

Sm-Nd dating of calcites from the Huize superlarge zinc-lead deposits of Yunnan Province, Southwest China

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More than 400 Pb-Zn-Ag ore deposits and ore spots have been found in the Sichuan-Yunnan- Guizhou polymetallic mineralization area of southwest China. The Huize superlarge zinc-lead ore deposits, composed by Kuangshanchang and Qilinchang ore deposit at a distance of 2 km, are situated at the center of this area. But there is not any dating data on these deposits. REEs are incorporated in calcite by substituting for Ca^{2+} in the crystal lattice. In recent years, some Ca-bearing minerals, such as fluorite, scheelite and tourmaline, have been used for Sm-Nd isotope dating. We have dated the ages of No 1 orebody of the Kuangshanchang deposit and No 6 orebody of the Qilinchang deposit by Samarium-Neodymium method in calcite.

The data for the calcites from the No 6 ore body yield a slope corresponding to an age of $(226\pm 15)\text{Ma}$ and $\epsilon_{\text{Nd}}=-10.8$, $\text{MSWD}=0.197$. The calcites from No 1 ore body define a slope corresponding to an age of $(225\pm 38)\text{Ma}$ and $\epsilon_{\text{Nd}}=-10.6$, $\text{MSWD}=0.129$. The ages of the two ore bodies are essentially similar, that is to say that the two ore deposits of the Huize superlarge zinc-lead deposits formed at the same stage. If plot all the data in one line, the slope corresponding to an age of $(222\pm 14)\text{Ma}$ and $\epsilon_{\text{Nd}}=-10.8$, $\text{MSWD}=0.695$.

The outskirts of most ore deposits (including the Huize superlarge zinc-lead deposits) in the Sichuan-Yunnan-Guizhou polymetallic mineralization area distribute a large amount of Emeishan basalt, erupted about 250Ma ago. At present, the understandings on the relationships between mineralization and Emeishan basalt activities have remained controversial. The ages of the Kuangshanchang and the Qilinchang deposit are close to the time of the Emeishan basalt eruption, maybe suggest that mineralization of the Huize superlarge zinc-lead deposits and the Emeishan basalt activities have some close relationships.

The abnormality of tellurium in deep sea sediments

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Tellurium is a rare and dispersed element in the Earth. The abundances of tellurium in the earth's crust and MORB are about 1 ppb and 4 ppb respectively (Wen Yi, 2000). Because of its low abundance and analytical difficulty, not many studies have been done on its geochemistry. The concentrations of tellurium in deep-sea sediments from C-C Zone of the East Pacific Basin were measured by ICP-MS in this study. It is found that the concentrations tellurium in deep-sea sediments are extremely high, ranging from 70 ppb to 380 ppb. The average value is 180 ppb, approximately 200 times of the value in the crust and 50 times of that in MORB. In order to understand the origin of abnormality of tellurium in deep-sea sediments, the isotopic compositions of helium and the concentrations of tellurium in their magnetic fractions and bulk are compared in this study. The $^3\text{He}/^4\text{He}$ ratios of deep-sea sediments are very high, varying from 1.10×10^{-5} to 2.69×10^{-5} with the average value of 1.79×10^{-5} . The $^3\text{He}/^4\text{He}$ ratios and the concentrations of tellurium in magnetic fractions are obviously high than those in bulk. The $^3\text{He}/^4\text{He}$ ratios of magnetic fractions vary from 20.33×10^{-5} to 25.60×10^{-5} , with an average of 22.56×10^{-5} . The concentrations of tellurium in magnetic fractions vary from 210 ppb to 710 with an average of 530 ppb, which is approximately 3 times as much as that in bulk, 500 times in the crust and 100 times in the MORB. Thus high concentrations of tellurium in deep-sea sediments could not result from pelagic sediments or under lying basalts. All data points of helium isotope of sediments sit in or close to the mixing curve between the interplanetary dust particles (IDPs) and the terrigenous sediments in the chart of $^3\text{He} - ^3\text{He}/^4\text{He}$. It shows that the high $^3\text{He}/^4\text{He}$ ratios in marine sediments result from IDPs, and the $^3\text{He}_{\text{IDP}}$ amount up to 99.9% of the measured ^3He concentration. There is obviously a positive correlation between the ^3He and Te concentrations in deep ocean sediments. As we know that the abundances of tellurium in meteorite are excessively high (2100 ppb). It may be even higher in IDPs. It is suggested that the abnormality of tellurium in deep-sea sediments may be caused by IDPs. Therefore the tellurium concentration in sediments may become a new and more sensitive indicator of impact event of meteorite or comet.

New genetic model for porphyry copper deposit

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Large amount of reduced-sulfur is necessary for the formation of porphyry copper deposit. At shallow crustal depths, the magma fluids will be partitioning in two phases: liquid and vapor^[1]. Sulfur tends to get into vapor phase, while copper tends to get into liquid along with chlorine^[2]. Therefore, it is very important how the two fluids mix and make the copper to precipitate as sulfides.

Xifanping porphyry copper deposit is located in the Kangdian porphyry belt, Southwest China. The ore bodies of the deposit are hosted in the two porphyries. The inner hornblend monzonite, outcropped, is earlier than the outer biotite-quartz monzonite buried 300 meters deep. Four stages of alteration assemblages are recognized: stage I, magnetite + biotite + quartz; stage II, k-feldspar(I) + actinolite(I); stage III, actinolite (II) + quartz + chalcopryrite + pyrite + chlorite; stage IV, albitite + serisite + pyrite. Types I and II are associated with the earlier hornblend monzonite and deep biotite-quartz monzonite, respectively. Significant Cu mineralization is associated with stage III. The veins of actinolite (II) + quartz + chalcopryrite + pyrite cut the earlies alteration assemblages. The temperatures of stage I is 600°C, and the daughter crystals of salt and sylvite were identified in quartz inclusions. The temperatures for stage II are 500 ~ 300 °C and a lot of chalcopryrite and salt daughter crystals were found in the quartz fluid inclusions.

Above evidence demonstrates the earlier fluids from magma hydrothermal fluids is rich in Na-K and the ore-forming fluids rich in Na and Cu is the mixture of two fluids from biotite-quartz monzonite and hornblend monzonite. Both of them secreted fluids during their ascending and cooling. The vapor from the earlier fluid escaped from intrusion into air, while its liquid stayed in the intrusion because of volcanism. When the later deep fluids rich in S (not escaped as buried deeper) superimposed on the earlier one, it provide reduced-sulfur and intensive mineralization occurred.

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Microbiological variation regulations of iron, manganese and sulfate in sediments of Lake Aha and Lake Hongfeng seasonally

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Fe-Mn-S cycling in Lakes can influence water quality, degrading of organic matter and variation of heavy metals. In the article, seasonal variations and microbe mechanisms of iron, manganese and sulfate in sediments of Lake Aha and Lake Hongfeng was studied. Sediment cores were collected at Lake Aha and Lake Hongfeng, which located in Yunnan-Guizhou Plateau, Southwest China. The later one has higher contents of iron, manganese and sulfate because more than 100 small coal mines around it.

Variations of iron, manganese and sulfate in sediment pore waters of Lake Aha and Lake Hongfeng in winter and spring shows that content of iron is relative low in several centimeters of upper layer sediments in winter and spring, however content of manganese is relative high then decrease to a lower content. They have change regulations differently that is affected by microbes and variation of sulfate. Content of sulfate in sediment pore waters is much lower in Lake Hongfeng than in Lake Aha, thus with different distributions and change regulations. However, a commonly change regulation is that content of sulfate decreases rapidly or keeps relative low one in several centimeters of upper layer sediments which is relative to distributions of SRB.

Molecular biological studies indicate that upper layer sediments among 7cm are main distribution locations of SRB. *Desulfobacter* and *Desulfovibrio-Desulfomicrobium* are main SRB groups. Distributions of all SRB groups are uneven, shown the difference and predominance. Due to activities of SRB, content of sulfate decreases rapidly, that S²⁻ produced combine with Fe²⁺ to precipitation results in different vertical variations of iron and manganese. Microbe culture experiments give the evidence of that iron and sulfate reduction are mainly microbe processes, but manganese reduction is not. The experimental results are in the follows. Two sediment cores are utilized to microbial culture experiments. They all keep the original state but microbes are killed in one sediment core. After keep anaerobic conditions, content of dissolve oxygen decreases. After 124 hours, the sediment cores are keep oxygen again. Iron, manganese, sulfate, DO and pH are determined in the processes.

Testing cosmogenic nuclide production rate scaling models using in situ cosmogenic ^{14}C from surfaces at secular equilibrium

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Theoretical models currently used for scaling in situ cosmogenic nuclide production rates (e.g., Desilets and Zreda, 2003, EPSL 206, p 21; Lal, 1991, EPSL 104, p 424; Dunai, 2001, EPSL, 193, p 197) are based on modern measurements of cosmic ray variation with latitude and altitude. In situ cosmogenic ^{14}C (in situ ^{14}C) in quartz provides a unique opportunity to test these theoretical models empirically using significant numbers of geologic samples. Unlike other commonly used in situ cosmogenic nuclides, ^{14}C has a short half-life that allows attainment of secular equilibrium, or “saturation,” in approximately 20-25 ky. Also, ^{14}C loss from decay far outstrips loss from erosion in many geomorphic settings. Under such conditions, the measured concentration of in situ ^{14}C is only a function of its integrated average production rate.

We are analyzing samples from saturated surfaces along mid- and low-latitude altitude transects to assess the altitudinal and latitudinal dependence of integrated late Quaternary in situ ^{14}C production rates. Sampling site altitudes for the mid-latitude transect range from near sea level in Death Valley, CA, to nearly 3.9 km in the Inyo-White Mountains, CA. Samples from the low-latitude transect, assembled from sites in Namibia, Australia and northern Chile, cover a comparable altitudinal range. In using samples from disparate locations, we are testing the assumption that the geomagnetic field averages to a geocentric axial dipole (GAD) over the exposure period of these samples.

Results from both transects are well-described by simple exponential functions. No systematic difference is observed between the low-latitude locations, suggesting a GAD adequately describes the effective geomagnetic field during exposure. Results from the mid-latitude transect are consistent with published scaling models, which do not differ significantly along the transect. However, the Lal (1991) and Dunai (2001) models for spallogenic production mechanisms predict higher production rates than those measured for the low-latitude transect. This suggests in situ ^{14}C production may have a significant muogenic component – consistent with the predictions of Heisinger et al. (2002, EPSL 200, p 357). Interestingly, the Desilets and Zreda (2003) model, which includes spallogenic and muogenic scaling factors, also overestimates the measured low-latitude production rates.

Burial of terrigenous and marine organic carbon in the Yangtze river delta and adjacent shelf sediments

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River delta and shelf system are one of the most important environment for organic carbon burial and may have a major contribution to the fate of carbon. However, organic carbon deposition in the delta and shelf sediments and their contribution to the carbon cycle were not well studied. Organic carbon $\delta^{13}\text{C}$, grain sizes, carbonate contents in sediments as well as the organic carbon burial rates of the Yangtze River Delta and adjacent East China Sea shelf were determined in order to understand sources of organic carbon, marine and terrigenous materials burial flux and their relative contribution to the study delta and shelf depositional system.

Large spatial variations of organic carbon, grain sizes and burial flux were observed in this study. Most terrigenous organic carbon were found in the Yangtze River Delta and inner shelf region. Away from the Delta and inner shelf in the west/east direction, organic carbon progressively shifted from mostly terrigenous in origin to predominant marine with organic carbon $\delta^{13}\text{C}$ varied between approximately -26 and -19 . Similar spatial variations of organic carbon concentrations in sediments and %fine-grained sediments were also found, with higher concentrations of organic carbon, and fine-grained sediments located mostly in the Delta and inner shelf. Organic carbon $\delta^{13}\text{C}$ increased linearly with decreasing organic carbon concentrations. Organic carbon concentrations also increased linearly with the fine-grained sediment contents. Large amount of detritus from the Yangtze River are controlling the distribution of terrigenous organic carbon distribution in the study region.

Approximately 80% of the terrigenous organic carbon exported from the Yangtze River were deposited in the Delta and inner shelf region with very limited amount of terrigenous organic carbon capable of depositing in other region. A great percentage of marine organic carbon were unaccounted and may be decomposed in the water column or escaping outside the Delta and shelf system.

Ca-Al-rich inclusions in the Ningqiang carbonaceous chondrite: Condensation, sintering, melting and alteration

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A systematic study of petrography, mineral chemistry, bulk compositions, rare earth and other trace elements, O and Mg isotopic compositions has been conducted on Ca-Al-rich inclusions (CAIs) in the Ningqiang carbonaceous chondrite. Our main purposes are to clarify condensation trajectory with regard to mineral assemblages, REE and other trace element patterns, and to evaluate any time differences between various events related to formation and evolution of the inclusions.

Abundant CAIs in Ningqiang are fluffy assemblages of condensates. They represent a wide range of condensation in the nebula, from hibonite-bearing Type A at high temperatures, melilite-spinel-rich, spinel-pyroxene-rich, to spinel-bearing amoeboid olivine aggregates (AOA) at low temperatures. Typical coarse-grained compact Type A (CTA), melilite-pyroxene-rich (Type B), plagioclase-pyroxene-rich (Type C), and plagioclase-olivine-rich (POI) inclusions were also found in Ningqiang, and they were sintered or melted by heating certain condensate assemblages in the nebula. Both CTAs and Type Bs can form through melting fluffy Type As (FTA), but precursors of CTAs are melilite-predominant and those of Type Bs contain more Ca-pyroxene. Type C inclusions crystallized from liquids that were probably produced by melting anorthite-spinel-rich inclusions (ASI). ASIs were found in Ningqiang, and they are alteration products of Type As, which took place at high temperatures. Spinel-bearing AOAs may be precursors of POIs.

Analyses of Mg isotopes of plagioclase in two POIs and one Type C inclusion in Ningqiang indicate absence or small excesses of ²⁶Mg ($\leq 2\%$). In addition, the preliminary data reveal secondary events after crystallization of these inclusions. More analyses of trace elements, O and Mg isotopes are going on.

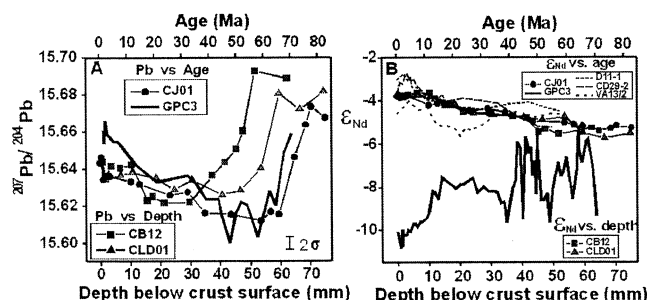
Pb and Nd isotope evolution of the Central Pacific Ocean over the Cenozoic: implication for contrasting source dominance

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In the past decades, isotope data of seawater and hydrogenetic ferromanganese crusts and nodules, ridge hydrothermal venting and riverine loads, have provided strong evidence on terrigenous sources for oceanic Pb and Nd. However, the ways for terrigenous Pb and Nd input into the ocean are not well constrained and are highly controversial. Here we present new Pb and Nd isotope data for three ferromanganese crusts (two with and one without phosphatization) from the central North Pacific. The three crusts, no matter phosphatized or not, display similar Pb isotope variation trends against depth, suggesting similar ages and different growth rates for these crusts. Estimation by constant Co flux model dating yields late Cretaceous age for the non-phosphorized crust (CJ01) whose variation pattern of Pb isotopes with time agrees well with the Pb isotope evolution of the silicate of eolian dust extracted from the central North Pacific Core (LL44-GPC3) whose sedimentation ages have been well constrained (Fig. A) (Pettke et al., 2002). Hence, we suggest that the central North Pacific seawater Pb as recorded in these crusts over the Cenozoic period should have a major eolian dust origin, and the Pb isotope record in the crusts has not been affected by phosphatization. In contrast, the Nd isotopic variations of the crusts studied and other Pacific crusts (Ling et al., 1997) are by no means similar to the Nd isotopic evolution of the core silicate (Fig. B), suggesting negligible contribution of eolian dust Nd to the central Pacific seawater Nd budget. The rise of Nd isotope ratio in the Pacific during the Cenozoic is likely due to an increase in volcanism and erosion in the Pacific rim.



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The effect of water on the solubilities of metals and accessory phases in granitic melts

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The solubilities of manganocolumbite, manganotantalite, wolframite (hübnerite), rutile, zircon and hafnon were determined as a function of the water content in a peralkaline (ASI=0.6) and a subaluminous (ASI=1.0) granite melt. All experiments were conducted at 1035°C and 2 kbar in TZM rapid quench autoclaves and the water contents of the melts ranged from nominally dry to approximately 6 wt% H₂O. Accessory phase solubilities are not affected by the water content of the peralkaline melt. By contrast, solubilities are affected by the water content of the subaluminous melt. There is a decrease in the solubilities of all the accessory phases at less than ~1 wt% H₂O, but at water contents higher than this value, solubilities are nearly constant. It can be concluded that water is not an important control of accessory phase solubility, although the water content will affect diffusivities of components in the melt, and thus whether or not accessory phases will be present as restite material. The solubility behaviour in the subaluminous melt supports previous spectroscopic studies, which have observed changes in coordination of high field strength elements only in subaluminous melt compositions, and only in nominally dry melts.

Wolframite solubility has an additional complexity because tungsten is potentially 4⁺, 5⁺ or 6⁺ in granitic melts. The experiments were conducted at constant hydrogen fugacity, thus the oxygen fugacities of the melts are progressively lower with progressively lower water contents. If wolframite dissolves as W⁵⁺, e.g., $\text{MnWO}_4^{\text{crystal}} = \text{MnO}^{\text{melt}} + 0.5 \text{W}_2\text{O}_5^{\text{melt}} + 0.25 \text{O}_2^{\text{melt}}$ then wolframite solubility should decrease with increasing the water content of the melt. The decrease of solubility with increasing water content will be even greater if tungsten is quadrivalent. However, wolframite solubility increases with increasing water content in the subaluminous composition suggesting that tungsten dissolved as a hexavalent species.

Water solubility in the lower mantle minerals

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Water storage capacity of the lower mantle becomes a matter of debate. Meade et al. (1994) reported 60-70 ppm H₂O in MgSiO₃-perovskite. However, Bolfan-Casanova et al. (2000) showed absence of water (<1 ppm H₂O) in MgSiO₃-perovskite. Murakami et al. (2002) reported 0.1-0.4 wt% H₂O in Al-Fe-Mg-perovskite, 0.3-0.4 wt% H₂O in Ca-perovskite and 0.2 wt% H₂O in ferropericlase measured by SIMS and FTIR. Bolfan-Casanova et al. (2002) reported less than 20 ppm H₂O in ferropericlase at 25 GPa. Here we report new data on water solubility in Mg-perovskites, Ca-perovskite, and ferropericlase in Al-Fe-bearing systems. Using the measured water content we estimate water storage capacity in the Earth's lower mantle.

The phase relations were determined at 25-26 GPa and the temperature range from 1000 to 1800°C. We used several starting materials corresponding to perovskite and ferropericlase. The hydrous composition was prepared by adding Mg(OH)₂ or Ca(OH)₂ adjusting the proportion of MgO and CaO. The furnace assemblies and experimental details are described by Litasov and Ohtani (2002). Water contents were measured by FTIR (Litasov et al., 2003).

IR spectra of pure MgSiO₃ perovskite synthesized at 1300°C show bands at 3397, 3423, 3448, and 3482 cm⁻¹. Calculated water content corresponds to about 100 ppm H₂O. Al-Mg-perovskite containing 4-7 wt% of Al₂O₃ shows broad IR spectra with bands at 3404, 3448, and 3565 cm⁻¹. Calculated water content is 1100-1400 ppm. IR spectra of MORB-related Mg-perovskite (Mg#=58-61, Al₂O₃=13-17 wt%) synthesized at 1000-1200°C show major bands at 3397 cm⁻¹. The H₂O content in MORB-related Mg-perovskites is 90-110 ppm. IR spectra of peridotite-related Mg-perovskite (Mg#=88-90, Al₂O₃=5-6 wt%), synthesized at 1400-1600°C, also show major bands at 3397 cm⁻¹. The H₂O content in Mg-perovskite related to peridotite is 1400-1800 ppm.

IR spectra of aluminous Ca-perovskite (2.0 wt% Al₂O₃) synthesized at 1900°C composed of two major bands at 3343 and 3607 cm⁻¹. Preliminary H₂O content in Ca-perovskite is near 5100 ppm.

IR spectra of periclase show weak bands at 3299, 3308, and 3404 cm⁻¹. Ferropericlase (Mg#=88) has major bands at 3299 and 3474 cm⁻¹. Calculated H₂O content in periclase is 11 ppm at 1400°C (Al₂O₃ in periclase is 1.2 wt%) and 20-25 ppm at 1600-1800°C (Al₂O₃=0.9 wt%). The H₂O content in ferropericlase is 14 ppm at 1400°C (Al₂O₃=0.9 wt%) and 80 ppm at 1800°C (Al₂O₃=2.4 wt%).

The present results indicate that Ca-perovskite has highest water solubility among the lower mantle minerals following by Mg-perovskite and ferropericlase. The maximum amount of water potentially stored in the lower mantle is estimated as 3.42x10²¹ kg. This is 2.5 times of the present ocean mass and comparable with the amount of water potentially concentrated in the transition zone.

Mantle genesis of diamond in carbonate-silicate-carbon melts of variable chemistry: Evidence from high-pressure experiments

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Carbonate-silicate nature of mantle melts responsible for formation of natural diamonds is revealed by contemporary data of high-pressure experiment and chemical mineralogy. Highly compressed multicomponent carbonate-silicate melts are of high carbon solubility. But, the melts can be considered as parent diamond-forming media only if labile carbonate-silicate-carbon melt-solutions oversaturated to diamond are originated. Experiments on diamond spontaneous crystallization in multicomponent carbonate-silicate-carbon melts (compositionally similar to fluid-bearing multiphase primary inclusions of $K_2O-Na_2O-CaO-FeO-MgO-Al_2O_3-TiO_2-P_2O_5-SiO_2-Cl-CO_2-H_2O$ chemistry in diamonds from Botswana [Schrauder, Navon, 1994]) showed that labile carbon oversaturations were run, and diamonds effectively formed [Litvin, Zharikov, 2000]. It is appropriate to recognize major (carbonate and silicate) and admixed (oxides, sulfides, phosphates, haloids, carbon dioxide, water, etc.) components in the compositions of natural parent media. Experiments show that silicate-carbonate-carbon melts with high silicate component contents (more than 60 wt.%) are not effective for diamond nucleation. By mineralogical data, essential composition variability of multicomponent carbonate-silicate parent media accompanying diamond formation evidently exists due to fractional crystallization of the melts. In the processes, contents of admixed components may increase to the levels comparable with the major component concentrations. Experiments on diamond spontaneous crystallization were realized in the labile Fe-Ni-Cu-S-sulfide-carbon [Litvin, et al., 2002], KCl-chloride-carbon [Litvin, 2003] and H_2O -carbon [Akaishi, Yamaoka, 2000] melt-solutions suggesting that local rise of admixed sulfide, chloride and water concentrations in the parent carbonate-silicate-carbon melts is perfectly combined with crystal growth of natural diamonds. Support: RFBR grant 02-05-64684.

