

Metal-silicate partitioning of U, Th, Nd, Sm at high P-T: Implications for heat and chemical budget in the core

NOMURA, Ryuichi^{1*}; HIROSE, Kei¹; KIMURA, Jun-ichi²; CHANG, Qing²

¹ELSI, Titech, ²IFREE, JAMSTEC

The excess abundance of siderophile elements in the mantle has been proposed that the core was equilibrated with the mantle at ~3500 K, ~30GPa and $fO_2 \sim \Delta IW-1$ at the Earth's formation (e.g. Righter, 2011 EPSL). Much more severe condition (>6500 K) is supposed immediately after the moon-forming giant impact based on the study of numerical simulation (e.g. Canup, 2012 Science). The occurrence of high-temperature equilibrium between the core and the mantle evoked that the early core had once incorporated heat-genic radionuclides (U, Th) and rare earth elements (e.g. Nd, Sm), which are known as highly lithophile elements, suggesting profound implications for the thermal history (Nimmo, 2007 Treatise on Geophysics) and early-formed geochemical reservoirs (e.g. sub-chondritic $^{142}\text{Nd}/^{144}\text{Nd}$, Boyet and Carlson, 2005 Science).

However, partitioning of these elements between liquid metal and silicate melt has been investigated only up to 20 GPa and 2500 K using multi-anvil apparatus (Malavergne et al., 2007 GCA). Here, we extended pressure and temperature conditions up to 138 GPa and 5200 K at $\Delta IW-2-1$ using laser-heated diamond cell (LH-DAC) and field emission-type electron probe microanalyzer (FE-EPMA, JXA-8530F, JEOL) and laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS, Kimura and Chang, 2012 JAAS). K (4wt%) and trace elements (U, Th, Nd, Sm, Hf, W, Pb) doped pyrolytic gel, and pure iron were used as starting materials. Iron-free pyrolytic gel was used as a thermal insulator. After high P-T experiments using LH-DAC, recovered samples were analyzed by FE-EPMA and LA-ICP-MS for major and trace elements, respectively. Fe and Mg were used as internal standards for metal and silicate, respectively for LA-ICP-MS. The diameter of ablated area was about 10 μm , small enough to measure each (silicate melt/liquid metal) phase.

The results are summarized as follows;

(1) Partition coefficient of U and Th are 10^{-3} - 10^{-2} at 3500-4000 K and $\Delta IW-1$ to -1.5, resulting in 0.02-0.2 ppb (<0.03 TW) U and 0.08-0.8 ppb (<0.04 TW) Th into the core assuming that the abundance of U and Th are 22 and 83 ppb in the Earth's mantle (McDonough and Sun, 1995). Total <0.1 TW (present-day) heat flow in the core has negligible effect on the thermal history of the Earth with <50 K change in the initial temperature at core-mantle boundary (Nimmo, 2007 ToG).

(2) The ratio of partition coefficients, $D_{Nd}(\text{metal/silicate})/D_{Sm}(\text{metal/silicate})$, was always unity despite of large temperature dependence for each D, suggesting that the core could not be a candidate for an early-formed (with sub-chondritic $^{142}\text{Nd}/^{144}\text{Nd}$) hidden reservoir.

Element partitioning between mantle minerals and melt under deep lower mantle condition

TATENO, Shigehiko^{1*}; SAKATA, Shuhei²; HIRATA, Takafumi²; HIROSE, Kei³

¹Dept. Earth & Planetary Sciences, Tokyo Institute of Technology, ²Dept. Earth & Planetary Sciences, Kyoto University, ³Earth-Life Science Institute, Tokyo Institute of Technology

Melting is a primary mechanism of chemical evolution of our planet. Earth's mantle would have been completely molten due to moon-forming giant impact, leading to a global magma ocean. Resultant fractional crystallization by secular cooling progressively induced the chemical evolution of the Earth. As a consequence, remnant silicate melt left at the present day at the base of the mantle is a possible explanation for the seismically observed ultralow-velocity zones (ULVZs). The knowledge of melting phase relations and element partitioning between mantle minerals and partial melt is crucial to understand the chemical evolution in the early Earth and the nature of ULVZs. However, melting experiments under the middle to deep lower mantle conditions are quite limited.

