The dissolution of hydrogen and carbon in reduced silicate melt

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The transport of volatile constituents from planetary interiors to surfaces provides the primary supply of material for the upper layers of the Earth and atmospheres. The major factor controlling that transport is the solubility of volatile species in magmas and the oxido-reduction evolution of the magma relative to their mantle sources. The iron-bearing silicate melt (ferrobasalt) + iron metallic phase + graphite + hydrogen equilibrium have been considered in this study to demonstrate that the carbon and hydrogen solubility in melt may have important implications for the formation of volatiles in terrestrial magmas. The experimental conditions (3.7 GPa, 1520 -1600°C) and hydrogen and oxygen fugacities (δfO²) were determined using Infrared and Raman spectroscopy techniques. The water concentration has been obtained by ion microprobe and by stepwise heating extraction. The last technique gave also the carbon content. It has been established that the liberated oxygen was consumed mainly to oxidized hydrogen into OH⁻, and to much lesser extent H₂O. Only traces of CO₂ and CO₂⁻ were formed. Dissolved carbon is mainly present as atomic carbon or amorphous carbon. The spectrum also suggested that the network units contain Si-C bonds. The amounts of C and H dissolved in melts are particularly low. Carbon solubility remains about one order of magnitude less than that of water (about 2 wt% H₂O and 0.2 wt% C). In the light of experimental data it appears that a large scale melting of terrestrial matter (an early magma ocean) is certainly controlled by the solubility of hydrogen, albeit the early Earth was likely a reducing environment.

A wiggle-matching technique applied to the dating of damaged cave deposits and compilation of a long-term paleoseismic record, Soreq Cave, Israel

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An innovative wiggle-matching dating technique is applied to a paleoseismic study performed in two caves near Jerusalem, Israel. Among them, the Soreq Cave has been intensely dated using U-Th TIMS method and shows continuous cave deposit (speleothem) growth for at least 185 kyr. High-resolution composite δ¹⁸O and δ¹³C profile was prepared for paleoclimate research (Bar-Matthews et al., 2000; Ayalon et al., 2002). Research of past earthquakes, typically retrieved records from soft sediment deformations, can benefit from the study of rockfalls and damaged speleothems. Dating of collapses and the speleothems overgrowing them constrain the dates of earthquakes. The caves, located 60 km west of the Dead Sea Transform (DST), record earthquake damage associated with DST earthquakes and, possibly, smaller local intraplate events.

One of the difficulties in accurately dating paleo-earthquakes using U-Th methods is the relatively large amount of calcite needed, which distances the sample material from the tectonic contact, and causes the age to be an average of many years of growth. In addition, to avoid contamination from the collapse there is a need to extract material at some distance from the contact (the boundary between collapse and regrowth).

In order to obtain an age as close as possible to the age of the tectonic event we first estimate the age by U-Th dating of the laminae on both sides of the contact. We then compared the high-resolution δ¹⁸O and δ¹³C profile for each collapse sample with the densely-dated δ¹⁸O and δ¹³C profiles of the Soreq Cave. The isotopic data point, 0.5 mm from the contact, enables us to accurately date the event.

Thirty-nine collapses were dated, of which at least 15 separate events were identified. Of the Holocene events, all correlate with archeologically and geologically recorded earthquakes. Of the 6 events between 70-20 ka, 5 correlate with lacustrine seismites in the Lisan Formation (paleo-Dead Sea). Events older than 70 ka are, at present, the only paleoseismic record of its age studied in the region.

References
Effects of biogenic substances on the light-induced redox cycling of iron in surface waters

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Chemical Characterisation of Biogenic Substances

Dissolved biogenic substances occurring in surface waters are complex mixtures of high- and low-molecular weight dissolved organic matter (HMW DOM and LMW DOM, respectively), and of hydrophilic and hydrophobic substances. We have characterised DOM fractions gained by ultrafiltration (1 kD) and C18 solid phase extraction of water samples taken from the River Tagliamento, Italy, by using spectroscopic methods including multidimensional solution-state NMR (Kaiser et al., submitted).

Effect of DOM Fractionation on the Light-Induced Redox Cycling of Iron

Irradiation of HMW and LMW DOM (from water samples longitudinally and seasonally collected from the River Tagliamento) with simulated sunlight resulted in the formation of Fe(II). Iron(II) steady-state concentrations (normalised to DOC concentration) were significantly higher in irradiated HMW DOM fractions than in irradiated LMW DOM fractions. This phenomenon may be explained by either Fe(II) being more efficiently formed in the presence of HMW substances and/or Fe(II) oxidation occurring faster in the presence of LMW substances.

Effect of DOM Origin on the Light-Induced Redox Cycling of Iron

Irradiation of unfiltered water samples from two Swiss lakes, Melchsee and Greifensee, with simulated sunlight revealed considerably faster kinetics of both Fe(II) formation and Fe(II) disappearance (after the light-source was turned off) in Melchsee than in Greifensee water, although Fe(II) steady-state concentrations were similar. Mathematical kinetic modelling and comparison with these experimental results suggest that superoxide is a key intermediate in the light-induced redox cycling of iron in these two lakes, and that superoxide steady-state concentrations are considerably higher in Melchsee than in Greifensee (Emmenegger et al., 2001). DOM present in the oligotrophic Melchsee is largely terrestrial-derived, whereas in the eutrophic Greifensee it is algal-derived.

References


Sulfate reduction rates in deeply buried marine sediments

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Bacterial sulfate reduction rates (SRR) in samples from three sites from the Nankai Trough, an accretionary wedge off Japan (ODP Leg 190), were directly assessed by injecting radiolabeled 35SO4 and measuring its turnover to reduced sulfur. At Sites 1173 and 1174 sulfate was depleted within the first few meters below the sea floor and reappeared at 200 m and 600 m respectively. SRR, however, were only measurable in the surface sediments. In contrast, Site 1177 exhibited significant sulfate turnover at depths of 500 to 700 m (up to 400 pmol/cm³/d). These depths comprise a turbidite sequence containing both high organic carbon content and near seawater concentrations of sulfate. These results are surprising in light of the age (10 - 15 Ma), and terrestrial provenance of the organic facies. For comparison we will also present sulfate reduction rates on samples just obtained from the Peruvian Continental Margin (ODP Leg 201) - sediments dominated by high marine productivity.
How unradiogenic is Pb in the core?
No limits to core-mantle exchange

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Interpretation of modern mantle melts with high $^{186}$Os/$^{188}$Os and $^{107}$Ag/$^{109}$Ag ratios as having a core-derived component is met by scepticism by those who expect the core to contain very unradiogenic Pb. Here we test in how far the paradigm of the core as a major reservoir of unradiogenic terrestrial Pb is supported by the latest constraints and data on core formation.

Two related issues need to be considered. Firstly, how much Pb is the core likely to contain and secondly, is the Pb really unradiogenic? With regard to the first question, we note that postulation of a Pb-rich core was based on the assumption that the Earth accreted with an U/Pb ratio similar to terrestrial Pb, indicating that the bulk Earth should have a present-day $^{206}$Pb/$^{204}$Pb ratio below 12. Mass balance would thus require that a large proportion (>75%) of the terrestrial Pb resides in the core or was lost during hydrodynamic escape. However, it is now widely agreed that the composition of the bulk Earth cannot be approximated by that of a single class of meteorite. It is significant that all other types of chondrites contain substantially more radiogenic Pb than CC. It will be shown that this radiogenic Pb is not an artefact of terrestrial contamination but an original feature of these meteorites. Because the inferred U/Pb of most ordinary and enstatite chondrites is similar to that of the silicate Earth there is no a priori reason to suspect the core to be particularly enriched in Pb.

The low terrestrial U/Pb paradigm was further cemented with the view that core formation provided a solution to the first terrestrial Pb-isotope paradox, because, as will be demonstrated, only very low bulk Earth U/Pb permit mean core formation times of <200 Ma. However, our new W-isotope data for the Allende CC show that core formation and accretion were very rapid processes (<40 Ma). Hence, core pumping even in a low U/Pb Earth does not provide a valid solution to the first Pb-isotope paradox nor does it help to constrain the bulk Earth U/Pb.

Published and new measurements of Pb-isotope ratios and Pb content in iron meteorites demonstrate that many contain substantial proportions of radiogenic Pb and that the Pb isotope content is too low to support substantial fractionation of Pb during silicate/metal segregation. Although much of the radiogenic Pb appears to be unsupported by U and Th, the possibility remains that at least the outer core could contain relatively radiogenic Pb.

In summary, the lack of unradiogenic Pb cannot be quoted as evidence against a core component in the source of mantle melts with high $^{186}$Os/$^{188}$Os and $^{107}$Ag/$^{109}$Ag.
Diamond-bearing magmas that form kimberlites in intracratonic settings are widely believed to represent metasomatised lithospheric mantle sources. As such they may supply information on the processes of diamond formation and the composition and origin of deep-seated metasomatic agents. Despite significant efforts in studying kimberlitic rocks the composition of their parental magma remains largely unknown. This is hampered by several factors: large and variable amount of lithospheric and crustal xenoliths and xenocrysts in kimberlites, pre- and syn-eruptive degassing, and significant alteration. Alternative to whole-rock studies, melt and associated fluid inclusions are abundant in both kimberlites and basic magmas. The existence of rough layering, mafic microgranular enclaves of gabbro and diorite are included often within the marginal part of the pluton. Aplitic veins and various dykes cut all intrusive rocks. The pluton is high-K, calc-alkaline, metaluminous to peraluminous and LILE enriched. Many peculiarities of the major and trace element variations are consistent with a fractionation. Geochemical variations (REE-patterns included) support the idea that granitoids of the Vejen pluton are derived from more primitive basic magmas. The existence of rough layering, mafic xenoliths, enclaves and cumulative packets of crystals and linear trends in the variation diagrams could serve as evidence to support also magma-mixing process. The applied discriminations are typical for volcanic-arc granites.

Rock paragenesis and mineral evolution are indicative of crystallization under moderate total pressure, high fO2, high P_H2O, high activity of silica. The applied geothermometers and geobarometers yielded an estimation of the temperatures between 730° and 770°C and depths of crystallization at ~18 km, ~15 km, ~13 km (Fig. 1). The subsolidus re-equilibriations are estimated at 2 kbar (~ 5 km) and at temperatures of about 600°C.

U-Pb dating on single zircons of the magmatic rocks from the pluton revealed an intrusion age of 314 ± 4.8 Ma for the granodiorite and a mantle contribution to its source.
Sr-isotope composition as a tracer for source identification of long-range transported Asian dust

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Introduction
Sr-isotope is one of the most useful geochemical tracers for the long-range transported terrestrial materials. In spite of its great possibility, it has not been successfully used for the source identification of Asian dust in the present time. In this study, we present the Sr isotope composition as well as the major and trace element composition, of the bulk aerosols and snow-trapped Asian dust particles collected over Japan in 2000 and 2001, and try to identify the source of long-range transported Asian dust.

Result and Discussion
The Sr isotope ratios (87Sr/86Sr) of the aerosol collected over Japan during spring were obviously higher than those of local possible source components. This suggests that Japanese aerosols in spring are considerably affected by long-range transported Asian dust of which Sr isotope ratios are higher than original surface soil in Japan. The potential sources of Asian dust are considered to be fine soil particles from arid and semi-arid regions of northwest or north China. Many studies have referred Sr isotope composition of loess in CLP and semi-arid regions of northwest or north China. Many studies have referred Sr isotope composition of loess in CLP as a representative of Asian dust. However, Rb-Sr isotope composition of atmospheric aerosols collected over Japan cannot be explained by the mixing relationship between local aerosols and reported Chinese loess. This discrepancy indicates that main source of Asian dust transported to Japan is not originated form CLP, but some other arid and semi-arid regions such as Inner Mongolia in China or Mongolia. Meteorological data analysed by SYNOP also shows the dust-storm events often occurred in Mongolia and Inner Mongolia. Thus we suggest that Asian dust affected to Japan is mainly originated around southern parts of Mongolia and/or northern parts of China and its Sr isotopic feature is distinctly different from loess of CLP. Unfortunately, the Sr isotope data in inland Asia is very scarce so far. To increase the possibility for source identification, we need the Sr isotope data accumulation.

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Isotope geochemistry of submarine lavas from South Arch volcanic field, Hawaii

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The Hawaiian Arch is a broad swell in the Cretaceous sea floor surrounding the Hawaiian Islands. Numbers of Tertiary/Quaternary volcanoes, which located on the Hawaiian Arch, are discovered in 1986 during surveys using the USGS GLORIA sonar system. The origin of the arch lavas may be somewhat related to the structure of the arch itself. The total area of identified arch lavas exceeds that of the subaerially exposed Hawaiian Islands. There has been a growing interest in the origin of these arch type volcanism to understand Hawaiian hot spot magmatism.

The South Arch Volcanic Field is one area of the arch volcanism located 200km south of Hawaii Island. The South Arch volcanic field consists of flat sheet flows and pillows in a 35 by 50 km area. It is reported that South Arch lavas erupted at 1-10 ka according to the palagonite thickness on lava surfaces, demonstrating South Arch volcanism is similar in chemical compositions to North Arch lavas which located 500km far from the center of the plume beneath Kilauea (Lipman et al., 1989).

Glassy fresh pillow lavas were collected from the young lava flow field in South Arch volcanic field by ROV-KAIKO during JAMSTEC 2001 Hawaii Cruise. The present Sr and Pb isotope data of the South Arch glasses plot in the limited ranges; 87Sr/86Sr: 0.70331-0.70342 206Pb/204Pb: 18.41-18.43, respectively. It is reported that two dredged glasses from the precursory South Arch have higher 206Pb/204Pb than peripheral North Arch lavas (Dixon et al., 2001). The Pb and Sr isotope data of fifteen North Arch lavas indicated that binary–like North Arch lavas (Dixon et al., 2001). The Pb and Sr isotope data of the South Arch glasses plot in the limited ranges; 87Sr/86Sr: 0.70331-0.70342 206Pb/204Pb: 18.41-18.43, respectively. It is reported that two dredged glasses from the precursory South Arch have higher 206Pb/204Pb than peripheral North Arch lavas (Dixon et al., 2001). The Pb and Sr isotope data of fifteen North Arch lavas indicated that binary–like North Arch volcanism and examine temporal special distribution of mantle components beneath Hawaiian hot spot region,


NMR evidence for a new water dissolution mechanism in alkaline earth silicate melts

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The dissolution of water in magmas significantly affects their phase relations, and physical and thermodynamic properties. Most of the spectroscopic studies on Al-free silicate melts/glasses thus far have concluded that water is dissolved as molecular H_2O and silanols (SiOH). However, these studies have been limited mostly to SiO_2, and Na-, Ba-, and Sr silicate compositions. We now report new 1H and 29Si NMR evidence for another water dissolution mechanism in silicate melts in the CaSiO_3 (Wo) - MgSiO_3 (En) - SiO_2 (Qz) system, that can be regarded as rough analogs for mafic to ultramafic magmas.

A hydrous Wo_{47.75}En_{47.75}Qz_{12.50} glass with 1.8 wt% H_2O was synthesized from anhydrous glass powder and deionized water at 2 kbar and 1450°C. The 1H 1-pulse and Hahn-echo MAS NMR spectra contain two partially resolved peaks at 1.4 and 4.6 ppm. The 4.6-ppm peak is broader and asymmetric with a shoulder near 14 ppm. Similar to those for hydrous Na-, Ba-, and Sr silicate glasses, this peak can be ascribed to molecular H_2O and SiOH with a range of H-bonding strengths. The 1.4-ppm peak is close to those of MgOH and CaOH in crystalline hydrous silicates, and thus can be attributed to (Ca, Mg)OH. These 1H NMR spectra are similar to those of another glass (Wo_{48.6}En_{39.2}Qz_{12.2} from probe analysis) with 3.85 wt% added H_2O, synthesized at 1 GPa and 1500°C (Xue et al., 2001). The 29Si MAS NMR spectrum of the anhydrous Wo_{48.6}En_{41.5}Qz_{12.50} glass contains a single asymmetric peak centered at ~82.3 ppm with a FWHM of 19 ppm. That of the hydrous glass is almost identical, with only a slightly displacement to higher frequency.

Our study clearly indicates that a substantial part of the dissolved water is in the form of cationic hydroxyls (Mg,Ca)OH, in addition to SiOH and molecular H_2O. The formation of cationic hydroxyls may be considered to result from the following reaction between water and non-bridging oxygens (NBO): 2SiO(Ca,Mg) (NBO) + H_2O = SiOSi (BO) + 2(Ca,Mg)OH

This reaction actually drives the silicate network to a more polymerized structure, and is thus expected to increase the melt viscosity, in contrast to the formation reaction for SiOH. Any models for the physical and thermodynamic properties of hydrous silicate melts must take this new water dissolution mechanism into account.

References
Paleoproterozoic positive carbon isotope excursion and organic carbon burial

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Paleoproterozoic sedimentary carbonates indicate that oceans were affected by a dramatic positive carbon isotope excursion between 2.2 and 2.1 Ga (Karhu and Holland, 1996). In the geochemical carbon cycle, a positive shift in marine $\delta^{13}C$ values requires an increase in the burial fraction of organic carbon relative to carbonate carbon. Higher rates of organic carbon burial, in turn, lead to higher rates of release of oxidizing power in the surficial environment. However, geological evidence for excessive organic carbon sedimentation seems to be missing from sedimentary successions deposited between 2.2 and 2.1 Ga (Melezhik and Fallick, 1996). Mantle subduction is a possible, alternative sink for organic carbon, causing a permanent change in the oxidation state of the Earth’s surface.

Following the Paleoproterozoic carbon isotope excursion the Fennoscandian Shield experienced a period of subduction and multiple island arc collisions in the Svecofennian orogeny. A post-collisional magmatic event at about 1.8 Ga comprises lamprophyres and peraluminous granites interpreted to have been derived from rapidly enriched lithospheric mantle (Eklund et al., 1998). The rock suite includes a carbonatite intrusion at Halpanen in southern Finland, characterized by unusually low $\delta^{13}C$ values of calcite, with an average at –12.3‰. The data are supported by results from lamprophyre calcite and contrast strongly with the signatures generally observed in mantle derived carbonatites. As the isotope composition of carbon in carbonatitites can be expected to provide a good estimate of the average $\delta^{13}C$ value in their mantle source, the results suggest an uncommonly high degree of $^{13}C$-depletion in the subcontinental mantle after the Svecofennian orogeny. This may be related to excessive subduction of organic light carbon into the mantle and derivation of metasomatizing fluids from the descending slab. The evidence for anomalous mantle compositions is limited to the Fennoscandian Shield, and clearly more data is needed to confirm the pattern and to evaluate the connection of the event to the Paleoproterozoic carbon isotope excursion.

References

Substrate preference of bacteria

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Biodegradation is important for the breakdown of toxic organic components. Better understanding of the controls on bacterial activity can aid the improvement of remediation strategies for soil and groundwater. Many bacteria prefer attachment to a substrate, to remain in a favourable environment or to insure a steady source of adsorbed nutrients. Before strains are developed for remediation in specific geological settings, mineral surface preference should be determined. A strain developed for oil-spill clean-up on sandy beaches, for example, would be useless if the bacterium only adsorbs to clay.

Our study takes a simple approach by using contact mode AFM to examine a selection of mineral surfaces that were exposed to solutions containing bacteria. Cleaved samples of calcite, gypsum, muscovite and biotite and a clean glass cover slip (as a model for quartz) were exposed to droplets of bacteria-containing solution. Water from a local pond produced bacterial assemblages that varied with mineral substrate. Many of the species found on one mineral surface were absent on the others. Experiments with a monoculture of Pseudomonas putida also showed substrate preference.

Figure 1: AFM picture of muscovite exposed to pond water. Pili attach one species to the substrate, but not the other. The bacteria are about 1 µm long.
 Contribution of fine exsolution lamellae of hematite-ilmenite to magnetic properties

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Hematite-ilmenite minerals play an important role in acquisition of rock magnetism. Samples of igneous rock with hematite exsolution in ilmenite, visible by optical microscopy, have indicated high and stable NRM, although the acquisition mechanism of magnetization is still unknown (McEnroe et al. 2001a). McEnroe et al. (2001b) have identified fine scale exsolution microstructures of hematite and ilmenite in metamorphic rocks with high natural remanent magnetization (NRM) using energy-filtered TEM, and suggested that the microstructure was related to the magnetic properties. In this study samples from the Sokndal Region, Norway, provided by S. McEnroe, have been examined by SEM, TEM with EDS, HRTEM revealed that the lamellae were parallel to (001) planes and the coherency strain is partially relieved by formation of the interface dislocations. TEM observations showed that within both the ilmenite and hematite, there are abundant fine lamellae (∼ in the order of a few tens on nm in length) of hematite and ilmenite respectively. TEM-EDS analyses revealed that the chemical compositions of the hematite and ilmenite were Ilm$_{14}$-19 Hem 81-86 and Ilm 99 Hem 1 . Our EDS results are similar to those reported by McEnroe et al. (2001b) who suggested that these phases alone cannot account for the magnitude of the NRM.

The strong strain contrast around the lamellae and observation of the interface between hematite and ilmenite by HRTEM revealed that the lamellae were parallel to (001) planes and the coherency strain is partially relieved by formation of the interface dislocations. Harrison and Becker (2001) calculated that the ferrimagnetic moment of the formation of the interface dislocations. Harrison and Becker (2001) calculated that the ferrimagnetic moment of the formation of the interface dislocations. Harrison and Becker (2001) calculated that the ferrimagnetic moment of the formation of the interface dislocations.

