxy of change in the global P burial record for the last 160 million years is based on a compilation of P accumulation rates, which were calculated from systematically measured P contents in a great variety of Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) cores (Föllmi 1995). Since its first publication three tests have been performed on this curve: The first test consisted in a re-examination of an important part of its early Cretaceous portion (137 to 132 myr; Valanginian-Hauterivian), which is based on relatively few data in comparison to younger parts. For this test, 575 P concentrations were measured in eight continental sections in central and southern Europe (Van de Schootbrugge, 2001). The resulting compilation correlates very well with the DSDP- and ODP-based data set, which suggests that the curve is robust for this time interval. The second test consisted in a close-up study of the last full glaciation phase. Here different P phases were analyzed in a selection of eight ODP cores using a sequential extraction method. An important result is that during this last phase of glaciation variations in P burial were coupled to climate change, albeit on a shorter time scale, in the range of the precession band frequency, and that glacial periods during this last glaciation show comparable to slightly higher P burial rates than interglacial stages (Tamburini 2001). The third test included a detailed analysis of the importance of biogeochemical weathering processes in glaciated areas. Here we selected the Rhône and Oberaar Glaciers catchments – both situated within the crystalline basement of the Aare massif (central Switzerland) –, and performed analyses on the geochemistry of the outlet waters, mineralogy of suspended material, and geochemistry and mineralogy of moraine material of different ages. One outcome is that glaciers have an important potential for increasing biogeochemical weathering rates during and especially immediately after glaciation phases (Hosein and Arn, in prep.).

Melt and source diversity under the ultra slow spreading Southwest Indian Ridge

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Glassy primary melt inclusions trapped within plagioclase and olivine phenocrysts and the matrix glass of basalts of the ultra-slow spreading Southwest Indian Ridge (SWIR), (49°E - 70°E) were studied to investigate the compositional evolution of parental melts, melt extraction and magma chamber processes during ultra-slow spreading. Specifically we test the hypothesis that the depth of melting, melt fraction, the extraction and mingling of melt increments and magma residence time change as spreading evolves from rift propagation in the East to steady-state in the West.

The matrix glass compositions of the SWIR show a unique MORB composition, with high Na₂O concentrations and enriched trace element and REE concentrations compared to a typical N-MORB (Meyzen et al, 2002). The melt inclusions show variable compositions along the ridge. Towards the East they show enriched compositions and more variability in major and trace element. Two groups of inclusions can be differentiated. One shows similar compositions to the matrix glasses, with flat HREE but enriched in LREE and LILE elements. The second group shows strong depletion in HREE and enrichment in LREE and LILE. They also show strong negative anomalies in Nb, Zr and Hf. The melt inclusion compositions towards the West of the ridge appear to be more homogeneous in composition and are depleted in LREE. They do also show negative anomalies in Nb, Zr and Hf. These variations in compositions can be related to enrichments of the melts by LILE carried out by metasomatic fluids coming from the mantle. Alternatively, Nb, Zr and Hf were held back by a mantle phase when these melts were segregated.

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Stability of hydrous minerals in subducting eclogitized crust: new experimental perspectives

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We have conducted experiments to study the phase equilibria of the basalt + H₂O system. The purpose of this work is to determine which hydrous phases are stable in the basaltic layer of a subducting slab and how deeply they may transport H₂O.

Previous experimental studies (Liu et al., 1996; Pawley and Holloway, 1993; Schmidt and Poli, 1998) reported contradicting results. It is possible that metastable growth of hydrous phases, such as chloritoid, occurred in the week-long runs of Schmidt and Poli (1998) as opposed to the month-long runs of Liu et al. (1996). For this reason, experiment duration for our study was either one week or one month for the same set of P and T conditions. Piston-cylinder experiments were undertaken between 2.2 GPa and 3.2 GPa at 650°C. Oxygen fugacity was buffered between 0.1 and 0.4 log units below NiNiO.

Our results show that a calcic amphibole (barroisite) is stable from 2.2 to 2.4 GPa. Above 2.4 GPa, it is replaced by a sodic amphibole (glaucophane) stable up to 2.7 GPa. Epidote is stable between 2.2 and 2.8 GPa. Chloritoid is present in week-long experiments between 2.6 and 2.8 GPa, but is not observed in the corresponding month-long experiments, except at 2.8 GPa and 650°C. At 3.0 and 3.2 GPa, neither chloritoid nor lawsonite are present in month-long experiments. Phengite is found in trace amounts from 2.2 to 3.2 GPa.

The stability field of chloritoid in our experiments is extremely reduced compared to Schmidt and Poli (1998). Metastability of chloritoid in some of their experiments is the most likely explanation for this difference, suggesting that chloritoid does not play an important role in the overall dehydration process in subduction zones.

Our results thus far show that no hydrous phases (except for trace amounts of phengite) are stable in the 3.0-3.2 GPa range at 650°C, implying that a slab following an intermediate P-T path would be completely dehydrated around 90 km depth.

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Metamorphic Monazite and the generation of P-T-t paths

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Monazite is fast becoming the mineral of choice for dating amphibolite- and granulite-grade metamorphism. The thermobarometric potential of monazite has also been recently realised with the generation of monazite-xenotime and monazite-garnet thermometers, which although complicated by assumptions of equilibrium, provide a suitable means of generating P-T-t points in a few restricted cases. In this contribution we discuss an additional, more widely applicable approach that allows a similar combination of monazite (and other U-Th bearing REE-phase) chronology with P-T.

A central aspect of the approach described here involves the chemical and textural characterisation of accessory minerals in a petrographic thin section. Simple textural relationships, such as included grains and grains restricted to rock forming mineral reaction zones, allow a first order link between accessory mineral chronology and P-T. Valuable additional constraints can also be generated through studies of accessory mineral chemistry. Monazite is particularly useful in this regard for two reasons. Firstly, metamorphic monazite appears to grow or recrystallise episodically throughout a metamorphic event, often over several millions of years. Secondly, the Y content of metamorphic monazite appears to reflect the abundance and stability of co-existing garnet; when garnet is absent or when garnet is breaking down, monazite tends to have a relatively high Y content (~2 wt%) and when garnet is growing monazite tends to have a relatively low Y content (~1 wt%). This feature is a consequence of garnets affinity for Y and can be used to link the ages of Y-distinct zones within single monazite crystals with P-T information.

