

An electrochemical cell across the core-mantle boundary

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The electrical conductivity of the lower mantle reaches ~100 S/m near the bottom of the lower mantle [1], and is likely to increase substantially over the bottom few km due to the temperature jump across the thermal boundary layer at the core-mantle boundary. The main mineral of the lower mantle is MgSiO₃-rich perovskite (MSPv), containing also Fe²⁺, Fe³⁺ and Al. There is an increasing body of evidence that MSPv is a mixed electrical conductor, with charge-hopping between Fe²⁺ and Fe³⁺ predominating at low temperature, but O²⁻ conductivity becoming important at high T [2].

The core and lower mantle are expected to be out of equilibrium with respect to the chemical potential of oxygen (μO₂), whether due to heterogenous accretion of the Earth, or metal/silicate segregation at different P-T conditions from those at the CMB [3]. There will also be a thermoelectric potential due to cooling of the mantle relative to the core over geologic time. Both ΔμO₂ and ΔT set up an electrochemical cell across the CMB; the presence of two modes of conduction allows current to flow, the flux of O²⁻ being balanced by the flow of electrons via Fe²⁺/Fe³⁺ charge-hopping in MSPv, perhaps also in magnesiowüstite.

Assuming a conductivity of 100 S/m at the CMB implies D_O of ~10⁻⁹ m²/s (Nernst-Einstein relation), hence a characteristic length $x=(Dt)^{1/2}$ of only 12 km over 4.5.10⁹ years. In a static mantle, therefore, the effect would be of minor importance. However, plume theory postulates that material from the lower mantle is processed by focussed flow through the bottom few km of the thermal boundary layer at the CMB. This is the advective mode that cools the core. The constant replenishment of material at the CMB greatly increases the flux of O²⁻ across the CMB. For a global plume flux of 3.10¹⁴ kg/a [4], and a velocity boundary layer at the CMB of 30 km [5], we calculate that ~10% of available oxygen would be coulometrically titrated from mantle to core. If "available oxygen" is identified with the Fe³⁺ content of the mantle, the flux of O²⁻ across the CMB of is ~10⁴ moles/s, corresponding to a current of ~2.10⁹ Amps. The amount of O transferred to the core over geological time is trivial (<0.1% of the mass of the core), but the effect may be locally important in altering the redox state of the mantle.

[1] Olsen N. (1999) *Geophys. J. Int.* 138, 179-187

[2] Xu Y and McCammon C. (2002) *J. Geophys. Res.* (in press)

[3] O'Neill H.St.C. and Palme H. (1998) *The Earth's Mantle* (ed. I. Jackson) pp. 3-126. Cambridge University Press

[4] Davies G. F. (1988) *J. Geophys. Res.* 93, 10467-10480.

[5] Davies G. F. (1999) *Dynamic Earth*. Cambridge University Press

Natural and Experimental Mass Fractionation of Transition Metal Isotopes

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Natural variations in the stable isotope abundances of Ti, Fe, Cu and Zn are now well-documented in both terrestrial and extraterrestrial materials (Zhu et al., 2000a, b; 2001; 2002a, b). Three isotope plots for Fe isotopes (ε⁵⁷Fe vs ε⁵⁶Fe) show that Fe in terrestrial biological and non-biological samples and in meteoritic material has isotope variations consistent with formation by mass fractionation of a single isotopically homogeneous Fe source of Fe formed at or before the time of chondrule formation.

Natural variations in Fe, Cu and Zn isotopes in biological materials, including metalloproteins from cultured yeast and bacteria demonstrate unequivocally that fractionations as large as 20ε units in Fe and Cu occur within a single cell.

Experiments carried out in aqueous solution at 25°C show that redox speciation reactions on Cu(I) – Cu(II) and Fe(II) – Fe(III) produces effects up to 40ε units. These inorganic mass fractionation are large, and the considerable variations observed in ε⁶⁵Cu and ε⁵⁷Fe in black smoker deposits are therefore not unexpected.

At the temperatures of silicate and Fe melt formation differences in ε⁶⁷Fe between silicate and metal of ca. 3ε units have been documented. Similar variations are also observed between olivine and pyroxene in spinel lherzolite xenoliths.

Experimental constraints on transition metal isotope fractionation at low temperatures in inorganic and biological systems now starts to produce a framework within which natural variations can be understood. The existence of measurable isotope effects at higher (ca. 1000°C) temperatures offers new opportunities in studies of igneous petrology and planetary differentiation.

Reference

Zhu, X.K. et al., (2000a), *Chem. Geol.* 163, 139-149.

Zhu, X.K. et al., (2000b), *Science* 287, 2000-2002.

Zhu, X.K. et al., (2001), *Nature* 412, 311-313.

Zhu, X.K. et al., (2002a), *Earth Planet. Sci. Lett.* 200, 47-62.

Zhu, X.K. et al., (2002b), *Int. J. Mass Spectrom.* (in press).

Determination of kinetic parameters for individual compounds on release from kerogen by thermal analysis

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Introduction

In order to obtain the activation energy (E) and pre-exponential factor (A) for an individual compound on release from thermal decomposition of kerogen, we analyzed kerogens (in Neogene sediments of the Shinjo basin, Yamagata, Japan) by a thermogravimetric analyzer with a gas chromatograph-mass spectrometer or a mass spectrometer. And we calculated depth profiles of release extents for individual compounds, using a mathematical model.

Results and Discussion

The obtained E and A for six released compounds are shown in Table 1. The rate constants of each compound at 120°C (the onset of the intense petroleum generation in the Shinjo basin) indicated in order of indene > benzene, toluene > phenol > hexane, heptane, whereas the E were inverse in order. Therefore, it was found that hexane and heptane were more strongly bound with kerogen matrix than benzene, toluene, and indene.

Table 1. E , A and rate constants at 120°C of individual compounds on release from kerogen in the Shinjo sediments.

Compounds	E (kcal/mol)	A (s ⁻¹)	Rate constants at 120°C (s ⁻¹)
Benzene	49.0	2.46x10 ¹²	1.41x10 ⁻¹⁵
Hexane	55.3	2.60x10 ¹⁴	4.69x10 ⁻¹⁷
Toluene	50.5	6.83x10 ¹²	5.75x10 ⁻¹⁶
Phenol	52.8	4.95x10 ¹³	2.19x10 ⁻¹⁶
Heptane	54.6	2.21x10 ¹⁴	9.77x10 ⁻¹⁷
Indene	46.7	4.90x10 ¹¹	5.34x10 ⁻¹⁵

The depth profiles of release extents for six compounds were different in temperature (therefore, depth) each other. Furthermore, the model indicated that hexane and heptane of aliphatic hydrocarbons were released in sediments deeper than benzene, toluene and indene of aromatic ones. These depth profiles were similar in pattern to those reported for solvent extractable aliphatic and aromatic hydrocarbons in the Shinjo sediments.

References

- Oba M., Mita H. and Shimoyama A., (2000), *Res. Org. Geochem.* **15**, 33-42.
Oba M., Mita H. and Shimoyama A., (2002), *Geochem. J.* **36**, 51-60.
Shimoyama A. and Oba M. (2002), *Res. Org. Geochem.* in press.

