

高温高压下における U, Th, Nd, Sm の金属鉄-ケイ酸塩間元素分配と熱的、化学的リザーバーとしての地球コア

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

野村 龍一^{1*}; 廣瀬 敬¹; 木村 純一²; 常 青²

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

¹ 東京工業大学 地球生命研究所, ² 海洋研究開発機構, 地球内部ダイナミクス領域

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 immediate aftermath 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 pyrolitic gel, and pure iron were used as starting materials. Iron-free pyrolitic 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.

下部マントル鉱物-メルト間の元素分配

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

館野 繁彦^{1*}; 坂田 周平²; 平田 岳史²; 廣瀬 敬³

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

¹ 東京工業大学・地球惑星科学専攻, ² 京都大学・地球惑星科学専攻, ³ 東京工業大学・地球生命研究所

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.

高圧下における FeO-SiO₂ 系の融解関係と沈み込んだ縞状鉄鉱層の行方 Melting relation on FeO-SiO₂ system at high pressure and the fate of the subducted banded iron formations

加藤 千恵^{1*}; 野村 龍一¹; 廣瀬 敬²; 三宅 亮³; 大石 泰生⁴

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

¹ 東京工業大学大学院地球惑星科学専攻, ² 東京工業大学地球生命研究所, ³ 京都大学大学院地球惑星科学専攻, ⁴ 高輝度光科学研究センター

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 $2 \times 10^8 \text{ km}^3$, 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*).

LA-MC-ICP-MSを用いたガラスと鉱物のNd同位体スタンダードレス測定 Standardless determination of Nd isotope ratios in glasses and minerals using LA-MC-ICP-MS

木村 純一^{1*}; 青 常¹; 川畑 博²
KIMURA, Jun-ichi^{1*}; QING, Chang¹; KAWABATA, Hiroshi²

¹ 海洋研究開発機構, ² 高知大学

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 $\text{NdO}^+/\text{Nd}^+ 0.01\text{--}0.05\%$, without significant sacrifice of the instrumental sensitivity ($\sim 70\%$). 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 $^{143}\text{Nd}/^{144}\text{Nd} = 0.511921 \pm 0.000013$ (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/ \sim 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.

キーワード: LA-MC-ICP-MS, Nd 同位体, ガラス, 鉱物
Keywords: LA-MC-ICP-MS, Nd isotope, glasses, minerals

氷多結晶体の粒界拡散の可視化 ~氷の塑性流動則の解明に向けて~ Grain boundary diffusion of polycrystalline ice I_h under confining pressure of 100 MPa

野口 直樹¹; 久保 友明^{2*}; Durham William⁵; 清水 以知子⁴; 鍵 裕之³
NOGUCHI, Naoki¹; KUBO, Tomoaki^{2*}; DURHAM, William⁵; SHIMIZU, Ichiko⁴; KAGI, Hiroyuki³

¹ 広島大学大学院工学研究科応用化学専攻, ² 九州大学大学院理学研究院地球惑星科学部門, ³ 東京大学大学院理学系研究科附属地殻化学実験施設, ⁴ 東京大学大学院理学系研究科地球惑星科学専攻, ⁵ マサチューセッツ工科大学地球大気惑星科学部

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 H_2O and D_2O 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 H_2O/D_2O 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.

キーワード: 氷, 拡散, 粒界拡散, 水素同位体, ラマン分光, レオロジー

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

先小御岳火山の微量元素及び Sr-Nd 同位体組成 Trace elements and Sr-Nd isotopic compositions of the pre-Komitake volcano

柴田 知之^{1*}; 吉本 充宏²; 藤井 敏嗣³; 中田 節也⁴

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

¹ 京都大学地球熱学研究施設, ² 北海道大学大学院理学研究院, ³ 特定非営利活動法人 環境防災総合政策研究機構, ⁴ 東京大学地震研究所

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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キーワード: 先小御岳, 微量元素, Sr-Nd 同位体, 富士山

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

HIMU – FOZO – PREMA の成因：極端な同位体組成の端成分と中間的な同位体組成を持つ端成分の違いに対する解釈 Geochemical connection between HIMU-FOZO-PREMA: link to chemical and water content variation in oceanic crust

下田 玄^{1*}; 小木曾 哲²
SHIMODA, Gen^{1*}; KOGISO, Tetsu²

¹ 産業技術総合研究所, ² 京都大学大学院人間・環境学研究科

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.