Here we carried out the melting experiments on KLB-1 peridotite and basalt to deep lower mantle conditions up to 179 GPa by a combination of laser-heated diamond-anvil cell experiments and chemical analyses of recovered samples. Textural characterization and chemical analysis on major and minor elements were made by a field-emission-type electron microprobe (FE-EPMA). Trace element abundances were determined by a laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Typical crater diameter was 2 or 5 μm by using ArF Excimer laser.

Results shows that the liquids phase was MgSiO_3 -perovskite at least above 34 GPa and further to post-perovskite in KLB-1 peridotite. The Fe-Mg distribution coefficients (K_D) between perovskite/post-perovskite and melt decreased considerably with increasing pressure, leading to strong Fe-enrichment in partial melts. It supports dense partial melts in a deep lower mantle, which migrate downward to the core mantle boundary (CMB). Furthermore, CaSiO_3 -perovskite (CaPv) was found to be a liquids phase under whole lower mantle condition in MORB bulk composition. We then investigated the minor/trace element partitioning between CaPv and melt in basaltic composition. Partition coefficient of alkali elements such as Na and K increases with increasing pressure. In particular, potassium, known as highly incompatible element, become compatible with pressure, whose partition coefficient exceeded the unity at 90 GPa. Although pressure effect on D_{Sm} and D_{Nd} was not found even to 80 GPa, D_{Sm}/D_{Nd} decreases with increasing pressure and will reach to the unity at around 100 GPa. Our results shows that Sm and Nd was equally partitioned to partial melt and residual solids upon fractionation of CaPv from primordial deep magma ocean. This has profound implications for the origin of the super-chondritic $^{142}\text{Nd}/^{144}\text{Nd}$ for all terrestrial rocks.

Melting relation on FeO-SiO₂ system at high pressure and the fate of the subducted banded iron formations

KATO, Chie^{1*} ; NOMURA, Ryuichi¹ ; HIROSE, Kei² ; MIYAKE, Akira³ ; OHISHI, Yasuo⁴

¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology, ²Earth-Life Science Institute, Tokyo Institute of Technology, ³Division of Earth and Planetary Sciences, Kyoto University, ⁴Japan Synchrotron Radiation Research Institute

Subduction of banded iron formations (BIFs) may have played a significant role on the evolution of the core-mantle boundary (CMB) region and the chemical stratification at the topmost core. Almost all of the BIFs that had been deposited on the seafloor must have been subducted into the mantle and only a small portion was left at the surface today. Because of their high density, BIFs may have fallen down toward the CMB region. The amount of subducted BIFs is estimated to be 2×10^8 km³, which roughly matches with the total volume of the ultra-low velocity zones (Dobson and Brodholt, 2005, *Nature*). BIFs would be composed mainly of FeO and SiO₂ in the lower mantle because its oxidation state is close to iron-wustite buffer. We have performed melting experiments on FeO-SiO₂ system by laser-heated diamond-anvil cell technique at 25 - 140 GPa. FE-EPMA and FIB-SEM chemical analysis and observation of the texture of the recovered samples revealed that the liquidus phase was SiO₂ when starting from Fe₂SiO₄ fayalite, and compositions of the quenched melt suggested that the composition of the eutectic point was extremely FeO-rich (<0.6 wt% SiO₂). The solidus curve was constrained by observing the existence or no-existence of tiny quenched melt pools in each recovered samples. The solidus temperature at CMB pressure was 3,100 to 3,300 K that were lower than the solidus of pyrolite and the geotherm (Nomura et al., 2014, *Science*). These results imply that when the BIFs reach the CMB, they generate FeO-rich liquid that would be mixed with the basal magma ocean (Labrosse et al., 2007, *Nature*). This liquid would form a thin layer spread along CMB and react with the topmost core. Silicon content in liquid iron varies inversely to the oxygen fugacity when equilibrium with silicate melt (Ricolleau et al., 2011 *EPSL*). Assuming silicon-rich bulk core, exchange of silicon and oxygen would occur between the topmost core and FeO-rich silicate melt. This mechanism may account for the seismic wave speed anomaly observed at the topmost core which is thought to be honor to chemical stratification (Helffrich and Kaneshima, 2010 *Nature*; Buffett and Seagle, 2010 *JGR*).