By combining textural, chemical and in situ isotopic analyses of accessory minerals from a variety of orogens with P-T pseudosections (assemblage stability diagrams) we demonstrate how successful this approach can be in the determination of prograde P-T-t paths.

Ross Sea ^{226}Ra and Ba profiles measured by MC-ICP-MS.

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The measurement of ^{226}Ra in seawater has several potential applications in oceanography, particularly as a tracer of water masses and of groundwater input into the oceans (Moore, 1996). $^{226}\text{Ra}/\text{Ba}$ also shows potential for dating marine carbonates, but the seawater $^{226}\text{Ra}/\text{Ba}$ ratio must be known. The majority of work on ^{226}Ra in seawater has used radio decay methods such as alpha scintillation, but the poor efficiencies of radiation counters limit the precision of these measurements to about 5% (Chung, 1980), and requires a sample size of at least 20 litres. Atom counting methods such as mass spectrometry significantly reduce these limitations. Thermal Ionisation Mass Spectrometry (TIMS) has a uncertainty < 2% and requires only 40ml. However, TIMS analysis is time consuming and can be subject to organic interferences. We have developed and tested the use of multiple ion counting ICP-MS to analyse ^{226}Ra on seawater samples using a Nu instrument. We describe the potential and limitations of this approach and demonstrate that 2% (2_σ) uncertainty can be achieved on 120ml of seawater. Backgrounds across the Ra mass range are very low (<1cps) when using clean cones, but molecular interferences of ~100 cps appear on several masses if the cones are contaminated with Ba. This problem necessitates the chemical separation of Ra from Ba prior to analysis. Nevertheless, MC-ICP-MS is significantly less time consuming than TIMS.

Three water column profiles from the Ross Sea and Southern Ocean have been measured in order to assess the variability of $^{226}\text{Ra}/\text{Ba}$ in the Ross Sea and the open ocean. We measure a surface water ^{226}Ra concentration of 0.386 ± 0.014 fmol $^{226}\text{Ra}/\text{kg}$ in agreement with a value of 0.386 ± 0.0048 fmol $^{226}\text{Ra}/\text{kg}$ from the same sample analysed independently using TIMS. ^{226}Ra concentrations are relatively constant with depth, and are close to those in the open Southern Ocean measured at GEOSECS station 287 (Chung, 1980). Ross Sea $^{226}\text{Ra}/\text{Ba}$ ratios are also within error of those measured at station 287 (4.9×10^{-9} mol/mol). This similarity indicated that there is minimal discharge of ^{226}Ra into the Ross Sea, either by surface weathering or by groundwater discharge – a reassuring result for the use of Ra/Ba dating of carbonates in the area.

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Experimental determination of the stability of aluminum-borate complexes in hydrothermal solutions

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Boric acid is an important component of granite-derived fluids and thermal waters whose concentration, as measured in fluid inclusions, may reach 30 Wt% (Peretyazhko et al., 2000). To check for the formation of Al-borate species, similar to aqueous Al-silicates, a series of experiments was performed including a ^{27}Al NMR spectroscopy study at 25°C, and gibbsite and boehmite solubility measurements from 50 to 200°C. ^{27}Al spectra performed at pH=9 in Al-B solution with $m(\text{B})=0.02$ show the presence of two peaks at 80.5 and 74.5 ppm which correspond to $\text{Al}(\text{OH})_4^-$ and a single Al-substituted Q_{Al}^1 dimer, respectively. When $m(\text{B})=0.02$, a third peak appears at 69.5 ppm which can be assigned to the Q_{Al}^2 trimer. The observed chemical shifts are close to those of the Al-Si dimer and trimer (74 and 69.5 ppm, respectively; Pokrovski et al., 1998) which demonstrates the chemical similarity of Al-B and Al-Si complexes. Gibbsite and boehmite solubility was measured in weakly basic solutions as a function of boric acid concentration. Equilibrium solubility was reached within several days at $m(\text{B})=0.01-0.1$, but Al concentration increased continuously at $m(\text{B})=0.2$ due to the formation of Al-polyborates. The constant of the reaction $\text{Al}(\text{OH})_4^- + \text{B}(\text{OH})_3^0_{(\text{aq})} = \text{Al}(\text{OH})_3\text{OB}(\text{OH})_2^- + \text{H}_2\text{O}$ decreases very slowly with increasing temperature to 200°C. The log K values deduced from the solubility measurements in $\leq 0.1\text{m}$ H_3BO_3 solutions are 1.58 ± 0.10 , 1.50 ± 0.15 , 1.50 ± 0.20 , and 1.25 ± 0.10 at 50, 78, 150, and 200°C, respectively. These results demonstrate that in a solution containing ~0.5g/l of boron at 400°C and 0.5 kbar, $\text{Al}(\text{OH})_3\text{OB}(\text{OH})_2^-$ accounts for ~50% of total aluminum. At boron concentration >1g/l the formation of Al-polyborates may considerably increase aluminum transport capacity of hydrothermal fluids. *This study was supported by CNRS and RFBR (grant 01-05-64675 to BT).*

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The climatic control of weathering in the Himalayan river system

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Physical erosion tends to favour weathering because it increases reaction surfaces in river basin. For most rivers, a rough positive correlation can be observed between chemical and physical erosions which suggests that physical erosion may exert a first order control on global weathering. Nevertheless, the Himalayan rivers, which have the highest rate of physical erosion among the major river systems, are not characterised by a remarkably high rate of chemical erosion. Depending on numbers accepted for the annual flux of sediment load, chemical erosion for the Brahmaputra and Ganga is between 3 and 7% in mass of the total erosion. Several factors explain this relatively low proportion including precipitation and transport dynamic. The comparison between the Brahmaputra and the Ganga drainages which have quite contrasted runoff (1.1 and 0.6 m/yr respectively) allow to test the importance of precipitation or runoff and transport on the efficiency of weathering in such basin undergoing very intense physical erosion.