Sea surface temperatures off the east coast of the Japanese Islands since the last glacial maximum inferred from oxygen isotope of foraminiferal tests

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The Northwest Pacific Ocean is a region where pronounced temperature changes occurred in the surface water between the cold Oyashio Current and the warm Kuroshio Current in the glacial-interglacial cycles. Four piston cores were collected from the Oyashio Current to the Kuroshio Current regions off the east coast of the Japanese Islands. The oxygen isotope differences between benthic and planktonic foraminiferal tests increased from the northernmost core (0.9 per mil) to the southernmost core (3.7 per mil) during the Holocene, due to increasing sea surface temperature (SST) towards the south. In contrast, these differences are much smaller during the last glacial maximum (LGM) than during the Holocene, especially in the case of the southernmost core (2.0 per mil). This suggests that the water mass similar to the present surface water off the east coast of the Japanese Islands shifted southward at the LGM.

The SST off the east coast of the Japanese Islands can be calculated from the relationship between the present temperature differences of the surface and bottom at the four core sites and the oxygen isotope differences of benthic-planktonic foraminiferal species. The results show that the SST at the northernmost core site remains almost the same as present, because the cold Oyashio Current has occupied the site since the LGM. On the other hand, the decreased SST of about 9 degrees centigrade is found at the southernmost core site, where the Kuroshio Current was replaced by the mixed water mass between the Oyashio and Kuroshio Currents at the LGM.

Such a water mass movement is also supported by the carbon isotope shifts of planktonic foraminiferal tests in the four cores. Furthermore, abnormal light carbon isotope values, which must be related to methane hydrate, are observed in the northernmost core during the LGM.

Limited Pleistocene glaciation in Deep Freeze Range, Northern Victoria Land, Antarctica, derived from in-situ cosmogenic nuclides

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The Cenozoic evolution of landscape and climate in Antarctica remains controversial. One hypothesis assumes that the Dry Valleys with their very cold and hyperarid conditions prevailing since at least Mid-Pliocene are representative for the entire continent (Denton et al. 1993). On the other hand, it was argued that the Dry Valley's tectonic block experienced a unique uplift history and thus a special climatic and landscape evolution (Van der Wateren et al., 1999).

The latter hypothesis can be tested by investigating ice free areas outside the Dry Valleys. The Terra Nova Bay region (75°S), Northern Victoria Land is one of the very few appropriate spots in Antarctica for this purpose. We determined ages of erratics and scoured bedrock with in-situ produced cosmogenic nuclides ¹⁰Be, ²¹Ne and ³He.

We investigated one site near an outlet glacier of the East Antarctic Ice Sheet (EAIS) and one near a local mountain glacier in order to evaluate potential differences in response to climate changes between ice sheet and local glaciers.

The ages obtained show that the mountains in Northern Victoria Land are free of ice since at least 4 Ma. This implies a formation of the landscape prior to Mid-Pliocene and very restricted erosion since then. Erratics on valley walls yield much younger exposure ages and thus indicate that subsequent ice coverage was restricted to valleys, both along the EAIS draining paths and in the local mountain glacier networks. At least three Pleistocene ice advances could be dated, the youngest of which is consistent with the Last Glacial Maximum of the northern hemisphere.

This set of exposure ages is consistent with the findings from the Dry Valleys: the Antarctic climate was cold and hyperarid since the Pliocene. Particularly, it indicates only restricted advances of both mountain glaciers and plateau drainage glaciers throughout the Pleistocene.

References

- Denton, G.H., Sugden, D.E., Marchant, D.R., Hall, B.L., and Wilch, T.I., (1993), *Geogr. Ann.*, **75A**, 155-204.
 VanderWateren, F.M., Dunai, T.J., Balen, R.T.V., Klas, W., Verbers, A.L.L.M., Passchier, S., and Hergers, U., (1999), *Global and Planetary Change*, **23**, 145-172.

The Fish Canyon Tuff: Ar-Ar versus U-Pb age discrepancy re-assessed

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Sanidine from the Fish Canyon Tuff (FCT; San Juan volcanic field, Colorado USA) is widely used as a neutron fluence monitor in ³⁹Ar-⁴⁰Ar dating. Intensive calibration work carried out over the last two decades has converged at an Ar-Ar age of ca. 28.0 Ma (Villeneuve et al., 2000, and references therein). This age, however, is distinct from a mean ²³⁸U-²⁰⁶Pb single-zircon age of 28.41±0.05 Ma (Oberli et al., 1990) and a similar, recently reported high-precision age of 28.478±0.024 Ma (Schmitz and Bowring, 2001).

New petrologic evidence suggests that the batholithic-scale magma chamber was cooling to near-solidus conditions before being partially remelted by mafic recharge, ultimately triggering eruption (Bachmann et al., in press). This model is supported by zircon U-Pb data and ³⁹Ar-⁴⁰Ar ages obtained on phenocrysts from the Pagosa Peak Dacite (precursor of FCT), the FCT (outflow facies), Nutras Creek Dacite (post-FCT lava) and three xenoliths from the FCT exhibiting FCT mineralogy. Partially resolved disequilibrium-corrected ²³⁸U-²⁰⁶Pb dates obtained for 24 out of 25 air abraded zircons span an interval of ca. 28.62–28.04 Ma and yield a weighted mean age of 28.36±0.06 Ma (95% c.l. ext.), with MSWD=26 indicating scatter grossly in excess of analytical precision (typically, 1σ ≤ 0.05 Ma for an individual measurement). There is no correlation of these U-Pb ages with lithology.

While 61 out of 62 ³⁹Ar-⁴⁰Ar total fusion experiments on sanidine phenocrysts from the three eruptive lithologies gave indistinguishable mean ages at 27.99±0.08 Ma, plagioclase, biotite and hornblende yield slightly higher ages of 28.2–28.3±0.2 Ma. CO₂-laser 24-step incremental heating on a feldspar megacryst from a pumice of the FCT produced a relatively flat plateau at 28.23±0.18 Ma (~75% of argon release), with the last eight steps (<20 % of argon release) yielding an inverse-isochron age of 28.75±0.32 Ma.

We interpret the pre-28.0 Ma age dates as evidence for extended magma chamber residence, which invalidates the use of FCT zircon ages as a constraint for Ar-Ar calibration.

References

- Bachmann O., Dungan M.A. and Lipman P.W., (2002), *J. Petrol.* **43** (in press).
 Oberli F., Fischer H. and Meier M., (1990), *7th Int. Conf. Geochr. Cosmochr. Isot. Geol., Abs. Vol. 27*, 74 (abstr.).
 Schmitz M.D. and Bowring S.A., (2001), *Geochim. Cosmochim. Acta* **65**, 2571-2587.
 Villeneuve M., Sandeman H.A. and Davis W.J., (2000), *Geochim. Cosmochim. Acta* **64**, 4017-4030.

Calcite formation by picoplankton

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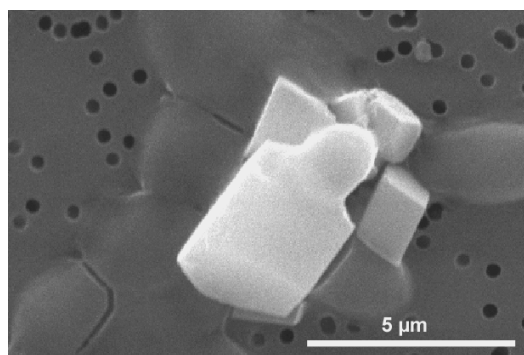
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Introduction

Calcite precipitation by picoplankton in hardwater lakes has been observed in a few recent studies. Biologically induced precipitation due to a change of the chemical environment near the cell wall or the biologically controlled process where the cell surface acts as a nucleation site are both possible mechanisms for biomineralization. However, not only the details of the mechanism but also the role of the calcite saturation state in precipitation still remain unclear.