キーワード: HIMU, FOZO, PREMA, OIBs, マントル端成分, リサイクル
Keywords: HIMU, FOZO, PREMA, OIBs, recycling, mantle reservoirs

南鳥島レアアース泥の調査結果概要と今後の調査・研究計画 REY-rich mud deposits around Minamitorishima Island -General overview and future re- serach plan-

鈴木 勝彦^{1*}; 飯島 耕一¹; 加藤 泰浩²; 藤永 公一郎²; 柏原 輝彦¹; 中村 謙太郎²; 町田 嗣樹³; 野崎 達生¹; 高谷 雄太
郎²; 安川 和孝²; 大田 隼一郎²; 原口 悟²; 荒木 修平²; 劉 漢捷²; 西尾 嘉朗¹; 白井 洋一¹
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

¹ 海洋研究開発機構, ² 東京大学院工学系, ³ 早稲田大学創造理工学部

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.

キーワード: レアアース泥, 南鳥島, 化学組成, 調査航海, 深海資源

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

サブボトムプロファイラで見た南鳥島 EEZ におけるレアアース泥の分布と特徴 Distribution and characteristics of REY-rich mud in the Minamitorishima EEZ inferred by sub-bottom profiling

中村 謙太郎^{1*}; 町田 嗣樹²; 藤永 公一郎¹; 加藤 泰浩³; 鈴木 勝彦⁴; 高谷 雄太郎³; 安川 和孝¹; 大田 隼一郎¹; 原口 悟¹; 荒木 修平¹; 劉 漢捷¹; 宇佐美 諒¹; 牧 亮太¹; 飯島 耕一⁴; 西尾 嘉朗⁴; 白井 洋一⁴; 野崎 達生⁴; MR13-E02 Leg2 乗船者一同⁴; KR14-02 乗船者一同⁴

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

¹ 東大・工・システム創成, ² 早大・創造理工, ³ 東大・エネルギー・資源フロンティアセンター, ⁴ 海洋研究開発機構
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

南鳥島 EEZ 北部に分布するレアアース泥の地球化学的特徴 Geochemical features of rare-earth elements and yttrium-rich mud from north region of Minamitorishima EEZ

藤永 公一郎^{1*}; 加藤 泰浩¹; 中村 謙太郎²; 鈴木 勝彦³; 町田 嗣樹⁴; 高谷 雄太郎¹; 安川 和孝²; 大田 隼一郎²; 原口 悟¹; 荒木 修平²; 劉 漢捷²; 宇佐美 諒²; 牧 亮太²; 飯島 耕一³; 西尾 嘉朗³; 白井 洋一³; 野崎 達生³; MR13-E02 Leg2 乗船者一同³; KR14-02 乗船者一同³

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; IIJIMA, Koichi³; NISHIO, Yoshiro³; USUI, Yoichi³; NOZAKI, Tatsuo³; MR13-E02 LEG2, Cruise members³; KR14-02, Cruise members³

¹ 東京大学大学院工学系研究科エネルギー・資源フロンティアセンター, ² 東京大学大学院工学系研究科システム創成学専攻, ³ 海洋研究開発機構, ⁴ 早稲田大学創造理工学部環境資源工学科

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

独立成分分析を用いた太平洋および南鳥島レアアース泥の地球化学データ解析 Independent component analysis to decouple geochemical components of REY-rich mud in the Pacific and Minamitorishima EEZ

安川 和孝^{1*}; 高谷 雄太郎²; 大田 隼一郎¹; 藤永 公一郎¹; 中村 謙太郎¹; 加藤 泰浩²; 岩森 光³
YASUKAWA, Kazutaka^{1*}; TAKAYA, Yutaro²; OTA, Junichiro¹; FUJINAGA, Koichiro¹; NAKAMURA, Kentaro¹; KATO,
Yasuhiro²; IWAMORI, Hikaru³