Carbonates represent the major source of dissolved ions representing 80 to 90 % in mass of the dissolved load of the rivers. The Ganga and most of its tributaries are over-saturated with respect to carbonates and the rivers transport up to 10% of carbonate particles in their suspended load. On the contrary, the Brahmaputra carries no particulate carbonates and is under-saturated in the Assam floodplain. Carbonate particles are however carried by the tributaries including 5 % in the Tsangpo-Brahmaputra but they disappear from the sediment load of the Brahmaputra over few tenth of km in the plain. It is likely the high precipitation over Eastern Assam (5 m/yr) which allow this very efficient carbonate dissolution. Precipitation therefore acts as the controlling factor for carbonate dissolution. They are insufficient in the Ganga basin to dissolve all the particles released by erosion.

Chemical erosion of silicates is low when compared to physical erosion as it represents less than 1 % of the total erosion for both Ganga and Brahmaputra. Taking into account only Na, K and Si which are unambiguously released by silicate weathering, the specific chemical erosion of silicate is double for the Brahmaputra than for the Ganga basin. This difference is even higher if we do remove the Tibetan area of the Brahmaputra where erosion is minor. Examined in detail, chemical erosion of silicate is strongly correlated to local runoff and suggests that it is strongly controlled by precipitation rather than by physical erosion.

The Role Of Metasomatising Fluids In The Genesis Of Orogenic Magmas. A Case Study From Sardinia, Italy

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Miocene High MgO Basalts (HMB) from Montresta (N Sardinia) and Mt. Arcuentu (S Sardinia) have been analyzed with the aim of identifying the physical state of the metasomatizing agents in the mantle wedge. These rocks represent near-primary mantle melts likely not interested by crustal contamination. They show typical subduction-related trace element features: LILE (Large-Ion Lithophile Elements) enrichment relatively to LREE (Light Rare Earth Elements), with Ba/La ranging from 10 to 23. LILE and LREE are both enriched relative to NMORB-like HFSE (High Field Strength Elements).

⁸⁷Sr/⁸⁶Sr ratios range from 0.70399 to 0.70631; ¹⁴³Nd/¹⁴⁴Nd ratios ranges from 0.51260 to 0.51274 and ²⁰⁶Pb/²⁰⁴Pb from 18.609 to 18.707, ²⁰⁷Pb/²⁰⁴Pb from 15.619 to 15.661 and ²⁰⁸Pb/²⁰⁴Pb from 38.408 to 38.747.

Sr, Nd and Pb isotopic data of Sardinia orogenic basalts indicate that, in addition to the input of fluids from altered subducted oceanic crust in mantle wedge, a further component from subducted oceanic sediments is to be considered. In order to constrain if subduction components are mainly fluid or melt phases, ratios among trace elements with strongly different solid/fluid and solid/melt partition coefficients (i.e. Th/Pb, Th/Nd and Sr/Nd) have been taken in consideration. Models based on elemental (Nd/Pb) and isotopic ratios (⁸⁷Sr/⁸⁶Sr and ²⁰⁶Pb/²⁰⁴Pb) indicate that small amounts of subduction fluid components in mantle wedge can account for the geochemical and isotopic features of Sardinia basalts.

In fact, mantle source of Mt. Arcuentu magmas can be modeled considering an enrichment of a DMM source by about 0.45% MORB fluid (derived from subducted oceanic crust) and 0.05-0.08% sediment fluid; for Montresta mantle wedge the amount of subduction components is about 0.1% MORB fluid and 0.03-0.04% sediment fluid. Such low values are consistent with the lack of negative Eu anomalies. It is noteworthy that, on the basis of Sr and O isotopic modeling, other authors proposed a much larger contribution of oceanic sediments (the same utilized in this work) (2-10%) for the Mt. Arcuentu basalts.

Paleoproductivity reconstruction: The on-going quest for a quantitative geochemical tracer

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The export of organic carbon from surface to deep water is one of the key aspects of the global carbon cycle controlling atmospheric CO₂ and the earth's radiation balance. A full understanding of the influence of greenhouse warming on secular changes in global climate thus requires the accurate reconstruction of this variable from the sedimentary record.

The residual organic carbon that is buried after reaching the seafloor is inadequate for this purpose, because of poor and variable preservation. Instead, indirect methods, which use geochemical or micropaleontological parameters that can be related to primary production, have been explored. In general, the main advantage of these tracers is better preservation of the productivity signal; the main drawback is that other processes, which may or may not be related to productivity, also affect this signal. One can attempt to mitigate this problem by combining different tracers of productivity that are influenced by different secondary processes, but we have yet to obtain a fully constrained system using this approach and it is becoming increasingly clear that one cannot expect to find a simple method of paleoproductivity reconstruction that would be universally applicable. Instead, different proxies will have different domains of applicability and it behooves us to clearly understand and define the limits of these domains. I will briefly review recent developments that have changed our views on the applicability of two geochemical tracers, sedimentary biogenic Ba accumulation rates and ex.²³¹Pa/ex.²³⁰Th, which were initially viewed as very promising and broadly applicable. As we gained a better understanding of their geochemistry, this initial optimism has given way to a more cautious approach towards their use for paleoproductivity reconstruction. While it is now clear that they cannot be used indiscriminately, however, they could still provide useful quantitative information under a more restricted set of environmental conditions.

Modelling the Cenozoic evolution of atmospheric CO₂

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In recent years, paleolevels of atmospheric CO₂ during the Cenozoic have been estimated from various proxy records, such as the ¹³C isotopic composition of marine organic matter (Pagani et al., 1999), the seawater pH recorded in boron isotopes (Pearson and Palmer, 2000; Lemarchand et al., 2000) and the stomatal density/index of fossil leaves (Royer et al., 2001). These proxy-based reconstructions provide Cenozoic evolutions of atmospheric CO₂ between two extreme scenarios: (1) CO₂ decreased from very high levels (2000-4000 ppmv) in the Paleocene-Eocene to present or lower than present values in the Miocene-Pliocene, (2) CO₂ remained relatively constant throughout the Cenozoic.