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UHP mineral inclusions hidden in zircons from amphibolites in Sulu terrane, eastern China

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The amphibolites occur sporadically as thin layers and blocks throughout the Sulu terrane, eastern China. All analyzed amphibolite outcrop and core samples from pre-pilot drillhole CCSD-PP1 and CCSD-PP2, Chinese Continental Scientific Drilling Project in the Sulu terrane, are retrograded eclogites overprinted by amphibolite-facies retrograde metamorphism, with characteristic mineral assemblages of amphibole + plagioclase + epidote ± quartz ± biotite ± ilmenite ± titanite. However, coesite and coesite-bearing ultrahigh-pressure (UHP) mineral assemblages are identified by Raman spectroscopy and electron microprobe analysis as inclusions in zircons separated from these amphibolites. In general, coesite and other UHP mineral inclusions are preserved in the cores and mantles of zircons, whereas quartz inclusions occur in the rims of the same zircons. The UHP mineral assemblages consist mainly of coesite + garnet + omphacite + rutile, coesite + garnet + omphacite, coesite + garnet + omphacite + phengite + rutile + apatite, coesite + omphacite + rutile and coesite + magnesite. Garnet inclusions in zircon separates from amphibolites, are characterized by low MnO content (0.25 wt %-0.57 wt %), with molecular percentages, Alm = 50.4-54.1, Prp = 22.9-26.1, Grs = 21.2-22.5 and Sps = 0.6-1.2. All omphacite inclusions show compositional ranges of Jd_{45.1-49.6} Aeg_{4.1-8.8} Aug_{44.4-48.6}. All phengite inclusions, adjacent to coesite, garnet and omphacite inclusions in zircon domains, have Si values ranging from 3.46 to 3.48 p.f.u. (O=11). Analyzed magnesite inclusions, coexisting with coesite inclusion in the same zircon domain, contain about 31.21 wt %- 32.47 wt % MgO and 17.47 wt %- 18.10 wt % FeO, and about 0.73 wt %- 0.81 wt % CaO. They have X_{Mg} (Mg/(Mg + Fe + Ca)) = 0.75-0.76, X_{Fe} (Fe/(Mg + Fe + Ca)) = 0.23-0.24, and X_{Ca} (Ca/(Mg + Fe + Ca)) = 0.01. Rutiles together with coesite, garnet and omphacite occur as inclusions in the cores of zircons from amphibolites. The TiO₂ content of analyzed rutile inclusions ranges from 97.48 wt % to 99.31 wt %, with FeO content ranging from 0.43 wt % to 0.47 wt %. Compositions of analyzed mineral inclusions mentioned above are very similar to those of matrix minerals from Sulu eclogites. These UHP mineral inclusion assemblages yield temperatures of 631-780°C and pressures of ≥28 kbar, representing the P-T conditions of peak metamorphism of these rocks, which are consistent with those (T=642-726°C, P≥28 kbar) deduced from adjacent eclogites. These data indicate that the amphibolites are the retrogressive products of UHP eclogites.

Characterization and leaching behavior of Fly Ashes from Power Plants in Yanzhou Mining District

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Method and Experiments

Mineralogy of the fly ashes were determined by X-ray diffraction. K, Na, Ca, Mg, Cu, Pb and Zn in ashes were determined by ICP-MS and spectrophotometer for As. 15 g fly ash samples (FA1) was placed in 1 L polyethylene bottles and mixed with 1 L of distilled water (pH=7). The bottles were shaken for 24 hours in a horizontal shaker at room temperature. Then, the supernatants were decanted and filtered through a 0.25 μm micropore membrane filter at the end of the leaching experiment, and the final pH in leaching solution was measured. The process of the same samples was repeated three times. The higher ratio between the ash and water was to prevent the solution achieving saturation and allowing all the water-soluble fractions in the ashes to be dissolved out.

Discussion of results

According to chemical composition, the ashes from the study power plants belong to $\text{CaO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system. The chemical composition usually fluctuates much due to the different mineral components contained in the coals. The analysis result showed that the content of the main minerals in coal is positive to the chemical and mineral composition of ashes. The trace elements are preferentially concentrated in fly ash, because of its small particles size and large specific surface. So much of K, Na, Ca, Mg and the partial of Pb, Zn, Cu, As, which are adsorbed on the surface of fly ash, are high in concentrations. Therefore, in the ashes of small particle size, the contents of trace elements are high. The leaching test results are shown in Table 3. From the Table 3, Ca and Na concentrations in the initial leachate are high. Cu, Pb, Zn concentrations were lower than the concentrations of Na, Ca, K and Mg. Zn Shows similar trend to that of Cu, but maintains a constant level. As were generally close to detection limit, but still detectable in all leaching solutions. Such continuous release of Cu, Zn, Pb and As might signify dissolution of the glass in the ash particle.

Conclusions

The major composition of ashes are SiO_2 , and Al_2O_3 , low amounts of Fe_2O_3 and CaO , and little content of SO_3 , P_2O_5 , Na_2O , K_2O and TiO_2 .

The leaching behavior of fly ashes indication that the trace elements in the fly ash particles are mainly associated with the surface but some of them are incorporated with the glass matrix as well.

Acknowledgements

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The influence of fluid components H_2O and CO_2 on the partial melting of upper mantle peridotite

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The importance of fluid components (especially H_2O and CO_2) in the partial melting of upper mantle peridotite is manifested by the explosive nature of the volcanism and much other indirect evidence. The role these fluid components play, however, remains as elusive as the fluid itself. Intensive discussion in the 1960s and 1970s ended inconclusively. Recent experimental studies also showed a marked lack of mutual consistency. This situation has mainly been caused by the lack of a suitable analysing technique and the lack of full evaluation of experimental techniques. In this study piston-cylinder experiments with long run durations are performed in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\pm\text{H}_2\text{O}$ at 11 kbar from H_2O -free condition to H_2O -saturation. Composition data are collected by electron microprobe and FTIR (for H_2O and CO_2 in melt), producing the first complete set of composition data for partial melts multiply saturated with the Sp-lherzolite phase assemblage. We find that in these nominally C-free experiments, the melts inevitably contain non-negligible amounts of CO_2 , up to ~ 0.7 wt%, which come from the hydroxides used to add H_2O or from graphite diffusion through the Pt capsule.

Our data clearly show that H_2O not only strongly affects the partial melting temperature but also the melt composition. It is found that 1 wt% H_2O in the melt decreases the solidus by ~ 40 degrees. The melt composition gradually changes from olivine basalt at H_2O -free condition to tholeiite at H_2O -rich condition. The melt also decreases its diopside component and eventually becomes corundum-normative. These data link together the previous results at H_2O -free condition (Presnall et al., 1979; Liu and O'Neill, in press) with those at H_2O -saturation (Kushiro, 1972).

In agreement with Egglar (1978), the effect of CO_2 on the partial melting temperature is essentially negligible. Its effect on the melt composition, however, is quite strong, stronger than but generally opposite to that of identical H_2O . Since CO_2 has always been detected here and in those fully analysed experiments in Gaetani and Grove (1998; up to ~ 1.3 wt%), its variation in abundance might explain some key discrepancies in previous hydrous partial melting studies.

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Fission track dating of authigenic quartz from the red residua overlying carbonate rock in Guizhou, China

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The dating of weathering crust have been documented by few authors. But, it is generally difficult to select suitable minerals for dating in many profiles. Fortunately, many authigenic quartzs are found in several red residua overlying carbonate rock in Guizhou, China. The aim of this paper is to present the data of fission track dating of authigenic quartz in these weathering profiles.

Three samples of the PB and XP profiles were taken from the bottom to upper respectively. two samples in the upper of HB and HC profiles were collected too, which the sample of HB profile was divided into two by its size. The data show quartz FT ages range from 25Ma to 1Ma, more younger than parent rock (T) (Fig.1). The thermal and tectonic history of Guizhou reveals that no heating event occurred during Cenozoic, which its temperature surpassed the annealing temperature of quartz (900-1000°C). The characteristics of

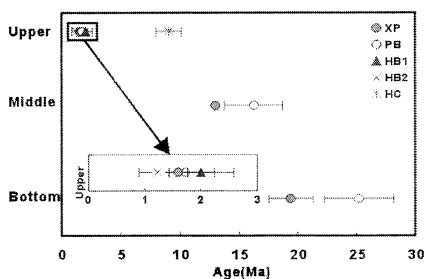


Fig. 1. Authigenic quartz FT ages of four profiles

track length (3-5 μ m) and track shape confirm further all samples are not annealed. So, the FT ages of authigenic quartz appear to reflect the age of formation. In other words, the age of the weathering crust would be outlined if the genesis can be known exactly, presuming formed either in bedrock or lower soil layer of profile. It is also very interesting to point out, from bottom to upper, the FT age of authigenic quartzs decrease gradually, just the opposite of weathering trend. The reason of this phenomenon need to be studied in detail.

Acknowledgments

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Formation of the Nb/Ta deficit in the continental crust: Insights with the Precambrian mantle-derived volcanics from North China craton

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A mass imbalance exists in Earth for Nb, Ta and possibly Ti: estimated bulk continental crust (BCC) and depleted mantle (DM) both have subchondritic Nb/Ta, Nb/La and Ti/Zr [1]. Mafic volcanics from the North China craton geochemically show an Archean-Proterozoic (A-P) boundary [2]. The Archean mafic volcanics (AMV) have average Nb/Ta = 20.0, Zr/Hf = 39.1 (Fig. 1a), which could be a potential silicate reservoir to complement the low Nb/Ta (and possibly Zr/Hf) of BCC and DM. However, Nb (and Zr) strongly fractionated from Ta (and Hf) with average Nb/Ta = 7.5 and Zr/Hf = 31.6 for the Proterozoic mafic volcanics (PMV). Given the fine correlation of Ti and Ca with HFSEs and Nb/Ta, Zr/Hf ratios in a large range, the highly fractionations of Nb from Ta and Zr from Hf for PMV could be related to the involvements of Ca-Ti-bearing phases during the mantle melting.

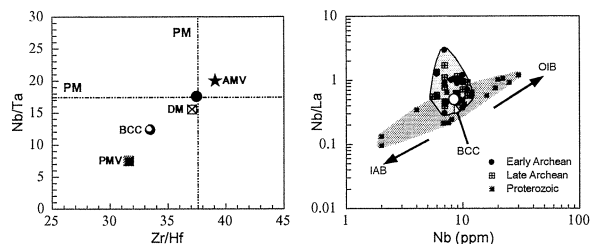


Fig. 1 (a) Average Nb/Ta vs. Zr/Hf for AMV and PMV. BCC is from <http://www.earthref.org/GERM>. (b) Nb/La-Nb variations of AMV and PMV.

Fig. 1b shows that Nb/La positively correlated with Nb ranging from OIB to IAB for PMV while no obvious correlation is found for AMV, which suggest that large-scale subduction could not have occurred until Paleoproterozoic time in the North China craton. The Proterozoic subduction could have largely contributed to the formation of Ca-Ti-bearing phases and subsequent totally Nb/Ta (and possibly Zr/Hf) deficit of PMV.

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Laojunshan-Song Chay metamorphic core complex and its tectonic significance

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The Laojunshan-Song Chay metamorphic core complex "LSMCC", embodied as a southeast-toward semi-moon sharp, located at the border between China and Vietnam.

Metamorphic core complex

The LSMCC made up of core, middle-layer, cover, detachment faults, and mesozoic granite pluton.

The core constituted with the ductile deformed high-grade metamorphosed Proterozoic(?) Formation and the Sillurian granites "430Ma". From down to up, the granites deformed to mylonitized granitic gneiss, augen gneissic mylonite and granitic mylonitized gneiss.

The middle-layer constituted with the later- Proterozoic and the early Cambrian schistose mylonite, and the deformation in there are ductile to brittle.

The cover consistent with the Paleozoic low-grade meta-sedimentary Formation, and deformation in there are brittle. The detachment faults included ductile ones in the upper parts of core, ductile-brittle ones in the middle-layer and dominoes-style brittle ones in the cover.

Isochronal ages "230~200Ma" gained from the core, the middle-layer and the cover, indicated that regional deformation and metamorphism coincided to the Indosinia movement.

The intruding of mesozoic granites "110~80Ma", reinforced upheaval of the LSMCC.

Tectonic significance

The LSMCC is north to the Ailaoshan-Honghe belts, south to the fold-fault belts, island arc and Ocean island basaltic rocks belts bordering Guangxi and Yunnan, and west to the Babu-Phu Ngu ophiolites. All of these mention above, formed to a typical Turkic-type orogen between the Indochina massif and the southern China massif, suggested that upheaval of the LSMCC should included two stages at least. First, iso-collision detachment at the Indochina movement "230~200Ma". Second, iso-intruding upheaving at the Yanshan stage "110Ma".

Natural and enhanced concentrations of heavy metals in surface sediments of Nonoc Island, Philippines

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A Nickel mining located in Nonoc island, Philippines operated for several years and ceased. In this study, heavy metals (Cu, Zn, Mn, Ni, Co and Fe) in surficial sediments from Nonoc Island were analyzed to examine the distribution of heavy metals and by linear regression model, sediment samples exceeding the natural level were determined.

Twenty four sediment samples were collected around the island and the total heavy metals were analyzed by AAS. Clustering analysis extracted three distinct clusters among the samples. The first cluster and the second cluster grouped the sediments having high metal concentrations. The third cluster grouped the sediments having the lowest concentrations of Cu, Zn, Mn, Ni, Co and Fe, averages of 9.6, 39.4, 352, 516, 81.5 ppm and 3.5 %, respectively. This cluster is considered to represent the natural level heavy metals in the study area. Using the metal concentrations in the third cluster, linear regression was generated with Fe as reference metal. Sediments in the first cluster exceeds the upper 95% confidence level for the Ni regression and is considered to be enhanced level.

REE and C, O and Sr isotopic compositions of hydrothermal carbonate minerals from Fankou superlarge Lead Zinc deposit, China

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Fankou is the largest Pb-Zn producer in Asia. Its ore bodies are embedded by D_{1-2} and C_1 carbonate strata. Hydrothermal carbonates, mostly calcite, is the major gangue mineral. Three stages of hydrothermal carbonates, pre-, syn- and post-metalliferous stages, are recognized in the mine. There exist a lot of opinions on its genesis, including "sedimentary-superimposed transformation" (Wu J. et al., 1987), "submarine hot spring outpouring" (Zhu S. et al., 1992); "contemporaneous fault hydrothermal filling and replacement" (Wang P. et al., 1995) and "submarine exhalation and syngenetic sedimentary" (Li Z. et al., 1997) etc. We analysed REE and C, O and Sr isotopic compositions of the hydrothermal carbonates and the results show that:

1.) The syn-stage carbonates possess the highest Σ REE (mostly $>120 \times 10^{-6}$) and positive Eu anomalies (δ Eu as high as 6.137), while both the pre- and post-stage carbonates have low Σ REE (mostly $< 30 \times 10^{-6}$) and negative Eu anomalies, indicating that the ore-forming fluid of the main metalliferous stage is of reduced, Cl⁻-riching, and relatively high temperature hot brine;

2.) The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the syn-stage carbonates are $-2.9\text{--} -8.0\text{‰}$ (PDB) and $14.7\text{--}19\text{‰}$ (SMOW), which are lower than those of carbonate host rocks (-2.5‰ and 20.5‰ respectively), and are also quite different from pre- and post-stage carbonates, suggesting magmatic (mantle-derived?) water might have been involved in the Pb-Zn metallogenesis;

3.) The Rb content of the hydrothermal carbonates is lower than 1×10^{-6} , that their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.712336–0.717972) may be used as $(^{87}\text{Sr}/^{86}\text{Sr})_0$ of the ore-forming fluids. Sr-isotopic exchange modeling indicates that the ore-forming fluids of Fankou mine mainly composed of basinal hot brine, and the Fankou is probably a basinal hot brine transformed deposit.

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Copper isotope study of copper and gold deposit of Dongguashan, China

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The Dongguashan deposit, located in Tongling, Anhui province, includes both stratiform sulphide (SHMS-type) and skarn orebodies. The massive sulphide ores occur between late Devonian sandstones and middle Carboniferous carbonates. The skarn orebodies were produced by intrusion of Yanshanian quartz diorite into late Palaeozoic carbonates. The $\delta^{65}\text{Cu}$ values of clusters of chalcopyrite and ring chalcopyrite around pyrite from massive sulfide ores are 0.45 ‰ and 0.78 ‰ respectively. The three disseminated chalcopyrite samples from skarn ores have the $\delta^{65}\text{Cu}$ values of 0.09 ‰, 0.23 ‰ and 0.83 ‰. The $\delta^{65}\text{Cu}$ values of veiled type quartz-chalcopyrite occurred in skarn ores and veiled type chalcopyrite from marble occurred in contact zone between quartz diorite body and its wall rocks are 0.36 ‰ and 0.38 ‰ respectively. The above copper isotopic compositions of chalcopyrite from the different types of ores are very similar to each other and are compatible with those of chalcopyrite from high-temperature magmatic hydrothermal deposits (Zhu et al., 2000), but are entirely different from those of samples from old inactive black smoker sulphide deposits (Zhu et al., 2000) and those of chalcopyrite in Jinman vein-type copper deposit in which the copper was thought to derive from sedimentary rocks (Jiang Shaoyong et al., 2002). This may implicate that the copper in both massive sulphide ores and skarn ores in the Dongguashan deposit has the same source, and probably comes from Yanshanian quartz diorite. According to the above copper isotopic data, together with a study on the geological features (Gu et al., 2000), a two-stage model of the formation of this deposit can be established. The first stage involves the formation of massive sulphide orebodies which contain dominantly pyrite, pyrrhotite and some gangue minerals, but little copper-bearing sulphide during early Carboniferous period. In the second stage the Yanshanian magmatic hydrothermal activities on the one hand form the skarn orebodies, on the other hand, overprint early massive sulphide orebodies and induce enrichment of large amounts of copper in these stratiform sulphide ores.

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Variation in surface characteristics of clay minerals in diagenesis processes and their relationship to the generation and primary migration of hydrocarbon

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In order to investigate the generation and primary migration of hydrocarbon in clayey source rocks comprehensively and attempt to determine the amount of hydrocarbon expelled approximately, some surficial analytical technologies, including XPS, nitrogen adsorption method, XRD, FTIR and TG, are employed to discover the combination pattern between organic matter and clay minerals and its variation during diagenesis processes. Both clay minerals and organ-clay complexes were isolated respectively from the tertiary clayey source rocks sampled from Dongying Basin, Bohai Depression. The calculation based on N₂ adsorption-desorption isotherm discovers that the BET area and the surface energy of clay isolation decrease gradually as the illitization of smectite occurred in diagenesis processes. But the change pattern of organ-clay complexes is quite different, the variation of BET area, pore-width-distribution and surface energy are influenced remarkably by the amount of soluble hydrocarbon in source rocks. It is of significance to find that the relative high energy sites on clay minerals take precedence over low ones disappear as the generation of hydrocarbon, and reappear lattermost as the primary migration of hydrocarbon. And it is also revealed that the hydrocarbon generated, especially low-molecular-weight hydrocarbon, could be absorbed in interlamellar space of smectite and on mineral surface as well, which decreased in BET area of organ-clay complexes and reduced amount of micropore because of screening and blocking effect of organic molecules absorbed. As the results of XPS, TG and DFT analysis of isotherm, the organic molecules generated prefer to be absorbed on the high energy site, and the desorption occurs in the latter stage of primary migration accordingly. In conclusion: a possible method employing the surface energy analysis of organ-clay complexes is proposed to determine the amount of hydrocarbon expelled from source rocks roughly.

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Geochemical anomalies possibly indicating occurrence of hydrate in the northeast of the South China Sea

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Gas hydrate, mainly composed of hydrocarbon gas and water, is considered to be the 21st clean energy. Many indicators such as BSRs which are thought to be related to gas hydrate are found in the South China Sea (SCS) in recent years. However, the northeastern part of the SCS are taken as one of the most potentials by many scientists in the area. It is situated in the conjunction of the northern divergent continental margin and the eastern convergent island margin, whose geological settings are much preferable for gas hydrate to occur.

Through our work, the bright temperature anomaly recorded by satellite-based thermal infrared scanning image before or within the imminent earthquake, the high content of hydrocarbon gas acid-degassed from subsurface sediment and the high radioactive thermoluminescence value of subsurface sediment are found in the region. Sometimes the bright temperature anomaly isolatedly exists in the surrounding of Dongsha island. The highest content of hydrocarbon gas amounts to 393 μ l methane per kilogram sediment and the highest radioactive thermoluminescence value is 31752 unit, whereas their geometric averages are 60.5 and 2688.9 respectively. What is more inspiring is that there are three sites where the methane contents are up to 243, 268 and 359 μ l/kg and their radioactive thermoluminescence values are 8430, 9537 and 20826 unit respectively, and which are in the very vicinity of one of the highest confident BSR locations identified by Chi (1998). In the paper, the reasons of these anomalies are preliminarily discussed. In allowance for other indicators such as headspace gas anomaly in the sediment and chloride anomaly in the interstitial water in the site 1146 of Leg 184, the above mentioned anomalies are possibly indicating the occurrence of gas hydrate in the northeast of the SCS.

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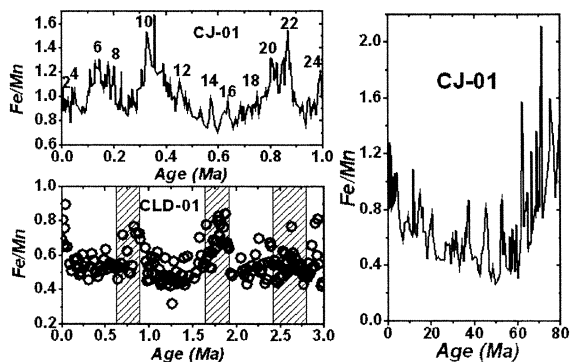
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Implications of Fe/Mn ratios in Fe-Mn crusts for paleoclimate changes

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Contents of Fe, Mn and other elements in two ferromanganese crusts recovered from the Central North Pacific were analyzed with electron microprobe for the study of the possible relationship between the deposition of Fe and Mn and the climate changes. Mn (IV) in hydrogenetic Fe-Mn crusts is mainly supplied as colloidal precipitates from the Oxygen Minimum Zone (OMZ), which concentrated high amount of dissolved Mn (II). The iron is derived from carbonate dissolution and silicate particles of eolian dust. Increase in paleoproductivity during a cooling period would lead to an expanded OMZ which would store more Mn (II), and thus to a decrease in Mn deposition. On the other hand, not effected by the OMZ, the iron depositing into the Fe-Mn crust would increase with the surface productivity and eolian dust input at glacial stages. As a result, the increasing Fe/Mn ratio should indicate a cooling climate. In the past 1 Ma profiles, Fe/Mn ratio fluctuates with glacial-interglacial cycles and roughly corresponds to 24 oxygen isotope stages. Within the past 3 Ma three episodes with high Fe/Mn ratios, approximately at 2.6, 1.8, 0.8 Ma, are detected and coincide with major climate transitions and cooling events: (1) the change of glacial cycles from 41 kyr to 100 kyr at about 0.6–0.8 Ma (Rutherford 2000; Williams et al., 1997); (2) a major cooling episode at Plio-Pleistocene boundary (1.6–1.8 Ma) (van Couvering 1997); and (3) another major cooling episode in Central Asia (Williams et al., 1997) at 2.8 to 2.6 million years ago. The secular evolution pattern of Fe/Mn ratio is broadly consistent with global deep-sea oxygen isotope records (Zachos et al., 2001), supporting that, during the last 80 Ma, Earth's climate system has drifted from expansive warmth to extremes of cold, with the transition at about 55 Ma.



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Origin of water on Earth and Mars

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Morbidelli et al. (2000) demonstrated on dynamical and chemical grounds that more than an Earth's ocean worth of water could have been delivered by large "planetary embryos" which grew in the asteroid belt during terrestrial planet formation. The source is consistent with current understanding of the water content of the asteroid belt (as informed by the chondritic meteorite record), early growth of the giant planets (especially Jupiter), and the isotopic record of D/H and the oxygen isotopes in Earth and chondritic meteorites (though the latter does cap the amount of water that could be delivered in this fashion). Alternative distal sources of Earth's water are ruled out on isotopic or dynamical grounds (especially, comets), and a local (1 AU, astronomical unit) source of water for the Earth would require very low nebular temperatures and seems to contradict the meteoritic evidence suggesting that material inward of 2 AU-3 AU was too dry to supply an ocean or more of water. Subsequent simulations (Raymond et al., 2003) confirm the essential details of this picture.

Mars' history is found to be different; to explain the present mass of Mars requires that it suffer essentially no giant collisions and the bulk of its growth is through addition of smaller bodies. Asteroids and comets from beyond 2.5 AU provide the source of Mars' water, which totals 6-27% of the Earth's present ocean (1 Earth ocean = 1.5×10^{21} kg), equivalent to 600-2700 meters depth on the Martian surface (Lunine et al., 2003). The D/H ratio of this material is 1.2-1.6 times Standard Mean Ocean Water, the smaller value obtaining for the larger amount of water accreted. The total water accreted, while many times less than that acquired by the Earth, is consistent with geological data on Mars, and the D/H value is that derived for Martian magmatic water from SNC meteorites. Both together are consistent with an interpretation of the high D/H in present-day Martian atmospheric water in terms of water loss through atmospheric escape.

