

## Geochemical features of deep-sea sediment in the eastern Indian Ocean: the first report of the Indian REY-rich mud.

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It was reported that deep-sea sediment contains high concentrations of rare-earth elements and yttrium (REY) in the eastern South and central North Pacific [1]. This REY-rich mud constitutes a huge potential resource for these elements.

Now, we confirmed the existence of deep-sea sediment with more than 1,100 ppm total REY contents in the eastern Indian Ocean. We will show the geochemical features of this Indian REY-rich mud for the first time.

[1] Kato et al. (2011) Nat. Geosci., 4, 535-539.

Keywords: deep-sea sediment, Indian Ocean, rare-earth elements

## Mn nodule field discovered in the EEZ around the Minami-torishima Island: occurrence and geochemistry of nodules

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The region which many manganese nodules are distributed with high density was discovered at approximately 300 km E of the Minami-torishima Island, where is in the exclusive economic zone (EEZ) around the Minami-torishima Island, by observation using submersible SHINKAI 6500 (dive #1207: observer is T.I.) during YK10-05 cruise of R/V Yokosuka, Japan Agency for Marine-Earth Science and Technology (JAMSTEC). A small seamount having 400 m height and 5 km in diameter situate at the region. Manganese nodules are broadly and densely distributed from the summit to northwest side of the seamount, and also the comparatively flat portion of a hillside. The region shows high acoustic reflectivity by survey using multi narrow beam. Such high reflectivity regions were also found in the other area of Minami-torishima Island EEZ. Then, these may also be the vast manganese nodule fields. In this report, we will present occurrence and geochemical compositions of manganese nodules collected by SHINKAI 6500 dive.

Keywords: EEZ around the Minami-torishima Island, Mn nodule

## Possible relationship between magnetic properties and rare-earth content of pelagic red clay

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Pelagic red clay occupies about 40% of the seafloor, but paleoceanographic and paleomagnetic studies were restricted so far mainly because sedimentation rates are very low and being devoid of calcareous or siliceous microfossils dating is difficult. Kato et al. (2011) presented occurrence of red clay with high contents of rare-earth elements in the Pacific Ocean, and its potential for resources has attracted attention. In this presentation, I will review red clay mainly from the viewpoint of rock- and paleomagnetism.

It is known that magnetostratigraphy is often lost in red clay older than about 3 Ma. This age coincides with that of increased eolian dust flux in the North Pacific. The eolian component of magnetic minerals in red clay may be carriers of stable remanent magnetization. If so, red clay of older than ~3 Ma without good magnetostratigraphy may have higher rare-earth contents because input of eolian dust would dilute rare-earth elements in red clay.

I examined possible relationship between magnetic susceptibility and rare-earth contents for the ODP cores that Kato et al. (2011) reported, when magnetic susceptibility data are available. I found a good correlation between magnetic susceptibility and rare-earth contents. It is considered that dilution by non-magnetic minerals such as calcareous and siliceous microfossils controls both magnetic susceptibility and rare-earth contents, but it may not be the only factor. If dilution controls, anti-correlation of magnetic susceptibility with sedimentation rate is expected. Although only a few cores have a good age control that enables estimation of variations in sedimentation rates, the limited data suggest that the correlation of susceptibility with sedimentation rate is not very good. More detailed rock magnetic studies are required to understand the correlation. At present it is not considered that contribution of magnetic minerals of hydrothermal origin is significant in deepsea sediments, but it might be important when sedimentation rates are quite low.

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Keywords: red clay, pelagic clay, paleomagnetism, rock magnetism, magnetic susceptibility, eolian dust

## Areal survey of rare-earth mud using sub-bottom profiler in the Minami-torishima EEZ

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See the abstract in Japanese.

Keywords: Rare earth elements, Seafloor resources, mud, Minami-Tori-Shima island, deep-sea, sub bottom profiler

## Geochemical features and origin of REY-rich mud in the Minami-torishima EEZ

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We report the distribution, bulk chemistry, mineral composition, origin, and chemical features of the rare-earth elements and yttrium-rich mud (REY-rich mud) in the exclusive economic zone (EEZ) around Minami-torishima.

Keywords: rare earth elements (REEs), REY-rich mud, deep-sea mineral resource

## Reports from KR13-02 cruise on spacial discription of REY-rich mud on deep-sea floor around Minami-Tori-Shima Island

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See the abstract in Japanese.

Keywords: Rare earth elements, Seafloor resources, mud, Minami-Tori-Shima Island, deep-sea

## REY-rich deposits around Minamitorishima -General overview-

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We report general overview of REY-rich deposits in the EEZ (Exclusive Economic Zone) around Minamitorishima.

Keywords: rare-earth elements (REEs), REY-rich mud, deep-sea mineral resource

## Systematic differences of I/Br ratios in kimberlites and their xenoliths related to their origin

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Kimberlite is an igneous rock originated from deep mantle. Compared to ordinary ultramafic rocks, kimberlite is rich in volatile components such as water and carbon dioxide. In addition, studies on the noble gas isotopes in kimberlites showed that kimberlite magmas have similar noble gas characteristics to those of ocean island basalts (e.g., Sumino et al., 2006).

The halogen elements (chlorine, bromine, iodine) have high aqueous fluid-silicate melt partition coefficients (Bureau et al., 2000). Thus, they (especially iodine) are enriched in pore fluid and have distinct elemental ratios in seawater, pore fluid, sediment, oceanic crust and mantle. Moreover, these elements are used as good tracers for pore-fluid subduction (e.g., Fehn et al., 2003; Muramatsu et al., 2007). Recently, halogens are revealed to be one of the reliable tracers for water cycling in subduction zones (Sumino et al., 2010). In this study, we analyzed concentrations of Cl, Br, and I in kimberlites and mantle-derived xenoliths from six localities to investigate the halogen characteristics and their origins in the kimberlite source regions.

Samples analyzed are 35 kimberlites collected from South Africa, China, Greenland, Brazil, Russia and Canada, and 4 xenoliths collected from South Africa and Russia. For the Cl, Br and I determination, we used the pyrohydrolysis method (Muramatsu et al., 2008) combined with ICP-MS and ion chromatography.

The result shows that the kimberlite samples are classified into two groups with respect to I/Br ratios. The first group (Group S) shows high I/Br ratios (about  $1 \times 10^{-1}$ ), which are distinctively observed in the kimberlites from South Africa, Greenland, Canada and Brazil. The xenolith from South Africa is also classified into the Group S. In addition, the I/Br ratios of the Group S are fairly similar to that of CI chondrite (I/Br ratio: about  $1 \times 10^{-1}$ , Anders and Ebihara, 1982). This suggests that these kimberlites preserve the characteristics of halogens in the mantle from which the kimberlite magmas formed. On the other hand, the other group (Group C) composed of Chinese and Russian kimberlite samples shows markedly low I/Br ratios (about  $6 \times 10^{-3}$ ). Similar low I/Br ratios have been observed in fluid inclusions in eclogites derived from seawater-altered oceanic crust (Svensen et al., 2001) and in seawater associated with halite precipitation (Zherebtsova and Volkova, 1996). This suggests an involvement of seawater-derived halogens having low I/Br ratios in the source regions of the Group C kimberlites.

Keywords: Kimberlite, halogen, I/Br ratio, South Africa, China, Russia



## Intrinsic and secondary noble gas components in olivine in kimberlites: how to reveal their source compositions?

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Kimberlites are unique igneous rocks, which occasionally brought diamonds from deep in the Earth. Although their origins are considered to be deeper than 150 km in the mantle based on the P-T stability of diamonds [1], they have not been well constrained yet [2].

We have been investigating noble gases in olivines in kimberlites to constrain the origin of kimberlite magmas. Sumino et al. [3] found plume-derived Ne in olivine phenocrysts in the Udachnaya kimberlite from Siberia and suggested that the origin of kimberlite is a plume rising possibly from the lower mantle or core-mantle boundary. Namely we may be able to use kimberlites as a window into the deep Earth.

In this study, we analyzed 7 fractions of olivines separated from 4 Udachnaya kimberlite rocks [4], 5 fractions from West Greenland kimberlites [5], and 3 fractions from Brauna kimberlite in Brazil [6]. Since magmatic noble gases are generally concentrated in fluid inclusions, stepwise crushing was applied to extract noble gases selectively from the inclusions.