References


Calcium isotope variation in Neoproterozoic carbonate rocks

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Neoproterozoic carbonate rocks from the eastern Kaokoveld (Namibia) house two glacial intervals each with a cap carbonate. Samples span the preglacial Ombaatj Fm, the postglacial Keilberg cap carbonates and the post-cap Maienberg Fm bracketing the glacial Ghaub Fm. The preglacial samples are fine grained limestones and dolostones near the top of the succession. The cap carbonates are pure dolomites, and dolomite is also present in the post-cap succession alternating with fine grained limestone. Samples have been analysed using a $^{44}$Ca-$^{44}$Ca-double spike and the Finnigan-Triton TIMS. Ca isotope ratios are given relative to NIST SRM 915a in the conventional ($^{44}$Ca) way. Calcium isotope data from the Namibia samples show consistent $^{44}$Ca values of -0.02 ± 0.17‰ (2σ std) through the both pre- and postglacial succession. Carbon isotope data from the same samples are characterised by positive isotope values in the preglacial rocks that decline to negative values within the postglacial carbonate rocks. The postglacial cap carbonates and the associated negative $^{13}$C values have been interpreted to reflect the physical record of carbon transfer from the atmosphere to the sedimentary reservoir by high weathering rates after glaciation (Hoffman et al. 1998). However, an increase in silicate weathering should affect the Ca isotope composition of seawater and hence, the $^{44}$Ca values of the precipitated carbonates. As yet, no such evidence has emerged from the study of Ca isotopes in these rocks. Ca isotope ratios of foraminifera display systematic temperature-dependent fractionation and are potentially a new proxy for past sea surface temperatures (SST). Recent data suggest that a 1°C change in temperature results in 0.24 ± 0.02‰ fractionation of $^{44}$Ca (Nägler et al. 2000). Thus, the uniform Ca isotope composition of the Namibia carbonates in rocks thought to reflect a wide range in temperatures suggests either (1) that the use of $^{44}$Ca as a SST proxy requires a biological contribution that was not present during the formation of these rocks, or (2) the temperature range during deposition was less than initially suggested.

References


Kinetics of the condensation of presolar SiC and its trace elements

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Equilibrium thermodynamic condensation calculations and collision theory were used to test whether the kinetics of trace element condensation, in an AGB star atmosphere, agree with the observed trace element abundances in presolar SiC grains (Kashiv et al., 2001, 2002). Condensation calculations of the major elements were done using D.S. Ebel’s ‘VAPORS’ code. The kinetic calculations set lower limits on all the rates below (since nucleation and evaporation were ignored, and the sticking coefficient, \( s \), was assumed to be unity).

Daulton et al. (2002) found that the presolar SiC polytypes condensed in the temperature range \( T_c \sim 1470-2000 \) K. This corresponds to a pressure range of \( p \sim 10^{-6} - 10^{-2} \) bar (1-10 \( ^4 \) dyne/cm\(^2 \)). Calculations were performed for the limiting case (i.e., slowest rates) for a gas of solar composition (except for C) with \( C/O = 1.05 \) and \( p = 10^{-6} \) bar (1 dyne/cm\(^2 \)) which give \( T_C = 1460 \) K for SiC.

The time it takes to grow a 1.5 \( \mu \)m SiC grain (the average grain size in Kashiv et al., 2001, 2002) is \( t = 1.9 \times 10^3 \) year, or \( t = 5.8 \times 10^5 \) year if one assumes that \( CO_{10} \) and SiS\(_i\) are inert. Both times are well within the astrophysical upper limit of \( \sim 1 \) year calculated by Sharp & Wasserburg (1995).

The trace element abundance patterns of Kashiv et al. (2001, 2002), combined with condensation calculations, indicate that trace elements condense mainly in solid solution in SiC. The relation \( dn_i/dn_j = (s_i/s_j)(n_i/n_j)(m_i/m_j)^{0.5} \) (where \( n_i = \text{number density of } i \), \( m_i = \text{mass of } i \), \( te = \text{trace element} \), and \( s_i = s_j = 1 \)) was used to calculate whether there was a kinetic limitation on observed abundances in presolar SiC. The results are that there is no kinetic inhibition for condensation in solid solution.

For example: The abundances of the enriched s-process elements in the grains (group 4 in Kashiv et al., 2002) – Y, Zr, Nb, Mo, and Ru, range from 1-146 ppm. The calculations show that under ideal conditions, including s-process enrichment, the collision rates for these elements will produce abundances in the grains of up to 530 ppm.

The possibility of condensation of trace element carbide sub-grains was also investigated. Of the four elements that start condensing before SiC – (a) condensation of Ti (as TiC) is not inhibited kinetically, (b) those of Zr (as ZrC), Nb (as NbC) and Mo (MoC) are kinetically inhibited (note that most of the Nb in the grains is the decay product of \(^{93}Zr\)).

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Climate change in Cenozoic inferred from carbon cycle model

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A global carbon cycle model based on GEOCARB-type model (e.g., Berner, 1994) during Cenozoic, in which \( CO_2 \) degassing from island arc and back-arc basin are considered, the contribution of the silicate weathering in the HTP (Himalayan and Tibetan Plateau) region is reevaluated, and degassing and regassing parameters are revised.

Our results show that: (1) the contribution of the silicate weathering in the HTP region is relatively small; (2) the warming from late Oligocene to early Miocene is due to the \( CO_2 \) degassing from the back-arc basin; (3) the cooling event in middle Miocene is caused by large amount of the organic carbon burial; (4) the atmospheric \( CO_2 \) level after middle Miocene is relatively low.

The age discrepancy between the \( CO_2 \) peak in our model and the period of MCO (the Miocene Climatic Optimum) could be attributed to the uncertainty of estimate of the BAB production rate (Kaiho and Saito, 1994).

The global mean temperature in our model does not show the cooling trend from middle Miocene and the cooling event at the Eocene/Oligocene boundary which are often argued in association with oceanic environment. However, we could say that the global mean temperature itself is not largely affected in these periods because these events might have occurred mainly in high latitude. This assumption of the small effect of the temperature variations in high latitude on the global mean temperature might be supported by our numerical test of the latitudinal sea surface temperature distribution.

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Geochemical Constraints on the Rise of Atmospheric O₂

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The rise of atmospheric oxygen was perhaps the most biologically significant environmental change in Earth history, as it allowed multicellular, eukaryotic organisms to evolve and proliferate. The rise of O₂ is thought to have occurred around 2.0-2.4 Ga, based on a variety of geochemical evidence [1]. More recently, Farquhar et al. [2] showed that Archean and early Proterozoic rocks contain mass-independently fractionated S isotopes, whereas rocks of younger age do not. According to current understanding, such anomalous fractionation patterns could only have been produced by photochemical reactions (e.g., SO₂ photolysis) in a low-O₂ atmosphere. A recent photochemical model study [3] places a firm upper limit of 10⁻⁹ PAL (times the Present Atmospheric Level) on the O₂ concentration at the time when these rocks were formed.

Seemingly at odds with this conclusion is organic biomarker evidence for the existence of cyanobacteria and isotopic evidence for rapid organic carbon burial as early as 2.7 Ga [4,5]. What then prevented atmospheric O₂ from accumulating? Kasting et al. [6] had suggested that volcanic gases became more oxidized with time as a consequence of H escape to space and the subduction of oxidized materials down into the mantle. This idea appears to be ruled out, however, by isotopic evidence for rapid organic carbon burial as early as 2.7 Ga [4,5].

References
**Metasomatic alteration of zircons from potassic granites**

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Zircon is a well known and a widely used geochronometer, since it is capable in retaining radiogenic Pb during high T metamorphic events. But often zircon has a complex behavior and can transform under hydrothermal conditions, especially when interacting with CO$_2$-rich fluid (Tugariniv, Bibikova, 1980, Rizvanova et al., 2000, Lifervich et al., 2001).

Zircons from some potassic granites of the Kola Peninsula, Russia were studied by cathodoluminescence (CL) and dated by ion-microprobe methods. Zircons show complicated structure under cathodoluminescence (fig.-1).

The originating of altered parts in zircons can be well explained as a process of metasomatic substitution of crystals - synchronous subprocesses of dissolving and growth. Under the influence of fluid some parts of zircons were dissolved and completely substituted with a newly formed zircon phase. Susceptibility of zircon to alteration can be enhanced by metamictization or mechanical fracturing during deformation. Zircons with high U and Th concentrations are more likely to be metamict and susceptible to leaching. We observed such type of internal structure in zircons from potassic granites only. Potassic granites are rich in U and Th, so zircon as a concentrator of U and Th is also rich in these elements. Its structure is initially disturbed by high foreign elements content and damaged from decay of incorporated U and Th. As well as metasomatic alterations of rocks often take place in zones of deformation where rocks become penetrative for fluids - all lattice defects in zircon play a role of channels for metasomatic solutions. Zircons with low U-contents from other rocks in the studied districts remained nearly unaffected by the fluid.

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**Reconstruction of paleoproductivity in the Sea of Okhotsk over the last 30 kyrs**

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Two sediment cores were taken from the central and western Sea of Okhotsk, which is located in the northwestern Pacific rim and is characterised by high biological productivity and the presence of seasonal sea ice. The cores were studied for phytoplankton-derived biomarkers (alkenones, brassicasterol and dinosterol), as well as biogenic opal and ice rafted debris (IRD), in order to reconstruct the paleoproductivity over the last 30 kyrs. Down core profiles of the phytoplankton markers suggest that primary productivity was restricted in the glacial period, but abruptly increased toward the deglaciation period and stayed high in the Holocene.

The comparison of three sediment cores including GGC-15 core taken from the southern Okhotsk Sea [Ternois et al., 2001] showed a propagative increase in the alkenone mass accumulation rates (MAR) from the last glacial maximum to the deglaciation. This increase started from the southeastern part of the sea and extended to the northwestern region. Spatial and temporal distributions of the phytoplankton productivity were found to be consistent with the changes in the reconstructed sea-ice distribution based on the IRD records. This study demonstrates that the progress and retreat of sea ice had controlled the primary productivity in the Sea of Okhotsk with the minimum productivity during the glacial period.

MARs of alkenones and biogenic opal indicate that the dominant phytoplankton species in the deglaciation was haptophyte, *Emiliania huxleyi*, whereas diatom overwhelmed haptophyte in the late Holocene. Such a phytoplankton succession from haptophyte to diatom was probably caused by the increase in the silicate supply possibly from the Pacific Ocean to the surface water of the Okhotsk Sea due to the changes in the hydrographic structure of the sea as well as the North Pacific Ocean.
Bacterial induced mineralization in the weathered sediments

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Introduction

Bacteria are widely distributed in various weathered rocks and sediments on the Earth surfaces. Recently, it has been shown that these bacteria have strong impacts on mineral formation by interaction of their cell surfaces with dissolved ions in pore waters. In this study, we investigated that the effects of bacteria on the formation of silicate minerals in a weathered pyroclastic deposit, southern Kyushu, Japan. Results of this study suggest that the formation of secondary minerals has been apparently promoted by the bacterial interaction.

Materials and methods

Weathered pyroclastic deposit (6,400 YBP) distributed around southern Kyushu, Japan was used in this study. The pyroclastic deposit consists of fine to coarse rhyolitic volcanic glass fragments with great amounts of allophane produced during weathering processes. To investigate bacterial mineralization in this deposit, we performed X-ray diffraction analysis (XRD), transmission electron microscopy (TEM), and energy dispersive X-ray analysis (EDX) for secondary products including biogenic and non-biogenic products. The pore water in the deposit was extracted by high presser press during weathering processes. To investigate bacterial mineralization in this weathering environment, we performed X-ray diffraction analysis (XRD), transmission electron microscopy (TEM), and energy dispersive X-ray analysis (EDX) for secondary products including biogenic and non-biogenic products. The pore water in the deposit was extracted by high presser press method, and then chemical analysis and geochemical calculation were also done to evaluate saturation states.

Results and conclusions

TEM indicated that the pyroclastic deposit contains allophane as a non-biogenic secondary product with the Al/Si and Fe/Al ratios are 1.76 and 0.20, respectively. Additionally, a great number of spherical to rod-shaped bacteria covered or decorated by biogenic poorly ordered silicate minerals with a thickness <1.0 μm was also present. EDX revealed that the biogenic minerals consist mainly of Al and Si (Al/Si = 0.6 to 1.5), and variable amounts of Fe (Fe/Si = 0.04 to 1.4) corresponding to the chemical compositions between protohalloysite allophane and chamosite. Thus, the biogenic minerals in this weathering environment have different chemical characteristics from those of the non-biogenic minerals, and are possibly present as early metastable phases of the non-biogenic allophane.

References

Melt transport in the mantle beneath oceanic spreading ridges

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Tabular dunites within the mantle section of the Oman ophiolite fulfill chemical and structural criteria for porous conduits that preserve disequilibrium between the mantle and migrating melts at depths from ~ 45 km to the base of the crust (Kelemen et al., Nature 95, JGR 95, Phil Trans Roy Soc London 1997, G-cubed 00).

Porosity in dunites can account for the transfer of pyroxene-undersaturated melt from > 1 GPa to the base of the crust (Braun & Kelemen, G-cubed 02). 226Ra excess is negatively correlated with 230Th excess in young MORB from the East Pacific Rise (Sims et al., GCA 02) as predicted (97). 226Ra excess likely has a shallower origin, perhaps by reaction of Th-bearing melt and depleted, uppermost mantle (Jull et al., GCA 02, submitted).

Transport of ~ 90-95% of melt in high porosity (~3%) dunite conduits, with the rest migrating by diffusive porous flow through residual peridotites, accounts well for available data. Obviously, melt transport in dikes is important in the cold “lithosphere”. Hydrofracture may generally arise within one compaction length of the base of the thermal boundary layer, where melt moving via porous flow begins to crystallize in pore space (Kelemen et al., JGR 95; Korenaga & Kelemen, JGR 97; Kelemen & Aharonov, AGU Monograph 98), and at shallower depths.

New studies (Braun & Kelemen, 02 in prep.; Hassler et al., 02 in prep.) confirm that Oman mantle dunites equilibrated with MORB-like melts (Kelemen et al., Nature 95). Trace cpx in Oman mantle dunites is in REE exchange equilibrium with MORB and with lavas that formed the crust at an oceanic spreading ridge. Spinel in Oman dunites have ~ 0.2 to 1 wt% TiO₂, similar to high Cr# spinels in MORB and dredged dunites from ocean ridges, but different from low-Ti spinels in residual peridotite worldwide, and in mantle dunites from some ophiolites (e.g., Bay of Islands, Suhr et al., G-cubed 02). Gradients in composition at Oman mantle dunite contacts are sharp, with width/independent of diffusivity. Dunite contacts formed via reaction with melt during porous flow, rather than in a static, diffusive boundary layer.

As may be common (e.g., Becker et al., EPSL 01), Oman dunites show higher whole-rock Os/²⁸⁸⁶⁸Os, and lower Os and Ir concentrations, than residual harzburgites (Hassler et al., 02 in prep.). Re-decay at measured concentrations cannot account for the isotope variation. If the differences are not due to alteration, then melts in dunites must have had higher Os isotope ratios than the surrounding peridotites, and must have been capable of dissolving Os- and Ir-rich phases during transport.

Thermal convection of the mantle wedge

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Thermal models suggest that partial melting of subducted material older than 20 Ma is unlikely beneath arcs. In contrast, geochronological and petrological inferences – e.g., explanations for high Th/La in basalts, as well as for data on “adakites” – suggest that partial melting of subducted basalt and sediment is common.

PT estimates for equilibration of primitive arc lavas with the mantle, and for metamorphic conditions in the Kohistan and Talkeetna arc sections, including our new results, require Moho temperatures of ~ 900-1000°C at ~ 1 GPa, ~200 to 400°C hotter than in thermal models. Crystallizing melts do not have to lie on a steady-state geotherm, so petrological estimates need not coincide with the thermal structure in models. However, other constraints suggest that high Moho temperatures are present over large regions for long periods of time.

Thermal models do not account well for the shape of low velocity anomalies in the mantle wedge beneath arcs. Observations of a 6% slow P-wave velocity anomaly at the base of arc crust for long distances along the strike of the NE Japan and Tonga arcs (Zhao et al., 92 to 00) suggest that there is melt in the mantle just below the arc Moho. In addition, arc topography and gravity data are better fit with a weak coupling between the subducting plate and the overlying mantle (Billen & Gurnis, EPSL 01).

If the mantle wedge viscosity is lower than has been considered in previous modeling, due to the effects of H₂O and/or melt, then cooling at the base of the arc and along the subduction interface could lead to thermal convection that is faster than the subduction velocity, thinning thermal boundary layers at the base of the arc and above the subducting plate. This will occur if mantle wedge viscosities are less than ~ 10⁹⁹ Pa s. Thermal convection in a weak wedge could raise temperatures at the top of the subducting plate by at least 10°C, suggesting that melting of subducted material in normal, steady-state subduction is inevitable, rather than impossible.

Other alternatives to explain high Moho temperatures are non-steady “delamination” of lower arc crust or advective transport of heat by rising diapirs and/or magma. However, these scenarios are unlikely to produce a weak, low Vp mantle wedge at steady-state, or to raise the temperature of subducting basalt and sediment.
Microbiology: What is next?
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The overall goal of microbiology is to understand ecology, physiology, evolution and interaction of microorganisms with their environment. Over the last decades the application of molecular-phylogenetic approaches resulted in the discovery of unique and previously unrecognized microorganisms. The vast majority of this unexpected microbial diversity is still inaccessible by a cultivation approach. Here we describe the development of a novel high throughput cultivation method using flow cytometry. This new method allows the rapid cultivation of many so far uncultivated microorganisms. The combination of this novel high throughput cultivation method with recombinant functional screening is an additional step towards the understanding of complex microbial communities.

Experimental determinations of Ar diffusion and solubility in plagioclase and leucite
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Plagioclase feldspar and feldspathoid (leucite and nepheline) minerals are becoming very important in the Ar-Ar dating of volcanic rocks, especially young volcanic systems. Despite the increasing use of plagioclase in Ar-Ar dating, very little is known about its Ar retention properties, and no laboratory derived diffusion parameters are available.

The Ar diffusion parameters for K-feldspar have been known since the early 1970’s, and have been confirmed by various techniques, most recently by ultra-violet laser depth profiling. However, very little is known of the diffusion parameters in other feldspars and feldspathoids.

Recent studies have used a new approach to determine Ar diffusion rates, measuring the ingress of 39Ar from carefully controlled laboratory experiments, which has the added advantage of offering combined Ar diffusion and solubility measurements. Studies have been undertaken to measure Ar diffusion and solubility in plagioclases and leucite, yielding information on Ar closure temperatures and diffusion rates, and determining the potential problem of excess Ar influx in these minerals.

Measured Ar diffusion parameters in plagioclase (E = 26.5 ± 0.3 kcal mol⁻¹, D₀ = 8.7 ± 1.3 x 10⁻⁹ cm² s⁻¹) yield values considerably lower than those for K-feldspar. The lower Ar diffusion rates mean that both grain size and cooling rate have a more pronounced effect on plagioclase closure temperatures than in the K-feldspar system. Plagioclase Ar closure temperatures are a few degrees lower than the equivalent K-feldspar, but in magmatic systems, plagioclase will retain Ar much longer than K-feldspar and this may explain the common observation of older plagioclase grains in volcanic systems.

A separate experiment was undertaken in leucite to determine Ar diffusion and solubility parameters across a known phase transition. Ar solubility in leucite was found to be extremely high, orders of magnitude higher than K-feldspar and plagioclase. The high concentrations of Ar precluded using the ultra-violet laser depth profiling technique, therefore, an electron microprobe was used. 2-dimensional X-ray maps of the Ar distribution in leucite samples were obtained, and the results represent the first images of Ar diffusion in a mineral.
Heterogeneity in the lower mantle: Constraints from numerical models and chemical geodynamics

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Numerical simulation of convection in the mantle, combined with observational and model constraints from heat flow, cosmochemistry, and geochemistry, is used to investigate models of possible compositional heterogeneity in the lower mantle. Geochemical and heat flow observations appear to require long-lived heterogeneity in the mantle. A variety of models have been proposed, including isolation of ancient subducted crust in the D" layer at the base of the mantle, or a dense layer in the lowermost 1000 km of the mantle, or viscous “blobs” in the lower mantle. These models are intended to reconcile diverse inferences about mantle dynamics and structure from geochemical and geophysical observations. Noble gas signatures from mid-ocean ridge basalts, oceanic island basalts, and the atmosphere imply that the mantle is incompletely outgassed. The global heat flow budget, in addition, requires a reservoir of mantle containing a higher concentration of heat-producing elements than the depleted mantle source of MORB. Numerical models of convection using homogeneous bulk composition exhibit rapid mixing, although models that include recycling of depleted lithosphere can yield streaks of mantle with apparently primordial helium isotopic signatures. The most straightforward explanation of all the observations is a compositionally heterogeneous lower mantle. A difference between the composition of the MORB source and the composition of the deep mantle is also consistent with recent estimates of the properties of perovskite at high pressures and temperatures. A transition to a different average composition in the middle of the lower mantle is also supported by recent seismic studies of lower mantle structure. Heterogeneity in the lower mantle may take the form of a hot abyssal layer of variable thickness starting at the mid-mantle or in the lowermost 1000 km of the mantle, or viscous “blobs” in the lower mantle. We prefer the hot abyssal layer model over the blob model, because hot, neutrally buoyant blobs are unlikely to persist for the long times required by chemical geodynamics. Chemical geodynamics and heat production put bounds on the volume of any dense layer and suggest that the transition to a dense layer should occur between about 1500-2000 km depth. The resulting layer would have to be enriched in heat producing elements compared to the depleted source of MORB. The D" region is unlikely to be the sole repository of any compositional variation; its volume is so small that excessive heat production would be required. Nevertheless, D" cannot be entirely ruled out as a source. Whatever its depth, a hot abyssal layer is likely substantially, but not entirely, isolated from the overlying depleted mantle.

