

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.

References

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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 1×10^{-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 1×10^{-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 6×10^{-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.

³He/⁴He ratios of the Udachnaya kimberlite olivines are ca. 6 Ra (Ra = 1.4×10^{-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 ³He/⁴He ratios. One group is characterized by ³He/⁴He 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 ³He, 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 ³He/⁴He 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; SiO₂ = 35-78.7; Al₂O₃ = 10.1-27.2; MgO = 0.005-11.9; CaO = 0.09-11.15; Fe₂O₃t = 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)_N 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 K₂O/Na₂O ratios, mafic rocks with Mg# = 47.7-66.3 in this area are further classified as sodic alkali basalts (K₂O/Na₂O < 1, dominant species), with one sample from the Lake Nyos area as potassic alkali basalt (K₂O/Na₂O = 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 (K₂O/Na₂O = 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 constraints on the petrogenesis of these lavas. Existing data for radiogenic isotopes in the OKVG ranges for ⁸⁷Sr/⁸⁶Sr = 0.70334-0.70382 and ¹⁴³Nd/¹⁴⁴Nd = 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 H_2O but as CH_4 or 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 H_2O .

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 SiO₂ (43 %) and higher FeO (18-19 %) contents, consistent with expansion of garnet stability field increasing FeO contents. The hornblendites have relatively lower Al₂O₃ (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 SiO₂ contents in increasing MgO contents, respectively. Secondary elemental movement accounts for the increase and decrease in SiO₂ contents because SiO₂ contents of magmas change a little compared with MgO, FeO and Al₂O₃ contents during fractional crystallization of basaltic magmas.

Except for the altered rocks with quite higher or lower SiO₂ 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 ~ 70 GPa and ~ 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 ~ 70 GPa and ~ 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 NH₃ dissociation and conversion of CO₂ to CH₄, 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.

References

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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 ~ 180 GPa.

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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. Zr⁴⁺ 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 Zr⁴⁺ is between 6 and 7. The eight-coordinated Zr⁴⁺ 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 δCe and δNd 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