<sup>3</sup>He/<sup>4</sup>He ratios of the Udachnaya kimberlite olivines are ca. 6 Ra (Ra =  $1.4 \times 10^{-6}$  for atmospheric He), which is higher than xenoliths in the same pipe (3 Ra), but similar to the Udachnaya diamonds reported by [7]. Neon and Ar isotope ratios show two different noble gas components; the plume-like one reported for kimberlite magma [3], and the other enriched in radiogenic/nucleogenic noble gases originate in Siberian subcontinental lithospheric mantle (SCLM). We also found that olivines with smaller grain size are highly affected by the SCLM component. This confirms a model proposed by [3], in which upwelling plume temporarily stayed at the base of the Siberian SCLM, formed diamonds and kimberlite magma, and then the kimberlite magma conveying diamonds ascended and erupted. It also suggests that noble gas compositions of the kimberlite magma were affected from surrounding SCLM during its ascent, resulting in addition of radiogenic/nucleogenic noble gases. This is consistent with the model that silica content of the kimberlite magma increased due to consumption of pyroxene in the surrounding SCLM [8].

In contrast to the Siberian kimberlites, olivines in the West Greenland kimberlites exhibit relatively low <sup>3</sup>He/<sup>4</sup>He ratios. One group is characterized by <sup>3</sup>He/<sup>4</sup>He values of ca. 1.5 Ra and the other much lower ratio of 0.5 Ra. Neon isotopic ratios are also different; the former is similar to the Siberian SCLM, the latter dominated by nucleogenic component. Since the West Greenland kimberlite olivines contain relatively small amounts of magmatic noble gases such as <sup>3</sup>He, radiogenic/nucleogenic components would become dominant after the kimberlite emplacement (600 Ma, [9]).

In the case of the Brauna kimberlite olivines, radiogenic/nucleogenic contributions are more significant. Their <sup>3</sup>He/<sup>4</sup>He ratios are ca. 0.02 Ra, and no magmatic Ne was observable.

These results suggest that whether olivines in a kimberlite can preserve magmatic signature or not strongly depends on their condition in each pipe, locality or environment, and also on their histories. Even though it preserves a magmatic noble gas signature, it itself could be severely contaminated by SCLM or other components during ascent of the magma. To obtain insight into the deep Earth, we should select samples and analytical methods carefully. If possible, comprehensive study involving other constituent components such as diamonds in the same kimberlite is more beneficial to clarify the relation of kimberlite magma with surrounding SCLM.

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Keywords: kimberlite, noble gas, olivine, Udachnaya, Siberia, Greenland, Brauna, Brazil

## Highly siderophile elements and Os isotope systematics of EM-1 basalts from Pitcairn Island

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It is well known that recycled materials are involved in producing the chemical and isotopic heterogeneities observed in oceanic island basalts (OIB). The type of recycled material present in the Enriched Mantle 1 (EM-1) source has been widely debated. Oceanic crust with pelagic sediment, delaminated subcontinental lithospheric mantle (SCLM), subducted oceanic plateaus, continental lower crust, and just single melting process involving pristine mantle have all been invoked as contributing to EM-1 flavor source (e.g., Chauvel et al., 1992; Hauri and Hart, 1993; Gasperini et al., 2000; Ishikawa et al., 2007; Collerson et al., 2010). The chemical composition of EM-1 is characterized by, for example, radiogenic Sr, unradiogenic Nd, unradiogenic Pb and radiogenic Os isotope compositions compared to the depleted mantle.

We have measured Os isotope ratios and PGE abundances in basalts from Pitcairn Island, south Pacific, which represent strong EM-1 flavor to identify the possible source components of these magmas. The range of the Os isotope ratios (0.138-0.161) have a similar to or slightly higher than those measured in previous studies on EM-1-type basalts (-0.150). The highly siderophile elements (HSE) patterns are characterized by fractionation between IPGE (Os, Ir, Ru) and PPGE (Pt, Pd). Among IPGE, Ir abundances of some basalts show depleted pattern compared to Os and Ru. The HSE patterns of the basalts from Pitcairn Island are clearly different from the HSE pattern of MORB (Rehkamper et al., 1999; Bezos et al., 2005). We will discuss the components of the source mantle of EM-1 and the magma genesis of Pitcairn Island basalts combining our data with previous studies.

Keywords: Os isotope ratio, EM-1, OIB, HSE abundance

## Geochemical characterization of lavas from the Oku Volcanic Group, Cameroon Volcanic Line, West Africa

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Understanding the origin and evolution of magma along the Cameroon Volcanic Line (CVL) has been a fundamental issue within the last 4 decades. The CVL is broadly divided into the oceanic, ocean continent boundary (OCB), and continental sectors, based on its lead and helium isotopic compositions. Mantle geochemistry using isotopes has been intensively studied in the oceanic islands and the OCB zones. On the contrary, very few isotopic data exist on the other volcanic centres of the continental CVL. As a result, most conclusions on this sector are drawn based on major and trace element data. In order to complement the understanding of the entire CVL, we are carrying out a detailed geochemical study of rocks from the Oku Volcanic Group (OKVG) located in the north eastern part of the CVL. As the first stage of the investigation, we here report preliminary geochemical data for eight volcanic rocks, alongside high quality literature data for rocks from the same area. Oku Volcanic Group lavas range from primitive mafic to highly differentiated felsic lavas. Major element compositions (wt. %) are; SiO<sub>2</sub> = 35-78.7; Al<sub>2</sub>O<sub>3</sub> = 10.1-27.2; MgO = 0.005-11.9; CaO = 0.09-11.15; Fe<sub>2</sub>O<sub>3</sub>t = 1.8-13.85. This compositional variation favours a fractional crystallisation model for the continuous evolution from a parent mafic magma to the more evolved felsic lavas. The high (La/Yb)<sub>N</sub> ratio (mean of 14.1) in most samples is an indication of melting in the presence of residual garnet. The low (< 66.5) Mg # of most mafic lavas of the OKVG confirms that they solidified from fractionated melts. Based on K<sub>2</sub>O/Na<sub>2</sub>O ratios, mafic rocks with Mg# = 47.7-66.3 in this area are further classified as sodic alkali basalts (K<sub>2</sub>O/Na<sub>2</sub>O < 1, dominant species), with one sample from the Lake Nyos area as potassic alkali basalt (K<sub>2</sub>O/Na<sub>2</sub>O = 1.30). The latter class is very rare and is reported for the first time along the CVL. Some three sodic alkali lavas in this range (Ba, Rb, K relative to Th) are classified as tholeiites (K<sub>2</sub>O/Na<sub>2</sub>O = 0.11-0.15; La/Yb = 3-4.6). These properties coupled with the high Ba/Th ratio could result from modification of the melts by processes such as meteoric alteration, metasomatism and/or crust contamination. Isotopic ratios of Sr, Nd and Pb of these samples will throw more constrains on the petrogenesis of these lavas. Existing data for radiogenic isotopes in the OKVG ranges for <sup>87</sup>Sr/<sup>86</sup>Sr = 0.70334-0.70382 and <sup>143</sup>Nd/<sup>144</sup>Nd = 0.5128460-0.512983. This is higher compared to the average ratio (0.7034 and 0.512867 respectively) of CVL lavas and thus in agreement with crustal contamination by the granitic basement rocks.

Keywords: geochemical characterisation, Oku Volcanic Group, Cameroon Volcanic Line, Sodic alkali lava, Potassic alkali lava, Tholeiites

## Utility of apatite as a proxy for solidification processes of magma revealed in the Nosappumisaki intrusion

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We have examined behavior of volatile elements during cooling and solidification of a magma in the crust based on morphology, chemical composition, and hydrogen isotopes of apatite in the Nosappumisaki intrusion, which has been extensively studied on the processes of crystal differentiation and solidification.

The Nosappumisaki intrusion is a sheet-like intrusion intruded into the Nemuro formation in the Nemuro peninsula, Hokkaido. The basic structure is a lower melanocratic cumulate zone overlain by an upper leucocratic monzonite zone. This structure is inferred to have formed by a quick and massive crystal settling from a magma initially laden with crystals in a sheet like magma body, (Simura and Ozawa, 2006) followed by a slow stage of fractional crystallization caused by compositional convection in a closed system (Simura and Ozawa, 2011).

In the intrusion, apatite occurs in all of the lithologies except for chilled zones showing short columnar to acicular euhedral morphology. The aspect ratio and number density of apatite increase from the lower cumulate zone to the upper chilled zone, suggesting that the cooling from the upper contact of the intrusion is more effective than that of the lower contact.