Relating mixing in the mantle to Nd, Sr, and Pb ratios in oceanic basalts

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We present an extension of the conventional geochemical reservoir model for the evolution of the Earth’s crust-mantle system in which we calculate not only the mean isotopic ratios, but also the distribution of those ratios within the reservoirs. Owing to low chemical diffusion rates, sub-reservoirs created by mass transport into and out of the mantle effectively exist as distinct geochemical entities for all time. By tracking these sub-reservoirs, we obtain a model of the full range of isotopic values represented in the mantle. Using results from numerical calculations of mixing, we also track the length scales associated with each sub-reservoir. Applying simple statistics, we obtain the distribution of expected measurements as a function of the stirring time, effective melt fraction, sampling volume, and mass transport history. These models allow us to connect isotope geochemistry with mantle dynamics without conducting full-blown thermo-chemical convection calculations.

We first present calculations of isotopic heterogeneity for two simple mantle evolution models and explore the sensitivity of geochemical observables to the variables mentioned. We focus on the Rb-Sr and Sm-Nd systems and are able to reproduce much of the observed complexity of oceanic basalts. Mixing time scales of ~500 Myr, in accordance with dynamical calculations of mixing rates, and sampling length scales of ~100 km yield distributions consistent with observation. We conclude that the differences between isotopic data from mid-ocean ridge basalts and ocean island basalts cannot simply be due to differences in sampling volume, but must also reflect differences in the source reservoirs and/or melting processes. Increasing the size of the ocean island basalt source region by 45% with respect to the mid-ocean ridge basalt source region reproduces the offset between the two distributions, but still fails to explain the more isotopically extreme measurements. Our results show that the argument suggesting that the absence of samples with a primitive isotopic signature indicates that no primitive material remains in the mantle is not valid.

The behavior of the U-Th-Pb system requires that we appeal to more complicated models. For example, we employ a two-layer crust to explain the observation that both the upper crust and depleted mantle appear to have “future” Pb compositions. We show that the \(^{207}\)Pb-\(^{206}\)Pb “isochron” as well as the (de)coupling of Pb with the other isotopic systems arise naturally within a continuously convecting and differentiating system.
Surface exposure ages of high elevation glacial erosion forms: an attempt to date deglaciation of the Last Glacial Maximum ice cap in the western Swiss Alps

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A reconstruction of the Last Glacial Maximum (LGM; approx. 18-20,000 yr B.P.) ice cap in the western Swiss Alps is based on high elevation glacial erosion features and provides a detailed representation of the former ice surface. Surface exposure dating is employed to determine the age of deglaciation from the last maximum ice surface. The timing of ice decay in the Alps is important for comparison with deglaciation on the Northern Alpine Foreland (NAF) as well as with the global ice age terminations.

The cosmogenic nuclide \(^{10}\text{Be}\) was measured in glacially eroded surfaces, 100-200 m below the maximum ice limit. Sampled surfaces were steeply inclined (40-90º) in an attempt to reduce the influence of a snow cover on the exposure ages. \(^{10}\text{Be}\) dates indicate that the last Alpine ice cap is LGM age and are consistent with surface exposure dates of the last maximum ice extent on the NAF (Ivy-Ochs, 1996). \(^{10}\text{Be}\) dates show that ice decay from the maximum level in the Saas Valley began by at least ~13,000 yr B.P. (Figure 1). This is 2500 yr after the initial deglaciation on the NAF.

**Figure 1.** \(^{10}\text{Be}\) surface exposure dates from Saas Valley.

Did the ancestral Hawaii plume interact with a mid-ocean ridge? The isotopic evidence

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The Hawaii-Emperor Seamount chain represents a record of mantle plume activity for at least 86 Ma. Systematic changes in incompatible element and Sr isotopic composition occur along the length of the chain, with the older seamounts showing much greater depletion than the younger Hawaiian lavas. In particular, the 81 Ma Detroit Seamount appears to have a MORB- like Sr isotopic composition, which Keller et al. (2000) attributed to the interaction of the Hawaii plume with a mid-ocean ridge in its earliest stages of evolution.

Following the recent success of ODP Leg 197, which penetrated a total of 1220 m into the basement of three Emperor seamounts (~80Ma Detroit, ~55Ma Nintoku, and 48Ma Koko), this hypothesis can be rigorously tested using Hf, Nd and Pb isotopes, coupled with trace element data.

Preliminary Hf-Nd isotope results for 65-85 Ma basalts recovered during DSDP Legs 19, 55 and 145 suggest that whereas younger seamounts trend towards Hawaiian compositions, the older Detroit Seamount has a similar range of \(_\text{Nd}\) to MORB. It is distinguished from MORB, however, by higher \(_\text{Hf}\) values for a given \(_\text{Nd}\), suggesting the involvement of a distinct high \(_\text{Hf}\) component. A similar trend is seen for \(^{207}\text{Pb}/^{204}\text{Pb}\), where Detroit has less radiogenic composition than N-MORB. This distinction is also confirmed by Nb-Zr-Y systematics.

Together, the data suggest that the Hawaiian plume contains a depleted component (with higher \(_\text{Hf}\) than Pacific N-MORB), which was sampled by the Detroit Seamount. An analogous high \(_\text{Hf}\) component has been identified in the Iceland plume system, where it is attributed to the entrainment of hot depleted material into the margins of the plume (Kempton et al., 2000). Such a model, however, contradicts Keller et al.’s hypothesis that the depleted component at Detroit seamount is the result of interaction with a spreading ridge. Work in progress on the new samples recovered during ODP Leg 197 will allow this model to be evaluated more rigorously for the Hawaiian mantle plume system.

**References**


References

Introduction

The involvement of siderophores in the dissolution of Fe containing minerals is well documented [1-4]. Recent studies explore the effect of siderophores on the sorption of actinide and heavy metals [5], further emphasizing their role in mediating the availability of Fe, other nutrients, and contaminants in soils. Our work employs a novel chemical force microscopy (CFM) technique that measures the forces of interaction between a siderophore and a mineral at the nanometer scale. Using these force signatures, we hope to obtain further insight into the mechanism by which siderophores release iron (and potentially other metals) from mineral surfaces.

Methods and Results

Azotobactin, a 1.3 kDa pyoverdin-type siderophore, was covalently attached to a hydrazide-activated AFM tips using a standard protein linkage reaction. Force measurements were then made between these tips and two minerals: goethite and its isostructural Al equivalent diaspore. Adhesion forces between azotobactin and the goethite surface (4.46±0.09 nN) were consistently 2-3 times the forces measured on the Al-oxide surface (1.52±0.12 nN) under the same solution conditions. Force magnitudes varied under different pH and ionic strengths, however, the relative force relationship associated with goethite and diaspore remained intact. Further, the large adhesion forces observed between the azotobactin and goethite surface could be suppressed upon the addition of soluble ferric iron, and partially regenerated with subsequent addition of high concentrations of EDTA.

Conclusions

We conclude that force signatures collected with this CFM technique reflect a specific interaction between azotobactin and goethite that correlates with azotobactin’s large affinity for aqueous Fe(III). Future investigation will attempt to identify the primary azotobactin functional groups involved during this surface interaction, and explore force signatures associated with siderophores.

References


Alkanes with a quaternary carbon centre: a 2,200 Myr. record of sulfide oxidizing bacteria

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Novel branched alkanes with quaternary substituted carbon atoms (BAQCAs) identified in hydrothermal waters escaping the ODP site 1026B on the flanks of the Juan de Fuca ridge (Northeast Pacific) are biosynthetic and occur in non hydrothermal modern and ancient sediments as old as 2,200 Myr. These hydrothermal lipids are dominated by families of 2,2-dimethylalkanes (2,2-DMAs) and 5,5-diethylalkanes (5,5-DEAs) with exclusively even and odd number of carbon atoms, respectively. These compounds (C15 to C26) were identified on the basis of their mass spectra. The structure of 5,5-diethylpentadecane (I), was verified by chemical synthesis of an authentic standard.

To determine if the paleobiogeographic range of the source organisms of BAQCAs extends beyond hydrothermal systems, the distribution of 5,5-DEAs was monitored in samples spanning the last ~800 Myr. of the sedimentary record. This record was extended to ~2,200 Myr. using the geochemical literature for gas chromatography-mass spectrometry data that indicate the presence of 5,5-DEAs. These compounds are present in the branched and cyclic hydrocarbon fraction of the lipid extracts of thermally immature Cenomanian and Turonian black-shales (Cretaceous, Canada) and other Mesozoic and Paleozoic shales where they were previously misidentified as 3,7-dimethylalkanes. 5,5-DEAs were also observed in extracts of immature Cenomanian and Turonian black-shales, microbial mats, and were released by hydrogenolysis of ~1.5 and ~2,200 Myr. pyrite (Mycke et al., 1988). 2,2-DMAs and 5,5-DEAs were also identified in modern and Holocene shelf sediments from the Russian Arctic and Abu Dhabi (UAE). The paleobiogeographic range of BAQCAs appears consistent with a bacterial microaerophilic sulfide oxidizing source.

References


Appendix

I
Isotopic and sequence stratigraphic constraints on the duration of Neoproterozoic cap carbonate deposition

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The timing and duration of strongly negative excursions in the $\delta^{13}C$ record have featured prominently in the current debate about Neoproterozoic glacial and associated carbonate rocks, and we think they represent the key. Positive carbon isotopic values were obtained from in situ peloids, ooids, and stromatolitic carbonate within Neoproterozoic glacial successions in northern Namibia, central Australia, and the North American Cordillera suggesting that the glacial oceans had normal marine carbon isotopic composition. Positive values are present at the base of postglacial cap carbonates, but become increasingly negative upward before returning to positive values in the overlying highstand sediments. These data constrain the negative excursion to the postglacial interval. Timing of the negative excursion and the anomalous alkalinity flux the cap carbonate records is possible in outcrop exposures in the Amadeus Basin of central Australia where the deposition of the cap carbonate can be compared to the rate of isostatic rebound recorded in the stratigraphic architecture that developed as a Neoproterozoic ice sheet withdrew. By analogy with modern rates of isostatic rebound, deposition of the cap carbonate occurred on the order of 10,000 y. This short duration argues for mechanisms that call on reorganization of pre-existing alkalinity within the oceans (the turnover models), or rapid release of alkalinity (clathrate model). These data argue against a silicate weathering origin for the cap carbonate as called on in the snowball Earth hypothesis because that hypothesis requires unrealistic weathering rates of 1000 times preglacial rates.

Modeling the influence of variable pH on zinc contamination in a quartz-sand aquifer

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A field-scale transport experiment was conducted to examine critical issues in modeling the influence of variable pH on the transport of strongly adsorbing metal ions. The experiment was conducted in a shallow aquifer that had been contaminated by 60 years of discharge of effluent from a sewage treatment facility serving a military base (USGS research site on Cape Cod, Massachusetts, USA). Groundwater velocities were approximately 0.4 meters per day. Uncontaminated groundwater with 2 mM chemically inert bromide (Br), added as potassium Br (KBr), and acidified to pH 4.5 by equilibrating with carbon dioxide was injected into a region where the pH was 6.0 and the aquifer was contaminated with dissolved and adsorbed sewage-derived Zn and phosphate (P). The tracer cloud induced fluctuations in pH, Zn, and other solute concentrations. For example, 2.4 meters downgradient from the injection, a decrease in pH from 5.9 to 4.9 coincided with breakthrough of Br and alkalinity. Increases in Zn concentrations from approximately 2 to 45 $\mu$M coincided with the decrease in pH. Following Br breakthrough, alkalinity and Zn concentrations returned to near-ambient values but pH increased more slowly, during which time P concentrations increased then decreased to ambient values (approximately 40 $\mu$M), and fluctuations in K, Na, and Ca concentrations were observed. The magnitudes of these fluctuations decreased with increasing transport distance except for alkalinity, which first increased then decreased with transport distance. Principal objectives of reactive transport modeling are to predict the influence of temporal variations in pH on Zn concentrations and transport using laboratory batch and column experiments for model calibration and to examine the trade-off between model parsimony (i.e., using the simplest reaction networks) and the ability to predict propagation of the pH pulse through the aquifer and its influence on Zn transport. A 2-site semi-empirical surface complexation model predicts the influence of the pH fluctuation on Zn concentrations during peak breakthrough but additional reactions are required to account for attenuation of the pH pulse, increase in alkalinity with transport distance, and the slow return of pH to ambient values following breakthrough of Br. Addition of surface protonation reactions improves prediction of the pH-pulse-attenuation and increase in alkalinity with transport distance but cannot predict the tail in the pH pulse. Work in progress involves assessing the relative contribution of ion exchange reactions and P adsorption to the evolution of pH during the transport experiment.
In situ Pb-isotope analysis by LA-MC-ICP-MS: Applications to geochemistry, geochronology, palaeoceanography and archaeology

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Variations in Pb-isotope ratios provide an unparalleled tool for isotope tracing and dating studies in the Earth Sciences and many other disciplines. Recent development of LA-MC-ICP-MS techniques allows rapid and accurate in situ laser ablation analysis of Pb-isotope ratios in a wide range of sample matrices, including silicate, titanate and phosphate minerals, silicate glasses, ferromanganese oxides and metals. In materials with sufficiently high Pb concentration (~>10 ppm) individual 30-60s Pb-isotope analyses can be made at a level of precision that approaches conventional (non double-spike) TIMS analysis, but requires just nanograms of matrix material and picogram to femtogram quantities of Pb.

In-situ Pb-isotope measurements, made using a CETAC 266 nm Nd-YAG laser in conjunction with an AXIOM multi-collector ICP-MS, have been successfully applied to a number of problems in the Earth and Archaeological Sciences. Rapid in situ single grain Pb-Pb dating of rutile, monazite,apatite and sphene provide detailed and precise (~± 0.2%) geochronological and thermo-chronological constraints on the evolution of ancient crustal rocks. High-resolution (~10-50 ka/analysis) Pb-isotope records of oceanic ferro-manganese nodules reveal changing Pacific deepwater Pb sources over the last 14 Ma, and combined Pb-isotope and LREE analyses (using a multistatic measurement technique) provide a detailed record of the relation between ocean bioproductivity and deep water circulation. Depth profile analyses of nodule surfaces provide Pb-isotope data at a spatial resolution of ≤5μm (~2.5 ka/analysis), and allow clear distinction of anthropogenic and the most recent glacial and interglacial Pb sources. Analysis of Pb-isotope ratios in feldspar, glass shards and groundmass from silicic pyroclastic rocks in Yemen and Ethiopia allow correlation of volcanic units across the Red Sea and to ash horizons in ODP leg 115 sediment cores ~2600 km from the eruption site. Analysis of metals provides rapid tracing of metal sources in archaeological material with minimal sample destruction.

Natural enrichment of organic halogens during peat formation

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There is an ongoing discussion on the natural formation and the fate of organic chlorine compounds in the environment. Recent studies on the formation of stable chlorinated organic compounds in weathering plant material (Myneni, 2002) provides interesting data about initial processes of the formation of organochlorines in the environment but also poses many questions. So, it remains unclear whether humification of plant material is the predominant process for the enrichment of organochlorines in nature.

Previously we have shown that peatlands are a major sink of organic chlorine (Kepler and Biester, 2002).

We now demonstrate that humification of plant material in peatlands is a major process to transform inorganic halides - originated from sea salt aerosols - into organically bound halides.

Two ombrotrophic peat bogs from remote pristine sites in the Magellanic Moorlands, Chile (53° S) were studied for the relationship between humification of plant material and the natural chlorination and storage of organic chlorine in wetlands. Concentrations of organic chlorine in peat were found to reach up to 0.2 % (d.w.). Based on our measurements and results from Canadian and continental European peat bogs (Silk et al., 1997; Müller et al., 1996), we estimate that between 300 and 1,100 million tonnes of organically bound chlorine have been stored in Earth’s peatlands since the last glacial period.

Moreover, concentrations of total organic chlorine (TOX) in environmental samples are often used to indicate pollution from anthropogenic sources. The observation that concentrations of naturally formed organochlorines in peatlands can exceed current threshold values of TOX to a large extent implicates that the use of this parameter requires critical discussion.

References

Atomistic simulation of the structure and reactivity of calcite surfaces

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Atomistic simulation techniques enable us to gain insight into processes occurring at the atomic level on mineral surfaces. We will describe recent work using two atomistic techniques, namely molecular dynamics and energy minimisation, to model the surface structure and reactivity of the most abundant calcium carbonate polymorph: calcite. The questions we are addressing are, does the surface structure and stability change with temperature? And to what extent are the surfaces likely to contain hydroxyl groups? In addition, we compare techniques that use inter-atomic potentials based on the Born model of solids to describe the total interaction energy of a system with electronic structure calculations using the VASP code (Kresse and Hafner 1993, 1994).

First we will review how we generate different calcite surfaces, their structures in dry and wet conditions as well as the structural change due to the presence of impurities, and their surface energy and how they compare with ab-initio calculations. We found that atom based potentials slightly overestimate the surface energies, e.g. the surface energy of the (104) surface calculated to be 0.59 J.m⁻² compared to 0.42 J.m⁻² using the VASP code. In the second part of the talk, we will present our use of molecular dynamics, using the DLPOLY code (Forester and Smith 1995), to model the interactions of water with the most significant low index surfaces and with growth steps. We found that water molecules bind strongly to the surface, this implies a layering of the water molecules in the vicinity of the surface as observed for MgO (de Leeuw and Parker 1998). The final section will describe the solid state reaction of calcite surfaces with calcium hydroxide and the implications for the presence of hydroxyl groups on the calcite surfaces as observed by experimentalists. Our calculations predict that the stepped surfaces are more likely to react than the flat surfaces, for example the energy of reaction of the hydrated acute step surfaces is −45.5 kJ.mol⁻¹ whereas that of the (104) surface is +13.5 kJ.mol⁻¹.

To conclude, atomistic simulation is a useful tool for relating surface structure and reactivity and provides a good complement to experiment.


Quantification of subduction zone metamorphic devolatilization from computed high pressure phase equilibria

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Devolatilization in subduction zones is essential to arc magmatism, seismicity and volatile recycling. Realistic modeling of metamorphic devolatilization of subducted lithologies is only possible for chemical systems that closely approximate actual bulk compositions. Volatile components are introduced into subduction zones by three contrasting lithologies: marine sediments, and hydrothermally altered mantle ultramafic rocks and oceanic metabasalts. Using free energy minimization (Perplex programs: erdw.ethz.ch/~jamie/perplex), phase equilibria were computed to 6 GPa (~160 km) to quantify the evolution of CO₂ and H₂O by prograde metamorphism of these lithologies. Serpentinites: for carbonate-bearing serpentinites (ophicarbonates) little CO₂ is released; for high-temperature (high-T) geotherms complete dehydration occurs under forearcs, and for low-temperature (low-T) geotherms major dehydration occurs under subarcs. Siliceous limestones: little devolatilization for all geotherms. Marl: with high-T geotherms devolatilization is complete under subarcs; in contrast, little devolatilization occurs with low-T geotherms. Carbonate-free pelites and turbidites: with high-T geotherms most dehydration occurs under forearcs, whereas along low-T geotherms substantial H₂O is released; for high-temperature (high-T) geotherms complete dehydration is negligible along low-T and intermediate-T geotherms and is limited along high-T geotherms; dehydration is complete under forearcs for high-T geotherms, significant under subarcs for intermediate-T geotherms, and very limited along low-T geotherms. Carbonate-free oceanic metabasalts: dehydration is complete under forearcs for high-T geotherms, and widespread under subarcs for intermediate-T and low-T geotherms. Because metamorphic devolatilization of subducted metabasalts and metasediments is continuous, no “pulses” of fluid release (corresponding to univariant devolatilization) are expected for these lithologies. Due to differences in the bulk compositions of volatile-bearing lithologies and in the P-T location of geotherms, generalized modeling of subduction zone volatile recycling is questionable.

References
Magmatic CO₂ degassing and global paleoatmospheric CO₂ contents

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Magmatic CO₂ degassing was undoubtedly a primary control on paleoatmospheric CO₂ levels. However, quantitative assessment of the flux to the atmosphere of magmatic CO₂ through time remains one of the most intractable aspects of modeling the global carbon cycle. Many geochemical models for the global carbon cycle quantify the magmatic CO₂ paleoflux by correlating with subduction rate; however, there are various reasons why this proxy is unsuitable (Kerrick, 2001). Estimates of magmatic CO₂ paleoflux coupling volumetric rates of magma production and melt CO₂ solubilities offers a viable alternative. Our current limited data base for the volume of arc magmatism through time, and uncertainties regarding CO₂ solubilities in melts of various compositions, confound this methodology for subduction-related magmatism. Flood basalts provide the most advantageous magmatic system for assessing the relationship between enhanced magmatic CO₂ degassing and elevated paleoatmospheric CO₂ contents. Because erosion and burial of flood basalts become more problematic with age, assessment of the volumetric record of flood basalt magmatism is more tractable with younger flood basalts. Using relatively conservative pre-eruptive CO₂ solubilities (i.e., 0.5 wt.%), eruption of flood basalts of the Ongtong-Java plateau could have produced 2-3 x 10⁶ moles/Myr and thus could have alone generated the estimated elevated atmospheric CO₂ contents (900-3,300 ppmv) during the middle-late Cretaceous. However, with pre-eruptive CO₂ solubilities of 0.5 wt.%, eruption of the North Atlantic igneous province, the major flood basalt volcanism during the late Paleocene-early Eocene (60-52 Myr ago), would have been insufficient to account for estimated atmospheric CO₂ contents (>2000 ppmv; Pearson and Palmer, 2000) during this time period. However, flood basalts may have pre-eruptive CO₂ solubilities >>0.5wt.% (Lange, 2002). With CO₂ solubilities of 2 wt%, degassing from the North Atlantic igneous province flood basalt volcanism could have resulted in CO₂ contents ~2X the pre-industrial value. The resultant global warming could have been a major factor in triggering the postulated massive CH₄ release by the dissociation of gas hydrates at ~55Ma (Dicks, 2001).