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Geochemical approach to the determination of the ^{100}Mo double beta decay half-life

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Double beta decay (DBD) is a rare second order decay, which involves the transmutation of one element of atomic number Z to another of $Z+2$. This decay occurs when normal beta decay is energetically forbidden, and is associated with the release of two electrons and either two neutrinos ($2\bar{\nu}$) or no neutrinos ($0\bar{\nu}$) depending on the neutrino mass. The two decay schemes ($2\bar{\nu}$ & $0\bar{\nu}$) have distinctly different decay half-lives, making double beta decay an excellent test for neutrino mass and lepton conservation.

In this work we look at the DBD of ^{100}Mo to ^{100}Ru , which has one of the highest decay energies compared to other DBD candidates. To date this ^{100}Mo DBD has been examined mainly through the use of direct counting, which suffers greatly from low count rates. Here we present the ongoing development of a geochemical method for the determination of its half-life, using geological time-scales for the accumulation of daughter species.

For our work, samples of molybdenites (MoS_2) were measured for Ru concentration and isotopic composition, and ages via Re-Os dating. Preliminary Ru concentration analysis resulted in concentration of natural Ru in Mt Mulgine and Osbourne molybdenites of 890 ppt and 255 ppt respectively. While Re-Os dating of the Mt Mulgine molybdenites via ICPMS indicates an age of 2807 ± 149 Ma, no meaningful date was obtained for Osbourne due to a possible disturbance of the Re-Os systematics in this sample.

Calculations using the half-life values of $(8.0 \pm 0.7) \times 10^{18}$ yrs, average of all "positive" $2\nu\beta\beta$ -decay results (Barabash, 2002), for the ^{100}Mo - ^{100}Ru decay, and natural Ru concentration in the 2.8Ga-old MoS_2 estimated in this study indicates that the ^{100}Ru isotope should see significant shift ($\sim 12\%$) due to DBD products. This anomaly will be easily detectable with the current analysis technique, given the elimination of Mo isobaric interferences. We hope to report detailed Ru isotopic data from the Mt Mulgine MoS_2 during the conference, and an estimate of the DBD half-life.

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Self-shielding of CO in the Surface of the Solar Nebula

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Self-shielding of $^{12}\text{C}^{16}\text{O}$ and concomitant depletion of the rare isotopologues of CO (e.g., ^{13}CO , C^{18}O) are well known to occur at the edges of molecular clouds. Self-shielding occurs because the predissociation absorption lines in the more abundant $^{12}\text{C}^{16}\text{O}$ become saturated at shorter pathlengths than for the CO isotopologues. The absorption lines of the isotopologues do not, in general, overlap those of $^{12}\text{C}^{16}\text{O}$, resulting in a higher photodissociation rate coefficient for the former. Recently Clayton (2002) suggested that the same process operated in the inner solar nebula (i.e., near the X-point in the X-wind model) and led to an $^{17,18}\text{O}$ enrichment in primitive solar system material (other than CAI's). Here we focus on CO dissociation in the cooler, surface layers of the nebula.

We utilize the disk model of Aikawa and Herbst (1999) for a flared disk with an isothermal vertical temperature profile. We also assume a dust grain population dominated by 3 micron particles and with a column abundance proportional to the column abundance of H_2 . The central star has a direct view of the surface of the disk, and FUV (far-UV) radiation can photodissociate CO in this region. To characterize mutual and self-shielding effects by H_2 and CO at CO photodissociation wavelengths, we employ the shielding functions of van Dishoeck and Black (1988) for the CO and C^{18}O isotopologues. We assume a protosolar FUV enhancement $\sim 10^4$ times the modern solar values at ~ 100 nm, consistent with the highest UV enhancements seen in T-Tauri stars.

In order to quantify total CO dissociation, vertical transport timescales must be considered. We assume an α -disk with $\alpha \sim 0.01$, which corresponds to turbulent velocities $\sim 0.01 - 0.1$ km s^{-1} and transport timescales $\sim 10^2$ to 10^4 years, depending on radial location in the disk. The source of the turbulence is presumably MHD instabilities (e.g., Balbus-Hawley). For a vertical transport timescale $\sim 10^3$ years, oxygen from dissociated CO has $\delta^{18}\text{O} \sim +1000$ ‰. Integrating all dissociated CO below this height in the disk yields $\sim 3 M_{\text{earth}}$ of oxygen at ~ 1000 ‰, which is enough to cause a 50 ‰ shift in all of the oxygen in a $0.02 M_{\text{solar}}$ solar nebula.

The excess $^{17,18}\text{O}$ liberated during CO photolysis is converted to H_2O via the reaction $\text{O} + \text{H} + \text{H}$ on grains, as suggested by Yurimoto and Kuramoto (2002). The timescales for H_2O formation will be presented.

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Experimental constraints on the mechanism of S isotope mass-independent fractionation during SO₂ dissociation

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The discovery of mass-independent fractionation (MIF) in Archean and Paleoproterozoic sedimentary sulfides and sulfates (Farquhar et al. 2000) offers the possibility of a quantitative proxy for atmospheric O₂ levels through time. Laboratory photolysis experiments on pure-SO₂ and mixtures of SO₂ and other gases show that photolysis at wavelengths < the dissociation wavelength for SO₂ (220 nm) can produce MIF similar (in sign) to that observed in ancient rocks. In the laboratory experiments, product elemental sulfur has $\Delta^{33}\text{S} > 0$, and product sulfate (presumably produced from SO₃ when an H₂O extraction is performed) has $\Delta^{33}\text{S} < 0$. This is consistent with the geochemical observation of $\Delta^{33}\text{S} > 0$ for pyrites and $\Delta^{33}\text{S} < 0$ for sulfates. However, the chemical mechanism producing MIF during photolysis of SO₂ is not understood, and is sure to be necessary for a complete understanding of sulfur isotope chemistry in the atmosphere.

Several processes can produce MIF: 1) symmetry-dependent non-equilibrium effects, such as those proposed for MIF during the O₃ association reaction (Gao and Marcus 2001); in the case of sulfur, the isoivalent S₃ association reaction ($\text{S} + \text{S}_2 \rightarrow \text{S}_3$) is an obvious candidate, but other such reactions are possible. 2) Because SO₂ undergoes at least partial predissociation at wavelengths < 220 nm, self-shielding during photolysis may also contribute to overall MIF in product sulfur and sulfate 3) Non-symmetry dependent MIF is also known to occur (e.g., $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$), and may play a role in sulfur dissociation chemistry. 4) Isotope substitution causes changes in absorption coefficients that yield measurable MIF and potentially large mass-dependent fractionations.

In the context of these mechanisms we will consider the available SO₂ photolysis data, and report results from recent spark discharge experiments on SO₂, in an attempt to elucidate the cause of MIF during SO₂ dissociation.

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Covarying molybdenum and organic carbon distributions in organic-rich sediments and sedimentary rocks

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The positive covariation between concentrations of Mo and organic C (OC) in black shales and the sediments of modern, oxygen-deficient marine basins is well known. While some of this correlation may be an artifact of dilution effects, such as in the modern Black Sea, Mo/Al ratios and Mo mass accumulation rates suggest true mechanistic linkages between the delivery/burial fluxes of the two components at many locations. This relationship is generally coherent over the Phanerozoic, but it is clear that no universal linear relationship exists for the covariation. In ancient sediments, shifts in the slope and scatter in the data can reflect selective loss of OC or Mo remobilization during burial and weathering. Our work in modern settings, however, reveals that primary differences can occur over comparatively short time intervals even within a single anoxic setting, such as the Cariaco Basin.

Ultimately, we agree with past workers that the availability of dissolved sulfide is central in Mo sequestration, and parallel OC concentrations may simply drive the hydrogen-sulfide-generating capacity of the system. A number of workers have suggested, however, that the requisite high levels of sulfide can occur in both pore waters and the water column—thus limiting the utility of Mo as an unambiguous indicator of euxinicity. Recognizing that persistent availability of dissolved sulfide is a function of bacterial production as well as loss through reaction, supplies of reactive Fe become an essential control in Mo enrichment. In addition to sulfide production, there is likely a more direct coupling between OC and Mo burial through reactions with the organic matter. If so, the type of organic matter may be critical—giving rise to regional variations in Mo (vs. OC) distributions in, for example, Carboniferous shales. Despite these and other complications and the potential for scatter in patterns of Mo versus OC burial, Mo-OC ratios show similarities among many temporally and spatially diverse organic-rich sediments, particularly for our Devonian and Carboniferous data. In general, the correlation is strongest where sulfide concentrations and/or organic matter type are most favorable to Mo accumulation.

Stable nitrogen isotopic chemistry of nitrate in GISP II ice

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We have analyzed twelve GISP II ice core samples for $\delta^{15}\text{N}$ of nitrate. Samples range from ~460 years to ~110,000 years BP in age. To our knowledge these samples represent the oldest precipitation samples ever analyzed for $\delta^{15}\text{N}$ in nitrate. The $\delta^{15}\text{N}$ values vary between 14.3 and 27.4‰. The mean isotopic value for Holocene age samples was lighter than the older samples (16.5 vs. 23.6‰). When compared to recent snow data from central Greenland, it is clear that the $\delta^{15}\text{N}$ of nitrate in the snow has decreased from 37,000 years BP through the Holocene into the anthropogenic period. These results may suggest that during glacial times a stronger stratospheric source of nitrate existed, or stratospheric photolysis rates were increased, or there was a change in the tropospheric nitrate source mix. However, as observed in previous ice core studies, the $\delta^{15}\text{N}$ values are inversely proportional to the snow accumulation rate. The results may indicate a preferential loss of the ^{14}N from the snowpack via post-depositional losses, especially at times of lower accumulation rates. There is no relationship between $\delta^{15}\text{N}$ and nitrate concentration. Further analysis should be undertaken in order to determine the exact cause of the $\delta^{15}\text{N}$ variation.

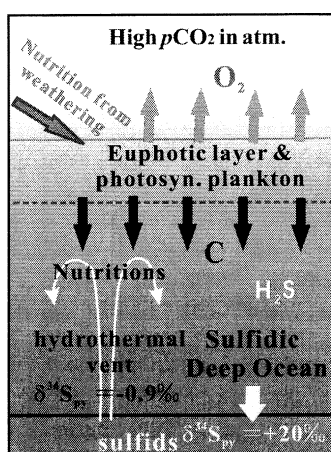
Sedimentary environments of lower Cambrian black shale in S. China

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The $\delta^{34}\text{S}_{\text{py}}$ of sedimentary pyrite from the Lower Cambrian black shale in NW Hunan of China have been determined. Except one sample with a $\delta^{34}\text{S}_{\text{py}}$ value of -0.97‰ from the Ni-Mo mineralized bed at the bottom Cambrian, total other 16 pyrite samples are all in the range from $+10\text{‰}$ to $+28\text{‰}$ with an mean value $+20\text{‰}$, obviously different from those in modern oceanic sediment (-20‰ to -10‰). If $\delta^{34}\text{S}$ of the seawater sulphate was identical with the world seawater at the early Cambrian, about $+34\text{‰}$, there was a small fractionation only 14‰ during sedimentation of the black shale. The high $\delta^{34}\text{S}_{\text{py}}$ value in the black shale should be caused by small fractionation between seawater sulphate and biogenic sedimentary pyrite in an anoxic sulfidic ocean in which the availability of sulphate is limited. Combining the data of $\delta^{13}\text{C}_{\text{org}}$, $\delta^{13}\text{C}_{\text{carb}}$ and trace elements of the black shale and related paleo-atmosphere and -ocean models, we propose a preliminary idea of paleoenvironments of the Lower Cambrian black shale in NW Hunan as follows.

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Hyperalkaline leachate-rock interaction and radionuclide transport in a fractured rock

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Introduction

The HPF project (hyperalkaline plume in fractured rock) at the Grimsel Test Site (Switzerland) comprises an underground field experiment including radionuclide transport in a shear zone, laboratory core infiltration experiments, reactive transport modelling, structural / mineralogical characterization, and studies on radionuclide stability. The aim is to quantify processes relevant for geologic disposal of nuclear waste in a cementitious environment. HPF is funded by ANDRA (F), JNC (J), NAGRA (CH), SKB (S), DoE (US).

Experimental results and modelling

Injection of K-Na-Ca-OH fluid (pH 13.4) into a natural shear zone in granodiorite induces marked changes to the flow field over two years, as recorded by hydraulic parameters and repeat dipole testing with radioactive tracers (Br, I, Na, Sr). The 3-D chemical evolution of the test zone is observed in 28 packed-off intervals in 10 boreholes. The overall transmissivity within the dipole is gradually decreasing while focusing of flow results in faster breakthrough times. Similar processes are observed in laboratory core infiltration experiments where formation of Ca-Si-hydrates is observed.

1-D reactive transport modelling of lab experiments is in good agreement with the measured chemical and hydraulic evolution. 2-D transport modelling (heterogeneous porous medium or discrete fractures) of tracer experiments in-situ is more difficult in an evolving natural system.

Discussion and conclusions

HPF offers challenges to experimental methods and reactive transport models, and created a unique hydraulic and geochemical data set of an evolving flow field controlled by rock-water interaction in a shear zone.

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Clathrate hydrate equilibria of methane and ethane

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Introduction

Equilibrium conditions of clathrate hydrate containing hydrocarbon gases are important to natural gas hydrate stability in marine sediment. Natural gas hydrate often contains methane with higher hydrocarbons such as ethane and propane. The ethane concentration up to 10 % was observed in natural gas hydrate containing thermogenic gases, for example, sampled in the Gulf of Mexico. On the other hand, it is known that clathrate hydrate equilibria of methane and ethane mixture are different from that of pure methane. In this work, clathrate hydrate equilibria of methane and ethane mixtures in pure water and NaCl solutions whose salinity is similar to seawater were experimentally determined. The experimental data were used to develop the statistical thermodynamic model of clathrate hydrate proposed by van del Waals and Platteeuw.

Results and Discussion

In this work, clathrate hydrate equilibria of methane and ethane mixtures with ethane compositions of 1%, 2%, 5%, 10% and 20% in pure water and 3wt% NaCl solution were experimentally determined. The results indicate that the addition of ethane to methane trapped in gas hydrate lattice shifts the hydrate equilibria to higher temperature and lower pressure and that the hydrate equilibrium decreases non-proportionally as ethane concentration in the mixture increases, which implies a hydrate structural change of Structure I to Structure II in ethane compositional range between 1% to 2%. The results also indicate that the equilibrium temperature differences of the hydrate in pure water and 3wt% NaCl solution are approximately 1 K over the compositional range investigated in this work.

Thermodynamic Modeling

The statistical thermodynamic model of clathrate hydrate proposed by van del Waals and Platteeuw was used to investigate the experimental results in this work. The intermolecular parameters between water and gas in the hydrate lattice, Kihara parameters, were optimized to fit the hydrate equilibrium conditions and implied structural change.

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Lithium isotope composition of arc volcanics from the Mt. Shasta region, N California

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Lithium isotopes can provide powerful constraints on the origin of the components in arc magmas. This is because of distinct isotopic signatures for altered oceanic crust and its eclogite residues [1]. Here we report lithium isotope ratios for high-Al olivine tholeiites (HAOT), basaltic andesites (BA), andesites and dacites from Mt. Shasta, Northern California. Lithium isotopes have been measured on Nu1700, a large geometry high-resolution mass spectrometer. Long-term reproducibility of international reference rock standards such as JB-2, AGV-2, or BHVO-2 is better than 0.5 ‰ (2 SE) [2].

The subset of Mt. Shasta region lavas does not show much evidence of fractional crystallization, crustal contamination or magma mixing [3]. Therefore, the observed range of $\delta^7\text{Li}$ values from 2.5 to 6.5 ‰ relative to L-SVEC most likely reflects distinct mantle components. The lowest $\delta^7\text{Li}$ values from 2.5 to 3.5 ‰ characterise near-anhydrous HAOT lavas erupted through the arc and back arc region towards the east of Mt. Shasta. HAOTs are thought to be generated by decompression melting of spinel lherzolite. However, lithium isotopes are inconsistent with models that assume melting of an old metasomatized peridotitic mantle source [4] because fluids in a subduction zone are thought to be ^7Li -enriched. $\delta^7\text{Li}$ values as low as -10‰ are reported for eclogites. Admixing $\leq 2\%$ of such eclogite to the mantle sources could explain low $\delta^7\text{Li}$ values of HAOTs. This is consistent with for example, the relatively radiogenic lead and the high concentrations of heavy rare earth elements (20 times chondritic) in HAOTs. $\delta^7\text{Li}$ values of BAs vary between 4.0 and 6.5 ‰. The lithium isotope composition of BAs is consistent with mixing Li into a former depleted mantle source by fluids derived either from low-T altered oceanic crust or sediments. Both HAOT and BA lavas form a linear array in $\delta^7\text{Li}$ -Y/Li space consistent with decoupling of Y and Li by fluid processes. Andesites and dacites show the same range of Li isotope ratios as BAs. Therefore, Li isotopes are consistent with generation of andesites and dacites from the same source as BAs.

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Geochemical evidence for environmental changes at Frasnian-Famennian boundary leading to the mass extinction

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Sedimentologic and geochemical evidence from Iran and south China indicate that environmental changes were concentrated in the F/F boundary interval. Typical feldspathic arkose with kaolinite and illite rich matrix suggest the intense humid weathering of feldspathic terrains. The ferruginous ooids with alternating micro lamina of hematite and dominance of kaolinite over illite (4:1 ratio) in clay matrix support intense chemical weathering under humid conditions. Significant positive excursion in ⁸⁷Sr/⁸⁶Sr ratio at the F/F boundary interval suggests an increased ⁸⁷Sr contribution from deep continental weathering. On the other hand, high Sr concentration of carbonates due probably to precipitation of aragonite indicates high alkalinity of sea water under the atmosphere of high CO₂ level. Collectively this evidence suggest the F/F boundary interval was a more intense warm and humid greenhouse condition superimposed in the general greenhouse condition in the Late Devonian. The synchronicity of the δ¹³C anomaly with the high concentration of redox sensitive elements such as U, As, and Th suggest a close causal relation between these two anomalies and the F/F boundary mass extinction.

Although the evidence for such variation is indirect at the Late Devonian, dissociation of gas hydrate in marine sediments is thought to be an important control of the global environmental changes across the F/F boundary. Widespread tectonic and geochemical evidence indicate that northern Iran was part of Turan Plate and the East European Platform, which experienced one of the largest volcanic episodes in the Phanerozoic. The Late Frasnian greenhouse was initially fed by volcanic CO₂. Increased climatic warming resulted in the dissociation of gas hydrate as suggested by the negative spike of δ¹³C at the base of F/F boundary interval. The methane released from the gas hydrate intensified greenhouse condition resulting in hyper greenhouse condition and poorly oxygenated seawater. The extremely warm and humid climate resulted in intense weathering on land. The subsequent dissociation of gas hydrate is supported by the sharp negative δ¹³C spike right at the F/F boundary resulted in global oceanic anoxia evidenced by widespread distribution black shale and anomalously high concentration of redox sensitive elements. Finally, subsequent anoxia resulted in the mass extinction of marine organisms.

Spectroscopic investigation of di- and trivalent ion interaction with sulfate in aqueous solutions

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Aluminum and iron are the most common metals in acid mine drainage (AMD) waters, and the most abundant counter ion in these waters is sulfate. Upon physical (e.g., temperature) or chemical (e.g., pH) changes, these waters may precipitate a variety of X-ray amorphous or crystalline solids. The goal of our study is to characterize the interaction of Al(III), Fe(II), and Fe(III) with sulfate in acidic aqueous solutions, before the solid precipitation takes place. Chromium (III) and nickel (II) were also included in the study for comparative purposes.

The solutions were prepared by dissolving appropriate amount of metal chlorides, Fe(NO₃)₃·9H₂O, and Na₂SO₄. The molality of SO₄ was always 15 mM, molality of the metals (Fe, Al, Cr, Ni) was 10, 20, and 50 mM. The solutions were acidified to the desired pH (1, 2, 3) by small amount of concentrated HCl. Using attenuated total reflectance Fourier transform infrared spectroscopy and Raman spectroscopy, we monitored changes in the spectral region of 1300-900 cm⁻¹, where the ν₃ and ν₁ bands of sulfate or bisulfate occur. X-ray spectroscopy at sulfur K-edge (~2480 eV) complemented the vibrational spectroscopy.

Among the metals probed, only Fe(III) shows stronger interaction with sulfate, as indicated by splitting, shift, or intensity variation of IR and Raman bands. The other metals, at all pH values, show only sulfate (1102 cm⁻¹) and bisulfate (1200 and 1050 cm⁻¹) bands in varying proportions, and occasionally a very weak ν₁ band at ~980 cm⁻¹.

In the Fe(III)-SO₄ solutions, we anticipate the presence of sulfate and bisulfate ions, inner-sphere iron-sulfate complex, and iron oligomers interacting with sulfate via hydrogen bonds. Interaction of Fe(III) with Cl⁻ or NO₃⁻ seems to have no effect on Fe(III)-SO₄ relations, as shown by no difference between IR spectra of Fe(III)-SO₄-Cl and Fe(III)-SO₄-NO₃ solutions. Hydrogen bonding between sulfate and iron oligomers is suggested by the shift of the bisulfate bands to ~1190 and ~1040 cm⁻¹. Approximately 10% proportion of the inner-sphere Fe(III)-SO₄ complex was determined by a linear combination of XANES spectra of copiapite, Na₂SO₄ and Fe(III)-SO₄ solutions.

We are planning to perform similar experiments on natural or more complex synthetic samples to address the questions of speciation of metals and sulfate in AMD waters.

Detection of bacterial population contributing to organoarsenic decomposition

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Arsenic, 20th most common in the earth's crust, is chemically similar to phosphorus, also in the same group. In aquatic environments, microorganisms take arsenate through their phosphate-concentrating mechanisms, bioalkylate to methylarsenic species and additionally produce more complex organoarsenic compounds. Decomposition of the organoarsenic compounds is thought to depend on bacterial activities. To understand the bacterial influence on the arsenic cycle in the environment, we observed the relationship between arsenic speciation and the bacterial population decomposing the organoarsenic compounds in lake water from April to December in 2002.

The cells number of bacteria involving organoarsenics decomposition were determined using the culture dilution method, MPN (Most Probable Number) method. The bacterial abundance was found to show a peak in July and November. After isolation of the dominant bacteria using agar plates, 43 isolates were classified to 13 groups by RFLP (restriction-fragment-length polymorphism) analysis of 16S rDNA. Especially, 32 isolates belonged to main 3 groups, of which one group continuously dominated and the other groups increased in summer and fall respectively. The concentrations of methyl and inorganic arsenic species were measured by atomic absorption spectrometry combined with the cold-trapping. Consequently, the methylarsenic was not detected, although the inorganic arsenic concentration remained over 5 nM during the experimental period. The organoarsenic was probably remineralized by the bacteria, which was suggested by culture experiment using the isolates.

In conclusion, this bacterial detection system is useful for monitoring the microbial activities that contribute to organoarsenic decomposition in aquatic environments.