Apatite crystals in three rocks representing earlier and later stages of solidification respectively were analyzed with NanoSIMS to determine the water content and hydrogen isotopic composition. The obtained average isotopic composition and water content are -109 per mill and 1.26 wt.% for the earlier stage of solidification and 18.2 per mill and 1.29 wt.% for the later stage of solidification. We also analyzed apatite with an EPMA to determine F and Cl contents. The Cl contents of apatite in the upper monzonite zone and the lower cumulate zone, which solidified earlier, are comparable. The Cl content decreases toward near the contact between the monzonite and cumulate zones, which solidified later. In contrast, the F contents of apatite are inversely correlated with the Cl contents. There are also zoned apatite grains, in which Cl content decreases from the core to rim with oscillation. Melt/fluid composite inclusions are present localized in a zone with lower Cl content.

The most important result of our study is the increase of F/Cl and D/H of apatite with solidification with minor variation of the water content. If the fractionation and solidification processes took place in a closed system, F/Cl in the magma decreases keeping D/H constant, because minerals crystallized with apatite after the intrusion are anhydrous minerals and biotite ( $\text{Mg}/(\text{Mg}+\text{Fe}) \sim 60$ ), to which F is more preferentially partitioned than Cl relative to silicate melts (Icenhower and London, 1997). However, the F/Cl and D/H increase contrary to this expectation, indicating that the variation of F/Cl of apatite was not caused by crystal fractionation. The most plausible scenario to account for the behavior is vesiculation/degassing at a certain stage of solidification of the intrusion. This inference is supported by followings: (1) F is more preferentially partitioned into melt than into gas as compared with Cl (Signorelli and Carroll, 2000; Webster, 1990), (2) the D/H of apatite has a variation, (3) melt/fluid inclusions selectively occur in Cl-poor zones in zoned apatite grains, suggesting vesiculation caused depletion of Cl in the apatite. In addition, the increase of D/H with fractionation suggests that vesiculation/degassing occurred not as  $\text{H}_2\text{O}$  but as  $\text{CH}_4$  or  $\text{H}_2$  (Kyser and O'Neil, 1983). This implies that differentiation and solidification of the Nosappumisaki intrusion took place under a reduced condition being undersaturated with  $\text{H}_2\text{O}$ .

Information of vesiculation/degassing, gas speciation, and oxidation-reduction state of magma can be obtained using F/Cl and D/H of apatite. Apatite is a useful proxy for behaviors of volatile elements during the solidification of magma.

## Petrology and geochemistry of amphibolite blocks in the earliest Archean orthogneisses, the Acasta Gneiss Complex

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The Hadean from 4.567 to 4.03 Ga is the earliest period of the history of the earth, and defined by no preservation of rock records in the earth. Although it is suggested that the earth underwent the whole earth differentiation related to the magma ocean, core formation and early crustal formation in the period, the details are not revealed yet. Many Hadean, >4.0 Ga, zircons, including a 4.4 Ga detrital zircon from the Narryer Complex, Western Australia are found, and their geochemistry and mineral inclusions implies that the mantle had been already differentiated to make felsic continental crusts in the Hadean. But, the interpretation of the zircon geochemistry and inclusions is still controversial because the zircons occur as detrital or inherited in the middle to Early Archean sedimentary rocks and orthogneisses and the host rocks are still unknown. Therefore, it is quite significant to study the Early Archean rocks and geologic bodies to understand the early evolution of the earth.

Acasta Gneiss Complex (AGC), located along the Acasta River in the westernmost part of the Slave Province, northwestern Canadian Shield, is one of the Early Archean complexes, and contains the oldest rock in the world. Bowring et al. (1999) reported the oldest, 4.03 Ga, zircon from a granodioritic gneiss. The AGC is divided into two main domains by a northeast-trending fault. The Eastern area is dominated by ca. 3.6-4.0 Ga white gneiss suites whereas ca. 3.9-4.0 Ga layered gneiss suites are predominant in the Western area. Gray gneisses, defined by geological evidence for intrusive structures by the white and layered gneisses, exist in the both areas. Iizuka et al. (2006) found a 4.2 Ga inherited core within a 3.9 Ga magmatic zircon. Furthermore, Hf model ages of zircons from the ca. 3.7-3.9 Ga granitic gneisses indicate the source materials were formed at ca. 4.2-4.0 Ga. The line of evidence suggests that the gray gneiss suites are older than the white and layered gneisses, and possibly goes back to the Hadean age. This paper presents field occurrence, metamorphic petrology and geochemistry of the gray gneisses to reveal the origin of the gray gneiss and early evolution of the solid earth.

The gray gneisses consist of hornblende + plagioclase + quartz ± chlorite ± epidote ± biotite ± apatite ± sphene ± garnet ± clinopyroxene ± opaque. The mineral assemblages indicate that these rocks were suffered from amphibolite to upper amphibolite facies metamorphism. Based on the mineral paragenesis, we classified the gray gneisses into three groups: (1) a garnet-amphibolite, (2) a hornblendite with over 95 % modal abundance of hornblende, and (3) amphibolite, respectively. The hornblendites occur ubiquitously, whereas the garnet-amphibolites occur only in the northern part of the eastern area.

We analyzed whole rock major element compositions of two garnet-amphibolites, four hornblendites and twenty amphibolites with XRF at Tokyo Institute of Technology. The compositions are basaltic, and are correlated with their petrography. The garnet-amphibolites have relatively lower SiO<sub>2</sub> (43 %) and higher FeO (18-19 %) contents, consistent with expansion of garnet stability field increasing FeO contents. The hornblendites have relatively lower Al<sub>2</sub>O<sub>3</sub> (3-5 %) and higher MgO (14-19 %) contents.

Some compositional trends are distinguished with MgO versus major element variation diagrams: for example, increase, constant and decrease trends in SiO<sub>2</sub> contents in increasing MgO contents, respectively. Secondary elemental movement accounts for the increase and decrease in SiO<sub>2</sub> contents because SiO<sub>2</sub> contents of magmas change a little compared with MgO, FeO and Al<sub>2</sub>O<sub>3</sub> contents during fractional crystallization of basaltic magmas.

Except for the altered rocks with quite higher or lower SiO<sub>2</sub> contents, the compositional variations are similar to those of modern abyssal basalts, consistent with geological evidence for supracrustal remnants within the earliest Archean orthogneisses.

## Chemical evolution of basal magma ocean and mantle structure of the early Earth

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Our recent study showed the experimental evidence on the gravitational stability of basal magma ocean against crystallized solid silicate at  $>76$  GPa conditions (Nomura et al., 2011 Nature). This dense, incompatible element-rich reservoir should be crystallized to form the stable layered structure at the base of the mantle in the early Earth.

To elucidate the chemical structure of the crystallized basal magma ocean, we performed silicate melting (crystallizing) experiments at  $\sim 70$  GPa and  $\sim 135$  GPa (correspond to core-mantle boundary condition) as follows. (1) Melting experiments of pyrolytic silicate at high PT, (2) The identification of the liquidus phases and partition coefficients between silicate melt and liquidus phases using field emission-type electron microprobe. (3) Calculation of the composition of fractionally crystallized basal magma ocean (4) Synthesis of the starting material with calculated (3) composition, and back to (1).

In this presentation, we will show the results of (1) pressure and compositional dependence of the partition coefficients (Fe, Al, Ca, K, Na) between silicate melt and solid, (2) liquidus phase relations at  $\sim 70$  GPa and  $\sim 135$  GPa in evolving basal magma ocean, and we will propose (3) the chemical layering structure of the early Earth.