Here we present a coupled model of the carbon and boron cycles. This model includes four carbon reservoirs (ocean-atmosphere, shelf/continental carbonates, pelagic carbonates and crustal organic carbon) for which carbon content and isotopic composition are calculated. A budget is also established for ocean alkalinity, ocean boron and its isotopes. A sub-model of the ocean-atmosphere system allows a redistribution of carbon and alkalinity among the atmosphere, the surface and deep ocean reservoirs. This sub-model calculates explicitly carbonate chemistry, pH, calcite and aragonite lysocline depths, as well as discrimination of carbon and boron isotopes in physical, chemical or biological processes. Surface temperature is related to atmospheric pCO₂ through a simple parametric law.

Various weathering rate laws or scenarios of spreading rates through time are tested with this model. Organic carbon deposition is derived from the δ¹³C of ancient seawater. It is shown that it is possible to produce simulations which are broadly consistent with a variety of proxy records, such as calcite compensation depth, ¹³C isotopic fractionation of marine biology and boron isotopes changes through the Cenozoic. Interestingly, in such reconstructions, Miocene levels of atmospheric CO₂ tend to be smaller than today.

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The Behaviour of ^{10}Be and ^9Be in the Arctic Ocean: Relationship to water mass distribution and particle flux

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The Arctic Ocean basin is confined by landmasses similar to the Mediterranean. There is only little deep water formed seasonally on the shelves of the Arctic Ocean despite the low temperatures. This is due to a freshwater lid at the surface which originates from the Arctic rivers. The deeper Arctic Ocean water masses can thus only be renewed at comparatively low rates through the only deep connection to the Atlantic Ocean, the Fram Strait. At the same time the biogenic particulate fluxes in the central Arctic Ocean are very low due to perennial sea ice cover and the organic matter produced in the surface waters is remineralised efficiently. Detrital particle fluxes from either eolian or riverine sources are also very low.

The distribution of particle-reactive natural radionuclides, (^{230}Th , ^{231}Pa) indicates differences in scavenging behaviour between the Canadian and Eurasian parts of the Arctic Basin, possibly due to different ventilation ages or lateral advection of particulate material from the shelves.

We will present the first combined dissolved ^{10}Be (cosmogenic) and ^9Be (continental sources) depth profiles from water samples of the major deep basins of the Arctic Ocean collected during the Swedish Arctic Ocean 2001 expedition. Be is 5-10 times less particle-reactive than Th or Pa and should therefore even at the low Arctic Ocean renewal rates serve as a quasi-conservative tracer for different origins of water masses (Atlantic Ocean/Norwegian Sea, Pacific Ocean, Arctic Shelves). ^9Be and Nd isotope analyses will provide complementary information on the pathways of dissolved material originating from the Arctic continents.

First results from near Svalbard indicate uniformly low ^{10}Be concentrations (500 atoms/g) over different water masses in the Eurasian part of the Arctic Basin. This suggests either small differences in initial ^{10}Be content of the mixed water masses or homogenisation through vertical processes.

Production and Isolation of Phytosiderophores

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The solubility of iron, a micronutrient, is far below the concentrations required by plants in well-aerated soils at circum neutral pH. Therefore, plants have developed two mechanisms to increase iron solubility so that it can be taken up by the root system. These mechanisms have been termed strategy I and strategy II. The strategy I mechanism relies on such mechanisms as the reduction of ferric iron to the more soluble ferrous state, excretion of protons from the roots, or the excretion of organic acids from the roots to increase iron solubility. The strategy II mechanism uses phytosiderophore (PS) to dissolve ferric iron in an analogous way to that of microbes who produce siderophores as an iron acquisition strategy--though this mechanism likely evolved independently between plants and microbes. PS are low-molecular weight, organic, hexadentate ligands of the Mugineic acid family (e.g. Fig. 1) that are secreted by the roots of some graminaceous

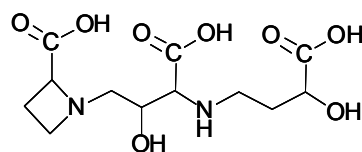


Fig.1 Mugineic Acid

plant species.

Although PS are characterized by their high affinity for Fe, these compounds also have high stability constants for other metal ions. Therefore, the specificity for this efficient iron acquisition strategy is thought to result from transporters that recognize iron-PS complexes and transport them across the plasma membrane, while excluding other metal-PS complexes. However, PS may influence the mobility of other metals in soils despite their irrelevance in plant nutrition.

Presently, studies of plant physiology regarding PS and the environmental significance of PS are hindered by a lack of PS reference material. The synthesis of PS and their isolation from root exudates are both rather involved procedures. In this presentation we will discuss details about the PS isolation procedure and how PS are involved in processes such as the ligand-promoted dissolution of iron hydroxides, the dissolution of precipitated actinides, and the adsorption of actinides to precipitated phases.

Mass Bias in ICP mass spectrometers

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It is well known that the uncorrected isotopic ratio measured using ICP mass spectrometers differs from the true value in a time independent manner. Experimentally it has been shown in high precision studies using multiple collector magnetic sector instruments that the following formula often applies:

$$\frac{\text{True Ratio}}{\text{Observed Ratio}} = \left[\frac{M_1}{M_2} \right]^\beta$$

with the value of β being close to 2.

We suggest that the origin of this mass bias arises from two parts, each contributing a factor of one to the beta value. The first part comes from the supersonic expansion process at the sampler, and the second from the space charge repulsion at the rear of the skimmer, in the region where the ions experience their initial electrostatic acceleration.

During the supersonic expansion process in the sampler's throat, the ion's forward motion is converted into a narrow velocity distribution, centred at a common value, equal to the velocity of the bulk argon carrier gas. The transverse velocity distribution is also narrowed, but the average velocity in this direction maintains the normal mass dependent variation. The higher transverse speeds for the lighter ions results in the lower transport efficiency of these species to the next stage of the instrument interface.