Standardless determination of Nd isotope ratios in glasses and minerals using LA-MC-ICP-MS

KIMURA, Jun-ichi^{1*}; QING, Chang¹; KAWABATA, Hiroshi²

¹JAMSTEC, ²Kochi University

We investigated an appropriate instrumental setup for a laser-ablation multiple-collector inductively coupled plasma mass spectrometer (LA-MC-ICP-MS) and found that a reduced oxide setting allowed accurate and precise analysis of Nd isotope ratios in samples with or without concomitant interfering elements. We used an Aridus II solution/excimer laser dual-intake system. The ICP interface used normal sample and skimmer cones with torch shield switched off and an additional large interface rotary pump. The setting accomplished reduced oxide levels NdO^+/Nd^+ 0.01~0.05%, without significant sacrifice of the instrumental sensitivity (~70%). Oxide molecular ions for the lighter elements were negligible and accurate internal mass bias corrections were achieved for both Sm and Nd using isotopic ratios derived from thermal ionization mass spectrometry measurements. This report reveals a novel setup that requires no external mass bias corrections (standardless analysis) for Sm and Nd isotope analyses by both solution- and LA-MC-ICP-MS methods. Solution analysis of La Jolla Nd standard gave a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.511860 +/- 0.000026, which is in excellent agreement with the reference value (relative deviation (RD) = +6 ppm). JMC Nd standard solution yielded a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512216 +/- 0.000044 (RD = -14 ppm) while a Sm-doped JMC solution showed 0.512211 +/- 0.000030 (RD = -23 ppm). For LA analyses, the observed ratios and RDs were $^{143}\text{Nd}/^{144}\text{Nd}$ = 0.511921 +/- 0.000013 (RD = -12 ppm) for NIST SRM 610 glass standard (430 ppm Nd/453 ppm Sm); 0.512490 +/- 0.000018 (RD = +14 ppm) for Durango apatite (1121 ppm Nd/147 ppm Sm); 0.512200 +/- 0.000009 (RD = -26 ppm) for Fish Canyon Tuff sphene; 0.512232 +/- 0.000003 (RD = +65 ppm) for EDR monazite; and 0.512890 +/- 0.000147 (RD = +34 ppm) for groundmass of a St. Helena lava (22.7 ppm Nd/~5.01 ppm Sm). All measurements were in good agreement with the reference values. Examinations on Sm/Nd elemental fractionation have also been made and we confirmed that this was originated from the ICP interface region rather than at laser ablation site.

Keywords: LA-MC-ICP-MS, Nd isotope, glasses, minerals

Grain boundary diffusion of polycrystalline ice I_h under confining pressure of 100 MPa

NOGUCHI, Naoki¹ ; KUBO, Tomoaki^{2*} ; DURHAM, William⁵ ; SHIMIZU, Ichiko⁴ ; KAGI, Hiroyuki³

¹Graduate School of Engineering, Hiroshima University, ²Department of Earth and Planetary Sciences, Faculty of Sciences, Kyushu University, ³Geochemical Laboratory, Graduate School of Science, University of Tokyo, ⁴Department of Earth and Planetary Science, Graduate School of Science, University of Tokyo, ⁵Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology

Ice I_h is a primary constituent of surfaces of the icy Galilean satellites and ice sheets at the Antarctica. Thus understanding rheological behavior of ice I_h will contribute to better knowledge about the dynamics and tectonics of the surface of the icy satellites and ice sheets. Stress applied by the tidal deformation to the surfaces of the icy satellites was predicted to be very low, ~1 MPa (Sotin and Tobie 2004), and diffusion and grain-size-sensitive creeps probably control the deformation of the surfaces of the ice satellites. The deformation map under such a low stress condition can be constructed, based on two diffusion constants, grain boundary and volume diffusion coefficients, of polycrystalline ice I_h. The volume diffusion coefficient of ice I_h was determined from experiments using a single crystal of ice I_h (Ramseier 1967; Itagaki 1967), while the grain boundary diffusion coefficient has not been determined yet. Thus we carried out experiments to determine directly the grain boundary diffusion coefficient of polycrystalline ice I_h.