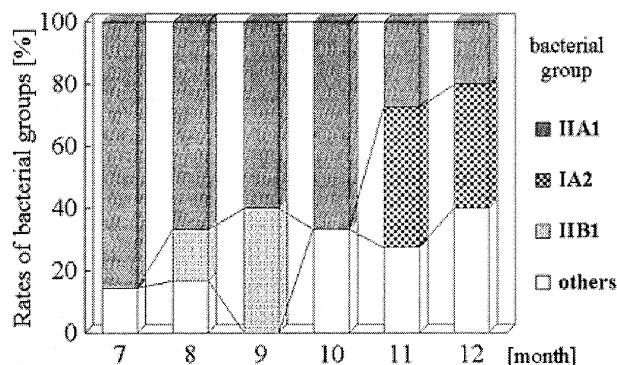


Figure 1. Seasonal changes in dominated bacterial groups

Simultaneous determination of Ru, Pd, Re, Os, Ir and Pt contents and $^{187}\text{Os}/^{188}\text{Os}$ ratios in geological samples using a new anion exchange chromatographic procedure

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We present a new group separation method for Ru, Pd, Os, Ir and Pt (PGEs) and Re in silicate samples employing less hazardous reagents and procedures. A silicate sample and isotope spikes were mixed, and digested with HF-HBr in a Teflon bomb at 518 K after *in situ* generated Br₂ treatment (M&N, 2001; Makishima et al., 2002). The sample was then dried and redissolved with 0.1 M HBr. After separation of fluoride residues by centrifugation, Re and PGEs were adsorbed on a 0.1 ml TEVA anion exchange resin, which has distribution coefficients (K_d s) of >1600 for Re and PGEs (Makishima et al., 2001). Re and PGEs were recovered into Re and Os fractions, by the combination of the eluents HCl, HBr and HI. Total recovery yields using this procedure were >90% for Ru, Pd, Os and Ir, and >70% for Re for ~1g of a peridotite sample. The Re fraction was further purified by 0.1 ml of cation exchange resin AG 50W-X8, and Re and PGE concentrations were determined by isotope dilution (ID) ICP-MS with a detection limit of <4 pg g⁻¹ except for Os. The Os fraction was purified by the micro-distillation technique, and its $^{187}\text{Os}/^{188}\text{Os}$ ratio was measured with negative thermal ionization mass spectrometry (N-TIMS). Total blanks were 2~3 pg for Ir and Os, 8 pg for Re, and 12~14 pg for Pd and Pt. This technique, therefore, enables us to determine simultaneously sub ng g⁻¹ levels of Ru, Pd, Re, Os, Ir and Pt and the Os isotope ratio of silicate samples. Furthermore, since only common distillable acids were used, Sr, Ce, Nd and Pb isotope ratios should be easily determined from the same sample. In addition, determination of calcophile elements such as sulfur, Ni and Cu in the same sample can be performed by simply adding S-Ni-Cu spikes together with the PGE spikes (M&N, 2001; Makishima et al. 2002)

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Iron corrosion product identification using micro-Raman spectroscopy

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Introduction

The corrosion of iron metal in aqueous systems results in the formation of a variety of iron bearing mineral phases. Many of these phases are highly redox sensitive, making their study by *in-vacuo* techniques difficult and potentially fraught with artefacts. Raman spectroscopy is a powerful technique that can be used to analyse environmental interfaces *in-situ* and we have used it to examine corrosion product formation.

Permeable reactive barriers containing zero-valent iron have been shown to be a viable technology for the remediation of contaminated groundwaters. Although contaminant-iron interactions have been fairly well studied, the changes that occur in the chemistry of the iron surface over time have not received as much attention. Here we describe *in-situ* Raman results obtained from column experiments conducted to examine the effects of various inorganic species and organic contaminants on iron interfacial composition.

Experimental

In-situ Raman spectroscopic measurements were obtained using a Renishaw 1000 Raman microscope system. This instrument consists of an Olympus microscope, a single spectrograph fitted with holographic notch filters, and a thermoelectric cooled charge coupled device (CCD) detector. An objective lens with 50x magnification provided spatial resolution of 2 μm^2 and a focal depth of 26 μm .

Results and Discussion

Upon contact with chlorinated hydrocarbon contaminants for a period of 308 days, the appearance of Raman bands at 425 and 504 cm^{-1} indicate the presence of the highly redox active species carbonate green rust and a band at 669 cm^{-1} that corresponds to magnetite. After 921 days, however, the bands for green rust have disappeared leaving Raman bands at 382 and 669 cm^{-1} , corresponding to the species goethite and magnetite.

In addition to temporal variations, interfacial corrosion product identity was found to be a function of solution composition and spatial distance along a laboratory column. These alterations indicate that the precipitates formed at the iron-water interface are both spatially and temporally heterogeneous. This result may partially explain observed variations in iron reactivity towards contaminant species.

This presentation will address the use of *in-situ* Raman spectroscopy for the analysis of the interfacial composition of a corroding surface. Additionally, this presentation will examine the use of *in-situ* Raman spectroscopy for the study of other surface-water interfacial systems where redox active species are present.

Paleozoic upper mantle of the southern frame of the Siberian platform: Structure and composition

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Abundant deep-seated xenoliths in lamprophyre dikes of the Western Sangilen provide information about composition, structure and evolution of the Paleozoic lithospheric mantle of the southern frame of the Siberian Platform. The mesostasis of camptonites and biotite and amphibole megacrysts have been analyzed with the Ar-Ar method and yielded a plateau age of 441.3 \pm 1.1 Ma (Izokh et al., 2002).

The camptonite dikes contain a lot of mineral megacrysts and phenocrysts as well as lherzolite, websterite and gabbro xenoliths. According to mineral composition the lherzolite nodules can be divided into primitive, depleted and enriched varieties. In turn, the depleted xenoliths vary from strongly to weakly depleted.

The HREE, Sr and Y contents in the clinopyroxenes from primitive spinel lherzolites are comparable with those in typical primitive mantle peridotites ($\text{Yb}_n = 10.2\text{-}13.8$), which have moderate HREE enrichment and minor depletion in LREE, Th, U and Nb. The La/Yb ratios in the clinopyroxenes vary insignificantly within a range of 0.44 to 0.97. All clinopyroxenes have small negative Zr-Hf-Ti anomalies. The HREE contents in clinopyroxenes from weakly depleted lherzolites are slightly lower than in those from primitive lherzolites ranging from 9.6 to 12.8. The REE distribution patterns are almost flat in the MREE and HREE regions and gradually slope down from Nd to La. La/Yb ratios in the clinopyroxenes are significantly lower ($\text{La/Yb} = 0.12\text{-}0.17$) than in the previous group. Likewise the clinopyroxenes from primitive lherzolites the clinopyroxenes of this group have small negative Zr-Hf-Ti anomalies.

The REE patterns in clinopyroxene from strongly depleted lherzolites are almost flat gradually sloping down from Yb to La. The HREE contents range from 4.6 to 11.7, whereas La/Yb ratios are < 1 (0.06-0.09). The negative Zr-Hf-Ti anomalies are less pronounced.

The chemical and mineralogical data obtained on the lherzolite nodules from Western Sangilen camptonite dikes allowed us to make several conclusions. The upper mantle domain beneath the Western Sangilen at a depth of the spinel facies consist of mainly 'dry' lherzolites varieties. The spinel lherzolites are dominated by depleted varieties (>50%). Mineral equilibria were attained at rather high temperatures of 1040–1190°C. This suggests a high geothermal gradient beneath the Western Sangilen during the capturing of xenoliths.

Andean subduction-related lithospheric mantle: Growth and isotopic evidence of chemical exchange in mantle and crustal reservoirs

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The Earth's sub-continental lithospheric mantle has a long-term evolution that records depletion and enrichment events and seems to have a close isotopic relationship to the continental crust formation. The heterogeneity of the mantle is well-constrained by chemical and isotopic data. Therefore, homogeneous compositions in MORB are related to large volume of melting unlikely other mantle-derived magmas as OIB and CFB. Sr and Nd isotopes have been thoroughly used to constrain mantle processes, while $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and T_{DM} (Sm-Nd) model ages comprise quite useful tools to characterize and date these processes, specially the lithospheric growth (continental crust plus depleted mantle). The subduction zones are special tectonic settings to modifications in the bulk, major, trace, REE and isotopic composition of the lithospheric mantle through processes like lithospheric growth (mantle depletion), asthenospheric upwelling, subducted-slab fluid percolations and interactions between host magma and mantle xenoliths. The Andean cordillera has a complex Phanerozoic history of terrane accretion and subduction processes. Two oceanic plates (Antarctic and Nasca) with different velocities, dipping angles and ages have been subducting beneath the continental South American Plate, which was made up by several and distinct crustal terrane ages. This active margin system presents four active volcanic zones (northern-NVZ, central-CVZ, southern-SVZ and austral-AVZ), separated by flat-slab or seismic ridge subduction segments, with samples of the lithospheric mantle hosted in alkaline basalts, except in the CVZ due to thickness and expressive crustal contamination. The well-marked 800-600 Ma peak in the T_{DM} model ages (based on literature and new data on mantle xenoliths and mantle-derived rocks) in all volcanic zones probably indicates the main period of crustal growth at the Andes. Sr and Nd isotopic ratios in spinel and/or garnet-bearing mantle xenoliths exhibit strong variations along the Andean cordillera ($^{87}\text{Sr}/^{86}\text{Sr}$ - NVZ: 0.7030-0.7053, SVZ: 0.7035-0.7045, AVZ: 0.7026-0.7052 and $^{143}\text{Nd}/^{144}\text{Nd}$ - NVZ: 0.5128-0.5135, SVZ: 0.5129-0.5134, AVZ: 0.5128-0.5131), apparently as a result of metasomatic process with chromatographic characteristics. In addition, interactions between mantle xenoliths and host lavas in crustal reservoirs tend to equalize chemical and isotopic ratios, masking the pristine signatures of the mantle.

Geology, age, and origin of Akilia supracrustal rocks, Greenland

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It has been proposed that supracrustal rocks on Akilia Island, Greenland, contain both the oldest marine sediments (Nutman et al., 1997), and the oldest evidence for active biological processes (Mojzsis et al., 1996). The interpretations rely on three strongly contested observations: the nature of crosscutting relations; the sedimentary origin of some lithologies; and interpretation of zircon ages (Myers and Crowley, 2000; Fedo and Whitehouse, 2002). Despite heated debate, the exposure has never been mapped at a scale appropriate to address the contested issues. New mapping (1:250) supports a >3.8 Ga sedimentary origin for components of the supracrustals.

Supracrustal lithologies comprise compositionally distinct, laterally continuous, mappable units of mafic amphibolite, ultramafic rocks, and two Fe-rich quartzites which contain C-isotope evidence for early life. The earliest structures are foliations parallel to lithologic contacts, with locally preserved upright fold hinges. Early foliations are isoclinally folded about a steep axial surface and refolded about a steep NS axial plane. Map relations reveal that Fe-rich quartzites are part of the stratigraphy, not later veins or intrusions. Contrasting whole-rock $\delta^{18}\text{O}$ values of quartzite (13‰) and adjacent metigneous units (8‰), and silica contrasts also preclude a metasomatic origin for the quartzite, while S-isotope data are consistent with a sedimentary origin (Mojzsis et al., 2003).

The age of Akilia supracrustals hinges on the nature of contacts with tonalitic gneisses. We identified two previously unrecognized crosscutting tonalites. U-Pb ion microprobe measurements of 21 zircons yielded ages of 3.6 to 3.83 Ga. 8 zircons are >3.8 Ga with tight age clustering at 3.83 ± 0.01 Ga. The oldest grains have higher Th/U and are interpreted to be the original magmatic population.

Thus our mapping, geochemistry and geochronology provide strong evidence for a sedimentary component to, and a >3.83 Ga age of, the Akilia supracrustals.

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Volatile cycling in subduction zones: Decreasing the deficit

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Tabulations of the volatile content of subducted materials suggest that more volatiles enter subduction zones than exit at mid-ocean ridges and arcs (Ito et al., 1983; Jambon, 1994; Bebout, 1995). This challenges models for the volcanic origin of the atmosphere and oceans, and supports mediation of Earth's volatile budget by supply of extraterrestrial volatiles (Chyba, 1990; Deming, 1999). However, surveys of volatile budgets do not account for the large potential for volatile transfer from arc magmas to the crust's metamorphic-fluid system. Hydrologic and mineral-solubility data suggest that the metamorphic-fluid system can accommodate sufficient subduction-derived volatiles to erase the "deficit."

Crustal permeability during metamorphism is sufficient to transport not only fluids produced within the crust, but also the entire deficit in subducted H₂O (~7x10¹⁴ g/yr; Ingebritsen and Manning, 2002), assuming delivery by degassing of magma ponded at the base of the crust. The volatiles may either diffusely transit the crust or be sequestered in minerals. Solubilities of volatile-bearing minerals in crustal fluids favor significant mineral storage because they are high and change little with pressure (*P*) between subduction depths and ~6 kbar, but decrease strongly with *P* decrease at lower *P*. For example, calcite solubility in H₂O increases by 10³ from 1-6 kbar at 600 °C, but by <10 from 6-20 kbar (Caciagli and Manning, 2003). Anhydrite (CaSO₄) shows similar behavior. NaCl increases total solubility, but does not change the large *P* dependence (Newton and Manning, 2002). The small changes in solubility with decreasing *P* at high *P* favor transport of CO₂ and S from depth to mid-crustal levels in rising fluids. However, decompression at shallower levels yields mineral precipitation. Allowing for mediation of the terrestrial volatile budget by the metamorphic-fluid system in arc crust implies no loss of ocean volume through time and minimal extraterrestrial volatile input.

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Calcareous foraminiferal test as a proxy of Cd in coastal marine environment

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Anthropogenic pressures exerted on estuaries and coastal areas necessitate to develop new methods for environmental assessments. In the perspective to develop a heavy metal proxy in coastal areas based on foraminiferal calcite, we present cadmium partition coefficients D_{Cd} : $([Cd]/[Ca])_{foram} = D_{Cd} \times ([Cd]/[Ca])_{SW}$, obtained from calcitic tests of the benthic foraminifer species *Ammonia beccarii* (Linné). Foraminifers were grown in sediment free cultures at 18°C and salinity of 28‰ with cadmium concentration at 4.3, 6.4 and 9.0 nmol l⁻¹. After reproduction or formation of new chambers, foraminifers or test fragments were collected, carefully decontaminated for cadmium and calcium analyses. Cadmium partition coefficients measured from culture experiments with controlled Cd concentration of 6.4 and 9.0 nmol l⁻¹ are 1.0±0.1 (n=8) and 1.2±0.2 (n=19) respectively. These values are comparable with the data published by Havach et al., (2001). They report an average D_{Cd} for *Ammonia beccarii* of 1.0 ± 0.5 with S= 35‰ and T= 10°C. Tachikawa and Elderfield (2002) estimated D_{Cd} relative to pore water for several species. Reported values are not significantly different from 1.0, with D_{Cd} were 0.9 ± 0.2 to 1.2 ± 0.2,

Reduced sample scatters showed an equilibrium of Cd/Ca ratios between sea water and calcite. D_{Cd} values ≈ 1.0 show that Cd/Ca ratios of sea water and foraminiferal calcite are also close to equality.

For culture with Cd concentration of 4.3 nmol l⁻¹, D_{Cd} is significantly different with 1.8 ± 0.2. The increase of D_{Cd} value is probably due to intracellular bio-accumulation.

The presence of 6% of deformed tests in culture with Cd concentration of 9.0 nmol l⁻¹ shows an impact of Cd on *Ammonia beccarii*. The comparison of $D_{Cd} = 1.5$ measured from abnormal foraminifers with others partition coefficients, does not seem to support the assumption of heavy metal enrichment of abnormal foraminifer test in polluted environments.

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Surface chemical heterogeneity of bacteriogenic iron oxides from a subterranean environment

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Bacteriogenic iron oxides play a significant role in the control of metal partitioning in pristine and contaminated environments.

This study quantifies the surface chemical heterogeneity of bacteriogenic iron oxides (BIOS) and its end-members (2-line ferrihydrite and intermixed intact and fragmented bacteria). On a dry weight basis, BIOS consisted of 64.5 ± 1.8 % ferrihydrite, and 34.5 ± 1.8 % organic matter. Enrichment of Al, Cu, Cr, Mn, Sr and Zn was shown in the solid versus the aqueous phase ($1.9 < \log_{10} K_d < 4.2$). Within the solid phase Al (69.5 %), Cu (78.7 %) and Zn (77.9 %) were associated with the bacteria, whereas Cr (59.8 %), Mn (99.8 %) and Sr (79.4 %) preferred ferrihydrite. Acid-base titration data from the BIOS and bacteria were fitted using FOCUS pK_a spectroscopy. The bacteria spectrum, with pK_a's of 4.18±0.37, 4.80±0.54, 6.98±0.45 and 9.75±0.68, was similar to discrete and continuous spectra for intact and fragmented bacteria. The BIOS spectrum recorded pK_a's of 4.27±0.51, 6.61±0.51, 7.89±1.10 and 9.65±0.66 and was deconvoluted to remove overlapping binding site contributions from the bacteria. The resulting residual iron oxide spectrum coincided with discrete MUSIC spectra for goethite and lepidocrocite with pK_a values of 4.10±0.43, 6.53±0.45, 7.81±0.76 and 9.51±0.68. Surface site density analysis showed that acidic sites (pK_a < 6) were contributed by the bacteria (37%), whereas neutral sites (6 < pK_a < 8), were characteristic of the iron oxide fraction (35%). Basic sites (8 < pK_a) were higher in the bacteria (57%), than in the BIOS (44%) or iron oxide fractions (47%). This analysis suggested a high degree of bacterial group masking and a similarity between the BIOS and goethite and lepidocrocite surface reactivity. An understanding of the BIOS surface chemical heterogeneity and inherent proton and metal binding capacity was obtained through the use of FOCUS pK_a spectroscopy.

The xenon record of the evolution of Mars

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SNC meteorites (Chassigny, ALH84001, Nakhilites Nakhla and NWA817 and shergottites NWA480, NWA856, NWA1068) contain xenon produced by the decay of ¹²⁹I (T_{1/2} = 16 Ma), the fission of the extinct radionuclide ²⁴⁴Pu (T_{1/2} = 82 Ma) and solar-like xenon presumably of Martian mantle origin.

The SNC source ratio (¹²⁹Xe/¹³⁶Xe)*, where ¹²⁹Xe* is decay product of extinct is systematically lower than expected from decay in a closed Martian mantle. The inferred low I/Pu ratio requires early degassing of volatile iodine with respect to refractory plutonium ≤ 50 Ma after start of solar system formation, which may represent the time of mantle-atmosphere differentiation through, e.g., large-scale magmatism.

Because the decay of ²⁴⁴Pu exceeds reasonable time interval for planetary formation and Pu is a refractory element, plutogenic xenon is a tracer of mantle degassing rather than of planetary formation ones. Both fissiogenic and trapped Xe isotopes are much more abundant than Xe isotopes in Earth's mantle-derived rocks, even after correction for degassing loss, outlining that the Martian mantle is less degassed and therefore less dynamic than the terrestrial mantle. Modelling of Pu-Xe suggests Martian mantle degassing could have continued for a few hundreds of Ma, but the major phases of magmatism ceased probably within the first Ga.

Petrological studies of nakhilite NWA817, which contains the largest amount of fissiogenic ¹³⁶Xe*, suggest fast cooling (Mikouchi and Miyamoto, 2001; Sautter et al., 2001), possibly due to magma crystallisation very close to the surface (less than 10 m, Mikouchi and Miyamoto, 2001). If this was the case, then volatile elements including xenon were degassed efficiently from the magma at the time of crystallisation. The quantitative occurrence of fissiogenic ¹³⁶Xe* in this meteorite suggests that magmatism having settled the composition of SNCs took place when ²⁴⁴Pu was still present, and that its chronometric age of 1.3 Ga is not related to a magmatic episode.

History of the Earth and life

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To provoke this session of the Conference, and to formulate the study of origin and evolution of life, I present a working hypothesis for the history of the Earth and life, covering the whole Earth from the central core through the mantle, ocean-atmosphere and biosphere, to the magnetosphere. The following seven biggest events are proposed. (1) Birth of the Earth by the collision-amalgamation of planetesimals and subsequent heavy extra-terrestrial bombardment at 4.55-4.56 Ga. (2) Initiation of plate tectonics, and resultant formation of continental crust and birth of life, presumably due to the formation of the ocean at 4.0Ga, as demonstrated by the surface records of the supra-crustal rocks in Isua, Greenland, and Acasta Gneiss, Canada. (3) Birth of a strong magnetosphere and initiation of photo-synthesis at 2.7Ga, as shown by the wide-spread occurrence of stromatolite and magnetic intensity variation with time, presumably by the mantle overturn. (4) Formation of first supercontinent at 1.9Ga. (5) Return of seawater into the mantle at 0.75Ga, deduced from the change of subduction zone geotherm with time. Return flow of seawater into the mantle decreased sea-level, and emerged a large landmass like today; the accumulation of terrigenous sediments prevented oxidation of organic matter. This increased the free oxygen in the atmosphere, which facilitated the proliferation of life. Released oxygen formed an ozone layer, which cut off ultraviolet rays, enabling life to move on land by 0.45 Ga. (6) Largest mass extinction at the P/T boundary (0.24-0.25 Ga). This may be related to the explosive volcanism by the breakup of Pangaea. The screened sunlight prevented the photo-synthesis and caused the super-anoxic events. (7) Birth of human-being and the initiation of science. At about 6 Ma, the African plume was activated extensively to change the climate of East Africa, enabling the appearance of ancestral human-beings.

The impact of sediment resuspension on mercury and methylmercury fate, transport and bioaccumulation in shallow estuaries

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Sediments could be a significant source to the overlying water column during resuspension events. The effect of resuspension on the cycling of Hg and methylmercury (MeHg) between the water column and the sediment during tidal resuspension was simulated using a mesocosms. A series of month-long experiments were with different levels of resuspension and with and without clams. While TSS was higher during resuspension, on a mass basis, MeHg concentrations decreased with increased TSS. The results suggest that Hg appeared strongly bound with little release during the resuspension events, while MeHg was actively accumulated in phytoplankton, and thus biota (zooplankton and clams) during the experiments. Overall, dissolved Hg and MeHg did not change in concert with changes in particulate load, suggesting that the dynamics between dissolved and particulate cannot be explained by an equilibrium partitioning. Finally, resuspension, by initially aerating the surface sediment and decreasing sediment acid-volatile sulfide (AVS) resulted in an initial increase in methylation rate but over time, as sediment AVS continued to decrease, methylation rate decreased. These results are consistent with the complex interaction between the amount of sulfide in sediments and its inhibitory role on Hg methylation. The biogeochemical dynamics as well as the bioaccumulation, fate and transport of Hg and MeHg during resuspension will be discussed.

Three discontinuous stages in progress of lanthanides (REE) geochemistry and potential further evolution

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1. Chondrite-normalized REE pattern gives us unique valuable information for various aspects. The present author has paid basic concern to logarithmic linearity of chondrite-normalized REE pattern determined with high precisions (1~2%) using the stable isotope dilution mass spectrometry. This category is related with development of authentic magmatism. 2. However, it was found that the foregoing logarithmic linearity does not hold for products related with the water-rock reaction. This is lanthanide tetrad effect. Tetrad effect is divided to W-type and M-type. The former is observed for aqueous (high-polarity) phase, whereas the latter for low-polarity one like silicate residue. This effect occurs in presence of both phases. Thus lanthanides are divided to 1st, 2nd, 3rd and 4th subgroups. It is important that this effect remains after removal of water.

Author proposed two ways to indicate the degree of tetrad effect, assuming the parabolic function for each of subgroups, based chondrite-normalized values. (There is no difference between them in mathematical meaning.)

Pragmatic quantitative treatment of tetrad effect:

Pm is extinct and Eu can be anomalous. Both belong to the 2nd subgroup. Thus it is assumed that the values of secondary coefficient for first and second tetrads are the same, and two parabolas intersect between Nd and Pm. Cusp point between 2nd and 3rd tetrads occurs at Gd, while that for 3rd and 4th ones is assumed to arise in the middle between Ho and Er. The degree of tetrad effect for each of 4 groups is calculated, with or without matrix of mathematics.

Two geochemical applications of lanthanide tetrad effect:

One application is for oceanography. Depth profile of secondary coefficients for 1st and 2nd subgroups is significant to investigate the currents of seawater. Another important meaning is for genesis of hydrothermal solution and deposits from it.

3. Implications for genesis of limestone. Attention was paid to limestone rich in fusulina or corals. Fusulina shows "dislocation" factor of 1.5 in diagram showing the abundance ratio between the samples of genetically close genesis (tropical coral reef). There is a systematic difference in features between coral and fusulina.

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Arsenic behavior in the modern sediments and the controlling factors of its release into groundwater

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Introduction

Highly arsenic contaminated groundwater causing serious toxicity widely occur in the modern sediments of the world without any anthropogenic source of arsenic. We analyzed the total and four different chemical forms of arsenic compounds (acid-soluble, oxidized, organic and sulfide compounds) with major chemical compositions of modern sediments to estimate the release process into groundwater. The sample sediments were taken from the Holocene sedimentary formation in Osaka Plain, where arsenic contaminated groundwater was occasionally observed, and from a mangrove forest in the Iriomote Island, far from highly populated areas.

Results and Discussion

Total arsenic contents of organic-rich mangrove sediments gradually increases with depth (up to 15ppm) from the surface to 2.7m depth, the bottom of the permeable layer. Below that depth, desorbed arsenic from the iron oxyhydroxide is fixed into the newly formed pyrite under reducing condition caused by microbiological activity.

Arsenic content is higher in a 22 m thick marine clay layer (7~20ppm) than in the freshwater sediments layers (<3ppm) from the Osaka Plain. Inside of the marine clay layer, sulfur decreases in each 3 m thick portions toward the above and below freshwater sediment layers. The arsenic also decreases in the almost same portions, however, it is concentrated with iron on the inflection depths of sulfur contents.