Keywords: basal magma ocean, early Earth, high pressure experiments, laser-heated diamond anvil cell, silicate solid-liquid partitioning



## Alkaline hydrothermal systems on Enceladus inferred from laboratory experiments

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The discovery of water-rich plumes with sodium salts erupting from warm fractures near the south pole of Enceladus suggest the presence of an interior ocean interacting with the rock components. The recent findings of silica nano-particles in Saturn's E-ring derived from the plumes imply the possibility of active geochemistry in the ocean. It is however highly uncertain the particular conditions of temperature, pH, and mineral compositions under which the reactions occur in the ocean. Here we report laboratory experiments of hydrothermal reactions between aqueous solution containing primordial volatiles with cometary compositions and primitive minerals simulating Enceladus' interior. Our results indicate that redox reactions of primordial volatiles, such as NH<sub>3</sub> dissociation and conversion of CO<sub>2</sub> to CH<sub>4</sub>, are highly inhibited kinetically even at high temperatures. These volatiles in turn would keep pH of the solution alkaline (i.e., pH 8-11). To generate silica nano-particles in Enceladus, we suggest that temperature should be at least ~100 degree in C or above with the presence of secondary minerals of serpentine and talc. These secondary mineral assemblages imply that the initial rock compositions of building block of Enceladus were CI chondritic. Our experimental results together with the findings of silica particles in Saturn E-ring suggest the presence of hydrothermal activities (temperature > 100 degree in C) with alkaline fluids in Enceladus' ocean in the recent past or even today.

Keywords: icy satellite, hydrothermal activity, astrobiology, planetary science

## Pressure effect on element partitioning between Fe-Ni Alloy and sulfide melt

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Understanding the partitioning behavior of elements between solid and liquid metal is key to resolving the evolution in metallic core of the terrestrial planets. Crystallization history of iron meteorites have been investigated from the partitioning data of trace elements at normal pressure conditions. In order to reveal evolution process in the larger bodies, partitioning data under high pressure conditions are required. Although a several high pressure researches on partitioning behavior have been reported, data are still insufficient. We performed high pressure melting experiments of Fe-Ni-S system at 10 and 25 GPa, and measured the partitioning coefficient of elements.

We synthesized Fe-Ni(95:5) alloy doped with 14 trace elements (Co, Cu, Ge, Mo, Ru, Ph, Pd, W, Re, Os, Ir, Pt, Au, Pb) in approximately 150 ppm, by arc-melting method. A small chip of this alloy and a small amount of FeS powder were packed in the MgO capsule, and high pressure melting experiments were performed using Kawai-type multi-anvil press installed at Tokyo Institute of Technology. Quenched samples were polished and major element compositions were measured by EPMA. Trace element abundances were determined by fs-laser ablation system with sector-type ICP-MS installed at Kyoto University.

The observed pressure dependences of partition coefficients in the present experiments were generally in agreement with the previous works (e.g., Hayashi et al. 2009, Chabot et al. 2011); partition coefficient of Cu, Ge, Pd, Au increased with pressure while that of Mo, Ru, W decreased. Partition coefficient of Re, Os, Ir, Pt showed no significant pressure dependence. However, in some elements, present results were slightly different from the previous works. For example, in previous works, it was suggested that partition coefficient of Co and Ni decrease with pressure, but our results showed no pressure dependence in partition coefficient of Co, and partition coefficient of Ni slightly increased with pressure. Therefore, more detailed experiments are required to resolve the pressure dependence of these elements.

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Chabot et al. (2011), *Earth Planet. Sci. Lett.*, 305, 425-434.

Keywords: element partitioning, metal, sulfide, high pressure



## In-situ X-ray structural analysis on laser-shock compressed iron

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The knowledge of high pressures ( $P > 1$  Mbar) behavior of materials as iron is crucial for modeling the planetary interiors. Despite important progress obtained in the last decade on macroscopic characterization including equation of state (EOS), microscopic studies are necessary to investigate finely the structure changes.

Here we present recent studies to obtain information on solid-solid phase transformation of iron under laser-driven shock compression

using picosecond time-resolved x-ray diffraction technique.

BCC-HCP phase transformation was observed at dynamic high pressure of  $\sim 180$  GPa.

This work was performed under the joint research project of the LULI, Ecole Polytechnique.

This work was partially supported by grants from the Core-to-Core Program of the JSPS, the Global COE Program CEDI of the MEXT, and the

CREST of the JST.

## XAFS study on Zr local structure in natural glasses and tektite

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The local structures of tektite and natural glasses were studied by Zr K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) in order to provide quantitative data on bonding distances and coordination numbers. The XAFS measurements were performed at the beam line BL-NW10A of the PF-AR in National Laboratory for High Energy Physics (KEK), Tsukuba, Japan. Zr<sup>4+</sup> ion in tektite have different kinds of coordination environment comparing with rock forming minerals. Various natural glasses are formed under different physical conditions. Impact-related glass, fault rocks, fulgurite and volcanic glasses are typical nature glasses. Sometimes, it is difficult to distinguish them because of their similar appearance and chemical composition. Analysis of local structure is help to compare their formation conditions and distinguish them. Tektite is a kind of impact-related silicate glass. Glass structure is affected by the pressure and temperature conditions existing during the glass formation and annealing process. This study indicated that different generation process of natural glasses gives different local structure of cation.

In order to interpret the Zr XANES spectra, the comparison between crystalline reference minerals and natural glasses is done. Comparison with other natural glasses shows that pre-edge peak heights and shoulder width are changing. The natural glasses are formed under different temperature and pressure conditions. Tektites are produced by impact event and experienced high temperature and high quenching rate presented low coordination number environment and shorter bonding distances than other glasses [1].

Zr K-edge XANES spectra of tektite had the double post-edge peaks with different heights and looked like the high temperature glass. Pseudotachylite fault rock, fulgurite, volcanic glasses and other impact-related glasses such as impactite possessed more simple local structure. Tektites are among the "driest" rocks, with average water content of 0.005%. The average coordination number of Zr<sup>4+</sup> is between 6 and 7. The eight-coordinated Zr<sup>4+</sup> shows different XAFS pattern in natural glasses.

Keywords: local structure of Zr, natural glass, tektite, XANES, EXAFS

## A new analytical bias correction for in-situ Sr isotope analysis of plagioclase crystals using LA-MC-ICPMS

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A new analytical protocol was developed for correcting baseline-induced biases during the analysis of Sr isotope ratios in plagioclase using excimer laser-ablation Aridus-dual-intake-system multiple-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS). Residual analytical biases of  $^{84}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  were observed after applying on-peak background subtractions and mass-fractionation corrections using the conventional  $^{86}\text{Sr}/^{88}\text{Sr}$  exponential internal normalization. The residual biases occurred only for samples analysed with LA and not for solution analyses using Aridus with the same instrumental setup. Based on observations from the ablation of NaCl and olivine crystals, we concluded that this was due to suppression and enhancement of the Kr baseline by loading of the LA sample aerosols and by the introduction of Kr from the samples, respectively. We also found that both the  $^{84}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios were affected proportionally by the baseline biases of the LA analyses of an isotopically/compositionally homogeneous anorthite plagioclase (MkAn) from Miyakejima, Japan, and similar results were seen in theoretical calculations. Therefore, the bias correction for the target  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios was available using the shift in the simultaneously measured  $^{84}\text{Sr}/^{86}\text{Sr}$  from the natural ratio. We then determined the correlation factors between  $^{84}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  by analyzing MkAn, which reproduced the theoretical factors obtained from numerical simulations. By applying the new correction protocol, the accurate measurement of unknown plagioclase samples was possible. This was confirmed by comparisons with the results of micro-milling thermal ionization mass spectrometry (MM-TIMS) of the same plagioclase crystals with various compositions. The new correction technique improved reproducibility by a factor five, providing a basis for an accurate Sr isotope analysis using LA-MC-ICP-MS.

Keywords: Sr isotope, laser ablation, MC-ICPMS, bias correction

## Mass-dependent isotopic fractionation of cerium and neodymium in geochemical samples

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We have developed a new analytical method to determine the mass-dependent isotopic fractionations on Ce and Nd in geochemical samples. Mass discrimination effects on Ce and Nd were externally corrected by normalizing  $^{149}\text{Sm}/^{147}\text{Sm}$  and  $^{153}\text{Eu}/^{151}\text{Eu}$ , being 0.92124 and 1.0916, respectively based on an exponential law. The reproducibility of the isotopic ratio measurements on  $^{142}\text{Ce}/^{140}\text{Ce}$ ,  $^{146}\text{Nd}/^{144}\text{Nd}$  and  $^{148}\text{Nd}/^{144}\text{Nd}$  were 0.008% (2SD, n=25), 0.006% (2SD, n=39) and 0.012% (2SD, n=39), respectively. The present technique was applied to determine the variations of the Ce and Nd isotopic ratios for five geochemical reference materials (igneous rocks, JB-1a and JA-2; sedimentary rocks, JMn-1, JCh-1 and JDo-1). The resulting ratios for two igneous rocks (JB-1a and JA-2) and two sedimentary rocks (JMn-1 and JCh-1) did not vary significantly among the samples, whereas the Ce and Nd isotope ratios for the carbonate samples (JDo-1) were significantly higher than those for igneous and sedimentary rock samples. The 1:1 simple correlation between  $\delta\text{Ce}$  and  $\delta\text{Nd}$  indicates that there were no significant difference in the degree of isotopic fractionation between the Ce and Nd. This suggests that the isotopic fractionation for Ce found in the JDo-1 could be induced by geochemical or physicochemical processes without changing the oxidation status of Ce, since the redox-reaction can produce larger isotopic fractionation than the reactions without changing the oxidation state. The variations in the Ce and Nd isotope ratios for geochemical samples could provide new information concerning the physicochemical processes of the sample formation.