The diffusion couples have been composed of a pair of disks of pore-free polycrystalline H₂O and D₂O ices. The glass beads with a diameter of 2 μm were doped in the diffusion couples to prevent the grain growth during diffusion experiments by Zener pinning effect. The volume fraction of the glass beads was approximately 1 %. The diffusion experiments were carried out under the confining pressure of 100 MPa using a gas apparatus surrounded with a cryostat (Durham et al. 2001). Temperatures were set in the range from 235 K to 256 K. After keeping the diffusion couples in the deformation instrument for 20 ~94 hours, we shaved off thin sections from the diffusion couples. Two-dimensional diffusion profiles of the thin section were determined with micro-and imaging- Raman spectroscopes and a cryo-stage. The Raman mapping or Raman imaging measurements were carried out with keeping the thin sections at -90 °C. The concentration of deuterium can be determined from the relative intensity of Raman band of OH stretching mode to that of OD stretching mode using a quantitative curve. The two-dimensional distribution showed enrichment of deuterium at the grain boundaries near the H₂O/D₂O boundary. It indicates that grain boundary diffusion of ice I_h is rapid. The diffusion profiles obtained by the experiments enable to estimate the grain boundary diffusion coefficient of ice I_h, which is essential to construct the deformation map.

Keywords: ice, diffusion, grain boundary diffusion, hydrogen isotope, Raman spectroscopy, rheology

Trace elements and Sr-Nd isotopic compositions of the pre-Komitake volcano

SHIBATA, Tomoyuki^{1*} ; YOSHIMOTO, Mitsuhiro² ; FUJII, Toshitsugu³ ; NAKADA, Setsuya⁴

¹Institute for Geothermal Research, Kyoto University, ²Faculty of Science, Hokkaido University, ³Crisis & Environment Management Policy Institute, ⁴Earthquake Research Institute, University of Tokyo

The chemical characteristics of magmas from pre-Komitake Volcano, which is a buried and old volcanic body beneath the northeastern flank of Mt. Fuji, show the differences to those of Mt. Fuji (Yoshimoto *et al.*, 2010). According to Yoshimoto *et al.* (2010), incompatible elements of former magmas increase with increasing SiO₂, whereas those of later magmas increase at nearly constant SiO₂. They emphasized that those changes of the magma chemistry at this area from 250 ka to recent may have occurred due to a change in regional tectonics around 150 ka, although this remains unproven. To elucidate this problem, geochemical study for the magmas from pre-Komitake is essential. Therefore, we analyzed trace element and Sr-Nd isotopic compositions of those magmas. The samples are selected from the entire group, which are classified by lithology and chemistry (Group 1-3, Yoshimoto *et al.*, 2010), and from 188-412m (core ERI-FJ2) and 426-624m (core ERI-FJ3) in depth. Trace elements are analyzed using by quadrupole inductively coupled plasma mass spectrometer following by the method of Chang *et al.* (2003). Sr-Nd isotopic compositions are measured by thermal ionization mass spectrometer following by the procedure of Shibata *et al.* (2007) and Yoshikawa and Shibata (2003). The enrichments of LILE's, Pb and Sr, which are general characteristics of island arc magma (eg. Wood *et al.*, 1979), are observed from the analyzed samples in the primitive mantle normalized multi-element diagram. High Sr/Y ratios (70 in max.) and the weak positive Eu anomalies ($Eu^* = [Eu]_N / ([Sm]_N/2 + [Gd]_N/2)$; N means chondrite normalized value) are also found from several samples. The Sr and Nd isotope ratios show the variations from 0.703320-0.703476, and 0.512885-0.513087, respectively.

The Sr-Nd isotopic compositions of pre-Komitake volcano show a similar range of Mt. Fuji presented by Nagai *et al.* (2004), indicating that those magmas can be generated from the same source materials. Although the variations of Sr isotope compositions are small, significant differences are found. Most of the samples show similar Nd isotope ratios, whereas few samples show lower significant differences. These observations can be explained by 1) difference of slab derived fluid and 2) different degrees of crustal contaminations. It is unlikely that Nd isotope ratio of slab derived fluid is changed, because it is difficult keeping isotopic heterogeneity during the deep processes. Crustal rocks, which have similar Sr-Nd isotope ratios of Tanzawa tonalities (Kawate, 1996), are the candidate producing the whole isotopic variation of pre-Komitake volcano. Therefore, we prefer the contributions of crustal materials to explain the Sr-Nd isotopic variations of pre-Komitake volcano. The Eu^* shows positive correlation with Al₂O₃. This may indicate the plagioclase accumulation contributed the magma genesis of pre-Komitake volcano, and cause the elevation of Sr/Y ratios.