Figure 1: SEM-image of calcite crystals on the cell surface of *Synechococcus* deposited on a 0.2µm filter.



Experiments and results

In order to investigate the influence of the saturation state we performed biomineralization experiments under controlled chemical conditions.

Crystal formation was induced by adding a culture of *Synechococcus* to supersaturated solutions of CaCO₃ (CaCl₂/NaHCO₃) of different concentrations. An abiotic calcite solution was used as a reference system. Due to the photosynthetic activity the uptake of CO₂ (corresponding to a rise of pH) by the microorganisms lead to an increase of CaCO₃-supersaturation. Precipitations occurred within 20 hours. The pH was monitored by an electrode. Within the precipitation period, samples were taken at a high time resolution to gain insights into the process itself.

The morphology of the precipitates was studied by Scanning Electron Microscopy (SEM, Fig.1) and in-situ Atomic Force Microscopy (AFM).

As illustrated in Fig1, cells are either incorporated in the crystals or aggregate with them. Thus, the biomineralization of calcite is most probably a combination of biologically induced and controlled mechanism.

Mineral chemistry of mafic and ultramafic xenoliths from Jurassic basalts in southern Sweden

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About 100 volcanic necks occur in the central part of the S-Swedish province Scania. The alkaline magmas of basanitic to melanephelinitic composition (Tappe et al. 2001) produced at the southern margin of the Fennoscandian Shield carried a variety of xenoliths from several levels in the Earth's mantle and crust.

Based on the mineralogical composition and textural features, two major groups of ultramafic to mafic xenoliths can be distinguished. One group comprises deformed porphyritic peridotites, the other consists of granular or banded rocks which represent cumulates. The samples of the first group are lherzolites or wehrlites, while the cumulates can be subdivided into ±olivine bearing websterites and clinopyroxenites, lherzolites and gabbros or anorthosites.

Microprobe analyses emphasize the differences between the various xenolith types. The deformed peridotites are both characterized by primary spinel phases, Mg-Al chromites and chromites, respectively. Especially in the wehrlites a secondary fine-grained Cr spinel phase occurs which is associated with olivine, clinopyroxene, glass and a hydrous mineral in discrete patches. Recalculation of all phases together points to existence of a former amphibole phase.

The ultramafic cumulates are characterized by relative large Cr-free spinel crystals, the gabbros and anorthosites contain tiny ilmenite or titanomagnetite grains. The olivine and both pyroxenes of the cumulates have lower Mg-numbers than those of the deformed peridotites, decreasing from pyroxenites towards gabbros as typical for layered intrusions. The distribution of pyroxene analyses in the quadrilateral and various bi-variate element plots, however, does not support the idea of belonging to one single layered sequence. Further, there seems no proof for a genetic relationship between gabbros and anorthosites.

Results of geothermometry calculations using two-pyroxene thermometer of Wells (1977) and Brey & Köhler (1990) range from 1000 to 1100°C for the deformed lherzolites – this is in accordance with values given by Griffin & Kresten (1987) – but scatter between 900 and 1200°C for the ultramafic cumulates.

References

- Brey G.P. and Köhler T. (1990), *J. Petrol.* **31**, 1353-1378.
Griffin W.L. and Kresten P. (1987), *John Wiley & Sons*, 101-106.
Tappe S., Obst K. and Solyom Z. (2001), *Terra Nostra* **5/01**, 65-68.
Wells P.R.A. (1977), *Contrib. Mineral. Petrol.* **62**, 129-139.

Is BET surface area proportional to reactive surface area?

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Introduction

It is universally accepted that one of the key variables that governs the amount of mineral dissolution that can take place is the amount of mineral surface area available for dissolution. In recognition of this fact the dissolution rates of minerals, as determined in the laboratory, are almost without exception normalised to mineral surface area, typically the specific surface area as determined by gas adsorption (normally N₂) and application of the BET isotherm. But what if the BET surface area of a mineral is not proportional to the reactive surface area of the mineral?

Previous work

Most workers accept that BET surface area is proportional to reactive surface area. However two studies that oppose this view stand out in the literature. Holdren and Speyer (1985, 1987) famously found that feldspar dissolution rates in batch experiments were not proportional to BET surface area over a BET surface area range of 0.05 – 4.48 m² g⁻¹. Gautier *et al.* (2001) dissolved quartz under far from equilibrium conditions using flow through apparatus and found that mass normalised dissolution rates remained constant whilst BET surface area normalised dissolution rates decreased as BET surface area increased from 0.07 to 0.37 m² g⁻¹. The BET surface area increase was attributed to unreactive etch pit walls exposed as etch pits deepened.

Current work

In this study powders of hornblende, anorthite and orthoclase ranging in grain size from 180 – 150 μm to 10 – 20 μm and BET surface area from 0.10 – 0.70 m² g⁻¹ (hornblende), 0.08 – 0.42 m² g⁻¹ (anorthite) and 0.07 – 0.48 m² g⁻¹ (orthoclase) were dissolved in pH 3 HCl in continuous flow reactors in order to determine whether the surface area normalised dissolution rates were constant for powders of the same mineralogy but differing BET surface area. No significant differences in dissolution rates were found. All grain sizes gave dissolution rates of c. 1 x 10⁻¹² mols m² s⁻¹ (hornblende), c. 5 x 10⁻⁹ mols m² s⁻¹ (anorthite) and c. 1 x 10⁻¹² mols m² s⁻¹ (orthoclase). These results indicate that BET surface area appears to be proportional to reactive surface area for these minerals under far from equilibrium dissolution conditions.

References

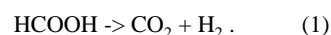
- Gautier J.-M., Oelkers, E.H. and Schott J. (2001) *Geochim. Cosmochim. Acta* 65 1059 - 1070
 Holdren G.R. and Speyer P.M. (1985) *Geochim. Cosmochim. Acta* 49 675–681
 Holdren G.R. and Speyer P.M. (1987) *Geochim. Cosmochim. Acta* 51 2311–2318

An experimental study of aqueous formic acid decomposition rates as a function of pH and temperature from 175 to 250° C

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The overall goal of this work is the improved understanding of rates of reactions among aqueous organic species at elevated temperature. Formic acid decomposition has been studied due to 1) its role as a reaction intermediary of the destruction of other aqueous organic species, such as oxalic acid 2) the overall potential importance of carboxylic acids in geochemical processes, and 3) its simple structure/formula. Aqueous formic acid decomposition rates were quantified through closed system experiments performed by heating initial solution containing HCOOH ± HCl or NaOH in rocking titanium reactors and in sealed quartz tubes. After a brief reaction removing residual oxygen in each reactor, aqueous formic acid was consumed exclusively by the reaction



Concentrations of the liquid and gas phases throughout the experiments were verified and quantified using Raman spectroscopy. Preliminary data indicates that the rates of this reaction (r) are first order with respect to aqueous HCOOH⁰ concentration ([HCOOH⁰]) and consistent with

$$r = k [\text{HCOOH}^0] \quad (2)$$

where k refers to a rate constant. This rate dependence is consistent with the assumption that reaction (1) is a homogeneous reaction which is not catalysed by the reactor wall surfaces (e.g. Akiya and Savage, 1998). As [HCOOH⁰] decreases with increasing pH due to aqueous formic acid dissociation, so do the rates of reaction (1). Regression of 250° rate data yield a rate constant of 9x10⁻⁴ s⁻¹ which is in rough agreement with formic acid decay rates reported by Small and Manning (1993). This rate suggests a formic acid half life of 2.6 days at pH 7, but less than one hour at pH<3. Preliminary data suggest this rate is strongly temperature dependent; a preliminary rate constant of 1.5x10⁻⁷ s⁻¹ was found for 175° C. Further work aimed at assessing the potential catalytic effect of the presence of mineral surfaces is planned prior to the meeting.