¹ 東大・工・システム創成, ² 東大・エネルギー・資源フロンティアセンター, ³ 海洋研究開発機構

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

南東太平洋および中央北太平洋の深海底に広く分布する「レアアース泥」は、様々なハイテク産業に不可欠なレアアースを豊富に含み、新たな海底鉱物資源として有望視されている (Kato et al., 2011). 2013 年には、KR13-02 航海により、日本最東端の南鳥島周辺海域でも海底面下 10 m 以浅にレアアース泥の存在が確認された (藤永ほか, 2013; 鈴木ほか, 2013). この南鳥島周辺海域のレアアース泥は、我が国の独自開発が可能な排他的経済水域 (EEZ) 内に存在し、かつ太平洋の他の海域で確認されていたレアアース泥の最高濃度 (2,230 ppm) を大きく上回る約 6,600 ppm という極めて高い総レアアース濃度をもつことで、大きな注目を集めている。

Kato et al. (2011) は、深海底堆積物中でレアアースの濃集に寄与している成分を推定するために、独立成分分析を用いてレアアース泥を含む太平洋の深海底堆積物の全岩化学組成データを解析した。その結果、生物源 Ca および生物源 Si にそれぞれ富む傾向を示しレアアースを希釈する独立成分と、Fe および Al にそれぞれ富む傾向を示しレアアースの濃集に関与する独立成分の計 4 成分が抽出された。このうち、レアアースが特に濃集する傾向を示した Al に富む独立成分については、主要元素組成の類似性から遠洋性粘土に通常含まれる phillipsite が端成分と考えられた。しかしながら、文献値から想定される phillipsite 自身のレアアース濃度では観測される全岩堆積物中のレアアース濃度を説明できない。そのため Kato et al. (2011) は、レアアースを濃集した別の鉱物が phillipsite の凝集体に取り込まれることで、phillipsite が堆積物中のレアアース濃集に寄与していると解釈した。その後、放射光を用いた XAFS 測定および μ -XRF 元素マッピングにより、堆積物中でレアアースと直接結合しているのは apatite であることが示された (戸田, 2013; Kashiwabara et al., 2014).

こうした経緯をふまえ、本研究では、太平洋広域および南鳥島周辺 EEZ から得られた深海底堆積物の包括的な化学組成データセットに対し、独立成分分析を適用してその起源成分の再解析を実施した。また、レアアース濃集に寄与する独立成分をより正確に解釈するため、堆積物中の phillipsite および apatite それぞれの単体をもつ化学組成を LA-ICP-MS で分析し、新たに端成分として用いた。本発表では、これらの結果について報告する。

キーワード: 深海底堆積物, レアアース, 独立成分分析

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

南鳥島 EEZ 内におけるレアアース泥の構成鉱物の特徴およびその成因への示唆 Mineralogical features of REY-rich mud in EEZ around Minamitorishima and implications for its genesis

大田 隼一郎^{1*}; 高谷 雄太郎²; 藤永 公一郎²; 安川 和孝¹; 中村 謙太郎¹; 町田 嗣樹³; 原口 悟¹; 加藤 泰浩²
OTA, Junichiro^{1*}; TAKAYA, Yutaro²; FUJINAGA, Koichiro²; YASUKAWA, Kazutaka¹; NAKAMURA, Kentaro¹; MACHIDA, Shiki³; HARAGUCHI, Satoru¹; KATO, Yasuhiro²

¹ 東京大学工学系研究科システム創成学専攻, ² 東京大学工学系研究科エネルギー・資源フロンティアセンター, ³ 早稲田大学創造理工学部環境資源工学科

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.

キーワード: レアアース, レアアース泥, 深海底鉱物資源

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

MORB 気泡中のヘリウム・ハロゲン組成 Helium and halogen compositions in MORB vesicles

鹿兒島 涉悟^{1*}; 高畑 直人¹; 佐野 有司¹
KAGOSHIMA, Takanori^{1*}; TAKAHATA, Naoto¹; SANO, Yuji¹