Since the distribution of the species in the expansion cone at the rear of the sampler maintains a memory of the distribution in the flame (for standard geometry's) the mass bias will alter as the torch position is changed. Similarly different elements will be ionised differently in the flame, resulting in differing spatial ionic distributions. This can result in minor variations in beta values between elements.

If no charge separation occurred at the skimmer, the transmitted ions would continue in an extremely narrow cone into the mass spectrometer, defined by the geometry of the sampler and skimmer orifices. However, the extraction voltage on the first ion optical element repels the electrons in the plasma, and accelerates the ions. These ions then experience a mutual repulsion, in this region of low acceleration potential. The heavier ions, which have a higher energy (since the forward velocity of all the species present is the same), will experience less repulsion than the lighter ions. This results in the second major contribution to the mass bias. It is to be expected that it should be possible to design an interface such that this repulsion is kept at a low enough level so that all ions which pass through the skimmer tip are transmitted into the mass spectrometer. In such a case, the overall beta value would approach unity.

Re-Os, Sm-Nd isotope- and REE systematics on komatiites and pillow basalts from the Earth's oldest oceanic crustal fragments (Isua Supracrustal Belt, W Greenland)

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Komatiites and pillow basalts from the Western and Northwestern sector of the Isua Supracrustal Belt (ISB) reveal a complex pattern of trace elements, mainly with respect to their rare earth elements (REE). The heterogeneity of LREE patterns, in combination with widely scattering $\epsilon\text{Nd}[T=3.81 \text{ Ga}]$ values, indicate that the REE systematics of the samples were disturbed by one (or more) metamorphic events which took place some considerable time after the original crystallization of the Isua belt. Furthermore, LREE-rich metasomatic fluids associated with the emplacement of tonalites into the supracrustals may have significantly altered the primary trace element budget. Extreme variations in whole rock $\gamma\text{Os}[T=3.81 \text{ Ga}]$ values of these rocks are favorably interpreted to derive from major metamorphic losses of Os, rather than from Re additions during fluid hydrothermal alterations. In contrast, the Re-Os isotope system remained intact in komatiite-hosted chromites from Isua and an average $\gamma\text{Os}[T=3.81 \text{ Ga}]$ value of $+1.3 \pm 0.9$ indicates that these komatiites were derived from a mantle source with a time-integrated slightly suprachondritic Re/Os ratio. Our data are the first to show early Archean mantle rocks with radiogenic initial $^{187}\text{Os}/^{188}\text{Os}$ isotopic compositions. Our data do not allow to further impinge on the petrogenesis of the ISB mantle-derived rocks. Similarities of unaltered pillow basalts with Phanerozoic boninites (Polat et al., 2002) may indicate a formation in an intra-oceanic subduction zone like geodynamic process, in which extreme early (Hadean?) depletion of a mantle source by melt extraction was followed by a second stage of melting induced by enriched subduction components. Alternatively, core-mantle interaction as a plausible mechanism for the ^{187}Os enrichments in these rocks remains a valid hypothesis.

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Fluid evolution and mineralogy during multi-stage hydrothermal alteration of quartz-depleted granites (episyenites)

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Episyenites are quartz-depleted granitic rocks that have the chemical composition similar to syenites. Episyenites do not have a magmatic origin, but are formed through late-magmatic to subsolidus alteration. In the German Fichtelgebirge, episyenites are known from several localities, forming spatially restricted lensoid to pipe-shaped bodies within Hercynian granites. Frequently, quartz-depletion is associated with, or subsequently followed by polyphase alteration of different types (albite, chlorite, sericite, hematite, fluorite, pyrite, stilbite and secondary quartz). Episyenites may even be associated with U-, Au- or Sn-W-mineralization. Although dissolution of quartz produces a porous rock, former magmatic textures are generally well preserved. Cavities are filled with later formed minerals, including chlorite, quartz and calcite. Sharp contacts between the altered rock and the fresh granite are characteristic. Sometimes there is a small transition zone with corroded quartz. Outside the quartz-depleted zone, large alteration halos are developed (e.g. chloritization), in which no quartz dissolution is observed.

The geochemical mass transfer during episyenitization is mainly characterized by the depletion of Si, but almost all major and trace elements may show large mobility (including REE), depending on the associated and subsequent alteration type. Chlorite geochemistry shows decreasing Fe and Al^{IV} from early to late chlorite, which correlates with decreasing temperature. Fluid inclusion studies indicate that aqueous fluids causing quartz dissolution have relatively low salinities, but high homogenization temperatures (Th) with a minimum T of 200 to 300°C. Fluids causing later alteration phenomena have higher salinities and lower Th.

Discussion of quartz dissolution conditions must include changes in T, P, pH and fluid salinity, because silica solubility strongly depends on these parameters. A silica undersaturated fluid is necessary for quartz dissolution within granitic rocks. For most natural hydrothermal conditions, increasing pH, T, P and salinity leads to an increase in silica solubility. However, under low pressure, silica solubility increases slightly with decreasing temperature (above the critical point of water). The timing of quartz dissolution in relation to the emplacement of the host granitic rocks is still a matter of debate.

High precision U-series isotope measurements of East Scotia back-arc basalts using single-collector sector-field icp-ms

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²³⁸U-²³⁰Th disequilibrium data are particularly useful to examine the process of recent (< 350 ka) fluid input from the subducting slab into the mantle source of arc lavas. Most island-arc lavas show (²³⁸U/²³⁰Th) > 1 which has been attributed to addition of an U-rich slab derived fluid to their mantle source. Very limited data exists for the U-series isotopic composition of back-arc magmas. Because of the transitional character of most of the back-arc basalts from MORB to arc-like it is not clear if recent fluid input will dominate to control the ²³⁸U-²³⁰Th disequilibrium in the melts.