Keywords: isotopic fractionation, cerium, neodymium

## Petrogenesis and magmatic process of the Ikoma gabbroic complex in Kinki district, southwest Japan

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The Ikoma gabbroic complex is one of the largest Cretaceous mafic pluton in SW Japan are exposed at Ikoma mountains, consisting of mafic rocks (the Ikoma gabbroic rocks) and intermediate to felsic rocks, the Fukihata tonalites and the Kyuanji quartz diorites. These rocks show two modes in whole-rock compositional relation, (1) as mafic rocks with SiO<sub>2</sub> <48wt.%, major oxide contents change widely for constant SiO<sub>2</sub> contents, and (2) as intermediate rocks with SiO<sub>2</sub> >48wt.%, major oxide contents show linear trends with respect to SiO<sub>2</sub> contents. On the compositional variation diagrams, plagioclase compositions included in mafic rocks is located to the end-member on the trend of mafic rocks. Moreover, some samples show cumulus structures and their plagioclase mode are shown by a positive trend with respect to the variation of CaO contents. It suggests that the Ikoma gabbroic rocks were associated with the accumulation and/or fractionation of plagioclase. On the other hand, whole-rock compositions of intermediate rocks vary linearly with increasing SiO<sub>2</sub> contents, and their <sup>87</sup>Sr/<sup>87</sup>Sr initial ratios at 82 Ma show a positive trend with variation of SiO<sub>2</sub> contents. These characteristics suggest a mixing of mafic and felsic magmas. The mafic end-member is plagioclase-poor mafic rocks. Granitoids occurred at the same time of the activity of the Ikoma gabbroic complex are plotted on the extrapolation of the compositional trend of intermediate rocks, suggesting that the granitoids may be the felsic end-member in a magma mixing.

Keywords: Ryoke belt, mafic rock, magmatic process, geochemistry

## Fe<sub>2</sub>O<sub>3</sub>/FeO ratios and K-Ar ages of the Tadamigawa granitic rocks, northeastern Japan

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The early Paleogene Tadamigawa granitic rocks are located around Hinoemata village in the southwestern part of Fukushima prefecture, northeastern Japan. The granites are divided into two rock types, the Tadamigawa granite and the Hinoematagawa granite. The Hinoematagawa granite is medium-grained biotite-hornblend granite. The Tadamigawa granite is coarse-grained biotite granite and it is characterized by the phenocryst of K-feldspar. On the field occurrence, the Tadamigawa granite intrudes into the Hinoematagawa granite. Because these granites are located at high-mountain area, precise field research has not been attempted. In this study, 7 samples of the Hinoematagawa granite and 34 samples of the Tadamigawa granite were analyzed for major, minor and REE compositions by XRF and ICP-MS, respectively. Moreover, we obtained K-Ar ages of biotite isolated from both granites, and Fe<sub>2</sub>O<sub>3</sub>/FeO ratios by titrimetry with potassium permanganate.

SiO<sub>2</sub> contents of the Hinoematagawa granite and the Tadamigawa granite range from 59.6 to 69.4 wt.% and from 62.8 to 74.6 wt.%, respectively. K-Ar ages of the Hinoematagawa granite and the Tadamigawa granite are 102.3 Ma and 102.7 Ma, respectively. These ages are much older than 67 Ma of the previous K-Ar age data obtained by Kawata and Ueda (1966). Both of granites may be formed at same time by Cretaceous igneous activity and generated from the same magma origin because they show similar trend on the Harker's diagram. Those granites are I type because almost all samples show low degree of alumina-saturation (A/CNK < 1.1). REE abundance patterns of all samples normalized by chondrite show high-LREE pattern. Many samples show negative Eu anomaly (Eu/Eu\* = 0.24-1.01), and the value of Eu anomaly increase with decreasing anorthite content calculated by CIPW norm. The value of Eu anomaly might be concerned with the crystallization differentiation of the original magma. The large Eu anomaly of the Tadamigawa granite shows much differentiation of the granitic magma. The anomaly is caused by the differentiation of anorthite in the Tadamigawa granite. The Hinoematagawa granite shows low Fe<sub>2</sub>O<sub>3</sub>/FeO ratio (0.28-0.39). It may be generated from the magma which has low oxygen fugacity.

Keywords: Fe<sub>2</sub>O<sub>3</sub>/FeO ratio, K-Ar age, REE, Granite, Tadamigawa, Hinoemata

## Generation of TH and CA suite magmas at Chokai volcano in the NE Japan rear-arc

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The Quaternary Chokai volcano is located in the rear-arc side of the NE Japan arc. Chokai volcano is a typical stratovolcano and the eruption activities are classified into Stages 1, 2, and 3 (Hayashi, 1984; Ban *et al.*, 2001). Stage 1 lavas are olivine two-pyroxene basalt to two-pyroxene andesite, and the lavas contain phenocrystic minerals in equilibrium with the host magmas with occasional dusty plagioclase, which exhibits disequilibrium. An-contents (An%) of the plagioclase phenocryst cores show unimodal distribution, and An% decreases with increasing SiO<sub>2</sub> in the host lavas (An<sub>90-80</sub> for basalts, An<sub>70-50</sub> for andesites). Stage 2 lavas are mostly amphibole-bearing olivine two-pyroxene andesite with a small amount of olivine two-pyroxene basalt. Stage 3 lavas are olivine two-pyroxene andesite. Most of the plagioclase phenocrysts in the Stage 2 and 3 lavas possess dusty zones or sieve textures. An% in these plagioclase cores exhibits wide range (An<sub>50-80</sub>). Bulk-rock compositions of the Chokai lavas plot near the boundary between high-K and medium-K. On the FeO\*/MgO vs. SiO<sub>2</sub> diagram, the Stage 1 lavas fall on tholeiitic (TH), whereas the Stage 2 & 3 lavas fall on calc-alkaline (CA) fields. The Stage 2 & 3 lavas collectively show straight trend on MgO vs. SiO<sub>2</sub> plots and MgO content is higher than those in the Stage 1 lavas. Sr isotope compositions of the Stage 1 lavas gently increase with increasing SiO<sub>2</sub> (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.70303 - 0.70341) contrasting to the steep increase shown by the Stage 2 & 3 lavas (0.70288 - 0.70342). The Stage 1 geochemical trends can simply be explained by fractional crystallization of a basalt magma with minor crustal assimilation. The Stage 2 & 3 trends can be generated by mixing between basaltic and felsic magmas. The Stage 1 parental basalt magma differs from the Stage 2 & 3 basalt mixing end-member, chemically and isotopically. The petrological and geochemical characteristics of the Chokai TH (Stage 1) and CA (Stage 2 & 3) suite magmas are similar to those in the Zao and Azuma TH and CA suite magmas found at the volcanic front of the NE Japan arc. Tatsumi *et al.* (2008) and Takahashi *et al.* (2012) have argued that the TH basalt with radiogenic Sr was formed by melting of the lower crustal amphibolite, whereas CA basalt with unradiogenic Sr was formed by magma mixing between a mantle derived-basalt and a felsic magma generated from the TH basalt by fractional crystallization. The same mechanism would explain the TH and CA suite magmas at Chokai. The Sr isotopic composition of the Stage 1 TH lavas overlaps with that of amphibolite xenoliths from lower crustal depth beneath Ichinomegata volcano (0.7032 to 0.7051; Yamamoto and Takeda, 2008). The geochemical features of the xenoliths and the TH basalt suggest that the Stage 1 TH basalt can be formed by melting of the amphibolite.