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Keywords: pre-Komitake, trace elements, Sr-Nd isotope

Geochemical connection between HIMU-FOZO-PREMA: link to chemical and water content variation in oceanic crust

SHIMODA, Gen^{1*} ; KOGISO, Tetsu²

¹National Institute of Advanced Industrial Science and Technology, ²Graduate School of Human and Environmental Studies, Kyoto University, Kyoto

One of fundamental concepts of the geochemistry is an existence of mantle reservoirs. Namely, isotopic composition of the ocean island basalts (OIBs) are explained by mixing of distinct and isolated reservoirs in the Earth (White, 1985; Zindler and Hart, 1986; Hofmann, 1997; Stracke, 2012). 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, those are HIMU (high-u: $u = 238\text{U}/204\text{Pb}$) EM1 (Enriched Mantle 1) and EM2 (Enriched mantle 2) whose isotopic compositions are enriched extremes. In addition to these reservoirs, importance of reservoirs whose isotopic compositions are common and 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 existences of these intermediate reservoirs are still in debated, the isotopic compositions of these reservoirs, in particular FOZO, have been frequently used to describe the isotopic distribution of OIBs. Therefore, elucidating the origin of these reservoirs should be important from the perspective of production of mantle heterogeneity (e.g., Hofmann, 1997; Stracke et al. 2005; Stracke, 2012).

To evaluate the origin of high-u (HIMU), focal zone; (FOZO) and Prevalent Mantle (PREMA), geochemical modeling was conducted from the perspective of chemical fractionation at mid-ocean ridges and subduction zones. For the modeling, MORB compositions from the Mid-Atlantic ridge are compiled for seven trace elements (Rb, Sr, Nd, Sm, Pb, Th and U) and used as representatives of oceanic crust compositions. Effect of chemical fractionation at a mid-ocean ridge is estimated based on magnesium number and frequency distribution. The results suggest that the chemical fractionation at a mid-ocean ridge can produce moderately depleted isotopic compositions those are suitable for PREMA if the age of recycled MORBs is 1-2 Ga. It may follow that subduction modification is unnecessary for the production of PREMA, suggesting the importance of recycling of dry MORBs. Dehydration process at a subduction zone can produce FOZO isotopic signatures if degree of dehydration is high (4 %) that may represent maximum amount of dehydrated water. Thus, FOZO-PREMA isotopic array can be explained by mixing between recycled strongly dehydrated and dry MORBs. Consequently, PREMA-FOZO arrays could be produced by mixing between dry and dehydrated MORBs. For the production of HIMU, U and Th enrichment during crystal fractionation at mid-ocean ridge and Pb depletion owing to removal of sulfur during subduction is required in addition to FOZO production condition. As sulfur content in MORBs should be controlled by degassing process at a mid-ocean ridge, key processes that can differentiate HIMU from FOZO may be magma evolution process at mid-ocean ridge.

Keywords: HIMU, FOZO, PREMA, OIBs, recycling, mantle reservoirs

REY-rich mud deposits around Minamitorishima Island -General overview and future reserach plan-

SUZUKI, Katsuhiko^{1*} ; IIJIMA, Koichi¹ ; KATO, Yasuhiro² ; FUJINAGA, Koichiro² ; KASHIWABARA, Teruhiko¹ ; NAKA-MURA, Kentaro² ; MACHIDA, Shiki³ ; NOZAKI, Tatsuo¹ ; TAKAYA, Yutaro² ; YASUKAWA, Kazutaka² ; OTA, Junichiro² ; HARAGUCHI, Satoru² ; ARAKI, Shuuhei² ; LIU, Hanjie² ; NISHIO, Yoshiro¹ ; USUI, Yoichi¹

¹JAMSTEC, ²Graduate School of Engineering, Univ. of Tokyo, ³School Creative Sci. Engineering, Waseda Univ.

We report general overview and future reserach planof REY-rich deposits around Minamitorishima Island.