¹ 東京大学大気海洋研究所

¹ Atmosphere and Ocean Research Institute, University of Tokyo

ハロゲン元素の海底火山からの脱ガス様式はよく分かっていない。我々は海嶺からのハロゲンの放出量を制約するために MORB の気泡に含まれるヘリウム・ハロゲン組成を決定した。世界中の 8 か所 (東太平洋海嶺の 13oN-17oS; 大西洋中央海嶺の 15oN-37oN; 中央インド洋海嶺の 24-25oS) で採取された試料を NaOH または NH₃ 溶液中に投入し、液体窒素の温度で溶液を凍結させた状態で破碎して気泡中の揮発性物質を抽出した。そしてヘリウムの同位体組成を希ガス用質量分析計 VG-5400 で、フッ素・塩素の含有量をイオンクロマトグラフィー ICS2100 で測定した。さらにガラス部分のフッ素・塩素濃度を二次イオン質量分析計 NanoSIMS で測定した。

気泡中の ³He 濃度は $(4.5 \pm 2.1) \times 10^{-15}$ mol/g, F/³He 比と Cl/³He 比は $(1.4 \pm 0.5) \times 10^6$, $(2.9 \pm 0.6) \times 10^7$ と得られた。そしてこれらの比と既知の ³He 放出量 530 mol/y から、フッ素・塩素の放出量として $(7.1 \pm 2.8) \times 10^8$ mol/y, $(1.5 \pm 0.4) \times 10^{10}$ mol/y が得られた。これらは海嶺からの放出量の下限值として考えられる。なぜならばフッ素・塩素のガラス中含有量は気泡中含有量に対してそれぞれ 7000 倍以上, 100 倍以上であり、海洋地殻中のこれらの元素の一部が海洋中へと溶け出すだけで放出量が大きく上がってしまうからである。気泡中とガラス中の F/Cl 比の差はフッ素・塩素の気泡-ガラス間における分配係数の違いを反映しており、これらの元素の海嶺における脱ガス様式には大きな違いがあると考えられる。また MORB に対して希ガス化法 (中性子を照射して試料中のハロゲンを希ガスへと変換し、それらの希ガスの同位体分析を行うことで元のハロゲン組成を決定する手法) を行った研究 [1] の結果から、気泡中の Br/Cl 比と I/Cl 比は $(1.8 \pm 0.1) \times 10^{-3}$, $(5.4 \pm 0.1) \times 10^{-5}$ と計算された。これらの値は同研究で報告されている固体ガラス中の元素の存在比とほぼ同じであり、このことは海底の玄武岩質マグマにおける塩素・臭素・ヨウ素の気泡-ガラス間の分配係数が似ていることを示している。Br/Cl 比、I/Cl 比および本研究で得られた塩素の放出量を基に、臭素・ヨウ素の海嶺からの放出量は $(2.7 \pm 0.8) \times 10^7$ mol/y, $(8.3 \pm 2.4) \times 10^5$ mol/y と計算された。これらは ³He の放出量に対して間接的に規格化することで得られた初めての臭素・ヨウ素の海嶺における放出量の推定値であり、塩素と同じ理由で下限値であると考えられる。本研究の手法と希ガス化法とを組み合わせることで、同一試料を分析することで、ハロゲン元素の固体地球内部からの脱ガス様式・物質循環について新たな展望が得られるだろう。

参考文献: [1] Kendrick et al. (2012) GCA 81, 82-93.

キーワード: 中央海嶺玄武岩, ヘリウム, ハロゲン, 放出量, 物質循環

Keywords: Mid-ocean ridge basalt, Helium, Halogen, Flux, Geochemical cycle

生駒山地における白亜紀深成複合岩体のマグマプロセス Magmatic process of Cretaceous plutonic complex in Ikoma mountains, SW Japan

小泉 奈緒子^{1*}; 奥平 敬元¹; 小川 大介¹
KOIZUMI, Naoko^{1*}; OKUDAIRA, Takamoto¹; OGAWA, Daisuke¹

¹ 大阪市立大学 院理
¹ Osaka City University

生駒はんれい岩類は、大阪府と奈良県の県境に位置する生駒山地に分布する白亜紀の深成岩体で、本邦における最大規模の苦鉄質岩体である。生駒はんれい岩類には、野外における観察から周囲に分布する中間質岩類と成因的に密接な関係が認められる(生駒山地領家帯研究グループ, 1986など)。このため、本研究ではこれらを生駒はんれい複合岩体として、岩石学的記載、全岩化学組成分析、鉱物化学組成分析を行い、そのマグマプロセスについて考察した。