References

- Akiya N. and Savage P. (1998) *AIChE J.*, 44, 405-415.
 Small, J.S. and Manning, D.A.C. (1993) *In Geochemistry of Clay-Pore Fluid Interactions*, Chapman-Hall, London, p181-212.

Water – rock reaction experiments for application to the formation mechanism of Kuroko deposits

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We performed water – rock interaction experiments using the artificial seawater containing no SO_4^{2-} and several kinds of rocks to clarify why the Kuroko hydrothermal solution contains high amount of K, Ca and Ba which are enriched in Kuroko deposits and surrounding altered rocks.

Experimental study on the fresh rock (basalt, andesite, rhyolite etc) – artificial seawater interaction indicates that the dissolution rate of K accompanying the interaction with the acidic rock is faster than that accompanying the interaction with other rocks, and consequently K is enriched in the solution reacted with acidic rocks. However, Ca which is the source of anhydrite and gypsum is taken into rocks accompanying the interaction with the fresh acidic rocks.

The experiments using weakly altered dacite containing small amount of smectite from the Kuroko mining area were also performed. The elemental mobility accompanying the interaction with the fresh acidic rocks is quite different from that accompanying the interaction with the altered acidic rocks. Namely, there are two (early and late) stages of the precipitation of smectite accompanying the alteration of acidic rocks. The incorporation of Mg and Ca and dissolution of Na and K occur in the fresh acidic rock experiments corresponding to the early stage of hydrothermal activity, and the ion exchange reactions accompanied by the incorporation of Mg into rocks and dissolution of Ca and K occurs in the weakly altered rock experiment corresponding to the late stage of hydrothermal activity. The dissolution rate of K in the late stage is still large, and Ca which is incorporated into rocks in the early stage dissolves into solution in the late stage. The degree of Ba mobility in the later is larger than that in the early stage. Therefore, the present study suggests that large amounts of barite, anhydrite and gypsum in the Kuroko deposits would have precipitated from the hydrothermal solution generated in the late stage due to the interaction of hydrothermal solution with altered acidic rocks.

Sources of the dissolved inorganic carbon in shallow coastal waters

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In the present study the sources of dissolved inorganic carbon (DIC) in pore water of surficial carbonate-rich sediments in the coastal marine zone in the Gulf of Trieste (northern Adriatic) were determined using stable carbon isotopes and chemical analyses.

Discussion of results

The diagenetic model developed by McNichol et al. (1988) was used to understand the observed variations of DIC and corresponding C isotopic composition. In this model major processes affecting the pore water concentration of DIC are considered: oxidation of organic matter, dissolution and precipitation of CaCO_3 , and irrigation by benthic infauna. The transport of DIC due to biological irrigation was described using the non-local source model (Emerson et al., 1984). Changes in the concentration of DIC by oxidation of organic matter or equilibration with CaCO_3 were described by the CO_2 -production rate, $R_c(z)$. $R_c(z)$ is assumed to decrease exponentially with depth and in our model it is described by two exponential functions. The same diagenetic model with the best-fit parameters obtained by fitting the pore water profiles of DIC, was used to describe the profiles of ^{13}C isotopic composition of DIC. It was found that this model does not reproduce the observed profiles. Data from all the cores showed that the inorganic carbon added to pore water during early diagenesis was enriched in ^{13}C with respect to C_{org} . The possibilities which could be responsible for this enrichment were further examined using the calculated value of $R_c(z)$ or by C isotope mass balance equation (McNichol et al., 1991).

Conclusions

Dissolution of carbonates in these sediments appears to be controlled by seasonal processes and contribution to DIC production was estimated to be 57%, 14% and 35% in June 1995, in September 1995 and January 1996, respectively. The enrichment of ^{13}C observed in DIC could be explained with isotopic exchange with bottom water, or the diffusion of ^{13}C -depleted H_2CO_3^* from pore water to bottom water.

References

- Emerson S., Jahnke R., and Heggie D. (1984) *J. Mar. Res.* **42**, 709-730.
- McNichol A.P., Lee C., and Druffel R.M. (1988) *Geochim. Cosmochim. Acta* **52**, 1531-1543.
- McNichol A.P., Druffel R.M., and Lee C. (1991) In *Organic Substances in Sediments and Water* (ed. R.A. Baker), Vol. 2, Chap. 12, pp. 249–272. Lewis Publishers.

Evolution of the groundwater geochemistry in sulphide-rich mine tailings remediated by applying soil cover, Kristineberg, northern Sweden

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At the Kristineberg mine in northern Sweden, sulphide-rich tailings were remediated in 1996 by applying till covers. The sulphides were isolated from the atmosphere to prevent oxidation. This was realized either by covering the tailings with till in combination with a raised groundwater level, thereby saturating the tailings with water, or by covering with compacted clayey till overlain by till (dry cover). During and after 1998, 14 groundwater pipes were installed in the tailings impoundment to study the effects of the remediation. Sampling has been performed on 32 occasions during a period of more than 3 years, and the samples were analysed for major elements and metals, anions, pH, redox and conductivity. The results show that the groundwater characteristics vary considerably in the impoundment, even under the same type of cover. The pH is generally increasing and redox is generally decreasing across the studied impoundment, where some areas showed quicker changes than others. The main source reaction of the pollution thus seems to have slowed down. Only As could be released at some locations, possibly as a result of an increased pH. Before the remediation, metals released by sulphide oxidation were partly secondarily retained in the tailings below the oxidation front. Such metals, mainly Fe, S, Mg and Zn, have been remobilised by a first washout as a result of the raised groundwater level. A second washout by the clean groundwater from the western till slope, combined with the slowing down of the acid-producing reactions should lead to significant and general decreases in the observed concentrations throughout 2004-2005. However, iron precipitations occur in some places, creating a secondary acidification, and resulting in a secondary buffering.

Iron Isotopes in Human Blood

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Introduction

The study of natural isotopic variation for heavy elements has had a significant influence in many research fields such as biology, planetary, earth, and environmental sciences (Anber et al., 2000, Beard et al., 1999, Brantrey et al., Zhu et al., 2001). Because Fe has a relative mass difference that is likely to be sufficient to record biologically-induced isotopic fractionation. In this study, precise Fe isotopes for several geochemical and biological materials have been measured by means of multiple collection-inductively coupled plasma-mass spectrometry (MC-ICPMS).