References

δ¹³C-, δ⁸⁷Sr/⁶⁶Sr-evolution trends of the Meso-Neoproterozoic carbonate deposits: west margin of the Siberian craton

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Reconstruction of the fragments of δ¹³C- and δ⁸⁷Sr/⁶⁶Sr evolution curves was performed over carbonate deposits (within 1500 to 850 Ma) of the Enisey ridge and the Baikit anteclise at the Western margin of the Siberian craton. Complex investigations of δ¹³C, δ¹⁸O (600 samples) and δ⁸⁷Sr/⁶⁶Sr (180 samples) were carried out with the boreholes carbonates taking account of sedimentological and petrographic data. Geochemical criteria for the selection of δ⁸⁷Sr/⁶⁶Sr in dolomites (limestones) were chosen as follows: Mn/Sr<2.5 (0.5); Fe/Sr<60 (5.0); Rb/Sr<0.005 (0.001). The most probable isotopic ratio for strontium - (⁸⁷Sr/⁶⁶Sr) was established as follows. Carbonates were decomposed sequentially in 4 stages. In all the fractions, the characteristics to be determined were ⁸⁷Sr/⁶⁶Sr, and the content of Rb, Sr, Ca, Mg. For each sample, a fraction (one of 4) with minimal ⁸⁷Sr/⁶⁶Sr, Rb and maximal Sr content was taken into consideration (Ponomarchuk, et al., 1998).

δ¹³C-values are distributed over the range –0.2±0.5‰ (PDB) within the age 1500-1350 Ma, while upwards along the sequence δ¹³C varies within –2.0 – 2.0±3.0‰. Larger variations of δ¹³C (from –2.0–3.0 to 4.0±6.0‰) are characteristic of the range 1000-850 Ma. Sharp negative shifts δ¹³C are observed near 1270-1250, 1100-1080, 1000, 950, 870 Ma (Khabarov et al., 2002). The δ¹⁸O values (PDB) are within the range –1.1 to –7.8‰, except one sample with δ¹⁸O=9.0‰. The behavior of δ¹³C- and δ¹⁸O-trends is anti-phase in the most cases.

(⁸⁷Sr/⁶⁶Sr) in carbonates are characterized by increasing values (from 0.70404 to 0.7055) upward along the sequence. This trend is destroyed by the shifts of (⁸⁷Sr/⁶⁶Sr) being increased. The highest (⁸⁷Sr/⁶⁶Sr) values are observed in carbonate rocks of the age about 1100 Ma. For the first time, low (≈0.7050) isotope ratio (⁸⁷Sr/⁶⁶Sr) was detected in carbonates from deposits younger than 1100-1080 Ma. Low isotope ratio (⁸⁷Sr/⁶⁶Sr) in mesoproterozoic ocean are the evidence of active process of paleoproterozoic supercontinent destruction and the formation of ocean. An increase of (⁸⁷Sr/⁶⁶Sr) in deposits aged ~1100 Ma is correlated with the closure of oceans and formation of the Rodinia continent. The moderate low (⁸⁷Sr/⁶⁶Sr),in the early neoproterozoic sequences are evidenced about active rifting and spreading processes.

References
Synchrony of the Bølling warming in the South China Sea (SCS) and Greenland: Implications for the regional diversity of deglacial warming, SCS reservoir ages, and the timing of MWP 1a

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Two high resolution alkenone (U K 37 ) sea surface temperature (SST) records from the southern South China Sea (SCS; sites 18252-3 and 18287-2) display an abrupt warming of >1 °C at the end of the last glacial period. According to AMS radiocarbon dates, the midpoint of this warming step occurred at 14,570 cal. ka, suggesting synchrony (within the recognized uncertainties of absolute chronologies) of the Bølling warming in the SCS and Greenland (GISP2 ice core record).

By comparing these SST records from the SCS to other available low-latitude SST records, we explore the regional variability in the timing and pattern of deglacial warming in the tropics and subtropics in the context of deglacial changes of ocean circulation.

Furthermore, we use an inferred synchrony of the Bølling warming within the SCS to assess the regional variability of reservoir ages within this semi-enclosed basin. Thus, a rapid warming during the last deglaciation in the northern SCS (site 17940-2) is AMS 14 C dated at 15,970 ±285/-260 years, suggesting locally increased reservoir ages of up to 1,400 years.

The rapid SST increase during the Bølling warming in the northern SCS (site 17940-2) is paralleled by a similarly abrupt decrease in the input of terrigenous organic matter to this site, as indicated by the concentration of an organic biomarker, n-nonacosane. We speculate that the rapid decrease in terrigenous sediment input to the northern SCS is caused by the extremely rapid inundation of the shelf during meltwater pulse (MWP) 1a. This correspondence, in turn, would imply a synchrony of the Bølling warming and MWP 1a.

Early Proterozoic continental growth in the Gyeonggi and Ryeongnam massifs, Korea

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Introduction

The Precambrian protolith of much of East Asia is: the North China Block, the South China Block, the Nangrim, Gyeonggi, Ryeongnam Blocks of Korea, and the Hida belt of Japan. Korea is a tectonic assemblage of three Precambrian micro-continents, two mobile belts, and one volcanoclastic basin. The Gyeonggi massif is dominated by Mesozoic felsic plutons which intrude the Precambrian gneisses and Paleozoic sedimentary rocks and in turn are overlain by Cretaceous rocks. The Ryeongnam massif is similar but has fewer paragneisses and more orthogneisses. Gyeonggi and Ryeongnam massifs are separated by the Ogcheon belt, which is a fold and thrust belt involving Precambrian to Jurassic rocks.

U-Pb Geochronology

The Gyeonggi and Ryeongnam terrains are essentially granitic terrains. They are composed of Precambrian ortho- and para-gneisses and Mesozoic felsic plutons. The Early Proterozoic plutonic activity that is manifested as orthogneisses can be grouped into 4 events: 2357-2342 Ma, 2120-2113 Ma, 1963-1890 Ma, and 1868-1826 Ma (Turek and Kim, 1996; Kim et al., 1999; Chang et al., 2002). The oldest plutons 2357-2342 Ma are in the Ryeongnam massif, rocks older than that are 2417-2413 Ma and are found in the Gyeonggi massif, but they are paragneisses. A peak period of plutonism can be identified as 1963-1918 Ma, in both massifs.

Conclusions

Proterozoic plutonic activity (2357-1826 Ma) contributed to the growth of the two massifs. They appear to have very similar plutonic and metamorphic history and hence were either joined together or physically close to each other in Early Proterozoic. Age correlations with China and Japan have been made (Chang et al., 2002). Ryeongnam and Gyeonggi massifs, in terms of ages, are comparable to the South China block rather than to the North China block.

References

Mercury speciation in bulk and colloidal mine wastes: origins, influences, and implications

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The speciation of mercury is one of the main factors dictating its potential bioavailability in the environment. Determining Hg speciation in Hg-bearing mine wastes is critical to understanding its release from such point sources and its distribution in surface aqueous systems. In this study the initial species of Hg present in contaminated mine wastes and the variables that may control or influence speciation in natural environments were investigated using extended X-ray absorption fine structure (EXAFS) spectroscopy. Additional techniques, including X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), inductively coupled plasma (ICP) spectroscopy, and BET surface area measurements, were utilized to further characterize the samples in terms of matrix mineralogy, particle size/morphology, and bulk chemistry.

EXAFS speciation analysis of roasted Hg ore (calcinates), waste rock, Hg condenser soot, gold mine tailings, distributed downstream sediments, and colloidal particles released from column experiments shows a variety of Hg-bearing phases present among the samples studied, with highly insoluble mercuric sulfides (cinnabar, metacinnabar) most common. Soluble Hg-chlorides, oxides, and sulfates were also identified in several samples and may represent more significant contributors of Hg to the environment.

Hg concentration and speciation in mine wastes were found to correlate closely with factors such as the initial conditions of Hg ore deposition, the roasting and weathering processes to which the samples were subjected, and particle size. Most notably, Hg in all samples, even those far downstream from their sources, appears predominantly in the crystalline phase and not as Hg sorbed to sediment particle surfaces. This discovery extends to the colloidal phase, where discrete particles of cinnabar (HgS, hex) as small as 20 nm in diameter were identified by TEM. This type of information is important to regulating agencies in assessing Hg-contaminated mining regions and devising remediation strategies.

Isotopic composition of uranium standards and sea-water determined using Finnigan Neptune multi-collector sector ICP-MS

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We have developed methods for U isotope measurements using a newly acquired Finnigan Neptune multi-collector ICP-MS. The instrument is equipped with a multi-cup Faraday (F) array and a single secondary electron multiplier (SEM) with a retardation lens system (RPQ) to eliminate tailing from intense near-mass beams. Uranium isotopes were measured in a two-step process. Firstly 234U (SEM), 235U (F) and 238U (F) were measured. Then, 235U (SEM) and 238U (F) were measured. The second step is intended to calibrate the SEM-Faraday-cup gain and the intensity of the 235U beam was sufficiently low (typically <700,000 cps) to avoid overloading the SEM. In principle, this step should account for all non-linearities between the two detectors other than count-rate dependent effects. There is significant tailing from 238U in the region of the 235U peak. The RPQ is able to reduce the scattered beam to negligible amounts with minimal loss of intensity. The RPQ lens parameters were adjusted to match the quality of the SEM peak shape to that obtained from Faraday cups. Initially the transmission through the RPQ was ~98%. However, this has subsequently deteriorated to about 75% for reasons that are not clear. However, the method for calibrating the SEM-FAR yield remains robust. NIST Uranium standard U-500 with subequal 235-238U was used to minimize the influence of tailing from 238U without having to use the RPQ. The results with and without the RPQ are identical within errors. Count-rate dependence of the results were tested and showed no significant effects within errors. All of the data are shown in the figure. For 234U intensities between 12 to 15 mV (10^11 Ohm resistor), the precision is better than ±1‰.

There is a discrepancy in the 234U/238U ratio in sea-water as determined from modern corals and directly from sea-water. Corals are close to 149 whereas mean sea water value is 143‰. Our results give values close to those measured in modern corals.

References

A major gold-bearing crust-forming event at 3.03 Ga

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The Witwatersrand Supergroup (WSG) located in the Kaapvaal craton of South Africa hosts the largest concentration of gold on the planet. Gold and rounded pyrite from the Vaal Reef (VR) of the WSG yield a Re-Os isochron age of 3.03 ± 0.02 Ga and an initial 187 Os/188 Os ratio of 0.1079 ± 0.0001 (Fig. 1).

Osmium concentrations of VR gold are 1-4 orders of magnitude greater than Os concentrations determined for other, younger gold deposits, implying both differences in mineralization processes and resistance to subsequent hydrothermal overprints (Kirk et al., 2001). The 3.03 Ga age is therefore not likely to have been significantly effected by latter hydrothermal fluids, which were likely Os-poor, as reflected by low Os concentrations determined for authigenic Ventersdorp Contact Reef pyrite.

Ages of Vaal Reef gold and rounded pyrite are older than the 2.92-2.71 Ga Central Rand Group conglomerates that host them (Robb and Meyer, 1995), indicating that the gold is detrital and was not deposited epigenetically via later hydrothermal fluids. The initial 187 Os/188 Os ratio of the VR gold and pyrite corresponds closely to the Os isotopic composition of the convecting mantle at ca. 3.0 Ga. As a result, Os and gold were likely sourced from one or more of the relatively contemporaneous mantle-derived rocks that helped to form and stabilize the Kaapvaal craton at ca. 3.0 Ga.


Precambrian/Cambrian Carbon Cycles and True Polar Wander: A Methane Connection?

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Over a dozen oscillations in the inorganic δ13 C with magnitude up to 4 %o punctuate Early Cambrian Time, starting in the Nemakit D’Aldyn zone at the Precambrian-Cambrian boundary and extending into middle Botomian time -- this is the classic interval of the Cambrian explosion. Several oscillations and large excursions are also present in middle and late Cambrian time. No other similar set of carbon cycle perturbations of this magnitude and duration (~15 to 20 million years) have been found in any other part of geological time, despite their proven use for stratigraphic correlation. The causes of these oscillations are unknown.

This same interval of time corresponds to large angular displacements in all of the apparent polar wander paths for the major continents; this has been interpreted as an inertial interchange true polar wander (IITPW) event, in which the magnitude of the principal and intermediate eigenvectors of Earth’s moment of inertia tensor become equal, and then cross. As a planet must spin about its principal moment of inertia, an IITPW event would cause the solid Earth to undergo a rapid burst of up to 90º of true polar wander, bringing parts of the globe initially located at the poles to the equator in a geologically short interval of time (~5-25 Myr). These large true polar wander events also predict dramatic sea level effects, the magnitude of which will vary greatly with geographic location. IITPW can be used to deduce the absolute paleogeography, including paleolatitude.

The IITPW reconstruction for Early Cambrian time implies that large areas of North America and Gondwana moved from the South polar region to the Equator. Methane clathrate deposits which formed in the cold polar regions were moved progressively out of their stability fields into warmer, tropical climates. The epistatic nature of global circulation, coupled with pressure changes induced by sea level variations, suggests that broad regions might be subjected to geologically sudden warming events, leading to fairly rapid bursts of methane emission. Such bursts are capable of producing large fluctuations in the carbon isotope record, such as has been suggested for the single blip at the Paleocene/Eocene boundary. A greenhouse induced transient thermal warming pulse is also expected to occur associated with these Cambrian carbon excursions, and might be detectable if carbonates with unaltered oxygen isotopes could be found. Many of the major negative excursions in the Early Cambrian carbon cycles are followed by a clear evolutionary burst in one or more phyletic groups, as also happened in the Eocene. As biological diversity correlates strongly with temperature, a series of repeated methane-induced warming pulses should have contributed to the biological radiation events during the Cambrian Explosion.
Possible tectonic control on the observed asymmetry of drainage networks across the Ladakh batholith

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Major rivers, in tectonically active regions, have been used as passive markers of diffuse strain with the clear suggestion that it is considered unlikely that they migrate laterally under conditions of large scale compression. Longitudinal valleys that parallel major thrust fronts are a possible exception to this observation. In Ladakh, northern India, asymmetry is observed in the transverse drainage pattern of the Ladakh batholith. The batholith is, in part, sandwiched between two major longitudinal rivers – the Indus to the south and the Shyok to the north. The course of the Indus is potentially affected by the northward deformation of the Zanskar fold and thrust belt.

Large-scale quantitative measurements and analysis of the landscape morphometry have been utilised to document potential feedback between tectonic uplift and longitudinal river systems. Quantitative geomorphological analysis of different portions of the batholith that are considered to be effected by thrusting, and those that are not, reveal significant differences in the degree of asymmetry across the batholith. The Digital Elevation Model (DEM) has been combined with field observations and preliminary low temperature thermochronometry (apatite fission track and U-Th/He). The denudational history of the batholith is revealed through the thermochronometry results and linked to major tectonic events in the wider Himalaya. Combined the datasets have been used to document potential translation and to test the hypothesis that local drainage form is a function of the horizontal motion of a major longitudinal valley in response to tectonic activity.

The $^{26}$Al ages of chondrules as the chemical records of the active proto-planetary disk

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Correlation of ages with chemical compositions

Recent studies of $^{26}$Al age of chondrules from various classes of chondrites indicated that they formed at average of 2 million years (My) after CAIs (Ca, Al-rich Inclusions), by assuming the homogeneous $^{26}$Al distribution in the early solar system. Our recent studies of 16 chondrules from ordinary chondrites suggested that the total span of their ages was at least 1 My. We further discovered that the olivine-rich (high Mg/Si) chondrules are older and generally depleted in volatiles (e.g. Mn and Na) than pyroxene-rich (low Mg/Si) ones. We considered the mechanism of the volatile enrichment (Si, Mn, Na) in younger chondrules as 1) evaporation of volatiles from older chondrules, 2) removal of older chondrules from the chondrule forming region, and 3) addition of evaporated volatiles to the precursor of younger chondrules.

Implication to the history of proto-planetary disk

The observed chondrules ages are comparable to the period of classical T-Tauri (CTT) stars. Recently, episodic (~hours) keV-range-X-ray flares were observed from many CTT stars with the energy $10^6-10^8$ times larger than the solar flare. The flare is repeated during the CTT stage and produces shock waves (~200 km/s), so that the $^{26}$Al ages of chondrules might record such an explosive magnetic activity of the proto-planetary disk. Evidence of volatility related chemical fractionation with chondrule ages implies that the episodic flares may cause high temperature gas/solid fractionation elsewhere in the proto-planetary disk. It has a significant implication to the cosmochemical fractionation among planetary materials.

References

Megascale isotopic anomaly in Cr?
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Undifferentiated meteorites provide many examples of microscale (spatial scale cm and smaller) isotopic anomalies, i.e. isotopic variations indicating incomplete mixing of stellar nucleosynthetic components, reflecting preservation of presolar solids [1]. Megascale anomalies, i.e. isotopic variations among different planetary bodies (e.g. in O [2] and arguably in Cr [3,4]), are fewer and smaller, and provide different constraints on solar nebula models.

Pursuant to better understanding of possible megascale anomalies in Cr, we have recently reported isotopic data for surface-correlated (putatively solar wind) Cr in lunar soil [5], finding excess $^{53}$Cr of at least 8 epsilon-units, and also excess $^{53}$Cr half that big. These results are well outside the envelope anticipated beforehand.

Perhaps these data do not represent presolar anomaly, but rather nuclear reactions within the solar system. The moon itself is a possible venue for such reactions; an interesting alternative is the atmosphere of the sun [6]. These two possibilities seem at the edge of plausibility [7]. They cannot be eliminated unambiguously but neither can they be supported in quantitative detail. In this work, therefore, we pursue ramifications of the interpretation that surface-correlated lunar Cr really is isotopically anomalous.

The direct interpretation is that the sun, or at least the source region of the solar wind, has a different isotopic composition than the terrestrial planets, reflecting different admixture or presolar nucleosynthetic components. This seems outlandish, but the difference need be only of order one permil. This situation could arise if the solar system’s antecedent interstellar cloud were itself spatially heterogeneous.

Alternatively, instead of solar wind Cr we may have measured meteoritic Cr. There is enough inferred meteoritic material in lunar soils to permit this interpretation, but its distribution is not known well enough for definitive evaluation. An immediate objection to this hypothesis is that known meteoritic (whole rock) Cr is not so anomalous, so a very unusual source of meteoritic material would have to be postulated. Thus, this interpretation would permit the tenet that the sun and terrestrial planets were made from the same material but at the expense of requiring that most meteoritic infall to the moon is not like known meteoritic material, e.g. is possibly from isotopically exotic comets.


Mercury in Carbonaceous Chondrites
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Introduction: There are many reports of isotopic anomalies in meteoritic Hg [1, 2]. Every such report is based on neutron activation analysis, which can only detect two of the seven stable Hg isotopes. As a result only anomalies in the $^{196}$Hg/$^{202}$Hg ratio have been reported.

We have developed a technique to measure low concentrations (pg/g levels) and isotopic abundances of Hg with a precision of $\pm 0.005 - 0.02\%$ using single- and multi-collector inductively coupled plasma mass spectrometry (ICPMS) coupled with continuous-flow cold-vapor generation. We first applied this technique to Murchison (CM) and Allende (CV), two meteorites which reportedly contain isotopically anomalous Hg. Our measurements suggest that the relative bulk abundances of all seven stable Hg isotopes in both meteorites are identical to terrestrial values within 0.7 \% [3]. Thermal analysis coupled with ICP-MS revealed distinct Hg release patterns for Allende and Murchison.

We have continued our study of mercury in primitive meteorites and expanded the suite of meteorites to include other members of the CM and CV chondrite group as well as CI and CO chondrites.

Methods: Clean, interior samples of the CI chondrite Orgueil, the CM chondrites Murray, Nogoya, and Cold Bokkeveld, the CO chondrites Kainsaz, Orans, and Insa, and the CV chondrites Vigaranj, Mokota, and Grosnaja were gently crushed under ethanol to obtain uniformly-sized powders. The samples were digested in a mixture of HCl/HNO$_3$/HF at 210°C/50 bar. Bulk abundance and isotopic composition measurements were performed using an ELEMENT2 (ThermoFinnigan) single-collector magnetic-sector ICP-MS. The continuous-flow, cold-vapor-generation apparatus is described in [3]. Thermal analysis was performed with a controllable oven coupled to the ICP-MS.

Results: The isotopic compositions of the meteorites show no significant isotopic anomalies greater than a few permil. These measurements will be repeated by MC-ICP-MS to determine if any fractionation is present below this level. Bulk abundances range from the sub-ppb level up to several ppm. Details of the thermal analyses are given in [4].