The observation of this study suggests that arsenic tends to stay or concentrate in the sediment when iron hydroxide or pyrite is stable under a given condition. Thus, the considerable arsenic would be released into the coexisting groundwater when the stability of and/or transition rates between those arsenic fixed phases become unstable.

Thermal stability of dissolved humic acid as revealed by *in-situ* UV spectroscopy

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Humic substances (HS) are considered to be carriers of environmental pollutants such as heavy metals and some organics. However, little is known on their long-term stability in the geochemical environments.

Of many influential factors on the stability of HS, we focused on the thermal stability of aqueous humic acid (HA). In order to determine precise kinetic parameters, we developed an *in-situ* heating system combined with UV spectrometer. The time-course of the reaction was monitored at 254 nm, which is considered to represent HA concentration, every 2.5 minutes at 80 to 160 C.

The decrease in absorbance at 254 nm for reagent HAS (Wako, Aldrich) was successfully fitted by the combination of 2 first order reactions and the activation energies were about 26 and 23 kJ/mol, respectively. These *in-situ* transformation rates are compared with those determined in batch experiments. The *in-situ* method was able to determine initial processes which could not be detected by the batch method. Moreover, the presence of more than one single reaction was discovered in our *in-situ* study.

These kinetic parameters for standard HA were also compared with some natural HA from groundwaters. Despite the differences in origin and character of HA, the transformation rates and activation energies were similar among them. This result suggests some common thermal transformation behaviors of certain functional groups. Therefore, similar experiments will be presented on model compounds such as carboxylic acids, cellulose and lignin and transformation mechanisms will be discussed.

Properties of aqueous fluids up to 200°C by ATR-IR spectroscopy

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In order to study physicochemical properties of hydrothermal and metamorphic fluids, attenuated total reflection (ATR) infrared spectroscopy of aqueous solutions were conducted from room temperature up to 200 °C. NaCl and Na₂CO₃ had opposing effects on water structure based on our previous model of 4 water molecular cluster components in IR OH stretching bands (Masuda et al., 2003). The competing effects of NaCl (longer hydrogen bond "loose" structure) and Na₂CO₃ (shorter hydrogen bond "tight" structure) could be represented quantitatively by the relative percentages of IR band components for the mixed solutions of 1M NaCl and 1M Na₂CO₃. The contrasted effect was also evaluated for the heated synthetic solutions up to 200 °C and compared with our data by *in-situ* IR microspectroscopy on heated natural fluid inclusions containing NaCl and CO₂ (Famin et al., 2003). The difference in "loose" vs. "tight" natures of these fluids became more pronounced at higher temperatures, suggesting their distinct wetting characteristics and permeability.

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A long term variability of a bathyal *Calyptogena* community in Sagami Bay off Japan based on pore water geochemistry

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Pore water samples were collected at the same patch in the largest *Calyptogena* community at the Hatsushima Site, Sagami Bay, central Japan (34-59.9N, 139-13.6E, 1146 m deep) with an *in situ* pore water squeezer (ISPS-S) by using a submersible, SHINKAI 2000, nearly once a year for 11 years from 1986 to 1996. ISPS-S squeezed at 6 depths from 0 to 45 cm below the sediment-water interface just below the living *Calyptogena* patch. Pore water samples were subjected to the analyses of major cations and anions, nutrients, H₂S, DIC and its $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$, methane and its $\delta^{13}\text{C}$, and $\delta^{34}\text{S}$ of sulfate and H₂S after appropriate chemical treatments. $\delta^{34}\text{S}$ values of gills of *Calyptogena soyoae* sampled at each dive were also measured.

In pore water samples collected during Dive 720 (26 Nov 1993), sulfate decreased remarkably below 9 cm depth and showed quite low minimum values between ca. 20 and 40 cm depth. Inversely hydrogen sulfide increased remarkably to a maximum value of 13.8 mM at 36 cm depth, and methane increased remarkably from 529 nmol/kg at 0 cm to 125,200 nmol/kg at 36 cm depth and decreased to 6850 nmol/kg at 45 cm depth. These methane concentrations were two to four orders of higher than those in usual deep and bottom waters of Sagami Bay (4-5 nmol/kg). The chemical stoichiometry and quite low $\delta^{13}\text{C}$ value of DIC such as -42 ‰ proved that microbial sulfate reduction using methane as reductant (Masuzawa et al., 1992) took place quite actively at ca. 20-40 cm depth just beneath the living giant clams.

Apparent isotope fractionation factor of sulfur (α') through microbial sulfate reduction in the pore water was estimated from the relationship between sulfate concentration and sulfur isotope ratio of pore water sulfate. The sulfur isotope ratio in gills of *Calyptogena* changed reversely to that of the estimated α' value. These results indicate that the activity of the patch of *Calyptogena* at the Hatsushima Site increased from 1986 to 1993, showed the highest activity in 1993 and after that it decreased.

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Impact of Asian emissions on the western North Pacific regions observed at JMA monitoring stations

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Introduction

East Asia is one of the major source regions for trace gases in the troposphere. The anthropogenic emissions in Asia will become more significant for global atmospheric chemistry due to a rapid economic growth in the Asian countries. In this study, we report an impact of Asian emissions on the western Pacific regions using trace gas data from three Japanese monitoring stations of the Japan Meteorological Agency (JMA).

Data analysis

Trace gases such as carbon monoxide (CO) as well as CH₄, CO₂ and O₃ had been observed using continuous measuring instrumentations at the three JMA stations of Ryori (39°02'N, 141°50'E) from 1991, Minamitorishima (24°18'N, 153°58'E) from 1994, and Yonagunijima (24°28'N, 123°01'E) from 1998. We analyzed these time-series data sets of CO to focus on pollution events due to an outflow from Asian emissions. Such events were identified on the basis of increased CO peaks compared with a background level in each station. The same data analysis was used for other trace gases to examine a chemical composition of air masses from the continent.

Results and discussions

Minamitorishima station is located in a remote island far from the Asia continent. The CO data in this station clearly revealed increased peaks, suggesting an impact of Asian outflow. It was confirmed by backward trajectory analyses that the CO enhancements were caused by a long-range transport from the continent driven by a synoptic-scale weather perturbation. These pollution events at Minamitorishima were found during winter and early spring, but there was no CO increase in maritime air masses during summer. A similar seasonality of the pollution events was also found at Yonagunijima and Ryori stations. In the both stations near the Asian continent, stronger pollution events appeared more frequently.

The CO elevation during the pollution event well coincided with the increased CH₄ peaks. This positive correlation clearly showed a seasonal change of the enrichment ratio of CH₄ to CO. These results suggested that chemical compositions of continental air masses were influenced by not only anthropogenic emissions but also biogenic products. We will discuss in detail on the air mass origin during the pollution events using multi-species correlations combined with meteorological analyses.

Inconsistent model uptake of anthropogenic tracers in the Southern Ocean

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Here we examine a suite of ocean biogeochemistry model experiments in their ability to ventilate the Southern Ocean. The experiments differ in their vertical and horizontal mixing schemes and hence in their large-scale overturning circulation. We gauge the performance of the experiments by comparing their simulations of natural $\Delta^{14}\text{C}$, anthropogenic CO_2 , bomb $\Delta^{14}\text{C}$, and CFC-11 with appropriate "observations". We find that no model is able to simultaneously ventilate the Southern Ocean on centennial time scale as indicated by natural $\Delta^{14}\text{C}$ and on decadal time scale as suggested by the other anthropogenic tracers. While some model experiments are able to simulate natural $\Delta^{14}\text{C}$ and CFC reasonably well, their uptake of anthropogenic CO_2 and particularly bomb ^{14}C is insufficient. In contrast, those simulations that take up about the right amount of anthropogenic CO_2 and bomb ^{14}C in the Southern Ocean have too old deep waters. This discrepancy is also evident in other coarse-resolution models that participated in the Ocean Carbon-Cycle Model Intercomparison Project. A partial resolution of this discrepant finding may have its source in the uncertainty of the "observed" anthropogenic CO_2 and bomb ^{14}C . The concentrations of these two tracers, unlike natural $\Delta^{14}\text{C}$ and CFCs, are not measured directly but estimated from the measured concentrations of nutrients and dissolved gases using rather complicated methods. It is also possible that our finding may be partially caused by too slow an air-sea gas exchange speed in our model. A faster gas exchange would likely enhance the transfer of anthropogenic CO_2 and bomb ^{14}C from the atmosphere to the ocean proportionally more than CFC-11, because the former two tracers have longer equilibration time scales than CFCs. There would be relatively little impact on CFC-11, which is already much nearer to equilibrium anyway. A faster gas exchange should therefore bring simulated anthropogenic CO_2 and bomb ^{14}C into closer agreement with CFC-11, whose uptake in the Southern Ocean was better simulated.

Chemical characterization of marine aerosol over the western North Pacific Ocean

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Introduction

Long-range transport of anthropogenic and mineral aerosols from the Asian continent to the North Pacific may have significant impacts on global radiation balance, atmospheric chemistry, and oceanic biogeochemistry. The author has conducted the observations of marine aerosol chemistry over the western North Pacific in the last decade^{1,2,3,4}, in order to understand seasonal and geographical distributions of chemical species in marine aerosols over the oceanic region as well as their chemical and physical properties. Here the author focus on the recent observations of aerosol chemistry in Japanese remote islands, and discuss chemical properties and long-range transport of ionic and carbonaceous species over the western North Pacific Ocean.

Long-range transport and chemical properties

Simultaneous observations of aerosols chemistry have been carried out at four remote islands (Rishiri, Sado, Hachijo, and Chichi-jima) since March 2001. Geographical distributions and temporal variations of land-derived chemical species in aerosols over the oceanic regions have been obtained in this study³. The outflows of continental air masses to the western North Pacific are accelerated by certain synoptic-scale weather systems. Post frontal outflows of continental air masses have been frequently found, especially during spring periods, which cause high loading of anthropogenic aerosols over the oceanic regions^{2,3}.

Particulate nss-sulfate mainly exists in fine particles as ammonium salt in marine atmosphere, whereas nitrate is associated with dust particles in East Asian Pacific rim region or with sea-salt particles in the remote ocean⁴. Nitrate and nss-calcium, especially nss-calcium, are effectively removed from the atmosphere during their long-range transport. Particulate organic carbon shows relatively higher concentrations over the remote ocean¹ probably due to oceanic sources, although elemental carbon is derived only from combustion sources.

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Biogeochemical implications of carbon isotopic compositions of sedimentary biomarkers from a meromictic lake

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We determined carbon isotopic compositions of lipid compounds in surface sediments collected from a meromictic lake, Lake Kaiike (12 m in maximum depth, area: 0.16 km²), Japan. As reported in our companion papers (Oguri et al. and Nakajima et al.), Lake Kaiike is characterized by an existence of an O₂/H₂S boundary around water depth of 4.5 m throughout the year. The sediments were collected at four sites from both aerobic and anaerobic environments. $\delta^{13}\text{C}$ values of phytol originated from side chains of chlorophyll *a* and bacteriochlorophyll *a* ranged from -29.1 to -23.8 ‰ with being relatively depleted in ¹³C in anaerobic sites (4.5 and 10.3 m) (Figure). The difference of $\delta^{13}\text{C}$ values between aerobic and anaerobic sites may be explained by source organisms. In aerobic site phytol could mainly be derived from cyanobacteria and diatoms, whereas in anaerobic site it is from purple sulfur bacteria Chromatiaceae forming a "bacterial plate" at the redox boundary. Farnesol covalently bonding with bacteriochlorophylls *e* is mainly produced by brown-colored green sulfur bacteria Chlorobiaceae in the lake. Generally, organic matter produced by Chlorobiaceae is relatively enriched in ¹³C due to the carbon fixation through reversed TCA cycle. However, $\delta^{13}\text{C}$ values of farnesol are -30±1 ‰ with being depleted in ¹³C relative to other compounds. It may be explained by a repressed growth rate of Chlorobiaceae or utilization of remineralized inorganic carbon. $\delta^{13}\text{C}$ values of PMI produced by archaea are almost constant in these sediments, suggesting that a methane cycle is not important in spite of the anaerobic environment in the lake. We are currently underway to determine $\delta^{13}\text{C}$ of DIC and suspended particulate matter to further discuss biogeochemical cycles in the lake.

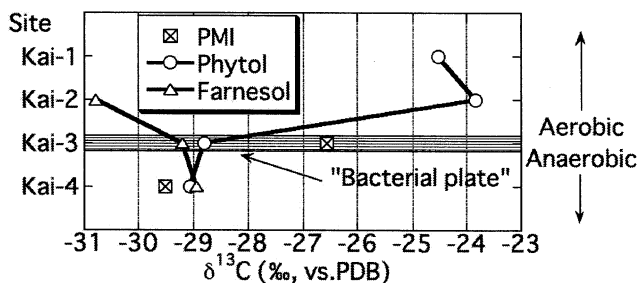


Figure. Carbon isotopic compositions of biomarkers in Lake Kai-ike

Kinetic study on trace element partitioning using *in situ* observation

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Introduction

Previous experimental studies on kinetic effects on element partitioning between minerals and melts have revealed the relationship between cooling histories and apparent partition coefficients [e.g., 1]. However, they have not been directly related to essential parameters of crystal growth, such as growth rate. For this reason, we applied *in situ* observation method [2] to kinetic study on element partitioning between forsterite and a melt.

Experiments

Forsterite crystals were grown from a melt (F_{0.20}-Di₄₀-An₄₀) doped with REE and Li in a heating stage under a transmission optical microscope. Cooling was induced by a few steps of isothermal cooling to investigate the dependence of growth rate on degree of supercooling. Growth rate was directly measured using *in situ* observation technique, and concentrations of elements of quenched run charges were determined using electron and ion microprobe analyzers. The partition coefficients (*D*) were calculated from the measured concentrations for crystals divided by those for the melt.

Results

Growth rate The crystal-melt interface moved almost linearly with time in each isothermal cooling step. The growth rate is linearly correlated with the degree of supercooling.

Trace element distribution in forsterite crystals Two types of zoning for Al and Li were recognized in the crystals; 1) sector zoning, corresponding to crystal orientations and 2) concentric zoning, corresponding to the cooling step. The outerpart, grown at the larger growth rate, is more enriched in Al and depleted in Li. The concentrations of Al and Li show a negative correlation with each other in both types of zoning.

Growth rate dependence of apparent *D* values The obtained *D* values for Al and Li are positively and negatively correlated with growth rates, respectively. This observation cannot be explained by any previous models in which one kind of substitution is simply assumed. The results require a model involving a coupling of at least two kinds of substitutions, such as AlAl-MgSi and MgMg-AlLi.

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Methane flux in accretionary complex: An example from the forearc basin and outer ridge of the Eastern Nankai trough

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Background and Objectives

Gas hydrate BSRs are widely distributed in shelf and slope sediments of the Nankai Trough off southwest Japan. Exploratory drilling in the eastern Nankai Trough in 1999-2000 has confirmed 20 to 30 m thick gas hydrate zones with 60 to 80 % gas hydrate saturation at about 250-270 meters below seafloor. Development of highly saturated zones in low TOC (<1%) sediments requires external supply of CH₄ into the zone of gas hydrate stability (<270mbsf). Assessing the amount and mode of transport of deep-seated CH₄ and CH₄-bearing fluids is critically important to understand the growth of gas hydrates, the resource potential, and environmental impact. Dai-ni-Hakurei 02DM cruise (Dec.02-Jan.03) recovered 30 piston and gravity cores from the eastern Nankai Trough. We analysed sulfate concentration of ~300 pore water samples to determined the depth of SMI (sulfate-methane interface) as a proxy of methane flux in marine sediments.

Results and Significance

SMI of the outer ridge sites, where major thrusts, earthquake faults, and methane seeps and seep-related phenomena have been observed, are unexpectedly deep, >10m, except for an active mud volcano site (~2m). Furthermore, the sulfate concentration is nearly constant for the top 1-2 meters, probably because of strong bioturbation. The observed "discrepancy" - low CH₄ flux at active seep sites, may indicate that venting and expulsion of methane are not steady state phenomena, but occur only intermittently and perhaps in very limited area. Active venting and release of methane may be related with such events as earthquakes.

Contrary to the outer ridge sites, the depths of SMI in the forearc basin sites are surprisingly shallow. Three sites in the Enshu basin range between 3.5 and 7.0 m, and two sites off Tokai are ~4.0 m. In addition to these five sites, two sites on the slope of the outer ridge, have also shallow SMI (1.5 to 3.5m). Enshu basin is characterized by three major E-W trending dextral faults and related high angle normal faults, which are traceable as deep as ~1 km on seismograms. A series of high angle faults are also observed in the top few hundred meters sediment in off Tokai area. Faults and fracture systems are thought to play an important role to transport CH₄ and CH₄-bearing fluids to gas hydrate stability zone and to the seafloor.

Observed depth variation in SMI would also provide critical constraints on the mode and amount of tectonically induced expulsion of fluids from the accretionary complex.

New noble gas data on basaltic glasses from eastern and western flanks of Loihi Seamount

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Characterization of noble gas isotopic signatures in deep and less-degassed mantle domain has a crucial importance in deciphering geochemical evolution of the Earth including its atmosphere. Loihi is undoubtedly one of the best places to study noble gas isotopes of such a primitive reservoir, but previous studies are largely focused on samples collected from currently most active rift zones. However, in order to fully understand evolutionary history of Loihi and to obtain isotope signature of possibly earlier stage of its activity, we need to target relatively older samples from Loihi. Thus, during a 2002 research cruise to Hawaii by JAMSTEC (Japan Marine Science and Technology Center), we have collected samples from the interior of the volcano which is exposed now in steep eastern and western flanks of Loihi due to mass wasting.

So far five samples of fresh glassy rim of pillow basalts have been subjected for noble gas isotope analyses by crushing extraction. These samples have systematically high ³He/⁴He ratios compared with population of ³He/⁴He ratios so far reported for Hawaiian basalts, indicating that the present samples represent some earlier stage of Loihi activity with lesser contributions from helium in the upper mantle reservoir. The sample with the highest ³He/⁴He ratio of 35Ra also yielded non-atmospheric xenon isotope ratios; about 13% excesses in ¹²⁹Xe and ¹³⁶Xe are the largest among those so far reported for plume-related samples (Poreda and Farley, 1992; Harrison et al., 1999; Trieloff et al., 2000) and comparable to the largest excesses found in MORBs (Staudacher and Allègre, 1982). This is probably the first unambiguous occurrence of non-atmospheric xenon from the glass rim of pillow lava from Loihi with very primitive helium signature. This finding indicates that excess radiogenic xenon is also present in the plume mantle region as predicted by steady state model for mantle noble gases.

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Isolation of presolar grains using fusion technique from Murchison CM2 meteorite

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Introduction

Primitive meteorites contain presolar grains. Conventionally, the method developed by group of Chicago University is widely employed for isolation of presolar grains [1]. This method basically treats an acid dissolution to dissolve silicates. Here we developed an isolation method of presolar grains using NaOH fusion from Murchison CM2 meteorite. Since the procedure is different from that of Chicago group, relative abundance of presolar grain species can be evaluated independently and it might be expected to identify new types of presolar grains.

Methods

0.1g of matrix materials were scraped carefully using a stainless steel dental pick. Matrix materials and 2g of NaOH pellets were well mixed in nickel crucible and fused at 500°C for 8 minutes in a muffled furnace. The fused sample was dissolved by 50 ml of deionized water. The precipitation of iron hydroxide was dissolved by adding of 30 ml of 6 mol/l hydrochloric acid. The pH of the solution was about 3. Then grains with the size larger than 0.5 µm were sunk by centrifugation. After 14 cycles of this dilution procedure, 5 ml of neutralized solution that contains the residual grains was prepared. 5 µl portions of solution were dried on the 7 mm x 7 mm sized pure copper substrate.

Morphology and chemical composition of the residual grains were analyzed by SEM-EDS. Isotopic compositions were analyzed by isotope-microscope system [2].

Results and discussion

We measured 300 residual grains. the residue consist of spinel, number percent: ~45%, grain size: 1-20 µm, chromite, ~20%, 1-20 µm, magnetite, ~10%, 1-20 µm, Forsterite, ~5% were, 1-5 µm, and unidentified phases (~15%). Other 5% of grains consist of hibonite (5-15µm) and graphite (~4µm).

Among graphite one grain showed about +4000‰ ¹³C excess relative to the terrestrial value. The grain was 4µm across with euhedral and hexagonal shape. This grain resembles to the presolar graphite grain previously reported by Zinner et al. (1995) [3].

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Hydrothermal environments in the primitive ocean and its implications on prebiotic evolution

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Hydrothermal environments in the primitive ocean could have been multi-functional in facilitating various phases of prebiotic evolution.

Reduction of carbon dioxide could be possible deep below the sea floor near heated magmas where both water and carbon dioxide coexist as contacting heated metal oxides at temperature about 1000 degrees C. Main products of the reduction include formic and acetic acids.

Synthesis of amino acids could be expected from nitrogen and other ingredient molecules in the supercritical conditions of water deep inside the hydrothermal vents at temperature above 400 degrees C.

Oligomerization of amino acids and its elongation are made feasible when the reactants recycle between hot and cold regions of water repeatedly. Since amino acids and their oligomers are vulnerable to hydrolysis at high temperatures, both the reactants and the half-made products cannot remain stable if they stay in the hot water for long. The best temperature of the hot water in which the reactants stay only for a limited interval for each visit is about 200 degrees C.

When saturated fatty acids such as decanoic acid are made from formic, acetic or oxalic acids via the Fischer-Tropsch-type reaction, they can be aggregated into vesicles in water. Decanoic acid vesicles can encapsulate amino acid molecules if they are also present in the reaction solution. Amino acid molecules encapsulated into the vesicles can enhance the extent of oligomerization, compared to the cases otherwise, when they are allowed to visit both the hot and cold regions of water repeatedly.

Oligomerization of nucleotide molecules such as AMP could also be possible in the hydrothermal circulation of the reaction solution between hot and cold regions. Oligomers of nucleotide molecule are, however, more vulnerable to hydrolysis compared to oligopeptides. The highest yields of oligomers of AMP are obtained when the temperature of the hot regions is about 100-110 degrees C.

A likelihood of co-evolution between oligopeptides and oligonucleotides could also be envisioned in water environments. To facilitate such a co-evolution, lipid vesicles encapsulating the both types of oligomer should further be required. The lipid molecules as ingredients for making lipid vesicles in the reaction solution utilizing the temperature difference between hot and cold should be those whose melting point is lower compared to that of saturated fatty acids (e.g. decanoic acid). Lipid molecules more suitable for lower temperatures are unsaturated fatty acids such as oleic acid or phospholipids.

Sr and Nd isotopic signature of late Cenozoic alkali basalts from Kibi-Sera and northern Hyogo areas in Chugoku district, Japan

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Trace element and Sr and Nd isotopic compositions were determined for Cenozoic alkali basalts from Kibi-Sera plateaus (KSP) and northern Hyogo Prefecture (NHP). The variations in Sr and Nd isotopic compositions for NHP basalts ($\epsilon_{Sr} = -9.6$ to $+42.3$ and $\epsilon_{Nd} = -4.5$ to $+3.6$) are remarkably large compared to those for KSP basalts ($\epsilon_{Sr} = -7.0$ to $+9.9$ and $\epsilon_{Nd} = +1.0$ to $+2.2$). It is noted that ϵ_{Nd} and ϵ_{Sr} values for NHP basalts are strongly correlated to each other, forming a linear array on an ϵ_{Nd} - ϵ_{Sr} diagram. We consider that the large variations in Sr and Nd isotopic ratios probably indicate isotopic heterogeneity in the mantle source rather than a binary mixing trend. Figure 1 gives a relationship between ϵ_{Nd} and longitude of sample location. Data for Cenozoic basalts from other areas in the Chugoku district (Fujibayashi et al., 1988, 1989; Morris & Kagami, 1989; Morris & Itaya, 1997) and Mesozoic rhyolites in the district (Terakado & Nakamura, 1984), which could be of lower crust origin, are also plotted. The results shown in the diagram suggest an intimate relation between lithospheric mantle and overlying lower crust materials in the district, that is, ϵ_{Nd} values for both of them decrease eastward. The large fluctuation of ϵ_{Nd} values for NHP basalts may suggest that the lithospheric mantle in the district is layered in terms of isotopic compositions.