Isotopic Analysis and Results

Precise and accurate isotopic analysis of Fe could be achieved by (a) reduction of polyatomic interference by utilising a desolvating nebulizer, (b) external correction of mass discrimination effect using Ni, and (c) chemical separation technique for Fe from complex organic compounds using 4-methyl-2-pentanone. The resultant precisions (internal precision or repeatability) of the measurements for both the $^{56}\text{Fe}/^{54}\text{Fe}$ and $^{57}\text{Fe}/^{54}\text{Fe}$ ratios were better than 0.01% for solution samples at the 95% confidence level. Using the present technique, the $^{56}\text{Fe}/^{54}\text{Fe}$ and $^{57}\text{Fe}/^{54}\text{Fe}$ ratios for human red blood cells were measured. The resulted Fe isotopic ratios for human red blood cells were approximately 0.17% per mass lighter than those for IRMM-014 reference material.

It was recognized that ferrous Fe was lighter than ferric Fe in aqueous solutions (Johnson et al., 2002), and generally vegetables and animals absorb ferrous Fe. This indicates lighter iron isotopic composition of human red blood cells can be caused by oxidation-reduction in food chain (Zhu et al., 2002).

References

- Anbar A. D., Roe J. E., Barling J. and Nealson K. H., (2000), *Science*, 288, 126-128.
- Beard B. L., Johnson C. M., Cox L., Sun H., Nealson K. H. and Aguiler C., (1999), *Science*, 285, 1889-1892.
- Brantley L. S., Liermann L. and Bullen D. T., (2001), *Geology*, 29, 535-538.
- Johnson C. M., Skulan J. L., Beard B. L., Sun H., Nealson K. H. and Braterman P. S., (2002), *Earth Planet. Sci. Letters*, 195, 141-153.
- Zhu X. K., Guo Y., O'Nion R. K., Young E. D. and Ash R. D., 2001, *nature*, 412, 311-313.
- Zhu X. K., Guo Y., Williams R. J. P., O'Nion R. K., Matthews A., Belshaw N. S., Canters G. W., Waal E. C., Weser U., Burgess B. K. and Salvato B., (2002) *Earth Planet. Sci. letters*, in press.

XAFS characterization of La and Nd coprecipitated with Mn dioxide and Fe oxyhydroxide

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Introduction

Ohta et al. (2000a, b) and Ohta and Kawabe (2001) have experimentally and theoretically studied the partitioning reaction of rare earth element (REE) between Fe-Mn deposit and seawater. When analysing their distribution coefficients theoretically, we need to correct the structural changes, because lanthanide (Ln) complexes are not usually isomorphous in the entire Ln series. Ohta and Kawabe (2001) pointed out that preferential adsorption of light Ln onto δ -MnO₂ is obvious compared with their adsorption onto FeOOH. We have tried to characterize the local structure of Ln coprecipitated with δ -MnO₂ and FeOOH with XAFS spectroscopy, which is recently used to examine structural information of the trace amount of element in poorly crystallized material.

Results and discussion

The δ -MnO₂ and FeOOH adsorbing La or Nd were prepared according to Ohta and Kawabe (2001). We express them as Ln/ δ -MnO₂ and Ln/FeOOH (Ln = La and Nd). The La-L_{III} and Nd-L_{III} XAFS spectra were recorded in the fluorescence mode at the BL12C of KEK-PF at under atmosphere and room temperature (Tsuno et al., 2000).

XANES spectra for Ln/ δ -MnO₂ are quite similar to those for Ln/FeOOH. This result indicates that a La and/or Nd form with δ -MnO₂ (Ln(OH)_n-mH₂O) is almost the same as those with FeOOH: the number of hydroxyl ions ligating Ln³⁺ ions does not change between Ln/ δ -MnO₂ and Ln/FeOOH (Ohta and Kawabe, 2001).

The EXAFS spectra of Ln/ δ -MnO₂ do not particularly differ from those for Ln/FeOOH. Fourier transfers spectra of Nd/ δ -MnO₂ and Nd/FeOOH have one large peak, but those of Ln/ δ -MnO₂ and La/FeOOH have the multiple shells. The fitting results of first shell (La-O and Nd-O) suggested that the coordination number of La coprecipitated with δ -MnO₂ is possibly different from those with FeOOH. This result will be explained by the hydration change of La.

References

- Ohta A. et al. (2000a), *Geochem. J.* **34**, 439-454.
 Ohta A. et al. (2000b), *Geochem. J.* **34**, 455-473.
 Ohta A. and Kawabe I. (2001), *GCA* **65**, 695-703.
 Tsuno H. et al. (2000), *PF Activity Report* **18B**, 126.

Geochemical behavior of minor elements and REE in loam and andosol

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Purpose

We studied the geochemical behavior of natural analogue elements, particularly rare earth elements (REE), U and Th in soil environment.

Samples and analytical methods

The samples were collected from outcrop along the mountain path in Yanagawa Hadano city, Kanagawa Pref., Japan. Point A is the cross section of only andosol and point B is the cross section of soil changing from andosol to loam. These samples were analyzed for major elements, minor elements and REE by using ICP-MS and XRF. Minerals in the samples were identified by X-ray diffraction method (XRD).

Results and Discussion

The minerals consisting of the soil for the primary minerals are feldspar, volcanic glass, olivine, pyroxene, magnetite, zircon etc and the secondary minerals are kaolinite, halloysite, allophane, smectite, maghemite, goethite etc. It is possible that the solubility of these minerals is causing a great effect to the soil elemental mobility. To see the behavior in soil, all the concentration is normalized by Al concentration by using its stability, because it is generally accepted that Al migration is very small due to very small solubility of Al-bearing minerals (halloysite etc). From the result, it is apparent that the concentration of minor elements and REE with depth, and the variation is different from element to element. These difference depends on the solubility of minerals and rock facies. Namely it was found that the behaviors are considerably different in andosol and loam. From the relation between loam and the elements in minerals, it is considered that physical parameters (ionic radius, ionpotential etc) are greatly affecting.

Conclusion

Variation of minor elements during weathering is affected by variety of primary minerals consisting of soil and solubility of minerals. There is significant relation between physical parameter, and concentration change in REE. As to the elemental mobility, REE removed from the soil due to the long-term (about 6,000 years) weathering, but the degree of elemental mobility of REE is less than that of alkali and alkali earth elements but more than that of immobile elements such as Fe, Al, and Mn. U and Th mobilities are very small.

Direct phylogenetic and isotopic evidence for multiple groups of archaea involved in the anaerobic oxidation of methane.

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The biological oxidation of methane by anaerobic microorganisms is a significant sink for methane in the marine environment. Although there is convincing biogeochemical evidence for anaerobic oxidation of methane (AOM) by methanotrophic archaea and sulfate-reducing bacteria, the identity of these uncultured microorganisms is only now being described. In this study, we examined the diversity of archaeal and bacterial assemblages involved in AOM using directly coupled isotopic and phylogenetic analyses at the level of single cells. The combined application of fluorescent *in situ* hybridization and secondary ion mass spectrometry (FISH-SIMS) identified two phylogenetically distinct groups of archaea (ANME-1 and ANME-2) from marine methane seeps that were extremely depleted in carbon-13 (-83 ‰) and appear to be capable of directly oxidizing methane. These archaeal groups were observed to exist as monospecies aggregates or single cells as well as in physical association with bacteria including, but not limited to, members of the sulfate-reducing *Desulfosarcina*. The results from this work illustrate the complexity of the microbial communities and possible mechanisms involved in AOM. FISH-SIMS is an effective approach for understanding the dynamic microbial interactions within diverse methane-associated communities and may provide a useful culture-independent tool for deciphering the metabolic function of other environmentally significant microorganisms *in situ*.