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Production rates of $^{10}$Be and $^{26}$Al in mid-latitudes and high altitudes

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Site Production Rates

The inner Titcomb Lakes moraine (43.12°N, 109°W), Wind River Range, Wyoming, USA has the attributes of a site suitable for determining terrestrial cosmogenic nuclide production rates for late Pleistocene exposures. The moraine was deposited between 12.9 and 11.6 ka during the Younger Dryas chron (1.3 kyr duration). Assuming constant GCR flux, exponential attenuation of the production rate below the rock surface, and negligible erosion, shielding, and inheritance, measurements of $^{10}$Be and $^{26}$Al in ten boulders yield annual production rates at the site of 53.8±0.9 $^{10}$Be atoms $a^{-1}$ g$^{-1}$ SiO$_2$ and 322±10.7 $^{26}$Al atoms $a^{-1}$ g$^{-1}$ SiO$_2$ (uncertainties reflect 1.6% and 3.3% 1 coefficient of variation about the mean).

Corrected for shielding due to topography and snow cover, the rates are 55.9±2.1 $^{10}$Be atoms $a^{-1}$ g$^{-1}$ SiO$_2$ and 335±6.0 $^{26}$Al atoms $a^{-1}$ g$^{-1}$ SiO$_2$. The $^{26}$Al/$^{10}$Be is 5.94 ±0.26 (uncertainties include external error, reproducibility at U. Pennsylvania chemistry and AMS, standardization at U. Pennsylvania, random errors associated with thickness, snow cover, and exposure duration).

Scaled Production Rates

Local production rates were converted to production rates at sea level and high altitude using the scaling approach of Lal (1991) as modified by Stone (2000) based on a geocentric dipole axis. The $^{10}$Be production rate at sea level and high latitude is 5.33±0.20 atoms $a^{-1}$ g$^{-1}$ SiO$_2$ and for $^{26}$Al, 32.0±1.9 atoms $a^{-1}$ g$^{-1}$ SiO$_2$. When scaled with the approach of Dunai (2000; vers. 1.3; 15°C at sea level, 45° lat.), the rates are 4.71±0.18 $^{10}$Be atoms $a^{-1}$ g$^{-1}$ SiO$_2$ and 28.2±1.7 $^{26}$Al atoms $a^{-1}$ g$^{-1}$ SiO$_2$.

Discussion

Because of the site’s insensitivity to variations in geomagnetic dipole paleointensity and axis positions, the site’s production rates remained within 5% of this value for the entire period from 22 to 6.0 ka. However, non-dipole field features in the region (e.g. persistent increase in inclination from the 13.5 – 0 ka Fish Lake record) could cause the time-integrated production rate at the site to be up to 3% lower than other sites for the same time. Effects of burial and erosion could also cause the scaled production rate to be lower than the others scaled similarly. Prevailing atmospheric effects in the Wind River Range may increase the site production rates by as much as 2% (Stone, 2000).

References

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Volatile-rich brine and melt in Canadian diamonds

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Micro-inclusions in diamonds provide pristine information on the composition of mantle fluids. Following the identification of carbonate and hydrous-silicic melts in diamonds from Congo and Botswana and brine inclusions in South African diamonds, we explored the composition of micro-inclusions in ten diamonds from the Diavik mine, Slave Craton, Canada. Three main types of micro-inclusions were found: brine-bearing inclusions, melt-bearing inclusions and a few mineral micro-inclusions.

Melt inclusions were found in a single diamond. Their composition is intermediate between the hydrous-silicic end-member and the carbonatitic (Mg-Ca-Fc-Ba-rich) end member of Schrauder and Navon (1994). The average melt composition is ($K$$Na$)$_{10}$($Si$$_3$Al$_5$)$_4$(Ca,Mg,Fc)$_{4}$Cl$_{10}$ ($H_2O$)$_{12}$ ($CO_3$)$_4$, with K/Cl molar ratio of 6.4±0.05. We did not find inclusions with intermediate compositions between the hydrous-silicic and the brine end-members.

Schrauder and Navon (1994) favored fractionation of carbonates and evolution from carbonatitic melt towards the hydrous silicic composition. However, such a model cannot explain the compositions between the carbonatitic end-member and the brine.

Johnson et al. (2000) found a wide range of Br/Cl and I/Cl ratios in Canadian diamonds (1 to 100 times the MORB ratio) and attributed it to fractionation of a Cl-bearing phases, such as apatite or mica from melts similar to those described by Schrauder and Navon (1994). We suggest that these diamonds trapped brine rather than melt and the high Br/Cl and I/Cl ratios are characteristic of the brine. If so, apatite or mica crystallization cannot explain the chemical evolution from carbonatitic melt to brine.

We favor a model where crystallization of carbonates from a carbonatitic melt leads to enrichment of the melt in silica, alkalies and chlorine and to its separation into two immiscible fluids: a hydrous silicic melt and a brine.

The source of the carbon, alkalies and chlorine cannot be easily identified as recycled or primordial. The carbon isotopic composition of fluid-bearing diamonds falls within the range of MORB and other mantle-derived melts. Br/Cl and I/Cl ratios converge towards the MORB values. The similarity of isotopic and chemical ratios to MORB values may reflect derivation either from subducted oceanic crust or from mantle reservoirs with MORB source signature.

References: Johnson et al. (2000) GCA 64, 717-732.
The extinct $^{182}$Hf-$^{182}$W isotope system has been widely applied to date core formation in planetary bodies [e.g., 1]. Recent studies report a $^{182}$W anomaly of about -2 ε units for the carbonaceous chondrite Allende relative to the terrestrial value [2] which significantly differs from the previously accepted value of $0.8±0.2\times10^{-4}$ [4] and $~1\times10^{-4}$ [2]. To address these issues, we obtained W isotope compositions for seven carbonaceous chondrites (CC) and a four point Hf-W internal isochron for the H chondrite Ste. Marguerite which is well dated with U-Pb (4.562±0.0006 Ga). Using the MC-ICPMS at Münster, $^{182}\text{W}/^{184}\text{W}$ can be measured with an external reproducibility of ±0.5 ε units (2σ). Hf/W ratios were measured using a $^{184}$Hf-$^{182}$W tracer that was calibrated against pure metals.

The seven CC Orgueil, Allende, Axtell, Murchison, Cold Bokkeveld, Nogoya and Karoonda exhibit uniform W isotope compositions with a mean of -1.9±0.2 ε units relative to the terrestrial standard. This value is consistent with the result from [2] and with Hf-W data on E chondrites. Most importantly, terrestrial samples now show a $^{182}$W anomaly of ca. +2 ε units relative to the newly defined chondritic value, which allows precise dating of terrestrial core formation. An internal Hf-W isochron for Ste. Marguerite defines the solar system initial $^{182}\text{Hf}/^{184}\text{Hf}$ ratio of $~1\times10^{-4}$ has been suggested [2] which is in stark contrast to the previously accepted value of $2.75\times10^{-4}$ [3]. To address these issues, we obtained W isotope compositions for seven carbonaceous chondrites (CC) and a four point Hf-W internal isochron for the H chondrite Ste. Marguerite defines the solar system initial $^{182}\text{Hf}/^{184}\text{Hf}$ as 1.1±0.1 $\times10^{-4}$ (2σ), which is significantly lower than the currently accepted value of $2.75\times10^{-4}$ [3], but in remarkable agreement with previously suggested values of $0.8±0.2\times10^{-4}$ [4] and $~1\times10^{-4}$ [2].

The redefinition of both the chondritic $^{182}\text{W}/^{184}\text{W}$ and the solar system initial $^{182}\text{Hf}/^{184}\text{Hf}$ requires the re-evaluation of published Hf-W ages for core formation. Assuming Hf/W = 34.6 for the HED mantle, 6.2 for the Martian mantle and 17.7 for the bulk silicate Earth, Hf-W model ages (after formation of CAIs) of ~4 m.y. for the HED parent body, ~16 m.y. for Mars, and ~30 m.y. for Earth can be calculated if our newly defined parameters are used. The Hf-W model age for the HED parent body is now consistent with results from the $^{53}\text{Mn}-^{53}\text{Cr}$ and $^{26}\text{Al}-^{26}\text{Mg}$ systems, which suggest HED mantle differentiation within the first ~3 m.y. after condensation of CAIs. The Hf-W model ages obtained for Mars and Earth are in excellent agreement with Wetherill-type models for planetary accretion that suggest a timescale of tens of m.y. for the formation of the terrestrial planets.


**Revised Hf-W ages for core formation in planetary bodies**

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**H2O in the mantle drives secular change in continental petrology**

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A model for Archaean granitoid magmatism is presented, which reconciles the geochemical similarities and differences between TTG and potassic granitoids. The model was developed with a sample suite from Barberton Mountain Land, South Africa. Since both investigated rock types share the typical trace element signature for arc magmatism (overabundance in fluid-sensitive elements; HFSE depletion) it follows that both granitoid types are derived from refertilised mantle above subduction zones (s.l.), where melting is triggered by fluids derived from slab dehydration. As parental melts hydrous basalts are envisaged, which underwent extensive fractional crystallisation. Experiments demonstrate that depending on initial water content of the melt, remarkably different fractionating assemblages crystallise (e.g. Sisson and Grove, 1993; Müntener et al. 2001). Importantly for TTG, high-H2O basaltic melts crystallise extensive garnet and/or amphibole whereas plagioclase and olivine crystallisation is suppressed. Such a fractionating assemblage ultimately leads to tonalitic derivative melts with (i) high LREE/HREE ratios; low HREE contents, (ii) absence of Eu-anomaly, (iii) low K/Na ratios and (iv) high abundances of highly compatible elements. While intermediate H2O-melts still crystallise garnet and/or amphibole, plagioclase and olivine are, in contrast, not suppressed. This results in derivative liquids with (i) high LREE/HREE ratios; low HREE contents, (ii) presence of Eu-anomaly, (iii) high K/Na ratios and (iv) low abundances of highly compatible elements. These characteristics are found in Archaean potassic granitoids. Low H2O-melts do not crystallise garnet and amphibole, but olivine and plagioclase resulting in ‘classical’ post-Archaean granites with (i) high LREE/HREE ratios; low HREE contents, (ii) absence of Eu-anomaly, (iii) high K/Na ratios and (iv) low abundances of highly compatible elements. We identify the initial water content of the parental melt as the key parameter to explain the secular change in continental petrology. The disappearance of TTG between 2.5-2.0 Ga and emergence of ‘classical K-granites’ is thus explained with secular decrease of aqueous fluid transport into the subduction zones and/or efficiency of deep fluid release from subducted slabs.

Metamorphic Pb-Ag mineralization at Albrunpass (Central Alps)

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Lead and silver occurrences are widespread in Triassic metasedimentary rocks of the central Alps. They are of interest as examples of mobilization and local enrichment of ore metals by regional-metamorphic fluids. The Binntal region in Switzerland hosts the Lengenbach deposit, which is famous for its exotic and partly unique Pb-As-rich sulfosalt minerals. At the southwestern termination of the same valley, near Albrunpass, an ancient mine produced Pb-Ag ore at a concentration ratio of 750:1. The mineralization lies exclusively in quartzite lenses within Triassic dolomite marbles enclosed by gneisses. Structural relationships indicate emplacement of the ore during late stages of Alpine deformation and regional amphibolite facies metamorphism, in semi-ductile to brittle shear zones and late-metamorphic Alpine fissure veins.

The Pb mineralization consists of coarse-grained galena, with subordinate pyrite, fahlores (tennantite and tetrahedrite), chalcopyrite and accessory Zn-, Sn-, Ag-, Te- and REE-bearing minerals (notably stannite and bastnaesite group carbonates). Open space filling of fissures includes rhombohedral quartz, dolomite, adularia, galena, pyrite and rutile.

Free-grown quartz crystals host 3 different generations of fluid inclusions that have been studied by petrography, microthermometry and LA-ICPMS elemental analysis. A CO2-rich, low-salinity (1-2 wt% NaCl eq) fluid with low metal contents represents the pre-ore stage fluid. Incursion of a high-salinity brine (~31 wt% NaCl eq), preserved in inclusions containing three daughter crystals at room temperature (halite, barite and probably sylvite), represents the input of the ore-forming fluid. It contains extremely high Ba, Pb and Mn concentrations. CO2-rich fluids progressively diluted the ore-forming brine, thereby probably triggering PbS deposition in veins but also in microcracks together with brine. Base metal concentrations in the fluids gradually decrease with decreasing salinity. CO2-rich fluid inclusions postdating the brines show variable salinities of 6 - 1 wt% NaCl eq and low base-metal content. The latest generation of fluid inclusions is a very low-salinity aqueous fluid trapped on secondary trails.

The ore metals at Albrunpass are interpreted to have precipitated by fluid mixing during late-metamorphic uplift and fissure formation. An exceptionally metal-rich aqueous brine probably originated from metamorphic equilibration with Triassic meta-evaporite units that may have contained dispersed Pb-Zn minerals of diageneric origin. These brines mixed locally in fissures with ambient low-salinity CO2-rich fluid of possible metamorphic basement origin, to generate a small but high-grade metamorphic ore deposit.

Some experimental constraints on major and trace element partitioning during partial melting of eclogite

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Isobaric partial melting experiments were performed to simulate partial melting of subducted oceanic crust. Experiments at 3.0 GPa yielded melts in equilibrium with garnet and aluminous clinopyroxene. Melt compositions show decreasing Si and alkalis, and increasing Ca, Mg and Ti contents with increasing temperatures. Experiments at 1200°C and 1300°C were rutile-saturated, whereas experiments at 1400°C contained no residual rutile. We argue that during the initial stages of subduction accessory rutile is likely to be stable in subsolidus eclogites of average MORB composition and that only large degrees of partial melting will eradicate rutile from an eclogite source. At 3 GPa any eclogites with a bulk TiO2 content of ≥1.5 wt% rutile will produce rutile-saturated partial melts, except at very high degrees of melting. At higher pressures all bulk Ti may dissolve in clinopyroxene and garnet, leaving no accessory rutile.

Trace element partition coefficients for 24 trace elements between clinopyroxene, garnet and melt were determined by SIMS analysis of experimental run products. Partition coefficients for the rare earth elements agree well with previous studies and have been evaluated using the lattice strain model. Partitioning data for high field strength elements indicate complementary DZr/DHf for clinopyroxene and garnet. Partial melting of an eclogitic component of different modal compositions may, therefore, explain both sub-chondritic and super-chondritic Zr/Hf ratios. Super-chondritic Zr/Hf has recently been observed in some ocean island basalts (OIB) and this may be understood as further evidence for components of recycled oceanic crust in OIB.
Differentiation rates and geochemical characterization of parental magmas for The Piton des Neiges Volcano (Réunion Island, Indian Ocean)

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A high-resolution K/Ar geochronological and geochemical study has been performed on the terminal activity of the now extinct central shield volcano of the Réunion hot spot (Indian ocean) : the Piton des Neiges. This ultimate stage of activity which lasted over about 300 kyr (from 350 ka to 25 ka), is characterized by the outpouring of differentiated products ranging from plagioclase-phyric basalts to quartz-trachytes and comendites. The high time-resolution of the chronostratigraphy allows two distinct and simultaneous geochemical evolution trends to be recognized. Based on brown amphiboles study, a two superimposed magma chamber model is proposed to account for the whole geochemical evolution of the Piton des Neiges volcano with a deep one (5-6 kbar) and a shallower one (2-3 kbar). Differentiation rates for magmas in the shallow reservoir are comprised between 0.4 and 1.3 wt.% SiO₂/ka. Such rapid differentiation occurred four times in the final history of the Piton des Neiges volcano. The parental magmas are Si-undersaturated with normative nepheline comprised between 0.8 and 4.8 wt.%.

Gradients in silicic bodies caused by mixing rather than chamber differentiation

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One widely accepted paradigm for compositional zoning in silicic eruptions is that such heterogeneity reflects vertical gradients in the source-magma reservoir developed gradually through in situ differentiation. Although the pattern of chemical and phenocryst variation in some eruptions may support magmatic gradients in the source reservoir at the time of eruption, evidence for protracted chamber differentiation is generally equivocal. In many instances the observed zonation is as readily explained by mixing during chamber replenishment just prior to eruption. Here we show that integration of textural and whole-rock geochemical signatures with mineral-scale isotopic variations in the rhyolite of Taylor Creek, New Mexico, can be used to identify and track the involvement of recharge in magma evolution and eruptive activity.

At Taylor Creek, a group of 20 high-silica rhyolite lava domes and flows totalling ~ 55 km³ in volume erupted in a period of 100,000 years or less at 27.9 Ma. For domes and flows showing time-related trace-element trends, phenocryst modal distributions vary systematically with relative age. Early erupted lava has moderate to high crystal contents (20–36 vol. %). Late erupted lava is relatively crystal poor (< 20 vol. %). Within these dome clusters, high 87Sr/86Sr, incompatible-element-poor lava is invariably first erupted. Mineral-scale isotope variations indicate the rhyolite formed by mixing of relatively low 87Sr/86Sr rhyolitic liquid into stagnant, partially solidified high 87Sr/86Sr magma previously intruded into, and contaminated by, Proterozoic granitic crust. Reinjection appears to have occurred prior to and during growth of the lava-dome field and may have triggered eruptions by slight reheating and/or addition of volatiles to resident magma. Mixing calculations suggest that addition of 10 to 90 % replenished liquid to resident magma can account for the entire compositional spectrum of Taylor Creek lava. Time variations in lava compositions and size distributions of phenocrysts indicate, however, that serial eruptions progressively tapped off most of the hybrid magma formed by mixing of contaminated resident magma with replenishment liquids prior to final dome emplacement. These observations link growth of the lava-dome field to reinjection events and are consistent with waning of eruptive activity following cessation of replenishment.
Geochemical clues on the origins of Rajahmundry Trap basalts, India

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40Ar/39Ar ages for plagioclase separates from Rajahmundry Trap basalts of eastern India reveal a mean age of 64.7 Ma (Knight et al., submitted), placing the eruption of the Rajahmundry Traps coincident with late stage Deccan Trap flood basalts, often associated with K-T boundary events and lying over 400 km to the west. Here, we further examine the plausibility of a petrogenetic relationship between these two provinces (e.g. Baksi et al., 1994). A recent set of published papers detailing the geochemistry of the north-eastern margins of the Deccan Traps (Mahoney et al., 2000; Peng et al., 1998) and a preliminary study of the preserved margins of eastern Deccan Trap volcanism (Bilgrami, 1999) provide the best-to-date basis for geochemical comparison. In light of these newly available data we use trace element data on 6 samples and isotopic data on 11 samples from the Rajahmundry Traps to better constrain the nature of a possible petrogenetic connection between the Rajahmundry and Deccan Traps. Rare earth element data for all samples normalised to chondritic abundances show slight enrichment in the light rare earth elements (La/Sr ~1.4) and no notable Eu anomaly. Pb isotopic data show three statistically distinct groups, with 206Pb/204Pb of 17.42 - 18.60. The Rajahmundry Traps reflect REE and isotopic ratios of north-eastern Deccan Trap flows pointing towards similar mafic magmatic sources and placing constraints on the origins and amount of crustal contamination present in the Rajahmundry Traps. Establishing the nature of a petrogenetic relationship between these two provinces also addresses melt transport mechanisms within flood basalt provinces and the original extent of the Deccan Traps.

References

Diversity of microorganisms mediating anaerobic oxidation of methane

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Methane is present in huge amounts in marine sediments. Little of the methane reaches the oxic water column because it is oxidized with sulfate to CO2 by microorganisms in the anoxic sediments. Recent studies demonstrated that the anaerobic oxidation of methane (AOM) is mediated by a structured consortium of sulfate-reducing bacteria belonging to the Desulfovibrio group and archaea belonging to the ANME-2 group, which is phylogenetically affiliated with the order Methanosarcinales.

The microbial diversity of AOM-communities was investigated by 16S rDNA clone library analysis of samples from different methane-rich submarine environments (Hydrate Ridge, Haakon Mosby Mud Volcano, Black Sea). The bacterial diversity was always high, and comparable with that of coastal sediments. The most abundant 16S rDNA sequences were derived from δ-proteobacterial sulfate-reducing bacteria (SRB), γ-proteobacteria and members of the Cytophaga/Flavobacterium cluster. In sediments from HMMV, however, the abundance and diversity of SRB was very low. Here, sequences related to methylotrophic bacteria (Methylomonas spp., Methylophaga spp.) dominated. The archaeal diversity was low in all habitats. Most sequences belong to recently described groups of uncultivated methanogenic archaea, ANME-1 and ANME-2.

Aggregated archaea and sulfate-reducing bacteria were present in all sediments investigated. In addition to structured consortia, consisting of an inner core of archaea partially or fully surrounded by SRB (Hydrate Ridge, Eel River Basin), we also found unstructured consortia (HMMV, Guaymas Basin, Gulf of Mexico) as well as consortia consisting of just two archaeal cells and a single SRB cell (Congo Basin). During submersible dives to methane seeps in the permanently anoxic Black Sea giant microbial structures were discovered, composed of massive microbial mats of centimeter to decimeter thickness, and producing large carbonate columns and platforms. Microbial 16S rDNA and FISH analysis of mat sections revealed that the massive mat is composed to 70% of archaea (ANME-1 cluster) which occur densely aggregated with SRB (Desulfosarcina group).

This presentation will give an overview on the different types of AOM consortia in methane seep environments.
Biological control of magnetite crystal formation in the magnetotactic bacteria: hints concerning the possible evidence from ALH84001 for life on Mars

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One of the strongest lines of evidence for the existence of ancient life on Mars is the possible presence of bacterial magnetofossils in the carbonate globules of the ALH 84001 meteorite[1, 2]. Of the ~seven magnetite-based criteria currently being used to identify life on Mars, one of the most distinctive features is the presence of magnetosome chains[3]; these structures are common in living magnetotactic bacteria and in a variety of terrestrial magnetofossils. However, there is a debate about whether they can form through other non-biological processes. In living magnetotactic bacteria, it is known that individual magnetite crystals are formed within a string of vesicles, each of which is composed of a proper lipid-bilayer membrane. At present, the biological process that forms these structures is completely unknown.