Here we present high precision U-series isotope data of an active back-arc spreading center, the East Scotia Ridge, determined with a newly developed procedure using sector-field inductively coupled plasma mass spectrometry (ICP-SFMS, Micromass PlasmaTrace 2) coupled with a desolvating micro-nebulizer sample introduction system (Cetac MCN 6000 with PFA spraychamber). The procedure involves conventional ion-exchange column separation with ²²⁹Th and ²³⁶U spikes. In general, the abundance sensitivity is critical for accurate determinations of ²³⁰Th/²³²Th ratios which are very low in rock samples (10⁻⁶). The continuously adjustable mass resolution of the PT2 instrument is advantageous for compromising abundance sensitivity (< 3 x 10⁻⁷ at 1100RP) with maximum transmission. Ionization efficiency (ions counted/ions introduced) is up to 1% (for U at 400RP) allowing precise measurements of ²³⁰Th/²³²Th with ± 2.5 (5) ‰ (2_) for 0.1 (0.01) pg ²³⁰Th. Linear working-range of the detector and wash-out protocols had to be carefully optimized to avoid analytical bias. Results for international rock standards show good accuracy within the error of accepted values ((²³⁰Th/²³²Th): TML 1.079 ± 0.008, JB-1 0.552 ± 0.006, AGV-1 0.921 ± 0.016).

The isotope ratios of the East Scotia Ridge lavas span a range in (²³⁰Th/²³²Th) and (²³⁸U/²³²Th) larger than reported of any other individual back-arc region. Most of the back-arc lavas have lower (²³⁸U/²³⁰Th) < 1 and are thus similar in composition to mid-ocean ridge basalts (MORB). Lavas from the centre and southern part of the back-arc have high (²³⁸U/²³⁰Th) ≥ 1, implying a recent addition of a U-rich slab-derived fluid.

Fluorescence Spectroscopic and Chromatographic Evidence for the Interaction of NOM and Metal Ions

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Introduction

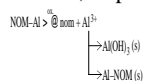
The presence of natural organic matter (NOM) in aquatic systems can strongly effect the transport of metal ions. Little is known about the influence of oxidation processes on the NOM complexing properties. As an example, the influence of photooxidation on the stability of NOM–Al complexes was investigated. The NOM sample originates from a brown water lake (Lake Hohloh, Northern Black Forest, Germany).

Experimental

The interaction of NOM and metal ions can be characterized by fluorescence spectroscopy and size-exclusion chromatography (SEC) coupled with inductively-coupled plasma mass spectroscopy (ICP-MS). Fluorescence spectroscopic techniques allow a non-destructive investigation of the metal-NOM system. Coupling of SEC and ICP-MS gives information about molecular sizes, metal distributions, and the metal mobility.

Results

At the beginning, fluorescence intensities of the NOM samples increased with increasing duration of irradiation due to cleavage of NOM molecules. Progressing irradiation and mineralization of NOM finally led to decreasing fluorescence intensities. The fluorescence signals in SEC chromatograms showed a shift towards higher elution volumes for the oxidized samples. The shift is probably attributed to the formation of smaller molecules (nom). A decrease of NOM–Al complex formation due to oxidation of NOM could be found. A shift of the Al signal towards higher molecular weight compounds indicates the formation of Al hydroxides and/or Al–NOM colloids, as pictured in the following reaction scheme:



Results of Pb and Zn will also be discussed.

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Dissolution experiments and natural weathering of carbonates.

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The rate of dissolution of natural dolomite and calcite, which show similar rates of weathering in the outcrops, were investigated using free-drift experiments on samples for which physico-chemical properties had been determined by scanning (SEM) and transmission (TEM) electron microscopy, EDS and ICP-AES. The surface morphology and grain-size of ground particles prior to, and after the experiments were observed by SEM, and compared with karst spring suspended sediment and naturally weathered surfaces. The experimental conditions were pH = 5.16, and T = 25°C, particle size $\phi = 90 \mu\text{m}$. Samples were precleaned in a sonic bath, and slightly acidified. The Solution pH and chemistry were measured at fixed intervals. Reactions approached steady-state after 21 hours for the limestone, and 27 for the dolomite.

Pre-reaction dolomite grain size distribution ranged from < 10 μm to 90 μm , in the same range as those of suspended sediments. Grain surfaces had ledges, macrokinks and original etch-pits. Pre-reaction calcite grains-size distribution was 90 μm , and grains had smooth surfaces. The dolomite reaction rate was more rapid than that of the calcite in the first 20 hours. After 1 hour, 0.203 mol. Ca and 0.200 mol. Mg were released to the solution by dolomite, and 0.046 moles Ca were released in the limestone reaction. Only after 22 hours, were the dissolution rates of calcite and dolomite similar. Post-reaction dolomite grain surfaces show the development of etch pits located along ledges and structural defects, and deepening and intersection of original etch pits. Post-reaction calcite grain surfaces show the development of ledges, etch-pits located along twins and cleavage planes, and preferred dissolution at subgrain boundaries, as observed in naturally weathered specimens.

The rates of dissolution seem to be affected by the original surface morphologies, and the distribution of defects. Pre-reaction dolomite grains had rugged surface morphology resulting from outcropping defects (ribbon microstructures, dislocations), and high surface/volume ratio in the smaller size-fraction. Pre-reaction calcite was almost defect-free, and had less reactive sites. Average grain surface/volume ratio was smaller than in the dolomite. Higher surface/volume ratio, and number of reactive sites are probably the cause of the initial, rapid dissolution rate for the dolomite. Dissolution rate of calcite reached that of dolomite (and then became faster) once a large number of ledges were exposed to the solution during the reaction. Experimental results are consistent with the physico-chemical properties of waters from aquifers that develop in the two carbonates of the present study.

The oxidation state of iron in the lower mantle

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Determining the redox state of the lower mantle is important because it will influence processes, such as chemical diffusion, electrical conductivity and volatile speciation. Using a multianvil apparatus we have measured the partitioning of Fe²⁺, Fe³⁺ and Mg²⁺ between magnesiowüstite and magnesium silicate perovskite in both Al₂O₃-bearing and Al₂O₃-free systems under variable redox conditions. In the Al₂O₃-bearing system perovskite Fe³⁺/ΣFe ratios are as high as 80%, which is over 3 times greater than for Al₂O₃-free perovskite. The variation in the Fe³⁺ solubility with the Al³⁺ content of perovskite is non-linear.