Lunar constraints on core formation: a new model with many implications

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The widely accepted iron-cores-by-percolation model is invalidated in two ways. The mantle has preserved, at least since 3.8Ga, a nearly chondritic Ni:Co (~20) despite Ni's tenfold higher liquid Fe/silicate partition coefficient. Although the coefficients do even up at mid-mantle pressure, most melting and segregation would have been at low pressure. Secondly, its essential corollary, the provision of a siderophile- and water-rich 'late veneer' after core completion (dated at ~4.45Ga by the ending of mantle Pb depletion, if attributed to Fe percolation), is denied by the Moon, which never underwent a late veneer (Taylor & Esat 1996), and was in Earth orbit by 4.50Ga (Lee & Halliday 1998).

The new core genesis model must work at least all the way from Mercury to Jupiter's Io, Ganymede and watery-surfaced Europa. In the presence of a dense and high-opacity radiatively cooled nebular disc the growing protoplanets would have acquired an accretion-rate controlled temperature and internal convection, largely independent of orbit radius. Erupted magmatic FeO was reduced to Fe by the nebular atmosphere and 'subducted'. The dense Fe-loading of the downwelling limb ensured its deep penetration, with the Fe dropping off at the bottom, thus accelerating convection and core formation. Transfer to the core of mantle chalcophiles and siderophiles took place across the CMB but was delayed by the expulsion of silicate dross from the core. The CMB was sealed at ~4.45Ga by the build-up of subducted primitive crust to start forming D", leaving a time-window for transfer, evident in the Hf-W data for Earth and Mars (Lee & Halliday). This function of D" denies that mantle plumes can start at the CMB. Planetary core formation was terminated (= 'age of the Earth') by nebula departure (4561Ma?), with comets and the Great Planets incorporating some of the potentially ~1000 Earth-ocean volumes of total reaction water expelled with it. The model makes C and S the preferred core diluents. Entry of U and Th is possible. Much water entered the early-Earth mantle, as seen in komatiites (e.g. -Nb anomalies), ensuring their high-melting magmagenesis without a need for plumes.

Such early acquisition of the Moon, its distinct siderophile composition and the dynamics of the Earth-Moon system suggest tidal-drag capture by a hot low-viscosity Earth, rather than by impact. The predominance of prograde satellites in the Solar System implies a tidal mechanism for their capture too (Counselman, 1973, *Ap.J.*), the retrograde ones (bar Triton) having 'wound in' to coalescence. So most non-gas planetary growth was completed in nebula-present conditions. Thus their growth would have been much faster than by impact alone because nebular-atmospheric drag, combined with their accretion-generated partially melted state, provided a much bigger (tidal) capture cross-section for planetesimals.

The extent to which asteroids possess cores is put in doubt. Small bodies would cease convecting and resurfacing themselves very soon after nebular departure, leaving iron and lavas on their surface as sources of iron and eucrite meteorites.

Productivity markers: inorganic and isotopic proxies versus biomarkers

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During ODP Leg 167 aiming at the long-term reconstruction of the California current system a dedicated hole (E) has been drilled at site 1017 60 km offshore Point Conception. Nowadays this location is situated within an upwelling center. The core interval presented here spans the continuous uppermost four sections – dated by ^{14}C AMS as the time frame of the last 25 ka with nearly constant sedimentation rates – and hence changes in concentrations equal changes in accumulation rates. The trace element contents point to oxygen depleted conditions at the sediment-water interface for the time interval investigated.

A variety of possible productivity proxies have been determined, ranging from inorganic measures as $\text{Ba}_{(\text{bio})}$, the nitrogen isotopic composition of the sediments, to a number of organic biomarker concentrations.

The signature of biogenic barium in the sediments is overwhelmed by the varying contents of Ba-rich K-feldspar, which account for more than 90% of the sedimentary Ba. The nitrogen isotopic composition changes rapidly from low values in the glacial to elevated values in the Bölling/Alleröd, then back to lower values in the Younger Dryas and finally to high values in the Holocene. But this change can be attributed likewise to a local variation in productivity or a more than regional variation in the influence of subtropical water masses with ^{15}N enriched nitrate.

The total organic carbon contents mimic the large changes of the $\delta^{15}\text{N}$ signal: Low values in the glacial and the Younger Dryas, elevated ones in the Bölling/Alleröd and the Holocene. The increase in the uppermost centimetres is attributed to incomplete early diagenesis. This is reflected by the highest biomarker concentrations there, too.

The chlorophyll- and pigment-derived compounds measured – total chlorins, phytol, loliolide, isololiolide – confirm the trend of TOC. And they confine the variations as changes in marine export productivity as the mentioned compounds differ in their resistance to degradation under varying diagenetic conditions.

The more producer-specific compounds as alkenones, alkandiolols, alkanketols and some sterols point to variations in the primary producer assemblage, especially during the glacial-interglacial transition. But in general they confirm the aforementioned productivity changes in time. And taken together they rule out an artificial alteration of the biomarker signal by diagenesis.

Therefore a combination of less organism-specific organic molecules (chlorins) and more specific biomarkers with different susceptibility to diagenetic alteration (e.g. alkenones and sterols) is suggested as the most practical tool to decipher changes in past ocean productivity in comparable settings.

Geochemical compositions of carbonate rocks and their acid-insoluble residues: implications for the genesis of dolomite

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This paper attempts to constrain the genesis of Paleozoic dolomites developed on the carbonate platform in Guizhou Province, China from studies on the mineralogy, geochemistry, Sr and Nd isotopic composition of carbonate rocks and their acid-insoluble residues from southwestern Yangtze platform. The contents of Na, Fe, Mn and Sr in carbonate rocks are: 371-593 ppm, 155-1787 ppm, 23-62 ppm and 62-136 ppm, respectively for the Triassic dolomites, and; 591-667 ppm, 622-933 ppm, 38-139 ppm and 358-117 ppm respectively for the Triassic limestones. Only the chondrite-normalized rare earth element distribution patterns of the Triassic limestones are approximate to those of shales and the upper continental crust (UCC) while those of most of the dolomite samples are consistent with the REE distribution patterns of seawater. An Early Triassic dolomite section is characterized by a high total REE amount, a remarkable Ce anomaly and abnormal MREE and HREE enrichments. As for the Sr and Nd isotopic composition of carbonate rocks are $^{87}\text{Sr}/^{86}\text{Sr}=0.7080\text{-}0.7083$, $\varepsilon_{\text{Nd}}(0) = -10.7\text{-} -8.4$ and $f_{\text{Sm}/\text{Nd}} = -0.44\text{-} -0.38$. The abnormal REE distribution patterns are corresponding to the positive $f_{\text{Sm}/\text{Nd}}$ values and $\varepsilon_{\text{Nd}}(0) = -6.2$. Geochemical characteristics of the acid-insoluble residues suggest that the composition of continental source region be an indispensable factor that constrains the formation of dolomites. Isotopic and trace elemental compositions suggest that dolomites developed from normal seawater. The formation of dolomites seems to have been reworked by later processes of diagenesis. A forming model has been suggested for the Early-Middle Triassic dolomites under our investigation.