Keywords: REY rich mud, Minamitorishima Island, chemical composition, research cruise, deep-sea mineral resource

Distribution and characteristics of REY-rich mud in the Minamitorishima EEZ inferred by sub-bottom profiling

NAKAMURA, Kentaro^{1*}; MACHIDA, Shiki²; FUJINAGA, Koichiro¹; KATO, Yasuhiro³; SUZUKI, Katsuhiko⁴; TAKAYA, Yutaro³; YASUKAWA, Kazutaka¹; OTA, Junichiro¹; HARAGUCHI, Satoru¹; ARAKI, Shuuhei¹; LIU, Hanjie¹; USAMI, Ryo¹; MAKI, Ryota¹; IIJIMA, Koichi⁴; NISHIO, Yoshiro⁴; USUI, Yoichi⁴; NOZAKI, Tatsuo⁴; MR13-E02 LEG 2, Cruise members⁴; KR14-02, Cruise members⁴

¹Sys. Innovation, Univ. of Tokyo, ²School Creative Sci. Engineering, Waseda Univ., ³FRCER, Univ. of Tokyo, ⁴JAMSTEC

In recent years, particular attention has been paid to the "REY-rich mud" (deep-sea sediment enriched highly in rare-earth and yttrium (REY)), because of its high potential as a REY resource. The REY-rich mud was originally reported from the central Pacific Ocean in 2011 (Kato et al., 2011). In January 2013, during KR-13-02 cruise, the mud was also discovered at southern part of the Minamitorishima within the Japanese exclusive economic zone (EEZ) (Kato et al., 2013; Fujinaga et al., 2013; Suzuki et al., 2013). Then, in the late 2013 and early 2014, we further conducted two more research cruises (MR13-E02 Leg2 and KR14-02 cruises) in the northern and eastern part of the Minamitorishima EEZ. During the cruises, we performed an acoustic survey using sub-bottom profiler (SBP), together with mud sampling by piston coring. In this presentation, we report the distribution and characteristics of the REY-rich mud in the northern and eastern part of Minamitorishima EEZ inferred by the SBP survey.

Keywords: rare-earth elements, REY-rich mud, Minamitorishima, EEZ, sub-bottom profiler

Geochemical features of rare-earth elements and yttrium-rich mud from north region of Minamitorishima EEZ

FUJINAGA, Koichiro^{1*} ; KATO, Yasuhiro¹ ; NAKAMURA, Kentaro² ; SUZUKI, Katsuhiko³ ; MACHIDA, Shiki⁴ ; TAKAYA, Yutaro¹ ; YASUKAWA, Kazutaka² ; OTA, Junichiro² ; HARAGUCHI, Satoru¹ ; ARAKI, Shuuhei² ; LIU, Hanjie² ; USAMI, Ryo² ; MAKI, Ryota² ; IJIMA, Koichi³ ; NISHIO, Yoshiro³ ; USUI, Yoichi³ ; NOZAKI, Tatsuo³ ; MR13-E02 LEG2, Cruise members³ ; KR14-02, Cruise members³

¹Frontier Research for Energy and Resources, University of Tokyo, ²Department of Systems Innovation, University of Tokyo, ³JAMSTEC, ⁴Department of Resources and Environmental Engineering, Waseda University

Recently, deep-sea sediment enriched in rare-earth elements and yttrium (REY) (called REY-rich mud) has been reported from a central part of the Pacific Ocean (Kato et al., 2011). Due to its great potential as a completely new REY resource, the REY-rich mud attracts particular attention from a wide field of scientists and non-scientists. In 2013, we have discovered the deep-sea sediments that are extremely enriched in REY (~6,600 ppm) from the south region of the Minamitorishima within the Japanese exclusive economic zone (EEZ) (Kato et al., 2013; Fujinaga et al., 2013; Suzuki et al., 2013). In 2014, in order to investigate the detailed distribution of REY-rich mud in the EEZ of Minamitorishima, we further conducted research cruises (MR13-E02 Leg. 2 and KR14-02) in the north region of the Minamitorishima. Here, we report the distribution, mineral composition, and geochemical features of the REY-rich mud from the north region of the Minamitorishima EEZ.