If, as some previous studies have indicated, the influence of Al on the Fe³⁺ content of perovskite is indeed independent of the oxygen fugacity, then for a typical mantle Al₂O₃ content of 4 wt %, silicate perovskite in the lower mantle would have an Fe³⁺/ΣFe ratio of approximately 70% and a bulk peridotite would have an Fe³⁺/ΣFe ratio of 50 %. Upper mantle xenoliths suggest an average mantle Fe³⁺/ΣFe ratio no higher than 3%, however, which would infer one of two possible scenarios for the lower mantle. Either the lower mantle contains more Fe³⁺ i.e. more oxygen, than the upper mantle or lower mantle perovskite must sequester oxygen by reducing vapour phases and through the precipitation of metallic Fe. As the vapour content of the mantle can account for only a minor proportion of the required oxygen the only feasible mechanism would be the disproportionation of FeO to produce approximately 1 wt. % metallic Fe. This metallic phase would also be supplemented by other siderophile elements. We have made a number of experiments in the presence of metallic iron in order to test this possibility. We also compare these results with analyses of inclusions found in diamonds which are considered to have formed in the lower mantle.

REE pattern of carbonaceous part of coals: a new proxy for the original plants of coals

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Introduction

It is generally thought that most coals are originated from trees and peat, and some of them are from algae. However, the inference of the original plants is sometimes a difficult problem. The study on REEs in coals is expected to provide us with some knowledge about the original plants of coal.

Experiment

Coal samples of the Taiheiyu coal mine, the Ashibetsu, the Ambalut coal mine, and boghead coal were collected in this study. Each sample was divided into carbonaceous part and mineral part by treating ashed coal with 10 % acetic acid solution. REEs in each part were determined with ICP-MS.

Discussion of results

The chondrite-normalized REE patterns of the carbonaceous part of all the coals can be classified into three types. The Ashibetsu coals, the Taiheiyu coals and some of the Ambalut coals are type I, which is featured with a medium slope and no depletion in Ce (no Ce anomaly). The others of the Ambalut coals are classified into type II, which is characterized with a steeper slope (greater LREE/HREE ratio) than type I and a Ce negative anomaly. The boghead coal was classified into type III, which is featured with a smaller slope than type I and a Ce negative anomaly. Compare with the extents of the Ce anomaly and slope of the pattern of plants we have surveyed so far, we can infer that coals classified into the type I, type II, and type III are originated from peat vegetation, trees and seaweed, respectively. This correspondence is consistent with the result of maceral study.

Conclusions

The REE pattern of the carbonaceous part in coals is shown to be a good proxy for the original plants to be coalified.

Acknowledgment

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Rb-Sr isotopic dating and its genetic significance to the Manaoko gold deposit, NW-Sichuan, China

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Introduction

The Manaoko deposit, hosted in Triassic turbidites, is a typical micro-disseminated gold deposit. With respect to its genesis, different models have been advocated. However, there is still much controversy about the timing of mineralization.

Mineralization at Manaoko occurs commonly as sheetlike bodies with distinct layering that is consistent with bedding of the host rocks. Main ore minerals include pyrite, realgar, stibnite, and arsenopyrite.

In order to constrain the timing of mineralization, Rb-Sr isotopes were measured for fluid inclusions in quartz.

Results and discussion

Rb and Sr contents in five quartz samples range from $0.731\text{-}2.702 \times 10^{-6}$ and $2.590\text{-}16.700 \times 10^{-6}$, respectively. The calculated $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values vary between 0.433-1.765 and 0.71010-0.71387, respectively. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the fluids (0.7085) is consistent with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater (0.7090). The data outline an isochron age of 210 ± 11 Ma.

The Rb-Sr isotope data show that gold mineralization at Manaoko is coeval with deposition of the host sedimentary rocks. It is thus suggested that submarine sedimentary exhalative processes were responsible for formation of the deposit, accompanied by deposition of the host turbidites. Gold and associated metals were introduced by episodic exhalation of metalliferous basinal brines.

Conclusions

The timing of gold mineralization at Manaoko is consistent with deposition of the Triassic turbidites. The deposit is defined to a sedimentary exhalative (sedex) type and is similar to the recently discovered gold occurrences in the Carlin trend (Emsbo et al., 1999).

Acknowledgments

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Sorption of As(V) on schwertmannite and its effect on the transformation

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Introduction

At abandoned arsenic mine in Nishinomaki, Japan, water discharged from mining and waste dump area is acidic and rich in arsenic. However, arsenic in the drainage is naturally attenuated due to the sorption by the ochreous precipitates, mainly composed of schwertmannite. In the present study, synthesized schwertmannite were prepared and served for the batch sorption experiment in order to examine the mechanism of arsenate sorption. Moreover, the alteration experiment of the specimen with different arsenate content was performed to determine the role of arsenate sorption on transformation of the schwertmannite in order to understand the long-term behavior of arsenic sorbed into schwertmannite.

Experimental methods

Sorption of arsenate in the schwertmannite suspension was examined as a function of arsenate concentrations (10^{-7}M ~ 10^{-3}M). The suspension pH was adjusted with HNO_3 to 3.2~3.4. After 24 hours, the suspensions were filtered. The solutions were provided for the analysis of Fe, As and sulfate. The reacted solids were examined by infrared spectroscopy.

The samples contained arsenate of 0~1.0 mmol/g were prepared by the batch sorption procedure. The samples were spread onto the glass slide, dried and then placed on the airtight containers in which condition was kept vapour pressure at 50 °C. The samples after aging were characterized by X-ray diffractometry.