Bacteria and their relevance during formation and preservation of sapropels

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Ongoing biological modification by metabolically active, unique bacteria

Up to 217,000 year-old sapropels and intermediate layers harbor unknown, metabolically active chemoorganotrophic bacteria and archaea. Sapropels exhibit higher cell numbers, higher activities of hydrolytic exoenzymes and higher anaerobic glucose degradation rates than the carbon-lean intermediate layers. This vertical pattern of metabolic activities suggests that the microbial carbon substrates originate from the sapropel layers themselves. Based on the analysis of 16S rRNA gene sequences, the majority of bacteria in sapropels belong to so-far-uncultured green nonsulfur bacteria and constitute up to 70% of total microbial biomass. In addition, Crenarchaeota were found in the microbial assemblage. Since both groups represent only a minor fraction of microbial biomass at the sediment surface, these previously unknown prokaryotes seem to be adapted to sapropels where they apparently still alter the subfossil organic matter.

Subfossil bacterial remains

Isorenieratene and its derivatives have been used as indicators for past anoxia of Mediterranean bottom waters. However, we found isorenieratene also in carbon-lean intermediate layers which were deposited under oxic conditions. Using a highly sensitive method, we could furthermore detect fossil 16S rRNA gene sequences of green sulfur bacteria not only in sapropels but also in the intermediate layers. Based on the vertical distribution of different sequences in the sediments, at least one type of green sulfur bacteria appears to be allochthonous and may have reached the deep-sea sediments via input from rivers or coastal lagoons, rather than representing a pelagic form which thrived in the chemocline of a stratified water column. During formation of at least some of the sapropels, an alleged anoxia of Eastern Mediterranean bottom waters therefore may not have reached the euphotic zone.

References

- Coolen M.J.L., Overmann J. (2000) *Appl. Environ. Microbiol.* **66**, 2589-2598
Coolen M.J.L., Cypionka H., Sass A., Sass H., Overmann J. (2002) *Science* (in review)

Migmatitic geochronology and geochemistry – a key to understanding the exhumation of the Madan dome (Bulgaria)

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The high-grade metamorphic rocks exposed at the area of Madan dome are part of the lower plate of the late Alpine Central Rhodopian core complex, exhumed at Eocene time (Ivanov et al., 2000). This study links U-Pb ages of accessory minerals and geochemistry of anatectic melts, generated in the dome core, with Alpine structural evolution of the dome.

High-precise U-Pb analyses of single zircon grains from orthogneissic mesosome, filled with thin millimeter scale leucosome, discordant leucosome and metric scale anatectic granite body usually show inheritance of lead components, post crystallization lead loss and yield a Variscan age of the protolith (310.7 ± 4.6 Ma). Newly formed zircon from a discordant leucosome give an age of 37.08 ± 0.38 Ma. The U-Pb analyses of single monazites revealed the age of their crystallization from anatectic melt at 37.8 ± 1.5 Ma.

The leucosomes have near a minimum melt composition for the major elements. The elements occurring as trace constituents in felsic phases (Rb, Ba and Sr) have concentrations similar to those of model equilibrium melts. The incompatible elements (REE, Hf, Zr, Y, Th, Sc, Nb, Ta) occurring as essential structural components in accessory phases or as trace constituents of mafic minerals show a positive correlation with Fe+Mg+Ti; this demonstrates a residence in refractory phases and low mobility during melting. LREE and Zr concentrations in some leucosomes coincide with those calculated for low temperature felsic peraluminous equilibrium melts. Leucosome samples with higher REE contents have negative Eu anomalies, whereas those with low total REE have positive Eu anomalies, which indicate that feldspar fractionation was important in their petrogenesis. Migmatitic geochemistry corroborates an assumption of low temperature melting and fast melts extraction that corresponds with rapid exhumation tectonic regime. This fact is confirmed by the narrow time bracket between peak of the metamorphism (37 Ma, > 600°C), core complex cooling (35 Ma at 300°C) and volcanic activity (32 Ma).

References

- Ivanov, Z., Dimov, D. & Sarov, S., (2000), ABCD-GEODE Workshop, Borovets, Guide to excursion (B), 6-17.

Noble Gases in Planetary Atmospheres

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The relative abundances of the noble gases and their isotopic ratios in the atmospheres of Mars, Earth and Venus provide clues to the origin and evolution of these atmospheres. The noble similarities between Mars and Earth stand in sharp contrast to the differences in the present masses and compositions of these two atmospheres. How closely linked are the noble gases to C, N, and H₂O? What carrier(s) brought these volatiles to the planets? We can examine the possible roles of impacts by comets/icy planetesimals and meteorites/asteroids. Venus does not share the similarities in noble gases found on Earth and Mars but the abundances of C and N in her atmosphere are close to those in the Earth's reservoir. Jupiter reveals the existence of icy planetesimals in the early solar system that have not been identified in recent times.

K-Ar age determination on Honolulu Unit, Oahu, Hawaii

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There are four stages of activity in Hawaiian volcanoes, i.e., pre-shield, shield, post-shield and rejuvenated stages. Alkalic basalt and tholeiite are effused during pre-shield stage, tholeiite during shield stage, and alkalic basalt during both post-shield and rejuvenated stages. Among these stages, the rejuvenated stage is characterised by a volcanic hiatus of several million years prior to the stage and the eruption from isolated vents which are unrelated to rift zones. It is not yet known why the hiatus exists prior to rejuvenated stage, and even the duration of hiatus is not well constrained. Rejuvenated stage volcanics comprise less than 1% of total volume of each Hawaiian shield volcano, but ages of those volcanics are important to better understand the relation between plume and hotspot volcanism.

Honolulu Unit, which consists of 37 vents or groups of vents on Koolau shield volcano, is most extensively and carefully studied rejuvenated stage unit. However, neither precision nor number of age data are enough for constructing history of Honolulu Unit or determination of duration of the hiatus. Because subaerial part of Koolau shield is dated as 2.6-1.8 Ma, Honolulu Unit is considered to be younger than 1.8 Ma. However, many of Honolulu Unit lavas contain excess argon, and there are only a few ages that can be trusted.

We sampled about 30 lavas and other rocks from Honolulu Unit and the top of Koolau shield for K-Ar analyses. We used only groundmass for dating because phenocrysts and xenoliths often contain sufficient amount of excess argon. We also collected and analyzed historical lavas from Mauna Loa and Kilauea in order to better document the systematics of excess argon in phenocrysts and groundmass.

References

- Clague, D. A. and Dalrymple, G. B., (1987), USGS professional paper 1350, 5-54
 Clague, D. A. and Frey, F. A., (1982), *J. Petrology* 23, 447-504
 Lanphere, M. A. and Dalrymple, G. B., (1980), *Am. J. Sci.*, 280-A, 736-751

Incongruent evaporation of olivine at low temperature

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Introduction

Partial evaporation of pre-existing minerals is one of important processes that caused chemical and isotopic fractionation in the solar nebula. Olivine was shown to evaporate stoichiometrically to magnesian olivine and gas with iron-rich olivine composition in both equilibrium and kinetic conditions (Nagahara et al., 1994; Ozawa and Nagahara, 2001), with large Mg-Fe fractionation. We, however, found that olivine evaporates incongruently to form Mg-rich pyroxene at low temperatures.