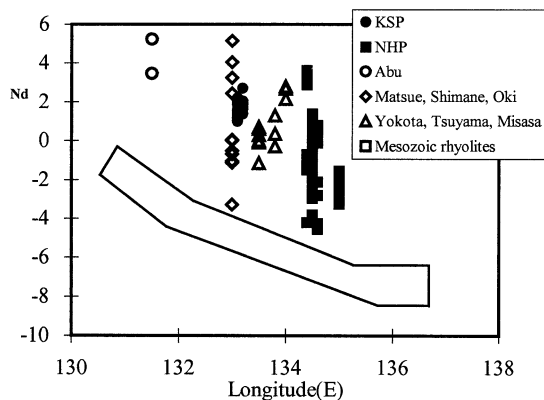


Fig. 1: Diagram showing a relationship between ϵ_{Nd} and longitude of sample location.

High-resolution stable isotopic analyses of an annually laminated tufa, Southwest Japan

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Material

Stable isotopic compositions of a tufa, a carbonate deposited in a cold freshwater, were analyzed with a high resolution in order to confirm the availability for a paleoclimatological tool. The objective tufa of this study collected from Shimokuraida (Okayama Prefecture, Southwest Japan) is annually laminated owing to regular air-water temperature changes. Chemical and isotopic compositions of the tufa-depositing water were monthly monitored from the locality.

Results

Results of every 0.2mm analytical intervals parallel to the laminae indicate cyclic seasonal changes in stable isotopic values, which correspond to the mm-scale lamination pattern. Both $\delta^{18}O$ and $\delta^{13}C$ values represent high in winter and low in summer. Since $\delta^{18}O$ value of the water has been stable throughout the years, tufa $\delta^{18}O$ variation indicates water temperature change at the sampling site. $\delta^{13}C$ variation mainly follows to the changes in the value of water dissolved inorganic carbon.

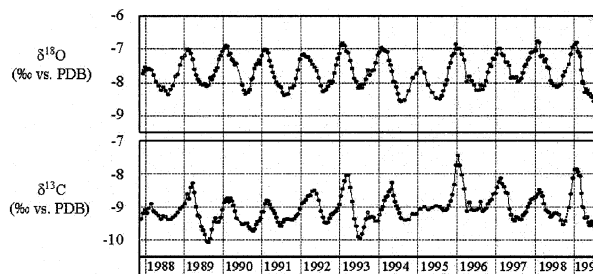


Figure 1: $\delta^{18}O$ and $\delta^{13}C$ variations of an annually laminated tufa deposit from Shimokuraida, SW-Japan.

Conclusions

The $\delta^{18}O$ and $\delta^{13}C$ variations of the tufa deposit clearly reflect seasonal changes in water and air temperature. These results were mostly identical to the values obtained from the previously analyzed tufa (Matsuoka et al., 2001). Therefore, this seasonal pattern can be largely applied to other laminated tufa deposits.

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Biogeochemical controls of iron isotope fractionation in organic-rich sediments

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This study explores the fractionation of iron isotopes ($^{57}\text{Fe}/^{54}\text{Fe}$) in an organic-rich mudstone succession, focusing on core and outcrop material sampled from the Upper Jurassic Kimmeridge Clay Formation type locality in south Dorset, UK. Two main types of iron-bearing assemblage are defined: mudstones with calcite \pm pyrite \pm siderite mineralogy, and ferroan dolomite (dolostone) bands. Mudstones and dolostones comprising the core section show a cyclic variation in isotopic composition, with lower values ($\delta^{57}\text{Fe}$ (IRMM-14) \sim -0.4 to 0.1 ‰) associated with the pyrite/ siderite-bearing mudstones, and higher values (\sim -0.1 to 0.5 ‰) related to the ferroan dolostones. Pyrite nodules and pyritized ammonites from the type exposure yield $\delta^{57}\text{Fe}$ values of -0.3 to -0.45 ‰, whereas the $\delta^{57}\text{Fe}$ values of the lithogenic source Fe(III) oxides represented by samples of Mid-Late Jurassic Fe(III) oxides, range from 0.2 to 0.9 ‰. Two fractionation models are proposed to account for the $\delta^{57}\text{Fe}$ variations. These relate the lower $\delta^{57}\text{Fe}$ pyrite and siderite values to variable degrees of biogenic reduction of the isotopically heavier lithogenic Fe(III) oxides. A consequence of this reductive dissolution is that a ^{57}Fe -enriched iron species may be produced that may be available for the formation of the higher $\delta^{57}\text{Fe}$ dolostones. However, an isotopic profile across a dolostone band sampled in both the core and type section reveals distinct zonal variations in $\delta^{57}\text{Fe}$, characterized by two peaks, respectively located above and below the central part of the band. This form of isotopic zoning is predicted in a one-dimensional model of diffusional-chromatographic exchange. Alternative zoning models envisage the infiltration of dissolved ferrous iron from variable $\delta^{57}\text{Fe}$ sources during dolostone growth.

The study shows that lithogenous source iron is partitioned into lower and higher $\delta^{57}\text{Fe}$ minerals during deposition of the organic-rich sediments. The isotopic fractionation is driven by biogeochemical processes, but physical processes of remobilization are a marked feature of subsequent diagenetic evolution.

Nature of rare earth element abundances in shallow marine platform carbonates

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Due to their unique 4f electron configurations, rare earth elements (La to Lu) behave as a coherent group and appear together in most geological processes. REEs in marine carbonate rocks have been studied by various workers to understand paleo-oceanic redox processes, reconstruction of paleo-oceanic REE abundance by calculating K_d and effects of diagenetic process on REE abundances.

In the present work we have determined the REE abundances in carbonate (limestone and dolomite) rocks from two late Neoproterozoic shallow marine platform carbonate sequences from India. The fundamental objectives of this paper are: (a) to portray the marked variations in REE abundance patterns in shallow marine continental platform carbonates, (b) to classify the REE abundance patterns into groups based on chondrite-normalized elemental ratios and curvatures of the abundance patterns, and (c) to discuss the possible physico-chemical factors which could have affected the nature of REE abundances.

The chondrite-normalized REE abundances in Krol and Bilara carbonates exhibit variable tetrad character. Based on chondrite-normalized Gd/Ho, La/Nd ratios, we have been able to classify the Krol and Bilara carbonates into three groups. (Y/Ho) and (Y/Dy) concentration ratios have been shown to reflect a combined effect of Y fractionation relative to neighboring trivalent REEs during carbonate precipitation from seawater and influence of continental contributions with chondritic ratios. The contrasting behavior of Y has been related to its different electronic configuration which determines its complexation behavior and partition coefficient. Ce anomaly values reported in this work are in agreement with the Ce anomalies in typical shallow marine conditions. However, absence of Ce anomaly and distinct positive anomalies in some cases reflect post-depositional Ce mobilization during early diagenesis possibly related to diagenetic mobilization of Fe and Mn.

Deep diamonds: Geochemical constraints on mantle dynamics

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Deep diamonds (i.e. those believed to come from the transition zone and lower mantle) provide some of the most compelling geochemical evidence of material transfer between the upper and lower mantle (reviewed in [1]). The geochemistry of these diamonds and their mineral inclusions places a number of constraints on mantle dynamics.

The phase assemblages in the inclusions reflect primarily the conditions of diamond crystallisation, but the original source rock material may leave some geochemical signature. For example, Ca silicate perovskite inclusions are enriched in trace elements many times above primitive mantle levels, suggesting an enriched source such as subducted crust. However, nearly all Mg silicate perovskite inclusions have low Al concentrations, which could only occur at the top of the lower mantle where garnet is also present. Together these observations support the idea that descending slabs pile up at the 660-km discontinuity.

Carbon isotopic compositions resemble those of the primitive mantle, in contrast to upper mantle diamonds, which show much lower and scattered values. This has been interpreted to indicate a lower mantle source for diamond carbon, with implicit implications for a restricted mixing of upper and lower mantle material. Recent suggestions, however, that redox conditions may play a role in carbon fractionation during diamond formation [2] introduce the possibility to account for observed carbon isotopic compositions through the redox dynamics of subducting slabs.

Nearly all lower mantle diamonds are classified as Type II, and the small amounts of nitrogen that are present show a high degree of clustering. Such behaviour generally indicates long mantle residence times and/or temperatures higher than are typical for diamond crystallisation.

To examine the degree to which deep diamonds and their mineral inclusions can be used to constrain mantle dynamics, I have compiled geochemical data from a number of sources. These include major and trace element geochemistry (including Mössbauer analysis) of the inclusions, carbon and nitrogen isotopic compositions of the diamonds, as well as information on growth and etching features. The result is a set of constraints on mantle dynamics that are consistent with the formation of deep diamonds with the observed geochemical signatures, their transport within the mantle, and eventual exhumation to the Earth's surface.

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Compound-specific $\delta^{15}\text{N}$ measurements of amino acids in dissolved organic matter from the central Pacific Ocean

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$\delta^{15}\text{N}$ values were measured for individual amino acids from high molecular-weight dissolved organic matter from surface to 4000m in the central Pacific ocean. To our knowledge these values represent the first compound specific $\delta^{15}\text{N}$ determinations for oceanic dissolved organic matter (DOM). Due to sample size and the complex DOM matrix, resolution was substantially more difficult than for other sample types we have examined, including particles and biota. However a subset of amino acids were resolved sufficiently to give reproducible values in most samples (Table 1). Overall, individual amino acid values tracked $\delta^{15}\text{N}$ of bulk DOM well. The similarity between amino acids whose nitrogen isotopic shifts tend to represent bulk protein suggests that despite the large fraction of nitrogen which cannot be identified in DOM, proteinaceous material- or a nitrogen source that is isotopically very similar - makes up the majority of HMW-DON. The only distinct change in $\delta^{15}\text{N}$ of amino acids within the water column profile occurs at the Chl. maximum zone. However, DON preserved at the oxygen minimum and in the deep ocean has both similar isotopic shifts and similar relative fractionation pattern to those in the surface Pacific. This suggests that, contrary to expectation, dissolved proteinaceous material that advects into the deep ocean is not substantially recycled. Very rapid mechanisms must act in the surface waters to protect this otherwise highly labile material from biological recycling processes over very long time scales.

$\delta^{15}\text{N}$ - AA Pacific DOM

12°S, 135°W

Depth (m)	2	100	375	4000
UDOM	8.3	8.5	7.9	7.8
Ala+Gly:	8.2	9.5	5.5	8.5
Ser+Thr	6.2	6.2	6.2	4.9
Val	9.5	9.9	5.0	9.9
Leu	**	11.6	5.7	4.9
Asp	8.8	12.6	4.9	12.0
Glu	4.7	6.3	7.2	10.3

Can the Eu oxygen barometer be applied to QUE 94201?

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QUE 94201 (QUE) has special significance among basaltic shergottites because (1) it likely represents a Martian melt composition and thus can provide valuable clues to magma petrogenesis on Mars; (2) it may be the most reduced of all basaltic shergottites (e.g. Herd *et al.*, 2002); and (3) its isotopic characteristics are the most primitive among basaltic shergottites (e.g., Borg *et al.*, 1997). Variation in oxidation state among the Martian meteorites, combined with systematic isotopic variations, may have important implications for the redox state of the Martian crust and mantle and the overall differentiation of Mars. Thus it is important to use multiple means to corroborate evidence that QUE is reduced.

One approach to determining oxidation state is through measuring the depth of the Eu anomaly in the REE patterns of near-liquidus minerals using SIMS (e.g., McKay *et al.*, 1994). In applying this approach to basaltic shergottites, Wadhwa (2001) assumed that the near-liquidus pyroxene crystallized from melt having the REE pattern of the bulk rock. This assumption is only valid if there is minimal fractionation of Eu from other REE prior to the crystallization of the volume of pyroxene analyzed by SIMS.

In the case of QUE, our experimental crystallization studies bear strongly on the validity of this assumption. QUE pyroxene is complexly zoned. Typical grains have Mg-rich pigeonite cores mantled by Mg-rich augite that abruptly begins to evolve towards more Fe-rich compositions. At the same point where iron enrichment begins, Al/Ti drops precipitously. Such Al depletions are generally thought to reflect plagioclase crystallization.

Dynamic crystallization experiments on synthetic QUE confirm the inference from Ti/Al: The drop in pyroxene Ti/Al and the commencement of Fe enrichment coincide and correspond to the onset of plagioclase crystallization. Because the potential of pyroxene to fractionate Eu is small, little fractionation can occur during crystallization of the initial Mg-rich pyroxene cores, only becoming significant after plagioclase entry. Thus, if SIMS analyses are of the Mg-rich pyroxene cores, little prior Eu fractionation can have occurred, and the assumption that the REE pattern of the melt was that of the bulk rock is valid. Provided appropriate partition coefficients are used, the Eu oxygen barometer can be applied to QUE.

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Bridging geochemistry and microbiology through ocean drilling

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In Jules Verne's adventure story, *Journey to the Center of the Earth* (1864), his heroes, while descending deep into the Earth's interior, discover a vast ocean teeming with pre-historic life. In the last 15 years, Verne's scientific fantasy has taken on new meaning within the context of the Ocean Drilling Program (ODP). Indeed, a major achievement of ODP has been the discovery of a sub-seafloor ocean comprising fluids moving through sub-seafloor formations in a wide variety of settings. Forming a continuum with the overlying ocean, this massive and dynamic plumbing system cycles the entire volume of the ocean through the seafloor every one million years, greatly influencing the chemical composition of the oceans. And, similar to the subterranean oceanic environment described by Jules Verne, this sub-seafloor ocean provides a unique habitat in which an extensive microbial population is active over a surprisingly broad range of temperatures, pressures and depths. Thus, another major achievement of ODP has been the recognition of the existence of a deep sub-seafloor biosphere, which may constitute as much as one-third of the living biomass on Earth. Together, the sub-seafloor ocean and the microbial communities therein are an important element coupling the biosphere with the geosphere.

Linking the biosphere and the geosphere provides a more realistic approach to delineate biogeochemical processes inducing carbonate biomineralization in marine sediments. Ocean drilling enables *in situ* studies of these biogeochemical processes associated with the deep biosphere, which, in turn, contribute to our interpretation of the evolution of marine sediments. For example, a combination of geochemical and microbiological analyses of samples, secured with recent ocean drilling during ODP Leg 201 on the Peru Margin, validates microbial mediation of dolomite precipitation in deep-sea sequences, providing tantalizing clues to understand the process of carbonate biomineralization under anoxic conditions. Geochemical signals incorporated into the microbial dolomite are a reflection of metabolic activity and document or confirm a microbial origin. The application of molecular biological techniques illustrates the intimate relationship between microbes and the *in situ* precipitation of dolomite. This geomicrobiological approach clearly demonstrates that microorganisms are instrumental in the modification and diagenesis of marine sediments. Future investigations of the biogeochemical interactions occurring within the sub-seafloor environment will undoubtedly provide new and exciting discoveries, as we continue to probe the oceanic depths with modern technologies and impending ocean-drilling campaigns within the framework of the Integrated Ocean Drilling Program (IODP).

Geochemical investigations of the hyporheic zone of the Columbia River, Hanford Site, USA

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The hyporheic zone, where groundwaters and surface waters interact at or near streambeds, is critical habitat for juvenile fish, and for organisms that act as the base of the aquatic food chain. The zone extends beneath the streambed and includes mixtures of surface water and groundwater. Although, in most environments, streams are *gaining* groundwater, they may also be *losing* water to the groundwater environment on a very local scale. The flux of nutrients and contaminants from groundwater to streambeds at any particular point thus may positively or negatively influence threatened or endangered surface water species such as salmon.

At the Hanford Site in southeastern Washington, the free-flowing Columbia River acts as critical salmon spawning habitat. The site also includes large plumes of contaminants, including dissolved uranyl and chromate, that move with aerobic groundwater through riverbed sediments. The river bottom is a cobble bed, with little apparent organic matter or fine sediment. We deployed passive multilevel samplers (MLS) in the riverbed to determine the chemical profile of the hyporheic zone and to estimate the concentrations of contaminants impacting riverbed biota. Stainless steel screens were driven into the riverbed using a jackhammer, and the MLS rods were placed in the uppermost 1.5 m, isolated from surface water by seals at the screen tops.

In the area of a known chromate plume, the samplers were allowed to equilibrate at high and low stage for ca. 24 h, then withdrawn. Hydraulic head measurements indicated the river was gaining at low stage and losing at high. In terms of electrical conductivity, the high and low stage concentration gradients had similar slopes, but conductivities near the river bottom at high and low stages were 125 and 375 μS , respectively; equivalent CrO_4^{2-} concentrations were 0 and 100 $\mu\text{g L}^{-1}$.

In the area of a known uranyl plume, the samplers were placed at varying (0 – 8 m) distances from the riverbank. At intermediate stage and 5 m from the bank, the uranyl concentration was relatively constant with depth, at ca. 100 $\mu\text{g L}^{-1}$, but at 8 m from the bank, the concentration gradient was steeper, from 100 to 250 $\mu\text{g L}^{-1}$ at 1 m beneath the river bottom.

Our results indicate that the hyporheic zone in this cobble-bed river presents variable and significant concentrations of contaminants to riverbed biota.

Shunga Event – Was it a case of Palaeoproterozoic mass extinction?

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The most significant accumulation of organic material (OM) and oil generation in the Proterozoic took place at c. 2000 Ma in the aftermath of the c. 2400-2060 Ma global perturbation of the carbon reservoir recorded in the isotopic composition of sedimentary carbonates and oxygenation of the terrestrial atmosphere. Occurrences of 2000 Ma-old, matured OM have been documented in northern America, Greenland, Africa and Fennoscandian Shield. In the Fennoscandian Shield, OM occurs in thick volcano-sedimentary successions with an estimated total carbon reserve of $>10 \times 10^{11}$ tonnes. The OM occurs in the form of a mineraloid, locally termed shungite (SH), which is a black, non-crystalline, glassy material with a strong lustre and contains >98 wt.% C.

The SH-bearing rocks were accumulated within continental rift settings, in non-euxinic lagoonal and lacustrine environments developed on the rifted margins of the Archaean craton. The occurrences of SH-bearing rocks represent a combination of a petrified oil field, and petrified organosiliceous diapirs and oil spills. These are exemplified by three types of deposit: (i) *in situ* stratified, (ii) migrated diapir, and (iii) redeposited clastic.

In situ stratified deposits are composed of metamorphosed oil shales (C<50 wt.%), rocks containing autochthonous kerogen residue and allochthonous OM (C = 50-75 wt.%), and migrated bitumen, originally liquid hydrocarbons (C>80 wt.%).

Diapiric deposits form non-stratified, cupola or mushroom-like bodies which are made up of SH rocks containing 35-75 wt.% SiO_2 and 20-55 wt.% C. These are considered to represent organosiliceous rocks, originally gels or mud. The SH rocks show abundant shrinkage cracks as well as cryptic fluidal textures and brecciation caused by multiple fluidisation processes. The current data are consistent with a diapiric or mud-volcanic origin or a combination of both.

Occurrences of clastic SH are hosted by lacustrine volcanoclastic greywackes deposited from turbiditic flow. SH occurs in rocks as clasts of lustrous SH ranging in size from <1 mm to 20 cm. The SH clasts are considered to represent redeposited, oxidised oil derived from oil spills.

Such unprecedented accumulation of OM might have been caused by a mass-extinction of old biological communities which were not adaptive towards oxygenation of the terrestrial atmosphere in the aftermath of the Palaeoproterozoic positive isotopic excursion of $^{13}\text{C}/^{12}\text{C}$.

Sm-Nd isotopic changes in sediments from the upper continental slope off southeastern Canada vs Laurentide Ice Sheet meltwater routing

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The influx rate and routing of Laurentide Ice Sheet (LIS) meltwaters exerted a tight control over North Atlantic thermohaline circulation during the last ice age and deglaciation. Sm-Nd isotopic analyses along NW North Atlantic margins can provide important information about the source of sediment supplies, thus about meltwater routes. Recent studies have shown that isotopic changes in sediments from the upper rise primarily record changes in the intensity of the deep Western Boundary UnderCurrent (WBUC). The present study shows that on the upper slope, off SE Canada, they vary as a function of sedimentary fluxes from the continent and thus reflect changes in the routing and influx of glacial meltwater. The study core was raised from a depth of 1400 m, near the outlet of the Laurentian Trough into the North Atlantic, in an area influenced by the Labrador Current. The upper 1600 cm span the Last Glacial Maximum (LGM)-present interval. AMS-¹⁴C measurements, benchmark layers and oxygen isotope stratigraphy indicate a major change in sedimentation rates during the early Holocene, from a late glacial rate of ~100 cm/yr to a post-glacial rate of ~38 cm/ka. ϵ Nd values range from about -10 to -20. The least radiogenic signatures (-10 to -11) characterize the LGM sediment. The overlying layer spanning the deglaciation (from ca. 16 until 9-8 ka BP) yield ϵ Nd values between -12 and -13, whereas in the upper ~350 cm of sediment (9-8 ka BP-Present), they range from -15 to -20. A thin layer rich in detrital carbonates and lithic fragments, assigned to Heinrich-event 1, separates the LGM vs. deglacial units. It shows a very low ϵ Nd value (-18.2). We attribute the major changes in sedimentation rates and ϵ Nd values at ca. 9-8 ka BP to a drastic reduction in meltwater flux and sedimentary supply from the SE margin of the LIS through the St. Lawrence Gulf. This is consistent with the opening of Hudson Bay, dated at 8.2 ka BP. The rerouting of meltwaters, from the Gulf of St. Lawrence to the Hudson Strait, resulted in a relative increase of low ϵ Nd sediments from Precambrian shield rocks carried by the Labrador Current to the study site, and a reduction in sedimentary supplies from the Paleozoic-dominated SE sector of the LIS margin. The upper rise and the upper slope sequences depict virtually opposite isotopic trends during the late deglacial period. This reflects the increased transport of younger sediment supplies from the mid-ocean ridge to the rise by the WBUC as a result of higher production of North Atlantic Deep Water.

The role of capillary pressure on the atmospheric noble-gas "excess air"

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Non-saturated zone (NSZ) of soils is defined by the coexistence of water and air above the water table. Such "suspended" water does not follow gravity and persists over air by decreasing its internal pressure below the atmospheric one, including the negative pressure domain. Mercury and Tardy (2001) have recently calculated thermodynamic properties of water in the stretched domain, to assess the consequences of the stretched water state upon the geochemical equilibria, within NSZ (Mercury et al., 2003). Particularly, it is predicted an increasing capability of the capillary water to dissolve noble gases.

Noble gases can be used as paleoclimatic proxies. It is assumed that atmospheric noble gases (ANG) are dissolved at the water table within the recharge area of aquifers, and their concentration is dependent of the air temperature during recharge. For waters of known age, we can obtain temperatures at the time of recharge from their measured concentrations. Often, noble gas concentrations in groundwater exceed those predicted by solubility equilibrium with the atmosphere, producing an "excess air" (Aeschbach-Hertig et al., 2000). One potential cause of the "excess air", often ignored or oversimplified in previous ANG studies, is the capillary pressure of water. The role of the capillary pressure of the solvent is here assessed using the dataset obtained by Stute et al. (1995) on the San Juan Basin groundwater, New Mexico. Paleocapillary pressures, paleotemperatures and "excess air" are simultaneously regressed to adjust the calculated dissolved ANG (using thermodynamic data from Shock et al, 1989) to the measured ones. Results fit well the measured dataset, and show that capillary pressure is generally close to, but not equal, 1 bar. This means that recharge of noble gases does not take place at the water table but at the top (or close to the top) of the capillary fringe, well-known to be very irregular and variable in some extent with the water level. Dissolution of noble gases may be a NSZ process, where simultaneous air entrapment can occur, facilitating the formation of "high" amount of excess air.

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Silicate stardust from comets

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Interplanetary dust particles (IDPs) collected in the Earth's stratosphere are 5 – 50 µm fragments of asteroids and comets [1-3]. Anhydrous IDPs have escaped significant parent body hydrothermal alteration [2] and are further distinct from meteorites in their greater abundances of volatile elements and C, fine grained (100 – 500 nm) textures, and unequilibrated mineralogies. Many anhydrous IDPs contain high abundances interstellar organic compounds [4] and grains of silicate stardust [5]. These observations are consistent with properties of comets inferred from remote astronomical observations.

Comets have been thought to be pristine aggregates of interstellar materials. However, spectroscopic observations of crystalline silicates in comets has challenged this notion, given their apparent absence in the interstellar medium.