Several inorganic processes using heavy metals are known to precipitate linear strings of similarly-sized crystals in a highly viscous media that contains large organic matrix molecules [4]. Our hypothesis is that organic material in ALH 84001 may have helped organize the chain-like magnetite structures. We will also report our attempts to observe the internal structures of the magnetosomes in the magnetotactic bacteria using electron microscopy, to test for the presence of a similar organic matrix.


The dependency of cosmogeneric nuclides to climate and surface uplift in transient landscapes

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Geomorphological and geological studies as well as drainage system analyses (e.g. Mortimer 1980, Wörner et al. 2002) point to the existence of 10-20 Ma-old surfaces in Northern Chile that have been preserved due to arid/hyperarid climate conditions. Because of the excellent preservation of these surfaces, they bear information on temporal and spatial variations in tectonic and climate forcing. In an effort to extract this information, we currently apply the cosmogenic stable 21Ne and radionuclide 10Be methodology to the Miocene bedrock and alluvial surfaces. The samples are collected in a transect from the Coastal Cordillera through the Longitudinal Valley, the Pre- and Western Cordillera from west to the east.

Measured concentrations of cosmogenic nuclides (without correction for erosion rates and surface uplift) imply Pliocene/Pleistocene apparent ages for the Miocene surfaces. These ages correlate with the topographic roughness and the content of moisture in the air (coastal fog, orographic precipitation). However, the correction for erosion rates of 20-50 cm/My as indicated by 21Ne /10Be - 10Be ratios (Ivy-Ochs 1996) yields Middle Miocene ages for the analyzed surfaces. These ages, however, are still significantly younger than expected (i.e. 10-20 Ma). Consequently, the difference between the corrected ages and the formation ages results from either unsteady erosion or variable surface uplift rates. Current efforts aim at analyzing depth profiles and modelling of erosion / surface uplift scenarios to detect possible unsteadiness in surface erosion and / or surface uplift.

Autigenic carbonate mineral ikaite originated from biogenic methane in the Kara Sea sediments.

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Various modifications of autigenic carbonates have been found during German-Russian expedition on board r/v “Akademik Boris Petrov” (2001) in Holocene sediments of the Kara Sea between the latitudes of 73 to 77° N, situated mainly along the Yenisei ancient channel. Among them there are carbonate concretia (nodules), dispersed carbonates (cement) and crystalline mineral ikaite (CaCO$_3$·6H$_2$O) specific to low-temperature (near zero) environments. Ikaite is a metastable mineral at the room temperature: it transforms to calcite and water. The all studied antigenic carbonates are characterized by depletion in the heavy carbon isotope. The ikaite carbon isotope composition varies from -24‰ to -49‰.

Figure 1: Kara Sea, St. BP-00-37

The pore water composition and methane concentration have been studied along with carbon isotope analysis. (Fig.1). Biogenic methanogenesis manifests itself by high content of isotopically depleted methane ($\delta^{13}$C = -102 to -104‰). Methane appears to be a source of isotopically depleted CO$_2$, which involves to ikaite precipitation. The methane transformation to CO$_2$ (“anaerobic CH$_4$ oxidation”) resulted from sulphate reduction, with the methane being used as a hydrogen source.

The role of dust in climate cycles

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Although atmospheric dust contributes significantly to the modern atmospheric aerosol load, even the sign of the direct radiative impact of dust on modern climate is unknown. Our ability to quantify the impacts of dust on the climate system depends on our understanding of (a) processes controlling the contributions and properties of naturally varying and anthropogenic dust emissions, (b) how these contributions change through time, and (c) how atmospheric dust then interacts directly and indirectly with the earth system.

The geologic record of dust from ice cores, marine sediments, and terrestrial records demonstrates that the glacial world was significantly dustier than today, suggesting that the climate impacts of dust were larger in the past. Glacial dust deposition rates downwind of tropical to subtropical regions were ~1-3 fold higher than today. Glacial areas of dust deposition were expanded in midcontinental regions, with highest glacial dust accumulation rates (~5000 g/m$^2$/yr) in the midcontinental USA. Dust accumulation rates across the Chinese Loess Plateau were 2-4.5 times larger overall, with regional median deposition rates of 310 g/m$^2$/yr. Combined with vegetation and lake status records, these data suggest that arid-to-semi-arid regions were expanded at the LGM.

Although the overall magnitude of high latitude glacial dust deposition rates remained small, they nevertheless increased 2-20 fold, and pose several interesting problems. First, dust provenance studies suggest that the most likely source for dust reaching the Greenland and Antarctic ice cores are Asian and Patagonian deserts, respectively. Second, the accompanying micronutrients in this dust may have been sufficient to impact marine biota and atmospheric [CO$_2$] uptake in key iron-limited oceanic regions.

Attempts to simulate these glacial-interglacial changes in dust have resulted in several advances of our simulation of the dust cycle. First, emissions in the most recent global dust models depend on changes in climate (i.e., winds and moisture balance) as well as land-surface conditions (e.g. vegetation cover, soil wetness, and preferential dry lake bed sources). Incorporation of these feedbacks results in a significant increase in global glacial dust emissions, in particular in Asian deserts at the LGM. Higher atmospheric dust concentrations at the LGM are also expected to have an impact on the global radiative budget. Although the high-latitude mean change in radiative forcing (LGM minus modern) is small relative to the forcing associated with ice sheets, the glacial decrease in radiative forcing in the tropics is of the same magnitude as the radiative cooling effect of low atmospheric [CO$_2$]. Finally, ocean biogeochemistry models show that the simulated impact of high LGM dust deposition rates in today's iron-limited regions produce a drawdown of atmospheric [CO$_2$] ranging from 8 to 40 ppm, suggesting that dust could provide a significant contribution to glacial-interglacial cycles of [CO$_2$] changes.
An experimental study of illite dissolution kinetics as a function of pH from 1.4 to 12.4 and temperature from 5 to 50°C

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The reactivity of clay surfaces are particularly significant in controlling the chemistry of surface waters due to their ubiquity and high surface area. To address these potential affects, natural illite (Illite du Puy) dissolution rates were measured from Si release rates during closed system experiments at pH ranging from 1.4 to 12.4 and temperatures ranging from 5 to 50 °C. Si release rate decreased with time during all experiments. This phenomena can be attributed to either 1) change in reactive surface area, 2) the affect of initial fine particle dissolution or 3) a sub-zero order of the illite dissolution reaction with respect to aqueous Al and/or aqueous Si (Oelkers et al., 2001). As such, illite dissolution rates generated from Si release rates measured during the initial parts of the experiments are significantly higher than those generated during latter stages of each closed system experiment. Such also seems to be the case for all published closed system clay mineral dissolution experiments reported in the literature (c.f. Heurtas et al., 1999).

After an initial preferential release of aluminum relative to silicon, the reactive fluid Al/Si concentration ratio evolution was consistent with stoichiometric illite dissolution for all experiments conducted at 4>pH>11. Measured dissolution rates exhibited a typical variation with pH; rates decrease with increasing pH at acid conditions, minimize at near to neutral pH and increase with increasing pH at basic conditions. The degree to which measured illite dissolution rates increased with temperature depends strongly on pH; apparent activation energies decreased from 18 to 5 kcal/mol with increasing pH and increase with increasing pH at basic conditions.

References


Shearing Melt out of the Mantle

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To extract melt quickly enough from beneath a mid-ocean ridge to satisfy geochemical constraints on transport times, melt must segregate from grain-scale pockets into melt-rich, high-permeability channels. As indicated by the occurrence of ductile shear zones in ophiolites and demonstrated by our laboratory experiments on partially molten rocks, such channels can develop during shear deformation. Melt organizes into melt-rich planar bands separated by melt-depleted, low-permeability zones provided the compaction length for the melt-solid system is less than the thickness of our sheared samples. Here, compaction length, \( \ell_n = k/f_J \), is defined in terms of the permeability, \( k \), and the ratio of the solid to the melt viscosity, \( f_J \). If the compaction length is significantly larger than the sample thickness, stress-induced pressure gradients cannot develop to drive melt segregation. In shear experiments, channels contain up to 20 vol% melt and are aligned antithetic to the shear direction at \( \approx 20° \) to the shear plane. Bands are already clearly present after a shear strain of \( \gamma < 1 \), and segregation becomes more intense with increasing strain reaching a steady-state microstructure by a shear strain of \( \gamma \approx 2 \). The spacing between the channels is controlled by the amount of melt available in the sample. Throughout formation, the orientation of the bands is independent of strain.

Two lines of evidence demonstrate that shear strain localizes on these melt-rich bands. First, samples of anorthite + 3 vol% melt sheared at constant rate weaken dramatically at shear strains \( \gamma \approx 2 \). Second, in samples of olivine + basalt, which do not form bands, the normal to the slip plane (b-axis) in the olivine grains is perpendicular to the overall sample shear direction. In contrast, in samples of olivine + chromite + basalt, which do form melt-rich bands, the b-axes are rotated backward by \( \approx 20° \) relative to the slip direction (i.e., the slip planes in the melt-depleted regions form an angle of \( \approx 40° \) with the melt-rich bands). Hence, the direction of shear in the melt-depleted regions compensates for that in the melt-rich bands to permit the sample to obtain a bulk shear consistent with the applied state of stress. In addition, the seismically fast a-axes in samples without bands are parallel to the overall shear direction, while the fast axes in samples with bands are rotated \( 90° \) from the shear direction.

Deformation-driven melt segregation will dramatically influence the physical properties of rocks. The presence of melt-rich bands will affect seismic anisotropy directly through their presence and indirectly through their influence of lattice preferred orientation. The redistribution of melt will modify the permeability network and create an anisotropic viscosity structure. If melt-rich bands occur in partially molten regions of the Earth, they will have important consequences for the flow of both solid and melt.
Seasonal oscillations in microbial iron and sulfate reduction in saltmarsh sediments

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Seasonal oscillations in heterotrophic microbial community structure at three saltmarsh sites on Sapelo Island, GA, USA were measured using culture enumerations for anaerobic Fe(III)- and Mn(IV)-reducing bacteria (FeRB and MnRB) and 16S rRNA probes targeted for sulfate-reducing bacteria (SRB). The observed seasonal trends are not identical for all microbial populations. Rather, at all sites, sulfate reduction rates (Kostka et al., 2002) and MnRB populations peak in summer, while FeRB populations collapse during summer.

Seasonal oscillations in SRR and MnRB populations trend closely with seasonal changes in temperature and aboveground live biomass in the saltmarsh, suggesting that these populations, unlike FeRB, are limited primarily by labile organic carbon availability and temperature. The collapse in FeRB populations during summer is consistent with a limitation by SRB, specifically, via production of sulfide that abiotically reduces available Fe(III) oxides.

The dependence of FeRB populations on sulfide production was further investigated using sediment slurry batch incubations. Increased temperature and increased availability of labile organic carbon led to increased SRR and to more rapid declines in culturable anaerobic FeRB populations. However, no decline in FeRB was observed with increased temperature when SRB were inhibited by addition of molybdate. Addition of sulfide with or without molybdate depressed populations of FeRB at all temperatures relative to no sulfide controls. Both the field and laboratory data are consistent with an iron reduction mechanism that shifts seasonally between periods of high sulfate reducing activity corresponding to periods of primarily chemical reduction of Fe(III) oxides by sulfide, and by periods of low sulfate-reducing activity when Fe(III) oxides are available for biotic reduction by FeRB.


δ¹⁸O of Permian and Triassic brachiopods: implications for coeval seawater and paleotemperatures

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A reconnaissance study of Permian and Triassic brachiopods from the Tethyan realm and the Germanic Basin yields a range of oxygen isotope values that may ultimately provide constraints for coeval seawater temperatures.

The δ¹⁸O of the Middle and Upper Triassic Tethyan brachiopods varies from -0.6 to -3.5 ‰ (VPDB). Some of these coexisted with reef-building corals that require permanent water temperatures of 18 to 32°C. Assuming 0 ‰ (VSMOW) for coeval seawater these Tethyan brachiopods would yield a comparable temperature range.

For Permian samples, the situation is more complex due to the large latitudinal variability of the studied specimens. The Dzhulfian (Upper Permian) δ¹⁸O from the equatorial Tethyan Jolfa section in Iran scatter between -2.4 and -4.3 ‰ VPDB. The calculated paleotemperatures, assuming a seawater δ¹⁸O of 0 ‰ VSMOW, would be ~ 26 to 36°C, an unlikely outcome considering that the confining sediments were deposited at a depth in excess of 100 m. Assuming -2 ‰ for δ¹⁸O VSMOW for the Upper Permian seawater would yield more realistic paleotemperatures of ~ 18 to 26°C.

The high latitude Asselian and Artinskian (Lower Permian) Cis-Uralian samples yielded δ¹⁸O of -1 to -3.4 ‰ VPDB, becoming more negative with decreasing age. This is consistent with the advancing deglaciation of the Gondwana. Assuming -1 ‰ and -2 ‰ VSMOW for the glacial and ice-free intervals, respectively, the seawater paleotemperatures would range between 12 and 22°C.

For the Germanic Basin, the lower Zechstein (Upper Permian) brachiopods are enriched in δ¹⁸O from -1.2 to 2.5 ‰ VPDB. One alternative could relate these high isotope values to influx of cold waters into the Germanic Basin from the northern Boreal Ocean. However, evaporitic sediments in the basin argue against such an interpretation, suggesting that high evaporation rates caused the coeval seawater to be impoverished in δ¹⁸O.

The brachiopods from the Germanic Middle Triassic Muschelkalk Sea, on the other hand, have δ¹⁸O from -2 to -6 ‰ VPDB, values that are difficult to explain as due solely to temperature effects. At these times, the connection between the Germanic Basin and the Tethyan Ocean in the south was often restricted or totally interrupted. Considerable influx of light meteoric water may have influenced the δ¹⁸O values of the seawater.
Hydrothermal fluids in the North Fiji Basin and Lesser Antilles

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Introduction

Hydrothermal fluids were sampled in the North Fiji Basin and in the Lesser Antilles island arc during two cruises with R/V Sonne (SO 134 and SO 154) funded by the "Bundesministerium für Bildung und Forschung" (grant nos. 03G0134 and 03G0154). In both cases, the low-temperature fluids emanate diffusely from the seafloor and show a distinct geochemical signature.

North Fiji Basin

The fluids were significantly enriched in CO₂, Si, Li, Rb, Cs, Ba, Mn, and several trace metals compared to ambient seawater, had high CH₄ and H₂S concentrations and a slightly decreased salinity (Koschinsky et al., 2002). Increased concentrations of Cr(III) compared to Cr(IV) indicate the reducing potential. The fluids derive from vapor-phase fluids produced by sub-seafloor boiling and phase separation, diluted with cold seawater. Compared to hot vents from other regions, trace metal concentrations are low. The fluids support high bioproducitivity, but no precipitation of sulfide mineral, as indicated by a very low Fe/H₂S ratio.

Lesser Antilles island arc

Though indications for active venting were less pronounced than in the North Fiji Basin, again distinct hydrothermal signals such as increased methane and Cr(III) concentrations were found at various locations. Fluids at the Kick'em Jenny submarine volcano appear to derive from phase-separated fluids as well and represent the condensed vapor phase. However, in contrast to the North Fiji Basin fluids, they are not enriched in H₂S and are not associated with a rich hydrothermal fauna.

Conclusions

In both study areas, phase separation has a major importance for the distinct geochemical composition (low metal and high gas concentrations) of the hydrothermal fluids and the overlying water column. Hydrothermal vents can be an important source for reduced metal species.

References


Isotopic composition of Li in foraminifera and their host sediments

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Tests of planktonic and benthic foraminifera have been extensively utilised as recorders of chemical composition of ancient seawater. Here we explore the utility of foraminiferal calcite as an archive of Li isotopic composition of past oceans. Specifically, we address the effects of temperature on Li isotopic fractionation and present the first well-constrained record of temporal variations in the isotopic composition of Li in foraminiferal carbonate and in the bulk host sediment.

We have successfully analysed 5–10 mg samples of planktonic and benthic foraminiferal tests (Orbulina universa, P. obliquiloculata, G. sacculifer, G. venezuelana, G. bullaoides and Pyrgo anomala) collected from surface sediments of the North Atlantic and fossil samples from the ODP Hole 926A in western equatorial Atlantic. The North Atlantic samples, rigorously checked for Holocene age, are from the coretop collection of Pflaumann et al. (1996). The ODP samples were taken from 32.5 to 304.5 mbsf corresponding to the age of 1.8 to 15.8 Ma. To avoid contamination by the host sediment, the foraminifera were crushed to break open their chambers and ultrasonically and chemically cleaned prior to dissolution and analysis by ICPMS (Kosler et al. 2001)

Li isotopic composition of the studied tests and their host sediments from ODP 926A varies from ca -30 to -15 ‰ and from 0 to +5 ‰, respectively. The data suggest that there was no significant isotopic equilibration of Li isotopes between the foraminiferal carbonate and the host sediment. Comparison of Li isotopes in recent foraminiferal tests from the North Atlantic with previously published results from the equatorial Atlantic and Pacific oceans was used to evaluate a potential role of temperature on Li isotopic fractionation between seawater and foraminiferal carbonate. Our data suggest that ambient water temperature does not appear to have any systematic effect on the isotopic composition of Li in foraminiferal carbonate, whilst we have observed systematic long-term changes in the Li isotopic composition of foraminiferal carbonate that may reflect changes in the composition of the oceanic Li reservoir.


A rigorous chemical analysis of the surface and subsurface material in a remote hostile environment such as Mars presents a truly daunting and unique challenge. To undertake such a mission, with the slightest hope of obtaining meaningful analytical data, requires instrumentation that can withstand rigors far beyond those encountered on Earth. In addition to mass, volume, and power constraints, the device must withstand temperature fluctuations that may range from -120 to 60°C, and anticipate any unexpected chemistry such an environment might present. We report here the initial development and evaluation of a prototype Robotic Chemical Analysis Laboratory (RCAL) equipped with an array of electrochemical sensors for measuring in-situ a variety of ionic species and parameters in the Martian regolith.

The RCAL instrument, shown below, is based on the Mars Environmental Compatibility Assessment (MECA) wet chemistry lab (WCL), a payload developed and flight qualified for the now-cancelled Mars’01 Lander. Similar to the MECA, RCAL will contain an array of sensors which will allow for determination of a wide variety of inorganic ions and electrochemical parameters, including, Ag⁺, Br⁻, Ca²⁺, Cd²⁺, Cl⁻, ClO₄⁻, Cu²⁺, HCO₃⁻, Hg²⁺, K⁺, Li⁺, Mg²⁺, Na⁺, NH₄⁺, NO₃⁻, SO₄²⁻, Pb²⁺, pH, oxidants, reductants, redox potential, conductivity, dissolved O₂ and CO₂.

The RCAL expands on the MECA concept by providing twenty individual sealed sample chambers mounted on a rotating carousel. The soil, after delivery by an external mechanism such as a robotic arm or sub-surface drill, is loaded into a dual soil hopper. Multiple small samples can then be taken from the hopper and delivered to the test chambers. After the chamber is punctured, one of a set of four electrodes mounted over the carousel can be inserted into the selected chamber. The RCAL will enable bench-top wet chemistry analyses of the Martian regolith, assessing its interaction with water, and ultimately providing unique scientific information about the geochemical history of Mars.
Spectroscopic studies (FT-IR, $^{13}$C and $^1$H-NMR) of macroaggregates in the northern Adriatic

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Introduction

The mucous macroaggregates in the northern Adriatic Sea are primarily the product of phytoplankton (mostly diatoms) production in favourable oceanographic conditions during late spring and summer. They are thought to be the result of aggregation of extracellular macromolecular DOM.

Experimental

Mucous macroaggregates, in the form of cloud-like structures and of gelatinous surface layer, were collected in the surface and water column in the southern part of the Gulf of Trieste (northern Adriatic Sea) during recent mucilage event in summers of 1991, 1997 and 2000. $^{13}$C and $^1$H NMR, and FTIR spectra of freeze-dried macroaggregates were recorded on a Bruker VVX 300 spectrometer and Perkin-Elmer System 2000, respectively.

Discussion of results

$^1$H NMR study of samples from summers of 1991, 1997 and 2000 identified four major classes of structural elements: carbohydrates ($\delta=3.4-5.8$ ppm), aliphatic component ($\delta=0.9-1.8$ ppm), functional groups such as ester and amide groups ($\delta=2.1-2.7$ ppm) and organosilicon compounds mostly of diatoms ($\delta<0.7$ ppm). FTIR and $^{13}$C NMR spectra confirmed this composition. XRD and EDS analyses indicated the presence of mineral particles especially calcite, quartz and silicates, entrapped into macroaggregate structure. They prevail in water-insoluble fraction and conversely, the water-soluble fraction was mostly composed of carbohydrates. During the mucilage event (maturation) the aliphatic structures bonded to Si and carbohydrates through carboxyl and amide groups increased contributing to the persistence and stability of macroaggregates. The observed temporal decrease of carbohydrate content was most probably due to microbial and photochemical degradation of reserve polysaccharides in the summer stratified water column when macroaggregate production and sedimentation was low.