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

Independent component analysis to decouple geochemical components of REY-rich mud in the Pacific and Minamitorishima EEZ

YASUKAWA, Kazutaka^{1*} ; TAKAYA, Yutaro² ; OTA, Junichiro¹ ; FUJINAGA, Koichiro¹ ; NAKAMURA, Kentaro¹ ; KATO, Yasuhiro² ; IWAMORI, Hikaru³

¹Sys. Innovation, Univ. of Tokyo, ²FR CER, Univ. of Tokyo, ³JAMSTEC

Rare-earth elements and yttrium (REY) are essential for state-of-the-art devices and green technologies including electric vehicles, fiber optics, smart phones, wind power generation etc. Recently, the deep-sea sediments enriched in REY (termed as "REY-rich mud") have been discovered in the Pacific Ocean, which have great potential as a completely new REY resource (Kato et al., 2011). In 2013, the presence of REY-rich mud was also confirmed within the Japanese exclusive economic zone (EEZ) around Minamitorishima (Fujinaga et al., 2013; Suzuki et al., 2013). The maximum total REY content in the REY-rich mud from Minamitorishima EEZ reaches as high as 6,600 ppm, although typical REY-rich mud in other regions of the Pacific Ocean contains less than 2,230 ppm of total REY.

In order to elucidate a component contributing to REY-enrichment in the sediments, Kato et al. (2011) performed independent component analysis (ICA) on the geochemical data set of Pacific deep-sea sediments. ICA is a relatively new multivariate statistical method established in 1980s, which can extract original independent source signals or factors from observed signals based on an assumption that the observed multivariate data are mutually independent but do not form a multivariate normal (Gaussian) distribution (Hyvärinen et al., 2001).

Four independent components (ICs) were found by Kato et al. (2011): two diluting components corresponding to biogenic carbonate and silica, and two components toward high REY contents with Fe and Al values, respectively. Kato et al. (2011) interpreted that the Fe- and Al-rich ICs that are responsible for the REY-enrichment of the mud correspond to end-member minerals of Fe-oxyhydroxide and phillipsite, respectively. Recently, however, X-ray absorption fine structure (XAFS) analysis and μ -XRF elemental mapping using high-energy synchrotron radiation revealed that most of REY are directly bonded to apatite in the REY-rich mud (Toda, 2013; Kashiwabara et al., 2014).

Here, we analyze a new comprehensive geochemical data set of deep-sea sediments from the Pacific Ocean and Minamitorishima EEZ by ICA. In this calculation, we utilize the new chemical composition data of individual crystals of phillipsite and apatite measured by LA-ICP-MS as new end-members for the ICA analysis. We will discuss the results and interpretation of our new analysis.

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Keywords: deep-sea sediment, REE, independent component analysis

Mineralogical features of REY-rich mud in EEZ around Minamitorishima and implications for its genesis

OTA, Junichiro^{1*}; TAKAYA, Yutaro²; FUJINAGA, Koichiro²; YASUKAWA, Kazutaka¹; NAKAMURA, Kentaro¹; MACHIDA, Shiki³; HARAGUCHI, Satoru¹; KATO, Yasuhiro²

¹Department of Systems Innovation, University of Tokyo, ²Frontier Research Center for Energy and Resources, University of Tokyo, ³Department of Resources and Environmental Engineering, Waseda University

The KR13-02 cruise was conducted in the southern part of the Minamitorishima to explore rare-earth elements and yttrium-rich mud (REY-rich mud) within Japanese Exclusive Economic Zone (EEZ) on January 2013. During the cruise, seven sediment cores were successfully collected. The results of bulk sediment analyses showed that one of the cores (PC05) has an extremely REY-concentrated layer with 6,596 ppm total REY (Kato et al., 2013; Suzuki et al., 2013) which is three times higher than the maximum concentration in the mud previously reported for the eastern South and central North Pacific Ocean (2,230 ppm; Kato et al., 2011). In addition to REY, P concentration in the layer is also noticeably high (Kato et al., 2013; Suzuki et al., 2013), suggesting that Ca phosphate (apatite) is mainly responsible for the REY-enrichment in the layer, as in the case for the mud presented in other areas (Kashiwabara et al., 2014). However, factors contributing the extreme enrichment of REY, which in turn might provide important insights into the genesis of REY-rich mud, are still uncertain. In the present contribution, we report mineralogical features of Minamitorishima REY-rich mud including the extremely REY-concentrated layer and discuss about its genesis.

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