生駒はんれい複合岩体の岩相は、(1)斜長石キュームレイト(Pl cumulate)、(2)普通角閃石?斜長石キュームレイト(Hbl-Pl cumulate)、(3)普通角閃石はんれいノーライト(Hbl gabbronorite)の3タイプに分けられる。Pl cumulateは中粒で、斜長石を集積鉱物として含み、それらの粒間には斜長石の他に角閃石や輝石などが見られる。Hbl-Pl cumulateは細粒で自形から半自形の斜長石および角閃石を集積鉱物とする。また、Hbl gabbronoriteは細流から中粒で、Hbl-Pl cumulateから遷移的に変化する。

生駒はんれい複合岩体における全岩化学組成は、SiO₂含有量44-63wt.%の組成範囲を示す。しかし、SiO₂含有量50wt.%前後を境として、SiO₂<50wt.%においては、他の主要および微量元素に対するSiO₂含有量の変化が小さいが、SiO₂>50wt.%では、SiO₂含有量は各成分と共に大きく変化する。Pl cumulate および Hbl-Pl cumulate は主に SiO₂ < 50wt.%の領域に含まれ、Hbl gabbronorite は主に SiO₂ > 50wt.%の領域に含まれる。

Pl cumulateに含まれる自形性の良い斜長石は、An₉₁₋₈₃付近に組成ピークを持ち、この斜長石の組成は、全岩化学組成におけるPl cumulateのトレンドの端成分にほぼ一致する。また、斜長石のモード組成と全岩組成におけるCaO含有量には相関が見られることから、このことから、Pl cumulateの組成トレンド形成においては斜長石の集積過程による寄与が示唆される。モデル計算を行った結果、SiO₂含有量約50wt.%の組成を出発物質として、最大70%程度の斜長石の集積によって全岩組成トレンドの再現が可能であることが明らかになった。Pl cumulateは岩体内でも標高の高い場所に分布しており、全岩組成におけるCaO含有量と標高に弱いながらも正の相関が見られることから、マグマだまりにおける斜長石の集積場所を反映していると考えられる。一方で、Hbl-Pl cumulate および Hbl gabbronoriteに含まれる斜長石は、バイモーダルな組成を示し、これらはAn₇₀₋₇₅付近に最大のピークを、そしてAn₈₅₋₉₀付近に小さなピークを持つ。このことから、生駒はんれい複合岩体における斜長石の晶出には少なくとも2つの段階があったこと、そして、Anに富む斜長石が集積したPl cumulateの形成後にHbl-Pl cumulate および Hbl gabbronoriteが形成されたことが示唆される。しかし、Hbl-Pl cumulateについては、角閃石と斜長石の集積作用のみで全岩組成トレンドを再現することは困難であり、その形成過程については更なる検討が必要である。

82Maにおける生駒はんれい複合岩体のSr同位体初生値とSiO₂含有量の間には、弱い相関が認められる。このことから、生駒はんれい複合岩体の形成時に苦鉄質マグマと、より珪長質でSr同位体初生値の高い物質との混合があったことが示唆される。生駒はんれい複合岩体周辺には、同時代に活動した花崗岩類が分布しており、これらの岩体の全岩化学組成は、生駒はんれい複合岩体のSiO₂>50wt.%における組成トレンドの珪長質側の延長線上に位置する。しかし、モデル計算の結果、これらの岩体のSr同位体初生値は、混合の珪長質端成分として考えるには低すぎるということがわかった。従って、生駒はんれい複合岩体は、同時代の花崗岩類よりも高いSr同位体初生値を持つ地殻物質と混合していたと考えられる。

【文献】生駒山地領家帯研究グループ(1986)地球科学, 40, 102?114.