Experimental

San Carlos olivine (Fo91-92) was cut into slab parallel to three major axes, which was heated in vacuum at temperatures of 1300, 1400, and 1500°C for 3 to 240 hours. The surface was observed and analyzed with after the run, and the compositional zoning from surface to interior in a vertical section was measured.

Results

The olivine evaporated keeping stoichiometry at 1500 and 1400°C, and the residue has become magnesian at the surface with compositional zoning toward interior. On the contrary, it evaporates incongruently leaving small crystals with lower Mg/Si ratio on the residue surface at 1300°C. The phase appears to be enstatite on the basis of X-ray intensity with EPMA, but we have not yet confirmed it with the X-ray diffraction method.

Discussion

Incongruent evaporation of olivine to magnesian pyroxene indicates the selective evaporation of FeO and formation of pyroxene at the surface. This is interpreted to be due to much higher volatility of FeO than SiO₂ from olivine. The present results predict that evaporation of olivine and Mg/Fe fractionation between solid and gas are highly suppressed once the surface of olivine is coated by enstatite, which prolongs the lifetime of Fe-bearing olivine. Enstatite, on the other hand, is shown to evaporate incongruently to forsterite and Si-rich gas (Tachibana et al., 2002) at a very small rate, thus remains long. Fe-bearing olivine thus remains long at temperatures as low as 1300°C and chemical fractionation is suppressed.

References

- Nagahara, H., Kushiro, I., and Mysen, B. O. (1994) *Geochim. Cosmochim. Acta* **58**, 1951-1963.
 Ozawa, K. and Nagahara, H. (2000) *Geochim. Cosmochim. Acta* **64**, 173-189.
 Tachibana, S., Tsuchiyama, A., and Nagahara, H. (2002) *Geochim. Cosmochim. Acta* **66**, 713-728.

Features of metals distribution in the bottom sediments of the Malaya Talmovaya River.

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Bottom sediments and water of the Malaya Talmovaya River were researched in this work Kemerovo region, Siberia), where the first tailings impoundment of the Salair Ore Recovering Plant is located. There were discovered the significant excesses of metal contents (Zn, Pb, Cu, Cd) to the background in 41, 39, 10, 1000 times accordingly, in three checkpoints, which show a state and a level of metal concentration in water and bottom sediment of the Talmovaya River

Contents of water soluble species of Zn (Zn [W]) are 2, 0.9, 1.95 ppm from upper to lower reaches and higher than the background level in 60 times (on average), the content of Cu[W] are 0.5, 0.45, 0.7 ppm and higher than the background in 6 times, the contents of Pb [W] and Cd [W] are below the limit of finding

Contents of exchangeable species of Zn (Zn [S]) are 280, 230, 390 ppm from upper to lower reaches and higher than the background level in 400 times on the average, the Pb [W] isn't discovered in any sample Cu [S] are 124, 165, 114 ppm and higher than the background in 100 times on the average, the amounts of Cd [S] are 3, 1.7, 3.2 g/t (from upper to lower reaches)

On the basis of the received data the following conclusions are made.:

There are speciations in solution: Me²⁺ (Me = Zn, Cd); MeOH⁺, Me(OH)₂ (Me = Cu, Fe); MeHCO₃⁺, Me(CO₃)₂²⁻ (Me = Pb).

The share of soluble forms of metals increases and the layer its contents raises by decrease of pH ,which is caused by the oxidation of FeS₂).

The irregular distribution of concentrations of metals in the water, sampled in different checkpoints, are bound up with sorption, which is fixed by content of organic substances in bottom sediments, area of clay surface, level of mineralization of water and accumulation of metals in phytoplankton. Moreover, there are different mechanisms of sorption for different metals (the higher content of Zn[W] in the middle checkpoint shows more active sorption of Zn in comparison with other metals).

As a whole, the contents of the mobile forms of metals increase from upper to lower reaches. The contents of Zn [W] and Zn [S] are higher than the background in 60 and 400 times accordingly, Pb [W] and Pb[S] no data, Cu [W] and Cu [S] are higher than the background in 6 and 100 times accordingly, Cd[W] is lower of the limit of finding, the content of Cd [S] is insignificant. Thus, the river is most polluted by Zn. It's danger for biota and consequently for people.

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Revisiting I-Xe systematics, an early solar system chronometer

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Xe, and other chronometers based upon short-lived activities, can provide valuable information about early solar system chronology. The objective of this paper is to reexamine I-Xe systematics concentrating on the composition that is implied for trapped Xe in meteorites. We show that the latter information is very useful in understanding elemental fractionation in proto-solar nebula, and also bears far-reaching implications on the age of the Earth.

Several workers have noted that there exists a negative correlation between the initial $^{129}\text{I}/^{127}\text{I}$ ratio and the $^{129}\text{Xe}/^{132}\text{Xe}$ ratio in a trapped Xe component in chondrules – hereafter called an I – R plot (Initial – Ratio) (e.g., 1, 2). Swindle et al. (2) interpreted that this negative trend was due to the decay of extinct nuclide ^{129}I in pre-chondrule environment. Swindle (3) further pointed out that if the pre-chondritic environment were of a closed system, the negative trend should be a straight line with a slope corresponding to I/Xe ratio in the pre-chondrule environment. Although the negative trend is apparent in Chainpur chondrules (2) and also supported by new Xe isotopic data on dark inclusions in Allende meteorite (4), the observed slope matches neither the solar I/Xe ratio nor values commonly observed in meteorites. We show that the characteristic features of Xe isotopic data seen in an I - R plot are consistently explained by assuming that Xe has been fractionated from I in the solar nebula that was dissipating exponentially with time

From the model, we also infer that the primordial $^{129}\text{I}/^{127}\text{I}$ and $^{129}\text{Xe}/^{132}\text{Xe}$ ratios are considerably smaller than the values deduced from meteorites, although the estimation of the primordial ratios involves large uncertainties. We note that some chondrules have the $^{129}\text{Xe}/^{132}\text{Xe}$ ratio of a trapped Xe as low as 0.9, well below the solar Xe ratio and even the least radiogenic $^{129}\text{Xe}/^{132}\text{Xe}$ ratio (Novo Urei meteorite). The new data on Allende dark inclusions (4) also support this smaller primordial $^{129}\text{Xe}/^{132}\text{Xe}$ ratio. If the primordial $^{129}\text{Xe}/^{132}\text{Xe}$ ratio were indeed as small as 0.9, this bears far reaching implications on early solar chronology. For example, the currently estimated value of the initial $^{129}\text{I}/^{127}\text{I}$ isotopic ratio of about 10^{-6} in the Earth (5) would become larger, and reduce the puzzling gap in an initial $^{129}\text{I}/^{127}\text{I}$ ratio (about 10^{-4} in meteorites) or in a formation age interval between the Earth and meteorites.

References

- (1) Podosek F.A. (1970) G.C.A. 34, 341-365.
- (2) Swindle T.D. et al. (1991) G.C.A. 55, 861-880.
- (3) Swindle T.D. (1998) Met. Planet. Sci. 33, 1147-1155. (4) Hohenberg C.M and Pravdivtseva O. (personal. com.).
- (5) Ozima M. and Podosek F.A. (1999) JGR 104, 25,493-9.