We measured the isotopic compositions of crystalline and amorphous grains in anhydrous IDPs to establish the relative proportions of solids of presolar and solar system origin in these materials. Stardust grains are distinguished from solar system materials by their exotic isotopic compositions as measured by NanoSIMS ion microprobe. Mineralogical characterization of some of these grains was performed by transmission electron microscopy (TEM) on 70 nm thick IDP microtome sections prior to isotopic analysis.

Roughly 1031 grains were measured for their O isotopic composition with sufficient precision to distinguish solar system material from stardust. Among these, 113 were characterized by TEM prior to analysis by NanoSIMS. We identified 6 grains of silicate stardust, two of which were previously analyzed by TEM where they were identified as an amorphous GEMS [6] grain and a forsterite grain. The remainder of the 1025 grains had O isotopic compositions indistinguishable from solar system materials.

The mineralogy of the isotopically solar grains include enstatite, GEMS, olivine, anorthite, Ca-Al-Mg-rich glass, diopside, and chromite. It has been suggested that interstellar grains may be rendered amorphous and isotopically homogenized by shock sputtering and re-accretion. However, crystalline silicates are very unlikely to form in the ISM. The most probable source of isotopically solar crystalline grains is the solar system itself.

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The Tono Natural Analogue Project: A system model for the origin and evolution of the Tono uranium deposit, Japan

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Natural analogue studies of the Japan Nuclear Cycle Development Institute (JNC) in the Tono uranium deposit, central Japan, are developing generic approaches for simulating geological perturbations within models describing radionuclide migration. Numerical model development is being made based upon extensive field and laboratory investigations.

The investigations are focusing on the Tsukiyoshi orebody, which is relatively large and accessible, being generally <150 m below the surface, about 3.5 km long, 500 m wide, and several metres thick. Approximately 2600 tonnes of uranium occur at an average concentration of 0.05%. Mineralisation is concentrated in lacustrine, lignite-bearing rocks of the Miocene (c. 18-20 Ma) Toki Lignite-bearing Formation, up to a few tens of metres above an unconformable contact with the late Cretaceous Toki Granite.

The sedimentary sequence contains several unconformities and mostly is cut by the Tsukiyoshi Fault (c. 30 m apparent reversed displacement). Marine Miocene rocks also occur at higher levels than the mineralisation. Thus, the deposit is preserved in spite of it being affected by exhumation, subsidence and sedimentation, marine transgression and faulting.

Conceptual and numerical models for these environmental perturbations were constructed using a novel adaptation of a Safety Assessment methodology. A 'reference scenario' was developed using a Systems Analysis approach. This scenario is a best estimate of how the geological system and the uranium deposit reached their present states and includes descriptions of all major environmental perturbations. Uranium is mobilized from the upper granite under relatively oxidizing conditions, and then transported by groundwater into the sedimentary rocks. There, reducing conditions cause uranium deposition. A specially-designed numerical model simulated the main features of this scenario.

Many simulations were performed to identify key uncertainties to which the simulated timing of ore deposition and uranium distribution are sensitive. The approach could be used elsewhere, in safety assessments of the high-level radioactive waste (HLW) geological disposal concept in Japan. A particular application would be at potential future waste disposal sites elsewhere, to prioritise site characterisation so that the most safety-relevant uncertainties are reduced.

Isotopic variations along the Southwest Indian Ridge, 30-50°E

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Isotopic studies of MORB (Mid-Ocean Ridge Basalt) have established the existence of a vast domain in the Indian Ocean where ²⁰⁶Pb/²⁰⁴Pb, and ¹⁴³Nd/¹⁴⁴Nd ratios are lower, but ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ⁸⁷Sr/⁸⁶Sr ratios are higher, than those of the Pacific and Atlantic Oceans (north of 25°S). In this domain, the Southwest Indian Ridge records a gradual, but irregular isotopic transition in the MORB source mantle from typical Indian-ocean type composition to the east and Atlantic like ones to the west of 26°E. Here, we present double spike high precision Pb-isotope and Sr-Nd-Hf isotope data for both basaltic glasses and basalts, dredged along the Southwest Indian Ridge (SWIR) between 30° and 50°E during the SWIFT cruise.

All samples from this ~2000 km section of the SWIR possess Nd-Pb-Sr isotopic signatures typical of Indian MORB. New analyses for lavas from the 39-41°E section, identified previously as exhibiting the most extreme DUPAL signature extend the previous range in ²⁰⁶Pb/²⁰⁴Pb (16.585-18.426) and ¹⁷⁶Hf/¹⁷⁷Hf (0.282880-0.283191) to some of the lowest values yet found among spreading centres worldwide. Modelling shows that the low ²⁰⁶Pb/²⁰⁴Pb and ¹⁷⁶Hf/¹⁷⁷Hf ratios from 39-41°E section cannot be accounted for by contamination of the upper mantle through recycled oceanic components (crust+sediment). The linear array defined by these lavas in ²⁰⁷Pb-²⁰⁴Pb-²⁰⁶Pb-²⁰⁴Pb intercepts the Pb crustal evolution curve at ~1.2 Ga similar to the mid-Proterozoic age of the lithosphere of southern Madagascar. The combined isotopic systematics suggest binary mixing between depleted mantle and a component of ultimate origin in the continental crust or mantle lithosphere. This component may have been thermally eroded by Marion plume when it lay beneath Madagascar some 90 m.y. ago.

The extreme isotopic compositions exhibited by lavas from the 39-41°E segment of the SWIR represent a local mantle heterogeneity with a localized explanation, and are separated from understanding the ocean-wide isotopic character of the Indian Ocean mantle.

Direct observation of immiscible fluids using X-ray radiography

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Revolutionary New Technique

The new method for the direct observations of immiscible fluids has been developed using X-ray radiography technique (Kanzaki et al., 1987) together with Kawai-type multi-anvil high pressure apparatus (SPEED-1500) installed at BL04B1, SPring-8, Japan. Hydrous Sr-plagioclase and hydrous CFMAS-basalt systems are used as starting materials. We developed a new sample container, which is comprised of a metal (Pt or AuPd) tube and a pair of single crystal diamond lids put on both ends of metal tube. The sample, which is put inside of the container, can directly be observed through the diamond lids and an aperture of the metal tube. The experimental conditions are at pressures of 3 to 6 GPa and at temperatures up to about 1400°C. Pressure is applied first, and then temperature is increased slowly.

Results

At around 800-900°C and 3 GPa in both systems, we observed some light-gray spherical bubbles moving upward in the dark-gray matrix. The light-gray spherules that absorbed less X-ray are considered to be aqueous fluid phase, whereas the dark-gray matrix is silicate melt. At least up to 1400°C in hydrous Sr-plagioclase system and 1200°C in hydrous system, immiscible two phases (i.e., both aqueous fluid and silicate melt) were observed at 3 GPa. One preliminary experimental result at 6 GPa in hydrous basalt system showed that there appeared no bubbles up to 1000°C.

Conclusion

Our new technique could be applied to the direct observations of various kinds of 2-fluids coexisting under deep mantle conditions.

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Major and incompatible trace elements in clinopyroxenes from different magmas

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We have compared a lot of compositions of clinopyroxene from different types of basaltic lavas.

We have studied tholeiites, traps and alkaline magmas that are common in Antarctica and nearby region of Southern Atlantic. Grains of clinopyroxene were picked from basaltic magmas of different ages: from Mesozoic basaltic flows related with traps in the region of Dronning Maud Land Province (DMLP) to Cenozoic alkaline lavas erupted in the segment of Hobbs Coast (Western Antarctic) and to contemporaneous tholeiites formed in the region of Western End of South-West Indian Ridge (SWIR). All magmas are of olivine-bearing type.

The variations of most lithophile elements in clinopyroxenes determined by ion microprobe were analogous to all studying regions and had well correlation on the graphs Mg# - element. At the same time clinopyroxene from the alkaline magmas from Hobbs Coast Province had visible enrichment in Ti. The clinopyroxene from traps of DMLP had enrichment in Cr. During the process of differentiation of magmas the maintenances of incompatible elements increased as well as increased the ratios of the most incompatible elements to less incompatible.

The petrogenetic compare of clinopyroxene from basalts from the Spiess Ridge and from the segment of Southwest Indian Ridge in the Bouvet region showed that paragenesis of minerals is similar and consists of olivine, plagioclase and clinopyroxene.

Using several methods for determent the pressures of origin of the basaltic rocks: Nimis, 1998; Yang et al., 1996, based on the abundances of major elements in basaltic glasses, we had estimated that pressures of liquid crystallization under the Spiess Ridge and in the Bouvet segment are similar and their values were from 2 to 5 kbar. And the analogous estimates fo r Hobbs Coast and Dronning Maud Land were 3-12 km and 1-6 km respectively.

Geochemical map of the Tohoku region, northern Honshu, Japan

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Geochemical characteristics of river sediments from the Tohoku region, northern Honshu, are studied, as a part of full-land geochemical mapping project of Japan, for environmental purposes and for understanding of a large-scale elemental distribution in an island arc.

The mapped region belongs to Northeast Japan Arc. This region consists of mountain areas, small basins and coastal plains. The Ou Mountains extends north to south through the region and correspond to the Quaternary volcanic front. Paleozoic to Mesozoic basement rocks are mainly exposed in the eastern part (Kitakami Mountains) and in the southwest part (Asahi Mountains). Other areas are widely covered by Neogene-Quaternary mafic-felsic volcanic rocks, sedimentary rocks and sediments.

About 390 river sediments were collected. They were analyzed for more than 50 elements by ICP-AES, ICP-MS and AAS.

The concentration patterns of Mg, Sc and Co in the geochemical maps accord with the distribution of mafic and felsic rocks in the whole area.

The areas showing high concentrations in light rare earth elements (LREEs), Th and U coincide with the distribution of pre-Neogene basement rocks, in many cases. The highest concentrations are obtained in the areas where the Cretaceous granitic rocks are exposed, especially in the Asahi Mountains. The area of the Jurassic accretionary complex in the Kitakami Mountains still shows higher concentrations than the area of the Neogene-Quaternary rocks. The relatively low concentrations in these elements are common characteristics for the whole area where the Neogene-Quaternary rocks are exposed, including sedimentary rocks and felsic volcanic rockst. The variations of the LREEs, Th and U in the geochemical maps are concordant with chemical variation of dominant rocks, and they possibly indcate the change of geological setting of the Tohoku region from continental margin to island arc in Cenozoic. The concentrations of K and Rb are low in the Ou Mountains, especially at the northern part, reflecting the chemical characteristics of the rocks at the volcanic front.

The areas especially rich in Cu, Zn, As and Pb coincide with the distribution of mineral deposits. The high concentrations related to Neogene Kuroko deposits, hydrothermal-vein deposits, and Cretaceous skarn-type deposits are recognized.

Mineralogy and petrogenesis of quenched angrite meteorites

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The angrites constitute an enigmatic achondrite group characterized by unusual mineralogy and ancient crystallization ages. Due to recent discovery of new angrites (Sahara99555, D'Orbigny and NWA1670), the current angrite collection is dominated by "quenched" angrite samples (samples listed above plus LEW87051 and Asuka881371) and distinct from the classic "slowly cooled" angrites (Angra dos Reis and LEW86010).

The quenched angrites show ophitic to porphyritic textures and often contain large olivine grains out of Fe/Mg equilibrium with the groundmass melt. Our previous studies pointed out that these olivine grains are essentially Cr-rich and Ca-poor than the groundmass olivines and are possibly xenocrysts [e.g., 1]. The similar mineralogy of the groundmass minerals as well as the presence of Cr-rich and Ca-poor olivine xenocrysts indicates that these quenched angrites are closely related and are co-magmatic.

We found strong correlations among major elements in these quenched angrites well understood by olivine control. Because olivine xenocrysts are absent or very rare in Sahara99555 and D'Orbigny, we suggest that their bulk compositions represent an angrite magma composition that is not contaminated by the xenocryst component. In contrast, LEW87051 and Asuka881371 contain ~10% olivine xenocrysts and appear that their bulk compositions include dissolved olivine xenocryst components. The newest angrite NWA1670 is also abundant in olivine xenocrysts and would be closer to LEW87051 and Asuka881371 in bulk composition. There is also a correlation between the core Fo components of the groundmass olivine and the bulk mg#s.

The origin of olivine xenocrysts is unclear. The forsterite component of xenocrysts ranges from Fo₉₆ to Fo₇₀. The presence of Fo₉₆ olivine is quite unique among achondrites and it is the most magnesian olivine except for olivines in aubrites and ureilites. Because it is hard to produce such a magnesian olivine by normal igneous differentiation processes, some reduction process may have been involved or it may be a completely exotic component related to the other class of meteorites. The heat source generating the angrite magma is also unclear. Either impact melting or endogenous melting is possible for producing rapidly cooled magma with xenocrysts.

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Alteration of marble and hyperalkaline groundwater evolution at Maqarin (northern Jordan)

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Introduction

Hyperalkaline Ca-OH-SO₄ type (pH>12.5) groundwaters are associated with the retrograde hydration and alteration of pyrometamorphosed bituminous clay biomicrites, at Maqarin (northern Jordan). Two groundwater systems ('Eastern' and 'Western') are differentiated on the basis of pH, Na, K, SO₄, Cr, Se and Re. The evolution of these groundwaters is being studied as a natural analogue for the evolution of the alkaline porewater environment of a cementitious waste repository.

Observations

The primary marbles contain larnite, spurrite, wollastonite, ellestadite, brownmillerite, periclase, brucite, portlandite, lime and other calcium aluminosilicate-sulphates and ferrites.

K and Na are present within major primary calcium silicate-sulphates, and in a discrete fine grained unnamed K-Cu-selenide-sulphide trace mineral associated with oldhamite (CaS). Oldhamite and K-Cu-selenide-sulphide are readily dissolved during early hydration. Calcium silicate-sulphates also alter early during hydration to produce secondary K-Na-free thaumasite. Brownmillerite, larnite, ellestadite and calcium aluminate-sulphate react more slowly to form a complex secondary assemblage which includes thaumasite, ettringite, portlandite, calcite, aragonite, vaterite, gypsum and and hydrated calcium silicates and aluminosilicates.

Discussion and conclusions

K and Na are leached from the marbles during retrograde hydration. Early alteration of the more reactive primary K-Na-bearing minerals would appear to explain the enhanced K, Na, Se and SO₄ in the highest pH (12.9) site. Groundwaters in this part of the site may represent an earlier stage of the cement alteration process, so providing an excellent analogue to long-term repository evolution.

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Domestication patterns of pigs (*Sus scrofa*) evidenced by carbon and nitrogen isotope analysis for prehistoric boar bone collagen

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Wild boar (*Sus scrofa*) might change the diet from natural resources to agricultural products or leftovers of human diet during the initial step of pig domestication. We have analyzed stable carbon and nitrogen isotopes of boar bone collagen to evidence this hypothesis in the Far East. Boar bones from archaeological sites at Ryukyu and other islands in Japan archipelago were analysed and compared with the results in Korea, Taiwan and Vietnam. Carbon and nitrogen isotope compositions in boar bone collagen from sites (ca. 4000BP) in central Japan showed a nearly similar range ($\delta^{13}\text{C} = -21 \pm 1\%$ and $\delta^{15}\text{N} = 4 \pm 2\%$) with that of deer in Japan, suggesting that the herbivores fed mainly on C₃ plants in natural system. However, boar from Ryukyu showed unusually higher $\delta^{15}\text{N}$, often increased to 12 ‰, although no change occurred in $\delta^{13}\text{C}$, strongly suggesting a significant contribution of animal diets. Such ¹⁵N enrichment was already found in the early Jomon period (ca. 6000BP) in Ryukyu. In contrast, some boar from Jeju island (ca. AD 2-3C), and historic pigs from both Ryukyu and east coast of Korea (Kan-wongdou: AD 1C) showed significant enrichment of ¹³C, indicating much contribution of C₄ plants or marine foods. We concluded that at least three feeding patterns were developed in domestication around the East China Sea. One pattern is mainly based on consumption of human leftovers, clearly marked by high $\delta^{15}\text{N}$ indicating similarity with humans. The second is a system feeding C₄ millets, although the degree of dependence on agricultural products should be variable according to the case. The third pattern is the feeding of marine resources. We suggest that boar found in early sites in Ryukyu might be the first pattern and were imported probably from main lands prevailing rice agriculture. While later sites showed the second pattern using millet products and seems to spread as popular domestication in the Ryukyus. Unreasonably domestication based on the marine resources might not be established in the Ryukyu archipelago.

⁸⁷Sr/⁸⁶Sr ratios in lake sediments in Lake Biwa, Japan — Environmental change in the last 200 years

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Lake Biwa is the largest lake of Japan and one of a few ancient lakes. The area surrounding the southern basin has many overpopulated cities, and has recently become polluted by remarkably increased human activities. In this study, three sediment cores from the northern basin, the southern basin and the boundary part of the basins were analysed for ⁸⁷Sr/⁸⁶Sr ratio and major and minor element compositions in order to study spatial variability and environmental change in the last 200 years.

Core samples were dried, pulverized and analysed for major element compositions by XRF. An aliquot of the sample was leached with 2M HCl to remove carbonates. The samples were digested with HF-HClO₄ and separated Sr and Rb using AG50WX8 cation-exchange-resin column. ⁸⁷Sr/⁸⁶Sr ratios were analyzed using Micromass Sector 54-30 mass spectrometer. Quantitative analyses of Rb and Sr were done by the isotope dilution method using Finnigan MAT THQ mass spectrometer. The sedimentation rate of the lake sediments was estimated by ²¹⁰Pb and ¹³⁷Cs.

⁸⁷Sr/⁸⁶Sr ratios of sediment cores in the southern basin are 0.7200 and radically decrease to 0.7184 at the depth of 10cm layer, deposited in approximately 1960, and show the low value within the surface layer. The Sr and Ca concentrations increase rapidly within the same depth layer, while Rb concentration is unchanged. The sediment cores in the northern basin have higher ⁸⁷Sr/⁸⁶Sr ratios (0.7210) and a little decrease at the 10cm depth layer, and show no increase in Sr concentration at the surface layer. The ⁸⁷Sr/⁸⁶Sr ratio profile from the boundary part of the basins shows an intermediate trend between the profiles in the southern sediments and northern sediments.

The residue after HCl-leaching for the southern sediments shows the high ⁸⁷Sr/⁸⁶Sr value similar to that of the northern sediments. The result suggests that the sediments in the southern basin and northern basin have originated from the same clastic components, and that an addition of any material with low Sr isotopic ratio to the surface layer in the sediments in the southern basin. Artificial activities might produce a large effect on Sr in lake sediments in the south basin. The surface sediments in the southern basin, however, could be disturbed and mixed by biological/physical turbulence because the southern lake is shallow.

Rare earth elements, Ir and Au from pallasite olivines

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Introduction

Pallasite consists of metal and olivine. As most pallasites are finds, they have more or less suffered contamination after their falls. Since olivine and metal are adjacent to each other, siderophile contents in olivine tend to be influenced by the neighboring metal phase. Incompatible elements like rare earth elements (REEs) in olivines are extremely low in their contents and, hence, may be increased by terrestrial contamination. Thus, initial contents of REEs and siderophile elements are hard to be accurately determined for pallasite olivines. In this study, rare earth elements (REEs), Ir and Au in olivine separates were determined by radioactive neutron activation analysis (RNAA) for four main-group pallasites (Brenham, Dora, Imilac, Esquel).

Results and discussion

Figure 1 shows CI chondrite-normalized REE abundances in pallasite olivines. V-shaped patterns were observed for HCl-leachates whereas the residual olivines show light-REEs depleted patterns. REE abundance patterns for the HCl-residue are similar to the partition coefficients of REEs in olivines but their inclination is more steeper than the partition coefficient pattern.

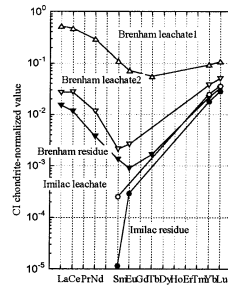


Fig. 1. REE from pallasite olivines

Ir and Au contents (1-20 ppt and 2-25 ppt, respectively) in the least weathered pallasite olivines are lower than those in weathered olivines (Fig.2) and are assumed to primordial values when pallasite olivines formed in their parent body. These Ir and Au contents coupled with Ir and Au contents in metal are consistent with the equilibrium partitioning of Ir and Au between liquid metal (core) and silicate mantle. Our results of REEs and siderophile elements (Ir and Au) suggest a cumulative origin of pallasite olivines.

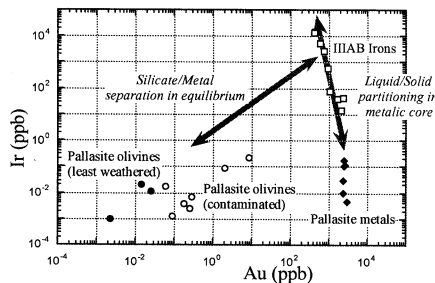


Fig.2 Ir vs. Au diagram for pallasite olivines and metals

Experimental study of gold, silver and water behaviour in endogenic processes at high temperature and pressure

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Water and gold behaviour at interaction of water-bearing melts of main and acid compositions with crystalline phases (T=900-1200°C and P=1 kbar) and fluid - solid phase (T=200-500°C and P=1 kbar) has been studied by use of hydrogen (³H) and gold (¹⁹⁵Au) radioisotope autoradiography. Gold and silver (¹¹⁰Ag) behaviour at leaching volcanites of main to acid compositions by hydrothermal solutions (T=200-500°C and P=200-1000 bar) has been investigated as well. A similarity in behaviour of water and gold has been revealed that is expressed by their higher contents on contact of the melt and solid phase, and their enrichment in hybrid formations when mixing the melts of main and acid compositions. A dependence of metal leaching on composition of silicate vein-stuff, P-T conditions and O₂ regime has been found.

The effect of water (fluid) concentration at the boundary of water-bearing basalt melt and plagioclase crystals as well as acid melt with host rocks has been established due to the use of tritium β-radiography in the T-water experiments. The effect results from water (fluid) influx to the front of melting (from melt) and can be employed in explaining the mechanism of magma replacement.

Higher contents of water as well as gold, iron and alkalis are also determined in the zone of water-bearing acid granite and basalt melt mixture. The effect of gold enrichment in the melt of mixed composition is elucidated by an increasing role of depolymerization factors in the mixed zone, particularly, such as H₂O and FeO due to their high activity in comparison with other elements-modifiers.

The experimental data obtained allow to explain close association of gold deposits with magmatic rocks that underwent complex interaction of basalt and granite magmas or their contamination by wall rocks. Thus, “andesite maximum” is revealed both for water and gold and it mostly causes the peculiarities of gold geochemistry during magmatic and hydrothermal processes.

The experiments on hydrothermal water-rock interaction show that metal leaching occurs from volcanites with the clark amounts of gold and silver (195 Au and 110 Ag). Rate and extent of leaching depend on T, P and P_{O₂}. In favourable conditions, up to 50% Au and about 100% Ag of the initial contents in rock can be leached. The rocks that contain these metals at clark level can be source of ore matter for gold and silver hydrothermal deposits.

The work has been carried out with financial support of Russian Foundation for Basic Research (grant 98-05-65110).

When did aqueous alteration occur on the Martian surface?

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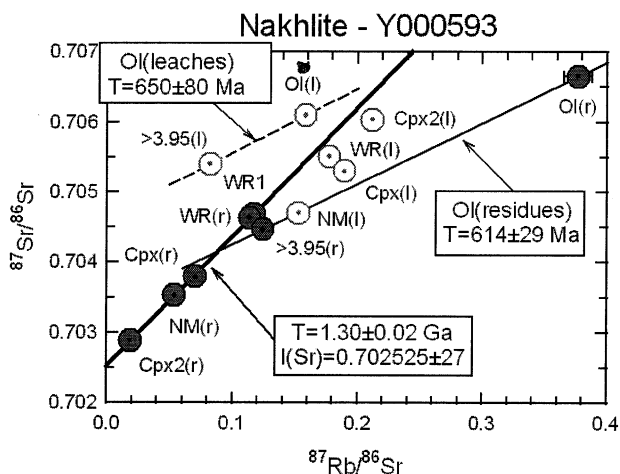
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We have been studying aqueous alteration products in Yamato nakhlite, Y000593, in an attempt to determine radiometric ages. The two-point Rb-Sr ages of olivine leachates (650 Ma) and of olivine residues (614 Ma) obtained by [1] are in good agreement with the oldest K-Ar age of 670 ± 91 Ma for the iddingsite sample [2] and with the Rb-Sr age of ~650 Ma for HCl leachates from the iddingsite-rich samples [3] from Lafayette. Our olivine samples (Ol and ρ>3.95) were obtained by density separation using heavy liquids of 3.60 and 3.95 g/cm³. The olivine (Ol) sample consisted of yellow olivines with lamellar exsolutions. Although adhering brown alteration products, iddingsite, are much less abundant in the Ol sample compared with the ρ>3.95 sample, the data point for the Ol residue is plotted far from the 1300 Ma isochron.