キーワード: 領家帯, マグマプロセス, 結晶集積
Keywords: Ryoike belt, Magmatic process, cumulate, accumulation

阿蘇火山火砕流堆積物中のアパタイトの揮発性元素組成 Volatile compositions of apatite grains from pyroclastic flow deposits of Aso volcano

道久 真理絵^{1*}; 小木曾 哲¹
DOKYU, Marie^{1*}; KOGISO, Tetsu¹

¹ 京都大学人間・環境学研究所

¹ Graduate School of Human and Environmental Studies, Kyoto University

本研究では、メルトインクルージョンの分析によりメルトの含水量が推定されている阿蘇火山火砕流堆積物中のアパタイトを分析し、アパタイトの OH 量とメルトの含水量との関係性について検討した。

地球の水は、表層や内部において生命活動やマントルダイナミクスなどに大きな影響を及ぼしている。そのような地球の水の起源の解明のためには、初期地球内部の水の量を明らかにすることが重要である。初期地球内部の水の量について知る手がかりとして、地球最古の鉱物である西オーストラリア・ジャックヒルズ変礫岩中のジルコンが包有する初生的なアパタイトがある。アパタイトはその結晶中に揮発性元素 (F, Cl, OH) を持つため、ジャックヒルズのアパタイト包有物から初期地球内部の水についての情報が得られることが期待される。しかし、アパタイトの OH 量からメルトの含水量を推定する際に必要となるアパタイト-メルト間の OH の分配についての知識は不十分であるため、これを明らかにすることを本研究の目的とする。

本研究の試料である阿蘇火山火砕流堆積物は、マフィック試料とシリシク試料があり、長石中のメルトインクルージョン組成の分析によって含水量はマフィックメルト>シリシクメルトであると推定されている。新たに試料からアパタイトを取り出して EPMA で分析した結果、1 試料中のアパタイトの Cl 濃度はほぼ一定である一方、F 濃度に幅があった。これは F と OH とが交換関係にあることを示している。また、アパタイトの OH 量とメルトの含水量は逆相関を示した。

この原因として、メルト中の Ca が F と化合物をつくり、アパタイトへの F の分配を妨げたということが考えられる (Mathez and Webster, 2005)。メルトの Ca 濃度はマフィック試料で約 3.34wt%，シリシク試料で約 1.44wt% であり、マフィックメルトの方が Ca 濃度が高かったため、F のアパタイトへの分配が強く阻害され、代わりに OH がアパタイトへ分配された可能性がある。

また、メルト組成を推定するために分析したメルトインクルージョンの含水量は、実際はメルト組成を反映していなかったということも考えられる。メルトインクルージョン中には気泡が多く存在し、気泡が多い試料ほど含水量は低いという傾向がみられる。すなわち、メルトインクルージョン中の水は気泡として抜けてしまっており、メルト組成よりも含水量を低く見積もっている可能性がある。また、斜長石の組成幅やメルト組成、温度から計算されたメルトの含水量はマフィック試料で 4.1-7.7wt%，シリシク試料で 4.1-5.7wt% で、マフィックメルトの方が含水量が多かったと見積もられている (Kaneko et al., 2007)。よって、実際はアパタイトの OH 量とメルトの含水量は正の相関関係である可能性がある。

1 試料中の F 濃度と OH 濃度に幅がある原因については、脱ガスに伴う F-OH の交換反応や結晶分化作用の進行によるメルト組成の変化を反映していると考えられる。

本研究の結果として、阿蘇火山火砕流堆積物中のアパタイトの OH 量とメルトの含水量は逆相関を示し、1 試料中の F 濃度と OH 濃度に幅があるということがわかった。今後メルトの含水量を推定したデータの信頼性や、メルト中の Ca やその他の元素がアパタイト-メルト間の揮発性元素分配に与える影響などを検討していく必要がある。

キーワード: アパタイト, 水, 揮発性元素, 初期地球, マグマ

Keywords: apatite, water, volatile component, the early Earth, magma

天然多結晶ダイヤモンド（カルボナド）のオスmium同位体比測定の試み Measuring osmium isotopic composition of natural polycrystalline diamond (carbonado) and implications for its origin

白石 智子^{1*}; 仙田 量子²; 鍵 裕之¹; 角野 浩史¹; 鈴木 勝彦²

SHIRAISHI, Noriko^{1*}; SENDA, Ryoko²; KAGI, Hiroyuki¹; SUMINO, Hirochika¹; SUZUKI, Katsuhiko²

¹ 東京大学大学院理学系研究科附属地殻化学実験施設, ² 独立行政法人海洋研究開発機構地球内部ダイナミクス領域
¹Geochemical Research Center, Graduate School of Science, University of Tokyo, ²Institute for Research on Earth and Evolution, Japan Agency for Marine-Earth Science and Technology