Results and discussion

The result of arsenate sorption experiment showed that schwertmannite sorbed arsenate up to 80 mg/g, and that the structural sulfate in schwertmannite was released to solution in response to the arsenate uptake. The result of alteration experiment showed that the schwertmannite with little arsenate transformed to crystalline iron phase after a week. On the other hand, no change in XRD patterns was observed in the samples with much amount of arsenate. The difference indicates that the transformation of schwertmannite is significantly retarded by arsenate sorption. By inhibition of the transformation, the attenuation process of arsenic in ochreous precipitates is irreversible in overall and expected to be maintained for long-term.

Reaction zones and composite veins around the metamorphosed basic dykes in the Hirao limestone, Fukuoka, Japan.

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This paper describes petrography and mass transfer analysis of the reaction zones and composite veins around the basic dykes in the Hirao limestone both of which are thermally metamorphosed by the Hirao granodiorite (Cretaceous). Reactions between the basic dykes and the limestone due to the contact metamorphism lead to the development of the reaction zones between them and the composite veins which were derived from the reaction zones by hydrofracturing and mass transfer along the fracture (Nishiyama, 1989). The peak condition of the contact metamorphism is estimated as T=650-700 °C and P<500MPa, based on thermodynamic analysis of metamorphic reactions in the Tagawa metamorphic rocks underlying the Hirao limestone.

The reaction zones consist of three zones: diopside zone, garnet zone and wollastonite zone in this order from the metabasite dyke towards the crystalline limestone. Dominant mineral assemblages of the rocks are; metabasite: biotite + diopside + plagioclase, diopside zone: diopside + plagioclase, garnet zone: grossular + plagioclase, wollastonite zone : wollastonite, and crystalline limestone : calcite. In plagioclase albite lamellae are observed in the matrix of Ab₆₂₋₇₆ plagioclase, of which compositional gap corresponds to the peristerite gap, indicating the reequilibration at approximately 400 °C. The total reaction leading to the development of the reaction zones can be modeled as:

biotite + calcite + plagioclase =
diopside + garnet + wollastonite + K₂O + 5Na₂O + 33CO₂ + 2H₂O

We employed the steady diffusion model (Joesten, 1979) to analyze the stability condition of the zonal sequence and to get exchange cycles, ignoring conservation of fluid species. As a result, the stability of the observed zonal sequence depends on $L_{\text{SiO}_2\text{SiO}_2}/L_{\text{Al}_2\text{O}_3\text{Al}_2\text{O}_3}$ and $L_{\text{SiO}_2\text{SiO}_2}/L_{\text{CaO}\text{CaO}}$ but not on $L_{\text{SiO}_2\text{SiO}_2}/L_{\text{MgO}\text{MgO}}$.

A composite vein consisting of garnet, plagioclase and wollastonite comes out from the reaction zones. The vein is rich in garnet near the reaction zones and rich in plagioclase at a distance of 2meters. This change in mode may reflect the relative magnitude of diffusivity of Al₂O₃ against that of SiO₂.

The continuous growth of aqueous aluminum nanoclusters

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Introduction

The geochemistry of aluminum in natural waters and soil has been debated for decades, mainly with respect to the formation of polynuclear species and hydroxide minerals. However, it is accepted now that the tridecameric molecule AlO₄Al₁₂(OH)₂₄(H₂O)₁₂⁷⁺(aq), known as Keggin Al₁₃, can form spontaneously in acidic waters from acid-mine areas or poorly buffered soil receiving acid rain mixes with neutral surface waters (Casey et al., 2001). For many years it was thought that the tridecameric nanoclusters in aqueous solutions is decomposed rather fast and that in a first step amorphous and then crystalline aluminum hydroxide solids are formed.

Discovery

Our new findings from long-term storage experiments confirmed these assumptions, however only partially. Five slightly acidic bulk solutions containing 7 mM Al₁₃ were stored on an office desk during 11 years at room temperature, gas tight but exposed to day light. In four glass containers the solutions were still fairly clear and about 95 % of the total Al(III) has been transformed into the larger nanocluster (AlO₄)₂Al₂₈(OH)₅₆(H₂O)₂₄¹⁸⁺(aq) (Al₃₀), which contains 30 Al(III) and bears an even higher charge (18+). In one glass container the solution became very milky; approximately 30 % of the total Al(III) has been transformed into crystalline gibbsite and the other 70 % into the Al₃₀ nanocluster. The chemical structure of the Al₃₀ nanocluster has just recently been resolved (Alloche et al., 2000; Rowsell et al., 2000).

Conclusion

So far it was thought that elevated temperatures were necessary for the synthesis Al₃₀ molecule. Our finding shows that the Al₃₀ nanocluster forms spontaneously in aqueous solutions of Al₁₃ even at ambient conditions. Since this process seems to have a time constant of a couple of years, we might find even larger aluminum nanoclusters one day.

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Multicomponent inverse modelling in aquatic sediments

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A comprehensive understanding of chemical mass transfer in aquatic sediments requires a comprehensive tool capable of deconvoluting all major processes that are heavily interrelated. Multicomponent reactive transport modelling can be the comprehensive tool when reaction and transport parameters are adequately constrained through a sufficient number of observations and prior knowledge of their interdependency. In the present study, a multicomponent inverse model written in Matlab was applied to a saltmarsh environment heavily affected by vegetation and bioturbating organisms, located in Skidaway Island, Georgia, USA. Depth profiles of most major redox species were directly measured, and transport parameters were determined using porosity profiles (for diffusion coefficients) and the relationship between ³⁵S-determined sulfate reduction rates and pore water sulfate concentration profiles (for irrigation coefficients). Consequently, the multicomponent inverse model could be used to quantify the reaction rates. The results indicate that within the upper few millimetres of intertidal sediments, carbonate mineral precipitation takes place during the low tide periods generating small pH maxima in the immediate vicinity of sediment surface. The results also show that the *in situ* rates of iron (III) reduction determined through modelling are comparable to the rates obtained by the *ex situ* incubation procedures. Inverse modelling of reaction rates can be especially useful where forward modelling with *a priori* application of rates is difficult due to complex reaction geometry and/or rapid recycling of redox species.