References


Gold and silver in massive sulfide deposits at Asian areas of Russia

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Massive sulfide deposits in Asian areas of Russia are represented by two types: volcanic-hosted and sediment-hosted deposits. The first type includes deposits situated in the NW Rudnyi Altai, in Salair Range, and in Eastern Tuva. All these deposits being formed in island-arc systems are associated with submarine volcanism of both bimodal and differentiated series. The second type involves two giant deposits such Ozernoe deposit in the Western Transbaikal region and the Kholodninsk deposit in the Northern Baikal region. Both these deposits are confined to shoshonite-turbidite sequences as in the intervolcanic depression so in riftogenous structure, respectively. Hydrothermal-sedimentary ore-forming processes are associated with dacite-andesite-basalt and tholeiite-basalt volcanism. At the Ozernoe deposit, ores occur in terrigenous-carbonate rocks and they show evidence of being formed under relative oxidizing conditions. At the Kholodninsk deposit, precipitation of ores in pyrrhotite-carbonaceous-siliceous shales is associated with very anoxic environment.

Ores of the first type of deposits contain gold (1-1.5 g/t) and silver (15-30 g/t). The irregular distributions of gold and silver within orebodies and the correlation between these elements have been found. The gold concentrations in ores of the second type are close to the abundance ratio of gold. Gold concentrations don’t depend on environment of basin sedimentation. The silver concentrations in these ores are 15-80 g/t. Obviously, submarine hydrothermal systems forming hydrothermal-sedimentary ores were initially depleted in gold, silver concentrations being the same or even higher than those in volcanogenic deposits. The different character of gold accumulation in ores of two types can be attributed to the nature of ore-forming systems. Sulfur of volcanogenic deposits is compositionally close to magmatic sulfur, whereas sulfur of hydrothermal-sedimentary ores is enriched in heavy sulfur.

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Physiological role of bioliths in plants life
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Examining conditions of forming biominerals in plants it is necessary take into account that in their tissues take place the restoration conditions – the biogenic restoration barriers in ways of biogeochemical migration of elements from environments in plants and inside plants. During decomposition of plants their bioliths, transformed or not transformed by oxidation processes, are entered in the small biological and in the great geologic rotation. Because of this bioliths are presented always in soils, bottom sediments of water drains, lakes, seas, oceans, and of course in sediments. Bioliths are known for 34 chemical elements. Three physiological functions of bioliths in plants may be discussed. 1) The participation in the mechanisms of non-barrier-barrier accumulation of chemical elements in various plant organs, tissues, sells and subsell structures. 2) The storing of some chemical elements in winter period of the relative physiological immobility for the intensive consumption in the summer period of intensive vegetation. 3) The active participation of corresponding chemical elements after dissolution of the accumulated bioliths in physiological processes in summer and autumn phases of intensive growth, development and fruit bearing. The first function of bioliths is characteristic for “old”, died, low-active and inactive tissues. It is connected with the transferring of the excessive quantities of chemical elements in the physiologically inactive forms of solid phase – bioliths. This function is established and investigated by us in suberized covering tissues (bark) of trees trunk and in their fruits, – in suberized cones of coniferous trees for example. The storing of chemical elements is well illustrated by forming of the calcium oxalate Ca (COO)2 crystals significant quantities in physiologically active sprouts and leaves of trees. It is described in thousands of publications. There are foundations to suppose that oxalatization are accompanied by the forming of some other chemical elements bioliths, the native gold for example. The dissolving in summer of bioliths accumulated in winter period of relative physiological immobility is one of the testimony that the most active ionic forms of the corresponding chemical elements arose from the bioliths take place in the determined physiological processes of the vital-functioned plant tissues. The work is carried with financial support of the Russian Fund of Fundamental Researches, grant 00-05-64698.

BILOGENIC MINERALS IN PLANTS
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Our investigations of 1970-2000 show that the most diversity of biogenic mineral – bioliths are observed in old suberized tissues of plants. It was established also that very convenient for their investigations are phytoshlichs (Kovalevskii, Kovalevskaya, 1992). It is probable that phytoshlichs may be excreted from other parts of plants and animals. The yellowed and dry defoliated leaves of trees and past years remains of grasses may be suitable also. By the scintillation emission spectral analyses (SESA) in them were revealed mineral particles of elements which were absent in green tissues. Gold is the example. It is presented in green leaves in water soluble forms of sell protoplasm (Kovalevskii, 1976) when absent even in small particles <0.2-2 mkm size. It is important that because of SESA high sensitivity, small weights of samples 0.1-0.2 g are suitable for investigations. The interesting peculiarity of bioliths is they ephemereity – the changing of one mineral into another. It is established specifically for silicon oxides and phosphates in plants. For the present time it may be stated that in plants may present bioliths of 34 chemical elements: Cu, Ag, Au, Be, Ca, Mg, Zn, Cd, Hg, Al, Si, Ti, Zr, Pb, P, As, W, O, S, Se, Mn, F, Cl, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt. It is no doubt that their number would be increased. SESA may assist in revealing and investigations of these and other chemical elements in great degree. Samples of various bioobjects whith probable presence of the largest bioliths, suitable for mineral investigations, may be revealed by SESA. Our long time (1977-1996) experience of exotic gold microbioliths investigations and recently beginning investigations of platinoids (1992-1999) made possible to state that the main peculiarities of forming and distribution of platinoids bioliths in plants are similar to the well investigated gold. It was established specifically that the largest (2-20 mkm) bioliths of gold and platinoids are formed in old parts of plants and also in roots. The most suitable for SESA among above ground parts of plants are outer suberized layers of the tree trunks bark, suberized cones and “old”, including rotten, stumps of coniferous trees. Small (<0.2-2 mkm) bioliths of gold, platinum and iridium were revealed by high sensitive SESA in twigs, sprouts and bast of trees trunk. The absence of gold microbioliths in green parts of plants corresponds with data that gold is presented in the sell protoplasm in ionic forms which are leached by distillated water (Kovalevskii, 1976, Kyuregyan, Burnutyan, 1972). It may be expected that similar phenomenon would be established for platinoids still not determined in saps of plants.
Stacking fault-enhanced argon diffusion in naturally deformed muscovite

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Recent advances in micro-scale 40Ar/39Ar geochronology have revealed non-Fickian argon concentration gradients interpreted to result from intragranular defect-enhanced diffusion. Defects observed by transmission electron microscopy (TEM) in naturally deformed muscovites with a significant intragranular argon diffusion component (Kramar et al. 2001) are evaluated as a potential pathway for argon diffusion. The heterogeneous presence of broad stacking faults is the most outstanding feature observed in the deformed muscovite. Some micro-cleavages were also observed in regions of medium-to-high linear stacking fault densities.

Two-dimensional defects, such stacking faults, occurring in ionic crystals is known to modify mechanical behavior or diffusion. Of particular interest for noble gas diffusion is the net dilatation that a stacking fault is able to generate in ionic crystals (Tasker and Bullough, 1981). In micas, partial dislocations defining the stacking faults and occurring in the interlayer, place the K ion into a hollow in the center of three oxygen ions of the adjacent tetrahedral layer (Caslawski and Vedam, 1971). Energy calculations based on electrostatic modeling conclude this configuration leads to an interlayer spacing on the order of 0.5 Å (Banos, 1985).

The interlayer spacing has direct implications for argon retention in micas. Numerical modeling of diffusion along the stacking faults was performed on the basis of the calculated interlayer spacing, the measured isotope data, and the observed linear stacking fault density. These calculations estimate the diffusivity ratios defined by volume diffusion and defect-enhanced diffusion which are comparable with diffusivity ratios in other materials (ceramics or metals).

In the absence of defects causing physical grain segmentation (e.g. kink bands or subgrain boundaries), stacking faults are potentially the main defect in the media controlling intragranular argon diffusion.


Volatile element abundances point to a H2O ocean on Earth at > 4.4 Ga

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Hydrogen, C, N, Cl, Br and I are highly concentrated in the Earth Surface Reservoirs (ESR: Atmo-hydrosphere, sediments and metasediments) and either reside in, or have been cycled through the atmo-hydrosphere. Their abundances in the ESR, normalised to AI in the whole Earth, show depletions of 10⁻³ - 10⁻² relative to Solar values, but solar-normalized patterns are broadly similar in shape to those of carbonaceous chondrites (CC). Notable features in the CC-normalised abundances of the ESR are an almost flat pattern for the halogens (~1.5×10⁻³) and a stronger depletion of H (~3×10⁻³), C (~3×10⁻⁴) and N (~8×10⁻⁴).

Possible sources for the volatiles, other than a CC-like component, are solar matter (either captured nebular gas or implanted solar wind, Podosek et al., 2000), and comets. A small solar matter contribution is required to explain Ne isotope ratios in the Earth’s mantle (Kunz, 1999) but does not significantly affect the depletion pattern for the elements studied. An important comet H contribution is ruled out because: (1) (For Oort Cloud comets) D/H ratios are around 3×10⁴, twice the terrestrial value (Meier et al., 1999); and (2) The H/C ratio of comets is chondritic or lower (Crovier and Bockelée-Morvan, 1999). CC accretion or co-accretion is thus the essential source for terrestrial H, C, N, Cl, Br and I. Importantly, the irregularities in the CC-normalised ESR abundance pattern are a robust feature, reflecting differential loss from the atmosphere following release by degassing.

129Xe(I) and 136Xe(Pu) systematics show that such loss occurred < 250 Ma after Allende (Azbel and Tolstikhin, 1993) most likely by hydrodynamic escape (Pepin, 1998), where the rate of escape of a species is inversely proportional to its mass, and proportional to its abundance in the upper atmosphere. All aspects of the process predict greater loss of H than of C or N. This paradox and the problem of high halogen retention can both be resolved and numerically modeled if most H₂O, Cl, Br and I quasi-continuously resided in a liquid water ocean during this early atmosphere loss, resulting in their underproportional loss from the atmosphere. This finding corroborates δ¹³O data on >4 Ga detrital zircons (Péck et al., 2001).

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Fingerprinting early continental evolution using Ca isotopes

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Questions concerning the formation of the earliest continental crust and its characteristics are highly debated but remain unclear. Does the scarcity of Archaean crust reflect a continuous growth of continental crust with time or very effective destruction? Do different geochemical characteristics mirror different crustal provinces and hence different mechanisms of crust formation? The K-Ca isotope system is highly suitable to address these problems due to: i) the short half-life of $^{40}K$, decaying to $^{40}Ca$, compared to the age of the Earth in non-linear growth of $^{40}Ca$, ii) the Ca isotopic composition of the mantle remains effectively constant because of its very low K/Ca ratio, and iii) K and Ca are strongly fractionated during crust formation processes.

We analysed ~3.6 Ga old felsic and mafic rocks from different Archaean Cratons. The Ca isotopic compositions of plagioclase and titanite separates in addition to the whole rocks were measured using the Finnigan-Triton TIMS. Ca is a major component in plagioclase and titanite, which are also characterised by low K/Ca. Therefore, both minerals should reflect the initial Ca isotopic composition of the source. The Ca isotope data show a clear distinction of the different Archaean provinces. TTGs from Zimbabwe show a Ca isotopic composition indistinguishable from our measured MORB value. Greenland samples, however, yield evolved radiogenic signatures of $\delta_{Ca} = +3$. The Akilia gabbros and the Itsaq gneisses show the same range of radiogenic $\delta_{Ca}$ values and plot on or above a single stage crustal evolution curve starting 4.5 Ga ago with a K/Ca ratio of 0.35.

Due to the fact that most Archaean rocks underwent metamorphism and alteration, the interpretation of back-corrected initial isotope values requires great care. A less radiogenic titanite compared to the corresponding plagioclase in the Zimbabwe samples indicates that the Ca isotopic composition of plagioclase might in some cases reflect a mixture of original, initial value and a ratio that evolved in the whole rock. It might also suggest that titanite more likely exhibits the pristine ratios and, therefore, more titanites will be analysed. However, exchange of the isotope signature due to recrystallisation during later thermal events can not explain the same back-corrected $\delta_{Ca}$ values obtained from different lithologies such as in Greenland. Felsic and mafic rocks have different K/Ca ratios and, thus, should yield different isotopic compositions. Only a very K-enriched crustal precursor comparable with the K-fraction of lunar KREEP basalts formed > 3.9 Ga ago can account for such radiogenic values up to $+3 \delta_{Ca}$.

Formation and dissolution of Zn-precipitates during reactive transport in a circum-neutral soil

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Recent spectroscopic studies have demonstrated the formation of layered double hydroxides (LDH) and phyllosilicates upon sorption of Zn$^{2+}$, Ni$^{2+}$, and Co$^{2+}$ to clay minerals and aluminum oxides at neutral to alkaline pH, and at relatively high initial metal concentrations (~1 mM). The intention of the present study was to investigate, whether such phases also form in soil under slightly acidic conditions (pH~6.5) and at lower metal concentrations. Columns packed with a loamy soil were percolated with aqueous solutions containing 0.1 mM to 0.2 mM ZnCl$_2$, NiCl$_2$, CoCl$_2$, and CdCl$_2$ in a 10 mM CaCl$_2$ background at pH 6.5. Metal breakthrough curves indicated a rapid initial sorption step, resulting in retarded breakthrough fronts, followed by further slow metal retention during the entire loading period of 42 days (~7000 pore volumes). Total metal sorption and the contribution of slow sorption processes decreased in the order Zn > Ni > Co > Cd. Leaching the reacted soil with 10 mM CaCl$_2$ at pH 6.5 remobilized 8% of the total retained Zn, 15% of Ni, 21% of Co and 77% of Cd (Fig. 1, 70-200 pore volumes). Leaching with acidified influent (pH 3.0) remobilized most of the remaining metals (Fig. 1, 200-800 pore volumes). Analysis of soil samples from the column experiments by X-ray absorption fine-structure (XAFS) spectroscopy showed that slow Zn sorption was due to formation of an Zn-LDH solid phase. Although Ni, Co and Cd concentrations were too low for XAFS analysis, their leaching patterns suggest that part of Ni and Co were also incorporated in solid phases, while most Cd remained as exchangeable sorption complex. A small but significant percentage of the sorbed metals (2% to 5%) remained in the soil even after leaching with more than 3000 pore volumes at pH 3.0, which may suggest micropore diffusion or precipitation of more stable mineral phases.
Spatial deuterium excess patterns in high-elevation Asian precipitation


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Stable water isotope (δD and δ18O) and deuterium excess (δD=8*δ18O data from precipitation collected in mountain ranges (Himalaya, Tien Shan, and Altai) surrounding the Tibetan Plateau display spatial patterns related to moisture source and transport. In the Himalaya (Mt. Everest and Tien Shan, and Altai regions), summer monsoon fresh snow d values are higher in glacier regions (5100-6500 m asl; 15.3‰) vs. lower elevation sites (4300 m asl; 4.1‰). The magnitude of the d difference between the two sites, coupled with synoptic observations, indicates that different moisture sources are likely involved (Bay of Bengal and the Indian Ocean). Our hypothesis is that source and transport. In the Himalaya (Mt. Everest and Tien Shan, and Altai regions). We will discuss and present 1 cores of >100m have now been recovered from the Everest, Tien Shan, and Altai regions. We will discuss and present 1 and 2-D isotope modelling results that are being used to interpret down-core δD, δ18O, and d records.

Where is geochronology going?
Migmatite petrology and isotope transport

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Geochronology may provide constraints on a number of important issues in metamorphic and magmatic petrology, which have a bearing on our understanding of large-scale geodynamic processes. Some of these issues are: (1) coupling of petrogenetic indicators (thermobarometry; trace element distributions; oxygen isotopes) with time constraints; (2) the time-scale of pro- and retrograde processes in migmatites; (3) melt extraction rates; (4) rates of processes in general.

Migmatite petrology is exemplified as a research field where an increased input from geochronology is required. A new migmatization model (Kriegsman 2001) incorporates four sequential processes: (i) partial melting producing restite (mesosome) and melt; (ii) melt segregation and extraction; (iii) reaction between melt and restite producing leucosome and biotite- or hornblende-rich melanosome; (iv) (mesosome) and melt; (ii) melt segregation and extraction; (iii) reaction between melt and restite producing leucosome and biotite- or hornblende-rich melanosome; (iv) crystallization of remaining melt at its solidus.

One of the implications of this model is that incompatible elements that entered the liquid phase during partial melting may re-enter restitic layers upon cooling. Zircon resorption followed by zircon growth in migmatites (Schaltegger et al. 1999) may be explained in a similar way. Zircon and monazite morphologies may therefore be strongly correlated to trace element (re)distribution at leucosome-melanosome-mesosome interfaces. The model is now being tested by trace element zoning and oxygen isotope distributions in garnet, zircon and monazite (EPMA, LA-ICP-MS, NORDSIM).

A next step is to constrain the rates of these processes, either through an assessment of the heating and cooling rates of the terrain (i); or by inferring the melt extraction rates from physical models for melt escape and melt percolation (ii) and the degree of (dis)equilibrium reached between melt and source rocks (iii). The first method is restricted by the current time resolution of isotopic techniques (commonly U-Pb) and therefore generally yields time scales > 1 Ma. Results from the other two approaches depend heavily on assumptions, but suggest rapid melt segregation (< 100 years).

Progress in this field requires a method that combines high spatial resolution (10 microns or less) with high time resolution (< 1 Ma) and is valid in minerals having low concentrations of relevant isotopes (e.g., U-Pb in garnet). This would open up possible applications such as deriving cooling paths directly from U-Pb zoning patterns in garnet.

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**In situ observations of reductive dissolution of colloidal Lepidocrocite (γ-FeOOH) in ascorbic acid**

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Ferric iron oxides and hydroxides play a major role in the immobilization of contaminants in environmental systems, but when conditions in aquifers become more reducing, incorporated toxic elements can be released to the groundwater. Better understanding of reductive dissolution is essential for our ability to predict the movement of heavy metals in natural systems. Lepidocrocite, γ-FeOOH, found in soils and sediments most commonly near the redox boundary, is vulnerable to attack by natural reducing agents.

We have used the high resolution capabilities of Atomic Force Microscopy to investigate reductive dissolution of micrometer-scale crystals of lepidocrocite in a closed fluid cell containing 10 mM ascorbic acid (C₆H₈O₆) as a model organic reductant.

Figure 1 shows a subset of images taken during dissolution of one single lepidocrocite crystal. We were able to determine that the reductive dissolution rate is about 4 x 10⁻³ g Fe m⁻² h⁻¹, which compares very nicely with macroscopic rates. Dissolution on individual faces was fastest on the ends of the longest dimension and slowest on faces of the shortest dimension, so that length-to-width ratio changed as a function of time. Contaminants that are adsorbed preferentially to these faces can either be released to solution again during dissolution, or they can inhibit dissolution, enhancing prominence of a new face and thus promoting a new morphology.

![AFM images of γ-FeOOH crystal](image)

**An isotope dilution, etch abrasion solution to the Akilia Island U-Pb age controversy**

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Two-stage (3.65 and 3.85 Ga) zircon populations, with a minor 2.7 Ga component, in tonalite intrusions that were sampled to constrain the age of a mafic enclave, reported to contain ¹³C-depleted graphite microparticles, Akilia Island, SW Greenland, have led to disparate interpretations (see review by Nutman et al., 2000). Nutman et al. (1997) ascribed the older age to the time of magmatic emplacement and the younger age to metamorphic growth, whereas Whitehouse et al. (1999) assigned magmatic growth at 3.65 Ga and the older age to inherited grains. Kamber and Moorbath (1998) suggest the latter explanation for the disparity between Rb-Sr, Sm-Nd, and Pb-Pb results versus ion probe ages throughout the region. Our initial analyses from the same sample sites (Krogh et al., 2000) supporting the younger age for magmatism are revised here based on our discovery that the few clear prisms analyzed have the same ages as the overgrowths and do not represent the main population of oscillatory zoned magmatic zircons.

The etch-abrasion method employed here exploits the extreme, radiation-induced solubility differences that render damaged domains visible, and leaves isotopically closed cores and tips, with the lowest U concentrations and the highest probability of concordance, unetched. Critical to this investigation is the fact that magmatic grains are typically highly zoned and turn white and friable where damaged zones are attacked, whereas metamorphic domains are not zoned and remain clear, so that the abundance distribution and habit of each stage is easily assessed.

Zircons from the tonalite sheet near the north contact with the mafic enclave are typically resorbed, 3:1 rounded prisms, with longitudinal cracks, and minor clear, pink overgrowths that together with highly etchable zones (3 hr NaOH 22°C) define the population as pre-metamorphic, primary magmatic. Metamorphic components comprise <10% of the population and occur as tips, rounded grains, and blocky prisms. Ages of 3760±4 Ma and 3658±3 Ma were obtained for the magmatic and metamorphic grains, respectively.

Zircons from the south contact sample only show two-stages of growth after etching (2.5 hr in HF at 220°C). Clear tips overgrow the dominant, zoned population and 5, 3:1 prisms and 3 equant grains of the latter type yield a colinear array (0.4% discordant) for an age of 3849±4 Ma to 2708 Ma (0.4% discordant). Overgrowth component (<10% of the population) gives a ca. 3670 Ma maximum age.

**References**

Syngenetic garnet of eclogitic/pyroxenitic composition included in a polycrystalline diamond aggregate from the Venetia kimberlite, Limpopo Belt, South Africa shows multiple inclusions of spherules up to ca. 50 µm, consisting of cohenite assemblage, implying that both compositions were immiscible melts and were trapped rapidly by the silicate. The oxygen fugacity of the metal-silicate system can be calculated using the mole fractions of Fe in metal and FeO in silicate and oxygen fugacity of the metal-silicate system can be calculated.