Keywords: rear-arc, tholeiitic series, calc-alkaline series, Sr isotope ratio



## Estimation of fluxes at mid-ocean ridges and geochemical cycles on the Earth's surface of sulfur and halogens

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### [Introduction]

Volatile elements on the Earth's surface have been accumulated by degassing from the solid Earth. Noble gases have been used as tracers to constrain the degassing history. Such studies suggested that the most part of the atmospheric argon had been accumulated in the early Earth [1], and estimated carbon and nitrogen cycles by comparisons with well determined helium-3 (<sup>3</sup>He) fluxes from the inside to the surface of the Earth [2, 3]. They constrain the evolutionary history of the Earth's surface. On the other hand, though sulfur (S) and halogens (fluorine (F) and chlorine (Cl)) form various compounds on the Earth's surface and significantly affect the environment, their geochemical cycles are not well understood. Fluxes of S and halogens at MORs (Mid-Ocean Ridges), where material migrations are dominant because of intensive volcanic activities, have been estimated based on compositions of quenched glassy rims of MORBs (Mid-Ocean Ridge Basalts) which retain those of magmas derived from the upper mantle. However, they may be overestimated [4], and plausible estimations based on compositions of both silicate melts and fractions released as hydrothermal fluids are needed. We determined compositions of hydrothermal fluid and melt components retained respectively in vesicles and solids of MORB glasses (Fig. 1) and estimated MOR fluxes of S and halogens to constrain the evolutionary history of the Earth's surface.

### [Analyses]

We analyzed glasses of MORBs collected at 2 sites on the East Pacific Rise, 2 sites on the Mid-Atlantic Ridge and 2 sites on the Central Indian Ridge. After volatiles in vesicles were extracted using the frozen crushing method [5], concentrations of <sup>3</sup>He were measured using a noble gas mass spectrometer (VG-5400) and those of S and halogens were measured using an ion chromatography (ICS-2100). Concentrations of S and halogens in solids were measured using a secondary ion mass spectrometer (NanoSIMS 50). We calculated relative molar ratios of S and halogens to <sup>3</sup>He (S/<sup>3</sup>He, F/<sup>3</sup>He and Cl/<sup>3</sup>He) and estimated MOR fluxes of S and halogens calibrating against the known <sup>3</sup>He flux (527 mol/yr [6]) [2, 3]. Using molar ratios, it is not necessary to discuss variations of volatile concentrations due to differences in porosities of each sample.

### [Results and Discussion]

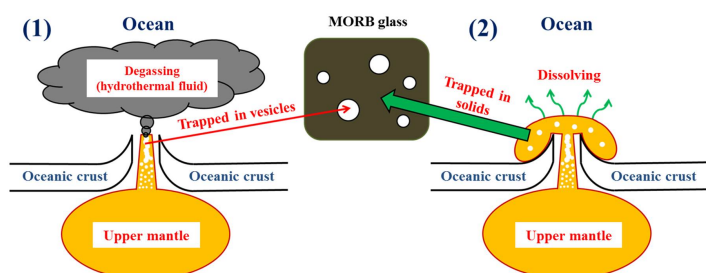
<sup>3</sup>He concentrations in vesicles were  $(1.8-6.3) \times 10^{-15}$  mol/g. Global averages of S/<sup>3</sup>He, F/<sup>3</sup>He and Cl/<sup>3</sup>He were calculated. For vesicle components, they are  $(4.2 \pm 1.6) \times 10^7$ ,  $(1.4 \pm 0.7) \times 10^6$  and  $(2.6 \pm 1.0) \times 10^7$ , respectively. For bulk compositions, they are  $(0.3-1.2) \times 10^{10}$ ,  $(1.6-6.5) \times 10^9$  and  $(0.7-3.0) \times 10^9$ , respectively. Using these ratios and the known <sup>3</sup>He flux at MORs, MOR fluxes were estimated to be  $(2.2 \times 10^{10}-6.6 \times 10^{12})$  mol/yr for S,  $(7.1 \times 10^8-3.4 \times 10^{12})$  mol/yr for F and  $(1.4 \times 10^{10}-1.6 \times 10^{12})$  mol/yr for Cl. Mass balances were discussed comparing MOR fluxes in this study with arc fluxes, influxes at subduction zones and rates of accretion to the continental crust. When we assume the continuous degassing with the low MOR fluxes estimated using vesicle (hydrothermal fluid) compositions, the amount of S accumulated on the Earth's surface are calculated to be 50 times lower than its surface inventory, and halogens are calculated not to be accumulated on the Earth's surface because of dominant influxes. This implies a possibility that significant amounts of chemically reactive volatile elements such as S and halogens were accumulated on the Earth's surface in the early Earth.

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Keywords: sulfur, halogen, helium, mid-ocean ridge basalt, flux, geochemical cycle





**[Fig. 1. A schematic view of degassing processes at mid-ocean ridges]**

(1) Bubbles connect each other and make paths in ascending magmas. Components fractionated into gaseous phases are released to the ocean.  
⇒ MOR fluxes dominated by hydrothermal fluid (volcanic gas) components can be estimated based on compositions of vesicles in MORB glasses.

(2) Erupted silicate melts are altered and bulk components are released to the ocean.  
⇒ MOR fluxes provided by intensive alteration processes of MORBs can be estimated based on bulk compositions of MORB glasses.

## Experiments for development of new method for measurement of diffusion gas

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### 1) Introduction

Ascent of magma causes gasification of volatile components in magma, which provides the driving force for explosive eruption. Release of volatiles from magma highly changes its physical properties such as viscosity and density, and thus influences the violence of explosions. Examination of the behavior of volatiles can provide a better understanding of degassing processes and volcanic eruptions.

Carbon dioxide is major constituent of volatile in magma after water and less reactive with ground water and subsurface material after degassing. The emission rate of diffuse CO<sub>2</sub> can increase drastically prior to volcanic eruption (Hernandez et al., 2001). Hence, studies of diffuse CO<sub>2</sub> have become a powerful geochemical tool for monitoring volcanic activity (e.g. Hernandez et al., 2001; Perez et al., 2011). It is very important to map surface CO<sub>2</sub> efflux anomalies and to estimate the total output of this gas regularly in order to have a better understanding of on-going volcanic processes (Salazar et al., 2001). Measurement of diffuse soil CO<sub>2</sub> has been usually performed in-situ by means of a portable infrared absorption CO<sub>2</sub> analyzer (LICOR-800 system) interfacing to a palm-top computer that processes data. Actually, handling of LICOR-800 system is simple and easy, however, surveillance for spatial distribution by means of this system is time-consuming. In this study, some fundamental laboratory experiments were performed to develop a new chemical method for monitoring flux of diffuse soil CO<sub>2</sub>.

### 2) Experiments

A vinyl chloride tube 20cm in diameter and 30cm in height is used for gas diffusion chamber. CO<sub>2</sub> gas diffuses through dry sand in the gas chamber. Small fan is equipped for convection of diffuse CO<sub>2</sub> in the chamber. A plastic box containing 5M KOH solution is within the chamber to absorb CO<sub>2</sub> in the chamber. Some experiments were performed parameterizing CO<sub>2</sub> gas flow rate, absorption time, surface area of the alkaline solution and so on.

### 3) Result and Discussion

Experimental results indicate that absorption for more than 2 hours can get the recovery efficiency of diffuse CO<sub>2</sub> gas reach around 1 although the flow rate of CO<sub>2</sub> is ten times higher than the diffusion rate at Kusatsu-Shirane and Usu volcanoes. Fan convection in the chamber has very positive impact for absorption of CO<sub>2</sub> in the alkaline solution. Further, flow rate of diffuse H<sub>2</sub>S is estimatable through analysis of dissolved sulfur in the alkaline solution. This method newly enables to estimate diffuse CO<sub>2</sub> and H<sub>2</sub>S flux in a short time, and monitor spatial distribution with high temporal resolution.

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Keywords: diffusion gas, chemical method

## Effective pair potential for Ca-O bonds in CaGeO<sub>3</sub> perovskite, garnet, wollastonite

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The CaGeO<sub>3</sub> perovskite and garnet were synthesized in a cubic anvil type apparatus under high pressure. The measurements of Ca and Ge K-edge XAFS spectra were carried out in the transmission mode at temperature up to 700 K. The effective pair potentials  $V(u)=au^2/2+bu^3/3!$ , for Ca-O bond in various phases of CaGeO<sub>3</sub> have been investigated by the temperature dependence of EXAFS Debye-Waller factors. The potential coefficient  $a$  for the Ca-O bond in perovskite-type CaGeO<sub>3</sub> is small, 4.4 eV/Å<sup>2</sup>, compared with those in garnet (6.0 eV/Å<sup>2</sup>) and wollastonite (6.4 eV/Å<sup>2</sup>). The potential for Ca-O bond in perovskite is broader than those in other CaGeO<sub>3</sub> polymorphs, which is one reason for the Clausius-Clapeyron's curve for perovskite-garnet phase boundary having a negative slope. The potential coefficients for the Ca-O in perovskite are significantly smaller than those for the longer Ge-Ge distances as the framework vibration though the potential coefficient decreases usually as a result of the larger bond distance.