An olivine grain oriented normal to [100] was observed by TEM. It contains exsolution lamellae, which are composed of symplectic intergrowth of magnetite (<3 wt % Cr₂O₃) and augite. The magnetite lamellae are ~150 μm in width, similar to those in Nakhla [4]. There are no obvious clues to the aqueous alteration in the symplectic exsolution. In the olivine grain, screw dislocations elongated to [001] were observed locally. Dislocation density is on the order of 10⁸ cm⁻². No signs of aqueous alteration were observed in the areas where dislocations were concentrated.

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Polyamino acid formation in the abiotic conditions

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Many model experiments had been performed to obtain information on the prebiotic formation of polyamino acids because those had gathered special interest as a model of protoprotein on the primitive Earth. Most of these investigations had revealed that aspartic and glutamic acids, their amides, and lysine. Recently, we revealed that molten urea (mp 135 °C) serves as a highly polar reaction medium in the nitrogen-incorporating thermal polycondensation of unsaturated dicarboxylic acids producing polyaspartic acid (Terasaki, *et al.*, 2002a). In addition, we reported that alanine, which had been known incapable of undergoing thermal polymerization, was polymerized in the molten urea (Terasaki, *et al.*, 2002b). This result showed that there was little restriction of amino acid specie to polymerized in the molten urea. We, therefore, attempted to polymerize many kinds of amino acid in the molten urea, and characterized produced polyamino acids.

We heated equimolar mixtures of amino acids and urea at 140 °C for 24 h in the sealed test tubes, and the aqueous extracts of the reaction mixtures were analyzed by LC-MS. We detected four types of oligomers those were free peptides, carbamoyl derivatives at *N*-terminus or *C*-terminus, hydantoin derivatives at *N*-terminus, and unidentified derivatives, from glycine, alanine, β-alanine, aminobutyric acid, norvaline, valine, norleucine, leucine, and aspartic acid. Oligomers of serine, diaminopropionic acid, and cysteine were not detected, and there were little remained amino acids in the extracts. It seemed that those amino acids were decomposed during the reaction.

The largest oligomers detected in the extracts were 13-mer from glycine, 11-mer from alanine, 7-mer from aminobutyric acid, 4-mer from valine and leucine, and 8-mer from aspartic acid. Long oligomers from valine and leucine were not detected on the LC-MS chromatograms, because of their low solubility. When the reactions were finished, reaction mixtures of valine and leucine were soluble in the molten urea, however produced oligomers did not soluble in the aqueous solution completely. Therefore, the molten urea played the role of a good solvent.

From the viewpoint of chemical evolution, this study offered a new candidate for a dehydrating agent or a polycondensation medium that can be present on the primitive Earth.

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Chondrule radius and evaporate fraction in viewpoint of shock-wave heating model

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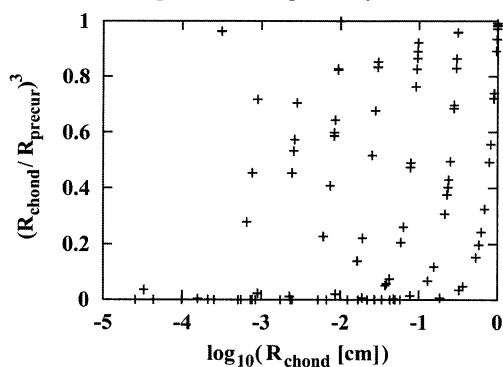
Shock-Wave Heating Model

The shock-wave heating model is one of the most possible mechanisms for chondrule formation. In this mechanism, formed chondrules in the postshock region are exposed by the hot gas in that region until the gas cools by emission of radiation. In this phase, most of small chondrules evaporate completely. On the other hand, some of larger ones shrink by the evaporation and survive to become the small chondrules (Miura & Nakamoto, 2003). From these results, it is naturally expected that the small chondrules have lost the greater portion of their initial mass than the large ones.

Numerical Results

We numerically simulated the chondrule formation by shock wave heating with various shock properties (shock velocity $v_s = 5 - 70 \text{ km s}^{-1}$ and preshock gas number density $n_0 = 10^{10} - 10^{15} \text{ cm}^{-3}$). Figure 1 shows the relation between the present chondrule radius and the evaporate fraction. In this study, as the indicator of evaporate fraction, we chose the volume ratio of the chondrule to its precursor. From Fig. 1, we can see that there are some chondrules which do not evaporate if their radii are larger than about 1 mm. However, chondrules whose radii are less than 100 μm (10 μm) must have lost their initial mass about 20% (40%) or more by the evaporation.

Figure 1: Evaporate fraction. R_{chond} and $R_{\text{precursor}}$ are the radii of chondrule and precursor, respectively.



Concluding Remarks

Our results suggest that it is possible to verify the shock-wave heating model by the measurement of mass-loss fraction as a function of the chondrule radius. Also, the mass-loss fraction may be related to the fractionation between refractory and volatile elements.

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Identifying silicate minerals incorporated by plants.

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It has been suggested that presence of higher plants could increase the weathering rates of rocks and minerals. Two mechanisms are commonly known to explain this phenomenon. One is mechanical breakdown of rocks and minerals caused by root elongation. Another is chemical attack following physiological activities of plants. Higher plants can change chemical conditions such as pH and redox condition around their root by excreting organic acids, proton, carbon dioxide, etc., resulting the dissolution of minerals. In any cases, inorganic elements in primary minerals are considered to dissolve into soil solution, and then taken up by plants or flow in drainage.

Recently, however, several studies indicate that some inorganic elements such as rare earth elements, calcium, and potassium in soil solution cannot completely explain the abundance of that in plant's body. This means inorganic elements in primary minerals may be rather directly transported to plants without taking free ionic form or complex form in soil solution.

In order to investigate whether the inorganic elements in plants are derived from primary minerals directly, neodymium isotope ratio provides powerful information. Nd isotope ratio is characteristic of each primary minerals and the value doesn't change during the weathering process and biological activity. The Nd isotope ratio of a plant is determined depending on the mixing proportion of each component from which Nd in the plant is derived.

Several species of plants were sampled from the Strengbach catchment, France. The Strengbach was chosen as sampling area because the age of bedrock was old enough to provide considerable difference between Nd isotope ratio of each minerals. Samples were ashed and digested with nitric acid and hydrofluoric acid. Separation of Nd was done using TRU and LN extraction resin columns. A thermal ionization mass spectrometer (MAT262) was used for the Nd isotope measurement. REEs in the plant specimens were also determined.

The result so far obtained indicate selective uptake of silicate minerals in soils. The present results would possibly affect the interpretation of weathering sequence of silicate minerals and of the REE signature of river water.

Noble gases in two hot desert eucrites, DHO007 and DHO275

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In recent years, a large number of meteorites have been collected from hot deserts (*c.f.*, The Meteoritical Bulletin). Noble gas data are helpful to understand terrestrial resident time and paring of specimens as well as thermal and ejection histories of meteorites. We report here noble gas results (only cosmogenic component in the abstract) on two eucrites from Oman desert, DHO007 and DHO275.

Cosmogenic noble gases including ⁸¹Kr ($T_{1/2} = 0.21$ m.y.) are summarized in the table below. One achondrite we have measured before is also given for comparison. The ages have been calculated with the manner similar to Miura *et al.* (1998). We found moderate discrepancy between the cosmic-ray exposure ages obtained from ²¹Ne and ³⁸Ar (T_{21} and T_{38}). Although T_{38} is close to T_3 , cosmogenic ³He and ³⁸Ar seems to be sensitive against weathering compared with ²¹Ne. Therefore, as more reliable cosmic-ray exposures we suggest 13 Ma (DHO007) and 12 Ma (DHO275), respectively. On the basis of these exposure ages and ⁸¹Kr-Kr ages, we obtain upper limits of the terrestrial ages of 0.02 Ma for DHO007 and 0.07 Ma for DHO275, respectively. The absolute concentrations of ⁸¹Kr are in the range reported for recently fallen eucrites (Miura *et al.*, 1998), suggesting that they do not have long terrestrial ages comparable to the ⁸¹Kr half life. For the terrestrial ages of meteorites from Oman desert, it has been reported that two achondrites (Martian and lunar meteorites) have long terrestrial ages of 0.34 Ma and 0.5-0.6 Ma (Nishiizumi *et al.*, 2002 and reference therein), whereas others present a terrestrial age peak around 0.015-0.020 Ma (Jull *et al.*, 2002).

	T_3^*	T_{21}^*	T_{38}^*	⁸¹ Kr-Kr*	⁸¹ Kr ^{&}
DHO007 #1 ⁺	10.9	13.6	10.2	13±2	0.087
DHO007 #2 ⁺	9.2	13.1	9.5	11±2	0.11
DHO275	7.2	11.7	8.5	11±3	0.096
NWA011 [§]	11	30	23	39±5	0.15

* in Ma. & in 10^{-12} cm³STP/g. ⁺ bulk chemical composition of the meteorite (Setoyanagi, Ebihara and Yamaguchi, personal com.) is used. [§] Yamaguchi *et al.* (2002).

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Cross-check of radiocarbon dating between the beta ray counting method and the AMS method

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A widespread tephra sedimentary layer is often used as a "key bed" in geology and geography. It means that the age of a tephra layer is used as a criterion to estimate the other layer's age. In Japan, we have a lot of tephra layers of probably less than 50,000 years, and radiocarbon dating is most suitable to date them. Therefore, it is important to establish radiocarbon dating method of tephra layer with high levels of reliability. Although many ¹⁴C ages have been reported for the tephra layer in Japan, they vary widely even for the same tephra in many cases. Hence, it is important to clarify the reasons for such scattering among the obtained ages.

Aira-Tn(AT) ash layer is one of the major widespread tephra distributed in Japan, covering almost the whole area of the Japanese Islands. Many ¹⁴C ages have been reported for the AT ash. However, ¹⁴C ages of AT ash vary widely. To obtain those ages, two types to measure ¹⁴C have been used. One of them is the use of a counter to measure the beta ray which is emitted when ¹⁴C decays. Another one is the Accelerator Mass Spectrometry (AMS) method.

In the reported values, the median value of AT ash, using the beta ray counting method is 21,500yr BP and that using the AMS method is 24,500yr BP. The difference between these two values is about 3,000 years.

Several possibilities are raised to explain the difference in the obtained ages between the two methods; (1) Some systematic bias in the laboratory, since only one laboratory measured ¹⁴C so far by the AMS method. (2) Sample heterogeneity, since the amounts of required carbons for the AMS method is one thousands of those by the beta ray counting method. (3) Difference in the chemical treatment of samples.

By using the AMS method, we determined the age of charcoals from the AT ash. Our results show similar ¹⁴C ages to those measured with the AMS method by the other laboratory. Further, multiple measurements from different portions of the same sample have shown similar ¹⁴C ages. Hence (1) and (2) are not likely to explain the difference and (3) remains as a possibility. To check this, we have been doing cross-checks on ¹⁴C ages of charcoal samples that were taken from the same AT ash layer, but measured with different methods. Through such experiments, we hope to reveal that the difference of chemical pretreatments might cause systematic differences of those ¹⁴C ages.

Sm-Nd and Rb-Sr isotopic characters of metamorphic rocks from Howard Hills, East Antarctica

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The Napier Complex in East Antarctica consists of high-temperature granulite facies metamorphic rocks. The Howard Hills is a wide exposure of the Napier Complex at the east of Amundsen Bay. Large blocks of granulites with ultramafic to mafic compositions were found in felsic gneisses at the central part of northern Howard Hills. One of the block was constituted by core portion with olivine orthopyroxene-spinel-phlogopite assemblage and mantle constituted by almost orthopyroxene. Much phlogopite was partly formed at the margin of the block. The possibility of partial melting during metamorphism was suggested for the felsic gneisses in this area. To understand the crustal evolution of the Napier Complex, especially for elucidating the behavior of isotopic compositions during the metamorphism, Rb-Sr and Sm-Nd isotopic analyses were done for the metamorphic rocks from the Howard Hills.

Sm-Nd and Rb-Sr compositions of bulk rock samples from the granulite block were regressed to simple lines on the respective isochron diagrams. The line defined by Sm-Nd composition of them gives an age of 2.66 ± 0.05 Ga with an initial ratio of $^{143}\text{Nd}/^{144}\text{Nd} = 0.50856 \pm 0.00004$. The line regressed by the Rb-Sr composition gives an age of 2.63 ± 0.03 Ga with an initial ratio of $^{87}\text{Sr}/^{86}\text{Sr} = 0.7357 \pm 0.0024$. The coincidence between the Sm-Nd age and the Rb-Sr age suggests that isotopic homogenization of neodymium and strontium at about 2.65 Ga among the metamorphic rocks associating the granulite block. It is possible that the Sm-Nd and Rb-Sr ages of about 2.65 Ga indicate the age of granulite facies metamorphism with partial melting.

Recent results of SHRIMP and CHIME dating of zircon and monazite in the granulites from the Napier Complex show many evidences of a regional geological event at about 2.4 to 2.5 Ga. The ages of about 2.65 Ga in this study probably indicate the age of granulite facies metamorphism at the Howard Hills preceding the 2.4 to 2.5 Ga geological-geothermal event.

20 μm spectroscopy from large ground-based telescopes: Primary results and its potential

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One of the most surprising results of recent infrared observations is the discovery of ubiquitous crystalline silicates in dust shells around young and evolved stars. The crystalline silicates have a lot of sharp emission features in the mid-infrared wavelengths around 10-40 micron. These features have been observed only from satellite observatories such as the Infrared Space Observatory (ISO) since telluric atmosphere is opaque in the mid-infrared wavelengths.

In this decade several large telescopes at high altitude where the atmospheric absorptions are relatively weak become available for infrared observations. The SUBARU telescope is one of the largest infrared telescopes at an altitude of 4200m, and thus useful equipment for infrared observations. We developed a new mid-infrared instrument named COMICS for the SUBARU telescope. It has imaging and spectroscopic capabilities with high spatial resolution in the N-band (~ 10 micron) and the Q-band (~ 20 micron). In the Q-band spectroscopy, spectra between 16-21 micron with a resolving power of 2500 can be obtained. This is a unique and a powerful tool to study crystalline silicate features seen in astronomical objects.

With the COMICS we have a plan to carry out Q-band spectroscopy of stars with the crystalline silicate and obtain spatial distributions of the silicate dust around stars. So far two evolved stars AC Her and HD44179 have been observed. In this presentation we will show details of the COMICS specifications and performances and the results of the Q-band spectroscopy of the stars. We also discuss the potential of the ground-based observations of crystalline silicate features around young stars.

DLA-modeling of metamorphic mineral growth

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Information on the degree of supersaturation is essential to evaluate P - T estimations and predict the pattern formation in metamorphic rocks. Instability of a growing interface at a high degree of supersaturation leads to irregular patterns (Mullins and Sekerka, 1963). The origin of irregular patterns of metamorphic cordierites can be modeled by DLA (Diffusion-limited aggregation) (Miyazaki, 2001), which is the simple statistical model for the universal fractal pattern. For DLA-like growth, the following processes are essential; (1) diffusion-controlled growth, (2) selective growth (enhancement and prevention of growth by surrounding matrix minerals), (3) random spatial distribution of matrix minerals. The processes (2) and (3) correspond to generation of random noise due to the sticking of a finite size random-walking particle in the original DLA model. Formation of DLA-like pattern is expected when diffusion-controlled growth is at a high degree of supersaturation. However, such a pattern is not common in natural metamorphic rocks. The effect of interfacial energy becomes important at a low degree of supersaturation. To simulate pattern transition with increasing effect of interfacial energy, I modeled mineral growth by DLA with a sticking probability depending on interface curvature and random-walk of particles on the grain-boundary. The results show that the pattern changes from a DLA cluster (c) to a compact pattern (a) with decreasing degree of supersaturation (Fig.1). The pattern at a cross-over (b) shares some features of an irregular pattern of garnet in a natural sample (d) (Fig.1). The results suggest that the diffusion-controlled growth pattern is a potential indicator for degree of supersaturation.

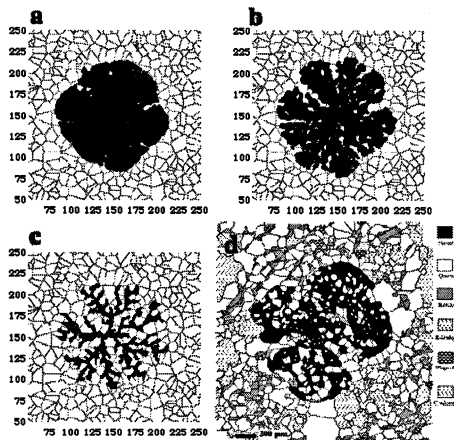


Fig. 1

Short-Term Temporal Variation of PM₁ Chemical Composition Measured in Tokyo

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Near real-time measurements of fine particle (PM₁) chemical composition were made with a 15-min time resolution at a ground-based site in urban city Tokyo in April-May 2003. The measurements were based on a Particle-Into-Liquid-Sampler (PILS), which collects particles into a flow of purified water for on-line analysis with a dual channel ion chromatograph. The measurements successfully revealed the transient events of the particle concentrations over a period of few hours. The maximum total ion mass concentration observed during the period was 30 $\mu\text{g}/\text{m}^3$. On average, nitrate, sulfate, and ammonium were the major components of a suite of inorganic aerosol ions. The most unique events were a sudden increase of nitrate concentrations up to 10-20 $\mu\text{g}/\text{m}^3$ especially in the morning or at midnight. During these events, nitrate concentrations were higher than sulfate concentrations by a factor of 2-5. Chloride concentrations also showed enhancement, which were strongly correlated with nitrate concentrations. The variable chemical properties of these events and insights into sources are presented and discussed.

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Distributions of oxygenated organic compounds in aerosols over the western Pacific and off the coast of East Asia

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Aerosol sampling for dicarboxylic acids, fatty acids, and levoglucosan was conducted from March 15 to April 20, 2001 on board the NOAA R/V Ronald H. Brown over the western North Pacific, East China Sea and the Sea of Japan, as part of the ACE-Asia campaign. Three types of air sampler (high volume air sampler, Micro-Orifice Uniform Deposit Impactor (MOUDI) and an annular denuder sampling system) were used for bulk aerosol sampling, size-segregated aerosol sampling, and organic-acid sampling in gas/particles, respectively. Organic acids and levoglucosan extracted from aerosol samples were derivitized with BF₃/n-butanol and N,N-bis(trimethylsilyl)fluoroacetamide (BSTFA), respectively, and determined by GC-FID and GC-MS.

Concentrations of total dicarboxylic acids, total fatty acids, and levoglucosan were found to be higher off the coast of East Asia than in the remote marine boundary layer. Particularly, concentrations of total dicarboxylic acids exceeding 1 µg m⁻³ were observed occasionally off the coast of East Asia. Due to their high (organic mass)/(organic carbon) ratios, their contribution to the total organic mass and oxygen contents was found to be substantial. The high positive correlations of dicarboxylic acids with nss SO₄²⁻ and NO₃⁻ was obtained, being consistent with the hypothesis that anthropogenic sources are important for diacid concentrations over the East Asia. For fatty acids, both terrestrial and marine biogenic sources were significant where their concentrations were high off the coast of the continent. The relative abundances of dicarboxylic acids between gas and particles were obtained, with C₂-C₅ diacids being found to be predominantly present in particles. The relative abundances between C₂-C₅ compounds were homogeneous throughout the cruise. This study suggests that wet and dry deposition was more important sink than chemical decomposition accompanying fractionation, and that they are stable end products of oxidation of organic compounds in the atmosphere.

Distribution and speciation of bioactive metals in the oceans

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There is increasing evidence that factors controlling the distribution of iron in the world's oceans determine the boundaries of vast areas where primary production is controlled by iron, phosphate and physical factors such as light limitation. Important features of the composition of phytoplankton assemblages, such as the abundance of diazotrophs and the relative abundance of diatoms versus coccolithophores, are also influenced by geochemical processes acting on iron and probably other metals as well. However, the boundaries of these regions are poorly defined, even with increasingly sophisticated biogeochemical models, because our knowledge of the distribution of metals is still quite limited over most of the oceans. This makes it difficult to define the boundaries of these biogeochemical regimes accurately and also makes it difficult to predict how changes in such factors as dust transport or ocean circulation might influence primary production through their influence on metal geochemistry. In this presentation, I will examine regions where new data are most needed, focusing on the direct benefits that additional data would provide. In particular, I will show how complimentary data obtained using isotopic data is an essential part of this project. I will also argue for the importance of speciation measurements, and ultimately, for novel molecular biological diagnostics of physiological conditions like P limitation, that could be incorporated into a measurement-intensive program. Incorporation of novel methodologies and interdisciplinary approaches could be facilitated by incorporating a strong educational component into the program.

Compound-specific isotope analysis of DOC in landfill Leachate

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In an attempt to better characterize the biogeochemical evolution of DOC in leachate, and to develop biogeochemical signatures for the origin of DOC in groundwater, we have developed a new approach focusing on the compound specific ^{13}C analysis of DOC. Samples were collected from the Trail Road Landfill site is located about 25 km to the west of the city of Ottawa in Canada, along with field measurements (Eh, pH, EC, TDS, DO, and T). High Performance Liquid Chromatograph (HPLC) is used to separate organic components into fractions. A Total Inorganic/Organic Carbon (TIC/TOC) Analyzer with He carrier gas then measures the DOC concentration and advects the sample to a Delta^{plus} continuous-flow -IRMS for $\delta^{13}\text{C}$ measurement. The HPLC fraction collector was used to collect dissolved organic compounds, classified by chromatograph peaks and their column retention times. Although each of these instruments individually is used in some laboratories, this is the first time that fraction-separated DOC compounds have been measured with a TIC/TOC analyser interfaced with IRMS. This represents a new operational system and a significant contribution to analytical technology. In addition, the isotopic characterization of each DOC component will be the first compound-specific isotope analyses of DOC in landfill leachate, which has never been attempted, and represents new knowledge.

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The oldest known sediments on Earth: Implications for exobiology

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What do we search for and how do we interpret data bearing on the appearance of the first life? What are the obvious pitfalls in interpreting the complex crustal history of the oldest rocks here or on any other planet? Without a clear understanding of geological relationships among outcrops and without geochronology or structural maps to guide sample collection, return missions from ancient planetary surfaces (e.g. Mars) will always face enormous obstacles. The oldest terrestrial rocks provide a medium for testing hypotheses to be used in the search for life elsewhere. They shed light on the timing and nature of the emergence of a biosphere on Earth-like planets, clarify when conditions became suitable for life and potentially provide a means for bridging what is known about the origin of life viz. molecular phylogenetic analyses and the preserved geochemical record.

As a case in point, isotopically light carbon found in >3.8 Ga metasediments from Akilia (island) and the Isua Supracrustal Belt, West Greenland, is suggestive of biological activity. This implies that metabolically sophisticated life had arisen prior to the end of intense meteoritic bombardments (~3.85 Ga) of the inner solar system. This inference has been challenged on the basis that: (i) the interpretation of zircon geochronology that that the crosscutting granitoid sheet which establishes the minimum age of an Akilia metasedimentary enclave as >3.8 Ga, is incorrect, and (ii) the Akilia Fe-rich quartzite enclave hosting the earliest proposed chemical fossils of life is instead a "metamorphosed (ultramafic) igneous differentiate". The second objection would preclude the presence of biosignatures from the pre-3.8 Ga rock record.

Age relations on Akilia have been studied using U-Pb age depth-profiles in zircons from three separate cross-cutting tonalites, thereby refining assessments of the minimum age of the supracrustals. Zircon cores have compositions consistent with crystallization from the host tonalites and thus their magmatic age is 3.83 ± 0.01 Ga; this establishes a minimum age of the surface hydrosphere and putative evidence for life at that time. Opx + grunerite common to meta-BIFs overprint the Akilia sediments. All trace element and stable isotopic data (PGEs, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\Delta^{33}\text{S}$) obtained thus far and new structural studies guiding the geochemistry (Manning et al., this meeting) instead support a primary sedimentary origin for the Akilia rocks hosting evidence for early life.