The origin of natural polycrystalline diamond, carbonado, has long been enigmatic. Carbonado is characterized as high porosity, no genetic relations to kimberlites, light carbon isotope ratio, and lack of mantle-derived mineral inclusions. Based on these observations, several hypotheses about the origin of carbonado have been proposed: transformation of subducted organic carbon into diamond in a cold slab (Robinson, 1978); shock metamorphism of organic carbon by meteorite impact (Smith and Dawson, 1985); radiation-induced diamond formation by spontaneous fission of uranium in crustal environment (Ozima *et al.*, 1991); formation in an interstellar environment (Garai *et al.*, 2006); crystallization from C-O-H fluid in cratonic upper mantle (Ishibashi *et al.*, 2012). However, no conclusive evidence has been provided to settle a controversy about the origin of carbonado. In this study, we first tried to measure Os isotopic composition of carbonados collected from placer deposits in the Central African Republic in order to identify its origin.

Natural samples have a wide variety of Os isotopic ratios, $^{187}\text{Os}/^{188}\text{Os}$, depending on their origin because ^{187}Re , the parent nuclide of radiogenic ^{187}Os , is a mildly incompatible element during mantle melting whereas Os is a strongly compatible element. $^{187}\text{Os}/^{188}\text{Os}$ ratio of upper continental crust ranges from 1.0 to 1.4 (Peucker-Ehrenbrink and Jahn, 2001), whereas that of primitive upper mantle is about 0.13 (Meisel *et al.*, 1996). Os isotopic ratio of the micro diamond crystal itself can reflect the environment where diamond grains crystallized. Carbonado is a porous aggregate of micrometer-size diamond crystals and original chemical characteristics of the grain boundaries could be heavily altered after the diamond growth.

This study was designed to determine Os isotopic ratios within diamond crystals of carbonados and in the grain boundaries separately. Two-step sample chemical leaching was carried out by Carius tube method (Shirey and Walker, 1995). First, carbonado samples were crushed to submillimeter grains and were sealed in a Carius tube with spike solutions and inverse aqua regia ($\text{HCl} + 3 \text{HNO}_3$). The solution was heated at 220 °C for 24 hours. This procedure was for extract Os in the grain boundaries. Second, the residue of solid samples was heated in a vacuum chamber to convert diamond to graphite. A graphitized sample was decomposed in acid solution in the same way as the first leaching process. The second process was to extract Os within diamond grains. Osmiums in the both solutions were purified with the solvent extraction (Cohen and Waters, 1996) and microdistillation (Roy-Barman, 1993). Osmium isotopic compositions of the samples were determined using thermal ionization mass spectrometry (TIMS). Blank levels of Carius tubes and inverse aqua regia solutions prepared from several chemical reagents were checked. As a result, a quartz glass tube was found to have the lowest blank level compared with other glass tubes made from borosilicate glass.

In the presentation, we will report preliminary results of Os isotopic ratios of the carbonado, which have the potential for a decisive evidence to close the debate on the origin of carbonado.

Keywords: carbonado, TIMS, Os isotope, diamond

ZnTiO₃ の高温高压相転移 High-pressure high-temperature phase transitions in ZnTiO₃

阿部 航平^{1*}; 糞谷 浩¹; 赤荻 正樹¹
ABE, Kohei^{1*}; KOJITANI, Hiroshi¹; AKAOGI, Masaki¹

¹ 学習院大学理学部

¹Department of Chemistry, Gakushuin University

ペロブスカイト型 MgSiO₃ は下部マントルの主要構成鉱物であると考えられている。MgSiO₃ は、22-24GPa、1400-1800 °C でイルメナイト型からペロブスカイト型に相転移する。イルメナイト型 MgSiO₃ のアナログ物質であるイルメナイト型 ZnTiO₃ は、約 20-25 GPa で ZnO + TiO₂ に分解する (Ito and Matsui, 1979)。しかし、その相関係は詳細に調べられていなかった。そこで、本研究では ZnTiO₃ の高温高压下での相関係を決定した。