## Development of an ultra high precision stable isotopic analysis of Sr by DS-TIMS technique

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Stable isotope fractionation is a frequently used geochemical tool to trace geological and geochemical processes, to estimate the temperature of the process, to discriminate the geological source of the material and to constrain marine elemental budgets (e.g. Hoefs, 2004). Application of the stable isotope fractionation of heavy elements, such as Fe, Zn, Cu and Sr to geology or environmental science is limited compared with the "traditional" light gaseous elements, such as H, C, O and N. One of the reasons for this is that the analytical precision is not small enough compared with the typical isotopic variability among geological and environmental samples. For example, the typical analytical uncertainty of  $\delta^{88}\text{Sr}$  measured by MC-ICP-MS is around 0.05 to 0.1 permil, while the typical isotopic variability is about 1 per mil and about 3 permil for geological and meteorite samples, respectively (Ohno et al., 2008; Moynier et al., 2010; Charlier et al., 2012). To discuss the sub-permil order stable isotopic difference in nature, improvement of the analytical precision is required.

We are developing a technique for ultra high precision stable isotopic analysis of Sr by double spike thermal ionization mass spectrometry (DS-TIMS) using Thermo Finnigan Triton at Kochi Core Center. DS-TIMS has advantages over MC-ICP-MS technique in sensitivity and higher analytical precision for measuring isotope ratios of elements with low first ionization potential, including Sr. We will discuss the current state of the analytical precision and accuracy as well as the sources of analytical error that may affect the analytical results.

Keywords: stable isotope, Sr isotope

## Ni isotopic analyses of meteorites using TIMS and MC-ICP-MS

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The isotope analysis of the meteorites can provide important information about the origin and evolution of our solar system. As for Ni, the isotopic anomalies on <sup>60</sup>Ni (decay product of <sup>60</sup>Fe), as well as <sup>62</sup>Ni and <sup>64</sup>Ni have been reported from both undifferentiated and differentiated meteorites (e.g. Shukolyukov et al. 1993, Steele et al. 2011). However, there have also been reports of disagreement between data obtained using different analytical approaches (e.g. Cook et al. 2008, Chen et al. 2009, Moynier et al. 2011), which need to be clarified in order to fully understand the cosmochemical implications of the isotope data. Here we report the results of Ni isotope analysis for carbonaceous chondrite Allende and iron meteorites Carbo, Toluca, and Buevaventura.

The Allende and iron meteorites were dissolved in HF-HNO<sub>3</sub> and HCl-HNO<sub>3</sub>, respectively, and Ni was extracted using a method modified from Yamakawa et al. (2009). The chemical yield and the level of impurities in the Ni cut were monitored using ICP-MS. The high-precision Ni isotopic analyses were performed using TIMS (MAT262, TRITON) and MC-ICP-MS (NEPTUNE). The activator for the analysis using TIMS was prepared by modifying the Si-Al-B type activator of Yamakawa et al. (2009) to gain higher beam intensity for a longer period of time.

The data for the iron meteorites obtained using both TIMS and MC-ICP-MS clustered around epsilon <sup>60</sup>Ni = 0. They were broadly similar to the data reported by Chen et al. (2009), however, no obvious correlation between the <sup>56</sup>Fe/<sup>58</sup>Ni and epsilon <sup>60</sup>Ni ratios was observed. Anomalies on <sup>62</sup>Ni and <sup>64</sup>Ni were also not detected in this study, but improvement in the analytical precision is necessary to further explore this issue. Bulk Allende also showed no anomaly on epsilon <sup>60</sup>Ni, implying the low abundance of <sup>60</sup>Fe in the early solar system and/or homogenization of Ni isotopes after the accretion of its parent body.

The data obtained so far in our laboratory is restricted to samples with relatively small variation in the <sup>56</sup>Fe/<sup>58</sup>Ni ratio. Thus, additional analyses of samples from different meteorite classes, as well as phases with high Fe/Ni ratio (such as troilite) is required to shed light on the nature of the Ni isotope in meteorites.

Keywords: Ni isotope, Meteorite, TIMS, MC-ICP-MS

## Metal-silicate partitioning of lithophile elements and implications for potassium and light elements in the core

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The partitioning of lithophile elements (K, O, Si, Mg, Al, and Ca) between liquid metal and silicate melt were investigated up to 138 GPa and 5450 K in S-free/S-bearing Fe + K-doped pyrolite system, in order to constrain the amounts of radioactive <sup>40</sup>K and other light elements in the core. The obtained iron-potassium exchange coefficients show strong temperature (T) dependence but negligible effects of pressure (P) and sulfur content, not supporting the transition-metal-like behavior of potassium at high pressure. As a consequence, present experiments suggest only ~10 ppm potassium in the core, which yields present-day heat production of ~0.1 TW, even when we assume the entire core-mantle chemical equilibrium at 136 GPa and 5300 K (liquidus of pyrolitic mantle). On the other hand, the core dissolves substantial amounts of silicon and oxygen as a consequence of reaction with a basal magma ocean at 4500-5000 K, which account for the 10% core density deficit. In addition, quenched liquid iron obtained in relatively high-temperature experiments included certain amounts of Mg, Al, and Ca, suggesting that these elements may have been once incorporated into the core at the time of giant impact. A more realistic model for the Earth's core must consider the combined effects of material that equilibrated at modest P-T with the material that was added at very high P-T, and the effect of latter components are focused in this study.

Keywords: metal-silicate partitioning, high pressure, core formation, magma ocean, potassium, light elements

## Rarotonga magma as a mixing product of EM-1 and HIMU in the Cook-Austral volcanic chain, the South Pacific.

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We present radiogenic isotope (Os, Pb, Nd, Sr) and major and trace element data on lavas from Rarotonga Island, the Cook-Austral volcanic chain in the South Pacific, and examine the origin of the source of these lavas. Relationship between Ni, MgO and Os concentrations of the lavas indicates that Os contents in magma are controlled by fractionation of sulfide. Osmium concentration of the samples with high- Os and Ni (over 80 ppt and 100 ppm, respectively) are least affected by magma differentiation. Since Os is a highly compatible element and is readily removed from magma during sulfide crystallization, shallow-level assimilation of crustal material and sediment with extremely high  $^{187}\text{Os}/^{188}\text{Os}$  during magma ascent significantly alters the original Os isotopic compositions of magma. The lavas with low-Os, therefore, do not preserve the initial Os isotopic composition of magma and possess the elevated Os isotope ratios. The  $^{187}\text{Os}/^{188}\text{Os}$  ratios of the Rarotonga lavas with Os concentrations more than 80 ppt (or Ni > 100 ppm) fall in a relatively limited range from 0.1282 to 0.1343 with an average of 0.132, which is possibly the initial Os isotopic composition of the Rarotonga mantle source. Evaluation of published data on the Pitcairn lavas known as originated from EM-1 in the similar manner to that used for that of Rarotonga data suggests that the lavas with high-Os and Ni (over 80 ppt and 300 ppm, respectively) keep the original Os signature of EM-1 with least assimilation. The Os isotopic compositions of such samples lie in a small range between 0.1350 and 0.1381 with an average of 0.1369. This value is much lower than the value of approximately 0.15 widely accepted as the  $^{187}\text{Os}/^{188}\text{Os}$  of EM-1. If in the case, the Os-Pb-Nd-Sr isotopic data of the Rarotonga lavas suggest that they are mixing products of EM-1 and HIMU.