Cohenite (iron carbide) and native iron formation within garnet included in polycrystalline diamonds by redox freezing in the cratonic lithosphere

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Isotopic constraints on the origin of the Bushveld Complex magmas in a back-arc environment

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Sr, O, Nd, Pb, Os, and Cl isotopic and concentration data indicate that the magmas of the Bushveld Complex contained variable proportions of crustal material prior to intrusion into the magma chamber. These magmas can be divided into three fundamentally different lineage’s, a harzburgitic-noritic Lower and Critical Zone (L&CZ) lineage, a gabbro-noritic Main Zone (MZ) lineage and a ferro-gabbro-noritic Upper Zone (UZ) lineage. Petrological modelling using the available isotopic data indicates that these represent mixtures of different mantle and crustal provenance’s.

Magmas with both high and low Sr concentrations and Sr isotopic ratios were injected into the magma chamber. 146Sr/138Sr ratios suggests that the first magma was less radiogenic (c. 0.7044) and that subsequent additions were more radiogenic (0.7085-0.7090).

The 818O characteristics of rocks from the whole stratigraphic extent of the Bushveld Complex indicates that there was a significant crustal content in the magmas higher in the succession and especially in the magma injected into the MZ. A strong positive correlation of very radiogenic 87Sr/86Sr initial ratios with the 18O values also supports this model.

Nd isotopic data indicate an upper mantle and old crustal sources, and the Sr/Nd relationship indicates an Archaean upper crustal source as the “contaminant” as Sr is highly radiogenic. The LREE enriched profiles can also be reconciled with this model.

Pb isotopic data indicates that the L&CZ magmas have a lower to middle crustal imprint on a “CHUR” type source, whereas the imprint on the MZ is upper crustal which is also consistent with the other isotopic data.

Os isotopic data on the chromitite layers and the Merensky reef indicate a substantial crustal signature in the upper CZ and lower MZ.

Heavy 37Cl and very high CUF ratios indicate a subducted altered ocean floor component.

Geochemical data on the Bushveld Complex and other cratonic rocks indicate that the c. 2.0 Ga Kheis-Magondi convergent tectonism and the Bushveld Complex are coeval. The combined isotopic and chronological data outlined above indicate that the Bushveld Complex is a back-arc phenomenon related to that convergent tectonism, which subducted a significant proportion of Archaean upper crustal material into the source region of the Bushveld Complex magmas.
Pb-Pb evaporation method on native gold grains

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Introduction
In this work is presented a new method of measure of isotope Pb ratios in native gold samples. In opposite of classical method of bulk chemical digestion and Pb separation for gold, this new method is faster and provides more information.

Analytical procedures
Small gold grains (0.3-1 mm) were rolled into foil, and were cleaned by the following acid sequence (using ultrasound and 100°C hot plate treatment): 10N HF; H2O; 6N HCl; H2O; 14N HNO3; H2O during 30 min for each step. After that, each grain was deposited on Re single filament with 5 µl of mixture of silica gel and H3PO4. Lead isotope ratios were analysed by Finnigan MAT-262 mass-spectrometer in ion counting jumping mode and static Faraday cups mode at temperatures 1330-1570°C. The typical error levels 2% for 206/204 ratios in non-radiogenic samples are 0.05-0.1%, in high-radiogenic samples are >0.5%.

Results and discussion
For Pb isotope studies were taken the native gold grains from veins of ore deposit Alemão (Carajas, Brazil) and ore-deposits Areal and Mina Velha (Gurupi belt, Brazil).

Gold samples from Gurupi belt deposits show non-radiogenic common lead composition and provide sufficiently high stable signal (~100 mV 206 mass) on Faraday cups and stable isotope ratios during measures. Samples points of Mina Velha lie near Doe-Zartman curve for mantle in age range 1200-1300 Ma.

Gold grains from Alemão ore-deposit show high-radiogenic lead composition and demonstrate low signal (<5 mV 206 mass) on ion counter. The 206/204 Pb ratio increased during analysis from block to block in most samples, in some of them up to 1.5 times and varied in range 50-1000. These big variations in 206/204 ratios are probably caused by small invisible impurities of other U-rich minerals. Because of these variations the 206-207 isochron calculations were made using separate block data. Three groups of 206-207 isochron data were obtained: 3529±50, 2770±24 Ma, 2132±17 Ma. The second age is concordant with 206-207 isochron age for sulfides.

Conclusions
The proposed new Pb-Pb evaporation method for native gold analysis may be useful for detail studies of gold mineralization and possible diagnostic tool for detection of origin of jeweler gold.

An update on the Köfels 10Be and 26Al production rates

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A giant landslide of Köfels, Tyrol, Austria occurred 9800 years ago. This site is ideal to determine the production rates of cosmogenic 10Be and 26Al for exposure dating, because the timing of the event could be dated dendrochronologically [Ivy-Ochs et al., 1998; Kubik et al., 1998]. The originally measured nuclide concentrations [Kubik et al., 1998] were scaled to sea level, high latitude using the scaling formalism of Lal [Lal, 1991]. Recent work [Stone et al., 1998; Heisinger et al., 2002a; Heisinger et al., 2002b] indicates that the contribution due to muons was overestimated. The original production rates have thus been revised in light of this. In addition, a new field campaign was conducted last year and this new data will be added to the existing data set.

References
The Kolmozero-Voron’ya greenstone belt is one of the most ancient geological structures of the Kola Peninsula. It is located between Upper Archaean terrains: Murmansk, Central Kola and Keivy. Within the Kolmozero-Voron’ya greenstone belt there are rare metal (Li, Cs with accessory Nb, Ta, and Be), Cu, Mo, and Au deposits. All rocks were metamorphosed under amphibolite-facies conditions and intruded by granodiorites, plagiomicrocline and tourmaline granites and pegmatitic veins. Four suites are distinguished within the belt: lower terrigenous formation, komatiite-tholeite, basalt-andesite-dacite and upper terrigenous formation. The Porosozero granodioritic complex, which intruded volcano-sedimentary units and granitoids of Murmansk block. Sm-Nd age of komatiites is ca. 2.87 Ga (Vrevsky, 1996). U-Pb age of zircon from biotite schist, which belong to acid volcanites is 2865 +/- 5 Ma. Quartz porphyries, which are considered to be intrusive vein analogus of acid volcanites has an age of 2828 +/- 8 Ma, that marks the final stage of the belt development. Dating of titanite from ovoid plagioamphibolites yielded an U-Pb age of 2595 +/- 20 Ma that probably is connected with the closure of the U-Pb isotopic titanite system during the regional metamorphism. The Porosozero granodioritic complex, which intruded volcano-sedimentary rocks of the belt has an age of 2733 +/- 6 Ma. Tourmaline granites are found all over the Kolmozero-Voron’ya belt occurring among volcanogenic-sedimentary rocks of the belt. Their Ppb-Pb age of 2520 +/- 70 Ma appears to denote the tourmaline crystallization at a post-magmatic stage of the complex formation. Preliminary age of rare-metal pegmatites is 1.9-1.8 Ga.

Thus, several stages can be distinguished in the evolution of the Archaean Kolmozero-Voron’ya greenstone belt: protoocean with komatiite-tholeite magmatism (3.0-2.9 Ga); volcanic arc with andesite-riolite magmatism (2.9-2.8 Ga); regional metamorphism and granitization with melting of granodiorite-granite magmas (2.7-2.6 Ga); regressive metamorphism and potassium metasomatism with the formation of tourmaline and microcline granites and rare-metal pegmatites within and outside the belt (2.5-1.8 Ga).
Evolution of the photosynthetic carbon isotope fractionation (\(\varepsilon_p\)) during the Late Paleozoic

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Photosynthesis is accompanied by a carbon isotope fractionation (\(\varepsilon_p\)) between the inorganic carbon substrate \(\text{CO}_2\) and the assimilated organic compounds. In fossil marine sediments \(\varepsilon_p\) can be defined as the difference between the carbon isotopic compositions of phytoplankton biomass (\(\delta_p\)) and dissolved \(\text{CO}_2\) (\(\delta_0\)). The magnitude of \(\varepsilon_p\) is dependent on (1) \(p\text{CO}_2\) and \(p\text{O}_2\) in the ocean-atmosphere-system, (2) cell-specific growth rate and (3) cell geometry.

This study investigates \(\varepsilon_p\) in marine phytoplankton in a series of Late Paleozoic time windows. Compound-specific carbon isotope analysis of acyclic isoprenoids preserved in immature marine sediments enabled us to determine \(\delta_p\) and carbon isotope data of well preserved brachiopod shells were used to calculate \(\delta_0\). While previous studies were limited to the calculation of \(\delta_p\), i.e. the carbon isotopic difference between total organic carbon (TOC) and carbonate carbon, our dataset provides the first genuine record of the Late Paleozoic evolution of \(\varepsilon_p\).

Our results show that \(\varepsilon_p\) commonly varies by several permil within individual Late Paleozoic time windows. This spread can be ascribed primarily to varying phytoplankton growth rates, associated with locally differing nutrient availabilities, and/or regionally varying compositions of phytoplankton communities. Yet, the longterm evolution of \(\varepsilon_p\) reveals a steady increase form the Devonian (ca. 16 – 21.5‰) to the Late Pennsylvanian (ca. 19.5 - 25‰), followed by a slight decrease during the Permian (ca. 21 – 23.5‰). This secular trend is interpreted in terms of an interplay between the significant increase of \(p\text{O}_2\) and the strong depletion of \(p\text{CO}_2\) in the ocean-atmosphere-system from the Middle Devonian to the Permo-Carboniferous, as proposed by a number of published numerical models. Our results suggest that Late Paleozoic \(p\text{O}_2\) variations had a stronger effect on \(\varepsilon_p\) than \(p\text{CO}_2\).

Density parameters in thermodynamic surface complexation models

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Thermodynamic surface complexation models (TSCMs) can realistically describe ionic sorption if characterization of a mineral-water interface helps to constrain stoichiometry and coordination of surface complexes, areas of surface types, and densities of the available binding sites. How can such information be utilized in macroscopic TSCMs in a rigorous way?

1. Reference density \(\Gamma_n\) (in mol m\(^{-2}\)) is to be taken the same for all mineral surface species. Then molar Gibbs energies \(G\) or equilibrium surface complexation constants \(K\) can be scaled to the same standard state if \(j\)-th surface species concentration is defined as \(\Gamma_j\), i.e. the carbon isotopic difference between total organic carbon (TOC) and carbonate carbon, our dataset provides the first genuine record of the Late Paleozoic evolution of \(\varepsilon_p\).

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2. While \(\Gamma_j\) takes part in standard state properties \(G^\circ\), \(\log K\), \(\Gamma_n\) (or \(\Gamma_\Omega\) for species competing on a surface type) can be used only in surface activity terms (SAT) that suppress the species density \(\Gamma_j\) at \(\varepsilon=1\). Coulombic terms in electrostatic TSCM also affect \(\Gamma_j\) of charged surface complexes as function of surface charge density \(\varepsilon_{\Omega}\), which itself is a function of \(\Gamma_j\).

3. In the linear adsorption region (close to the reference state at \(\varepsilon=0\) and \(\Psi=0\)), the densities \(\Gamma_j\) (and mole quantities \(x_j\)) of surface complexes depend only on \(G_j\), chemical potentials in the system and the surface type area, but not on \(\Gamma_n\) or \(\Gamma_{\Omega}\) parameters. Hence, if concentrations of mono-, bi-, tri-... \(n\)-dentate surface complexes are referenced to the same species density at standard state \(\Gamma_j\) then their behaviour will differ only at approaching the site- or surface-type saturation.

4. Thus, \(\Gamma_{\Omega}\) parameters and SAT equations (initially defined for monodentate surface complexes) must be re-derived for \(n\)-dentate surface complexes by careful interpretation of \(\Gamma_j\), \(\Gamma_{\Omega}\) and \(\Gamma_{\Omega}\) parameters in terms of “available site density” and “species density”. For that, statistical analysis of surface site geometry (following Benjamin, 2002) is promising, especially when enhanced by micro-spectroscopic molecular-scale data about the binding site types and their spatial distribution.

Some developments will be exemplified by comparing TSCMs for mono- and bidentate \(\text{U}^{19}\) sorption on oxides, to conclude about usefulness of the new species/site- density concepts in mechanistic model description of heterogeneous sorption, as well as in compilation of a uniform chemical thermodynamic database for surface complexes.

References

Helium studies in the Mojave Desert, California: Quantifying mantle and crustal additions to the regional groundwater system

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We report helium concentrations and isotope results measured on deep groundwaters from the western Mojave River Basin (MRB), 130 km east of Los Angeles. The aquifer is composed of Quaternary alluvial fan and basin fill deposits (interbedded gravel, sand, silt, and clay) that overlie a crystalline complex of pre-Tertiary igneous and metamorphic rocks. Samples were collected along two groundwater flowpaths that originate in the San Gabriel Mountains and discharge to the Mojave River ~30 km to the northeast. The basin is adjacent (~10 km) to the NW-SE trending San Andreas Fault (SAF) system. The primary objective of this study is to quantify the crustal and mantle helium contributions to the regional groundwater system.

A total of 25 groundwaters, sampled previously for chemistry and isotope systematics (including C-14 activity), have measured helium concentrations which increase along flowpaths from $9.9 \times 10^{-8}$ to $1.0 \times 10^{-4}$ cm$^3$ STPg$^{-1}$ H$_2$O. Concomitantly, $^3$He/$^4$He ratios decrease from 0.84 $\text{RA}$ to 0.11 $\text{RA}$ ($\text{RA}$ equals the $^3$He/$^4$He ratio in air = $1.4 \times 10^{-6}$). In no samples did we measure $^3$He/$^4$He ratios equivalent to crustal production values (~0.02$\text{RA}$).

Measured helium concentrations were resolved into components associated with solubility equilibration, air entrainment, in-situ production within the aquifer and an extraneous flux. Young groundwaters close to recharge areas were dominated by the first 2 components – older groundwaters by the latter 2. The $^4$He/$^3$He ratio of the extraneous component is ~0.11$\text{RA}$, indicating addition of mantle-derived He to a (deep) crustal flux. If the mantle component is characterized by $8\text{RA}$, then addition of 1-2% is sufficient to account for the observed ratios. Therefore, this study confirms findings of Kennedy et al. (Science, 1997) of the presence of mantle-derived fluids proximal to the SAF. By comparing $^4$He and C-14 ages and assuming a range of porosities between 10-25%, the calculated crustal flux of helium varies between $3 \times 10^6$ and $3 \times 10^7$ cm$^3$ STP cm$^{-2}$ yr$^{-1}$. This range is comparable to values published for other regions of the western USA (e.g. Carrizo aquifer, Texas and San Juan Basin, New Mexico).

Weathering through Earth history: controls and consequences

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Chemical erosion of the continents is the predominant source of solutes to the ocean. The chemistry of the ocean is expected to have varied in response to changes in chemical erosion over Earth history, but by how much is poorly known. Most proxies of chemical erosion rates (e.g., changes in the radiogenic isotope composition of the oceans as recorded in limestones) are ambiguous because they respond both to changes in the magnitude and isotopic composition of the riverine inputs. Use of multiple proxies holds the promise of unravelling these influences.

One of the most hotly debated topics is the extent to which chemical weathering provides stability to long-term climate through feedback in the carbon cycle. The fundamental issue is what controls chemical erosion rates on global scales, yet much of the debate has focused on controls on individual watersheds. Tectonic uplift (shedding of the soil mantle) is clearly a limiting factor for a number of watersheds, whereas a climate limitation, especially a temperature dependence for chemical erosion, has been more elusive. Using Ge as a proxy indicator for transport vs. weathering limitation (after Stallard and Edmond), one finds that the world as a whole is strongly weathering limited. Thus, those factors that control weathering (climate, rock composition) are limiting the rate of chemical erosion today. During periods of tectonic stasis, transport limitation could have dominated.

Limits on the range of global chemical erosion rates over geologic time are likely tied to the water cycle. Extreme continental aridity might have caused erosion rates to fall near zero in the Neoproterozoic, Late Permian/Early Triassic, and Paleoproterozoic (ca. 2.0 Ga), as indicated by extreme enrichments and rapid swings in carbon isotope composition. Maximum rates of chemical erosion would have been realized when the water cycle was accelerated and rivers were saturated with CaCO$_3$. Under the most favorable conditions, chemical erosion rates could have been 50 times today’s.
Is CO₂ the Phanerozoic climate driver?
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There are good reasons to suspect that atmospheric pCO₂ has been a primary climate driver in the geologic past, but the evidence is not conclusive. Numerical carbon cycle models and pCO₂ proxies generally support the suspected relationship between climate and atmospheric pCO₂. However, the oxygen isotope paleotemperature record from 600 Ma to the present displays notable intervals for which temperature and inferred pCO₂ are not correlated. One of these occurred during the early to middle Miocene (about 17 Ma), a time well established as a warm interval but with proxy evidence for low atmospheric pCO₂. Moreover, whereas climate models predict warming at all latitudes in response to elevated pCO₂, geologic evidence is not conclusive. Numerical carbon cycle models predict warming or even cooling at low latitudes while higher latitudes warm.

Is the CO₂-climate relationship refuted by these and other apparent mismatches between climate and CO₂ proxies? Not necessarily. The “cool tropics paradox” and the longer-term mismatch between pCO₂ and temperature proxies could be artefacts, the consequence of inevitable blurring of the signal by diagenesis. Even if the proxies survive further scrutiny and the mismatches remain, we shouldn’t necessarily expect highly correlated records of atmospheric pCO₂ and climate. A pCO₂ increase whose radiative forcing drives a slowly changing climate component (e.g., the extent of continental ice sheets during glaciation), or triggers the release of other greenhouse gases (e.g., CH₄) could produce a proxy climate record (e.g., ice-sheet volume as expressed in the oxygen isotope record, indicate muted warming or even cooling at low latitudes while higher latitudes warm.

Noble Gases from the deep mantle: new evidence from oceanic volcanism

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The “standard model” for terrestrial helium isotopic evolution is that high ³He/⁴He ratios reflect undegassed deep mantle reservoirs having high He/(Th+U) ratios. High ³He/⁴He ratios from oceanic islands such as Hawaii, Iceland and Galapagos would then reflect relatively undegassed reservoirs brought to the surface by mantle plumes. This model has been challenged on a number of grounds, as geochemists and geophysicists increasingly attempt to explain the geochemical diversity of oceanic basalts by recycling processes. In order to address this important issue, we report new helium and neon data from submarine glasses of the Galapagos archipelago, and compare them to the most recent noble gas data from Hawaii. The new Galapagos samples come from the submarine western flank of the archipelago, and were collected during a 2001 cruise of the R/V Revelle which combined multibeam bathymetry, sonar mapping, and dredging. The highest Galapagos ³He/⁴He ratios, up to 30 times atmospheric, are found at Fernandina, and on the seafloor directly to the west of Fernandina. The geometry is similar to Loihi Seamount, Hawaii, in the sense that Fernandina is at the leading edge of the archipelago with respect to plate motion. We interpret the high ³He/⁴He ratios, coupled with active volcanism, as an indication that the plume melting center presently lies beneath Fernandina. The Galapagos submarine glasses have less radiogenic ²¹Ne/²²Ne ratios than MORB or Loihi seamount, and the neon isotopes are consistent with the helium isotope systematics in suggesting relatively undegassed mantle. Overall the helium-neon systematics are consistent with the correlation identified by Moreira et al. (EPSL 185(2001) 15-23) and demonstrates that Loihi Seamount does not adequately characterize high ³He/⁴He mantle sources. Correlations between helium and other radiogenic isotope systems, at Galapagos and Hawaii, provide some important arguments in favor of the standard model for noble gases. The most plausible explanation for high ³He/⁴He ratios remains undegassed deep mantle reservoirs, perhaps from the core-mantle boundary: the noble gas data cannot be explained by recycled material.
Regional Pb-Nd-Sr isotopic differences of the Mesozoic granitoids in South Korea: Implications for the basement structure

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The isotopic ratios of granitoids can provide important information about the nature of the lower crust, since granitoid magmas are generally formed by the partial melting of the lower crust rocks. The initial isotopic ratios of Pb, Nd and Sr of this and previous studies for the Mesozoic granitoids from widely separated parts of South Korea show regional differences regardless of their intrusion ages. The isotopic differences are most prominent between the granitoids in the Gyeongsang basin and those in other tectonic provinces (the Gyeonggi massif, the Okcheon belt and the Yeongnam massif). The former has mantle-like signatures: ⁸⁷Sr/⁸⁶Sr = 0.705 to 0.707, ⁴⁰Nd/⁸⁷Sr(T) = -6.6 to +3.9, ²⁰⁶Pb/²⁰⁴Pb = 18.2 to 18.4, ²⁰⁷Pb/²⁰⁴Pb = 15.53 to 15.59, ²⁰⁸Pb/²⁰⁴Pb = 38.1 to 38.5, whereas the latter has old crust-like signatures: ⁸⁷Sr/⁸⁶Sr = 0.709 to 0.717, ⁴⁰Nd/⁸⁷Sr(T) = -8 to -21, ²⁰⁶Pb/²⁰⁴Pb = 16.9 to 18.8, ²⁰⁷Pb/²⁰⁴Pb = 15.49 to 15.81, ²⁰⁸Pb/²⁰⁴Pb = 37.6 to 39.8. In detail, those granitoids with the crustal isotopic signatures can be further divided into five regional zones: Northeast, Southwest, Central, West and Southeast. The first two zones have most enriched signatures, and the last two zones have least enriched signatures. The Central zone has intermediate signatures. These isotopic zones appear to have no direct geographic relationships with the NE-trending tectonic provinces, and are considered to reflect the basement differences. We also note that the regional differences in the gravity anomaly of South Korea more or less agree with the regional isotopic differences. Namely, the zones with the most and least enriched isotopic signatures have strong negative and positive Bouguer anomalies, respectively, suggesting that the crustal thickness of South Korea may correlate with crustal formation age. We present a model for the basement structure of South Korea on the basis of the above observations.