出発物質のイルメナイト型 ZnTiO₃ は、ZnO と TiO₂ をモル比 1:1 で混合し、800 °C で 32 時間加熱することにより合成した。川井型 6-8 マルチアンビル高压発生装置を用い、出発試料を 13-35 GPa、1000-1400 °C の条件で 1-2 時間保持後、急冷回収した。回収した試料について、粉末 X 線回折法を用いて相の同定を行った。

15-20 GPa、1000-1400 °C で実験した回収試料は、LiNbO₃ 型構造であった。イルメナイト型と LiNbO₃ 型の相境界線は $P(\text{GPa}) = 19.9 - 0.0038T(^\circ\text{C})$ と決定された。イルメナイト型 FeTiO₃ は、約 15 GPa 以上でペロブスカイト型に転移し、減圧過程で LiNbO₃ 型となり、イルメナイトとペロブスカイトの相境界線は負の勾配を持つ (Ming et al., 2006)。一般的に、イルメナイト型からペロブスカイト型への転移では 2 価陽イオンの配位数が 6 から 8 へ増加するため、正のエントロピー変化となる。このため、相境界線は負の勾配を持つ。一方、LiNbO₃ 型の 2 価陽イオンは 6 配位であり、仮に LiNbO₃ 型構造が安定だとしたとき、予想される相境界線の勾配は正となる。したがって、FeTiO₃ と同様に、ZnTiO₃ は高压下でペロブスカイト型であったものが、減圧過程で LiNbO₃ 型に転移したと考えられる。

約 20 GPa 以上で行われた実験の回収試料は、ウルツ鉱型 ZnO と α -PbO₂ 型 TiO₂ であった。ペロブスカイト型と ZnO+TiO₂ の相境界線は $P(\text{GPa}) = 9.5 + 0.010T(^\circ\text{C})$ と決定された。ZnO は約 6 GPa でウルツ鉱型から塩化ナトリウム型に転移し (Kusaba et al., 1999)、TiO₂ は約 17 GPa で α -PbO₂ 型からバデレアイト型に転移する (Tang and Endo, 1993)。そのため、分解相の安定領域では、ZnO と TiO₂ はそれぞれ塩化ナトリウム型とバデレアイト型で存在すると考えられる。

キーワード: ZnTiO₃, LiNbO₃, ペロブスカイト, 高压

Keywords: ZnTiO₃, Perovskite, LiNbO₃, High pressure

Quantitative multi-element imaging of geological materials by femto-second LA-ICP-MS Quantitative multi-element imaging of geological materials by femto-second LA-ICP-MS

常 青^{1*}; 木村 純一¹

CHANG, Qing^{1*}; KIMURA, Jun-ichi¹

¹ 海洋研究開発機構

¹ Japan Agency for Marine-Earth Science and Technology

Elemental mapping analysis of geological materials using X-ray related methods (EPMA, XRF) or SIMS suffers from insufficient sensitivity and poor quantification. LA-ICP-MS has advantages of high sensitivity and less matrix effect, therefore has been developed for elemental and isotopic imaging analyses over the last decade. However, quantification problem by this method remains unsolved because of the lack of a suitable sampling volume correction method and necessity of matrix-matched standard. This work presents multi-element imaging/mapping analysis of orthopyroxene and plagioclase minerals by femto-second LA-ICP-MS using a novel normalization process. Laser sampling volume is corrected for by analyzing ten major elements (SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO, CaO, Na₂O, K₂O, and P₂O₅) followed by normalization of the analyzed total sum to 100 wt% to obtain correction factor. This correction method is free from any external analysis (e.g., EPMA) for at least one internal standard element (e.g. Ca), and can be applied for both spot and line scanning LA mode. This allows LA-ICP-MS method standalone and liberates from errors inherited from any local heterogeneity of the samples picked up differently by the different analytical techniques used. Use of USGS basalt glass as a standard eliminates matrix effect in the levels less than 10% RD for these silicate minerals. Two-dimensional elemental distribution images of 43 elements were acquired from 4-6 μm depth of the sample surface with a ~40 μm lateral resolution. An area of 500×500 μm can be scanned simultaneously for 43 elements in less than 2.3 hours. Trace elements in silicate minerals can be imaged at sub-ppm concentration level, while major elements were mapped at sub-percent concentration.

Key words: femto-second LA-ICP-MS, elemental mapping, minerals