Keywords: Polyneisa, hot spot, Rarotonga island, EM1, HIMU

## Re-Os mineral isochron age of peridotite xenoliths from Hannouba, China: Implications for Os behavior in mantle

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Geochemical and isotopic data on mantle peridotite xenoliths provide key constraints on the evolution of lithospheric mantle beneath the thick continental crust. Especially, Os isotopes could give us information on the age of continental roots (Pearson, 1999) and genetic relation of the lithospheric mantle to the overlying continental crust. The continental crust was possibly formed by extraction from primitive upper mantle to form both the lithospheric mantle and the continental crust. However, Re introduction from the host magma or through metasomatism leads to rarely observed reliable Re-Os isochron for peridotite xenolith suites. Gao et al. (2003) successfully obtained the Re-Os whole-rock age of  $1910 \pm 220$  Ma with an initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio of  $0.1156 \pm 0.0009$  for peridotite xenoliths from Hannouba, China. However, five out of thirteen analyses were plotted out of the isochron trend and were eliminated from the regression, which indicates disturbance of the Re-Os system of the samples or analytical problem. In this study, we have analyzed whole-rock samples and minerals such as olivine, orthopyroxene, clinopyroxene and spinel of fresh peridotite xenoliths in continental basalt in Hannouba to make detailed age constraints on the evolution of sub-continental mantle in this area.

As shown in the figure, most of the Re and Os isotopic data of the whole-rock samples obtained in this study are plotted on the isochron line reported by Gao et al., (2003), implying the geological event at 1.9 Ga. Preliminary results of mineral analysis suggest a Re-Os mineral isochron with a younger age for a suite of Hannouba peridotite xenoliths, indicating that minerals possibly record a younger geological event such as metasomatism or shallow-level processes within the continental crust.

Keywords: Hannouba, peridotite xenolith, dating, Re-Os system, sub continental mantle



## Does E-chondrite relate to the chemical state of the Earth?

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The chemical state of the Earth has been estimated based on chemical and isotope analyses of terrestrial materials which compose the crust and the mantle, taking the physical and geological information on physical properties account. However, to understand the chemical state of the early Earth and the whole Earth from the view of material science, it is required to use materials which could represent them even as approximated ones. As geochemical approaches to pursue this purpose, CI-chondrite has been generally used, because it maintains most abundant volatile elements among meteorite groups and show similar chemical compositions of the Sun which have been estimated by spectroscopy.

However, it does not always guarantee that CI-chondrite directly represents the chemical state of the Earth when it was formed. Hence, some different models have been proposed so far based on the other meteorite groups. Here, noting the importance of similarities with the Earth in oxygen isotopes, the significance of E-chondrite group is reexamined to estimate the chemical state of early and deep Earth.

Three oxygen isotopes of terrestrial and extraterrestrial materials have been extensively studied since 1970's, initiated by R.N. Clayton's group and followed by some other groups. Through such studies, it has been revealed that in the ( $\Delta$ )17O/16O- ( $\Delta$ )18O/16O diagram data of terrestrial materials lie on an isotope mass fractionation line (TFL) and the other extraterrestrial materials are mostly off the line and each group forms a different isotope mass fractionation line. Among extraterrestrial materials, only lunar samples and E-chondrite group lie on the TFL. Even Martian meteorites do not lie on the TFL. Such results indicate that the Moon and E-chondrite group might have been possibly formed in the similar chemical state to that of the Earth. This is compatible with the observation that stable isotopes such as C and N of the Earth are more similar to those of E-chondrite rather than C-chondrite groups.

In the (Fe+FeS)/Si-FeO/Si diagram, it has been clearly demonstrated that E-chondrites represent quite reduced conditions, while C-chondrites show much oxidized conditions. In the same diagram, mantle xenoliths are plotted in a rather reduced region. It has been suggested that the surface condition of the early Earth might have been in a relatively reduced condition. The Redox state of E-chondrites and the Moon might reflect it.

Furthermore, the estimated chemical state of the lower mantle would highly depend on the model of the reference material. If we assume C-chondrite as a starting material to form the Earth, the Redox state of the lower mantle would be estimated to be less reduced condition. However, if E-chondrite is assumed to have been related to the early Earth, the inferred state of the lower mantle would be in a rather reduced state. It might be compatible with the observation that kimberlite magma, which might have been originated in the lower mantle, show a rather reduced condition which is different from those of the other volcanic rocks.

It should be noted, however, that the chemical composition of the E-chondrite does not always represent that of the whole Earth, just as in the same manner that the Moon does not have the same composition of the Earth.

Keywords: Earth, chemical state, E-chondrite, relationship

## Role of crystal fractionation and effect of degree of dehydration in producing FOZO and HIMU reservoirs

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It has been widely accepted that recycling of oceanic crust with/without sediments produced at least three enriched reservoirs in the mantle (HIMU, EM1 and EM2). This fundamental concept of the geochemistry is called 'mantle reservoir model' (White, 1985; Zindler and Hart, 1986), in which isotopic composition of the ocean island basalts (OIBs) are explained by mixing of distinct and isolated reservoirs in the Earth's interior. The origins of enriched components are usually explained by recycling of oceanic crust (HIMU) with variable amounts of sediments (EM1 and EM2).

In early research on the mantle reservoirs, the isotopic composition of OIBs was mainly explained by the mixing of depleted MORB mantle (DMM) and three enriched reservoirs (HIMU, EM1, and EM2) whose isotopic compositions are enriched extremes. In addition to these reservoirs, the importance of reservoirs whose isotopic compositions are intermediate has been pointed out, these are, FOZO (Focal Zone, Hart et al., 1992), C (common component; Hanan and Graham, 1996), PREMA (Prevalent Mantle, Zindler and Hart, 1986) and PHEM (Primitive Helium Mantle, Farley et al., 1992). Although the existence of these reservoirs is still controversial, the isotopic compositions of these reservoirs, in particular FOZO, have been used to designate the isotopic distribution of OIBs.

In the present study, geochemical modeling has been conducted to evaluate the origin of HIMU and FOZO reservoirs. For the modeling, MORB compositions from East Pacific rise and Mid-Atlantic ridge are compiled from published data (PetDB: <http://www.earthchem.org/petdb>). The results suggest that crystal fractionation at a mid-ocean ridge can increase U and Th concentrations relative to Pb content, producing high U/Pb and Th/Pb ratios in evolved MORBs. In addition, dehydration beneath a subduction zone can increase U/Pb and Th/Pb ratios of recycled oceanic crust, i.e., strongly dehydrated oceanic crust can be a suitable source material of HIMU magmas and less dehydrated MORBs can produce material with FOZO isotopic signature. Although depleted Sr isotopic composition of HIMU magma seems to contradict with high Rb concentration of evolved MORBs, high degree of dehydration beneath subduction zones can produce large Rb loss, producing depleted Sr isotopic composition of recycled crust that is suitable for the HIMU source. In this context, magma evolution at mid-ocean ridges and variable degree of dehydration beneath subduction zones play an essential role in producing the isotopic variations between HIMU and FOZO. Combination of crystal fractionation at mid-ocean ridges and degree of dehydration beneath a subduction zone can produce observed isotopic array of OIBs.

Keywords: Mantle reservoir, Recycling, HIMU, FOZO, Mid-ocean ridge, Subduction zone

## Geochemical variations in Quaternary magmas along the volcanic front of Kyushu, Japan

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The Quaternary magma genesis of central Kyushu, Japan, was investigated by geochemical lateral variations. This area is underlain by the Philippine Sea Plate including the older Kikai Basin segment (60-40 My old) and the younger Shikoku Basin segment (26-15My old) divided by the Palau-Kyushu Ridge. Sr/Y ratios of the Quaternary lavas of the Quaternary lavas decrease from north to south along the volcanic front of the Kyushu arc. All analyzed Sr-Nd-Pb isotope compositions plot close to or along mixing curves between MORB-type mantle wedge and Philippine Sea Plate sediments, or between Shikoku Basin basalts and the Shikoku Basin sediments on the plate. <sup>87</sup>Sr/<sup>86</sup>Sr ratios negatively co-vary with the Sr/Y ratios and increase from north to south. These geochemical characteristics suggest that Quaternary magmatism in central Kyushu was controlled by various contributions of the materials from the Philippine Sea Plate slab. The negative correlations between Sr/Y and Sr isotope ratios suggest that extent of addition of the partial melts derived from the subducting slab is the prime control of the spatial variations. These observations also suggest that the high Sr/Y slab component in the north would have been derived from the partial melts from the hot and young Shikoku Basin slab, whereas the low Sr/Y flux in the south may have derived from slab fluids from the older Kikai Basin slab.

Keywords: adakite, Philippine Sea plate, volcanic front, trace elements, Sr-Nd-Pb isotopic compositions