

海洋地殻の層状構造と2段階脱水：HIMU-FOZO-PREMAの成因に関する解釈 Geochemical connection between HIMU-FOZO-PREMA: two-stage dehydration of oceanic crust with layered structure

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 京都大学人間・環境学研究科

¹Geological Survey of JAPAN, ²Graduate School of Human and Environmental Studies Graduate School of Human and Environmental Studies

Isotopic composition of the ocean island basalts (OIBs) can be explained by mixing of 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 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). In addition to these reservoirs, importance of reservoirs whose isotopic compositions are common and intermediate has been pointed out, such as, FOZO (Focal Zone, Hart et al., 1992) and PREMA (Prevalent Mantle, Zindler and Hart, 1986). Although these intermediate reservoirs have been used to describe the isotopic distribution of OIBs, existences of the intermediate reservoirs, themselves, are still in debate. Therefore, elucidating the origin of the intermediate reservoirs should be also important from the perspective of production of mantle heterogeneity (e.g., Hofmann, 1997; Stracke et al. 2005; Stracke, 2012).

To elucidate the origin of mantle reservoirs, geochemical modeling has been conducted, in which origin of HIMU, FOZO and PREMA is discussed. The results suggest that MORBs with high frequency (common MORBs) have chemical composition that is suitable for production of PREMA if chemical modification during subduction is negligible. It may suggest the importance of recycling of dry MORBs for the production of OIBs source. Dehydration of common MORBs beneath an arc can produce FOZO isotopic signatures if amount of dehydrated water is large (4 %) which may represent maximum amount of dehydrated aqueous fluid at sub-arc area. Thus, FOZO-PREMA isotopic array can be explained by recycling of common MORBs that release various amount of aqueous fluid during subduction. For the production of HIMU, additional dehydration (~2%) at high pressure is required. As high pressure dehydration release supercritical fluid, chemical fractionation during dehydration is different from the sub-arc process. This difference can explain isotopic difference between HIMU and FOZO.

キーワード: HIMU, FOZO, PREMA, MORBs, OIBs

Keywords: HIMU, FOZO, PREMA, MORBs, OIBs

Ocean Basalt Simulator version 1 (OBS1): 輝石岩を含むマントルかんらん岩断熱融解における微量元素マスバランス
Ocean Basalt Simulator version 1 : Trace element mass balance in adiabatic melting of a pyroxenite-bearing peridotite

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

¹ (独) 海洋研究開発機構, ² 高知大学
¹JAMSTEC, ²Kochi University

We present a new numerical trace element mass balance model for adiabatic melting of a pyroxenite-bearing peridotite for estimating mantle potential temperature, depth of melting column, and pyroxenite fraction in the source mantle for a primary ocean basalt/picrite. The Ocean Basalt Simulator version 1 (OBS1) uses a thermodynamic model of adiabatic melting of a pyroxenite-bearing peridotite with experimentally/thermodynamically parameterized liquidus/solidus intervals and source mineralogy. OBS1 can be used to calculate a sequence of adiabatic melting with two melting models, including (1) melting of peridotite and pyroxenite sources with simple mixing of their fractional melts (melt-melt mixing model), and (2) pyroxenite melting, melt metasomatism in the host peridotite, and melting of the metasomatized peridotite (source-metasomatism model). OBS1 can be used to explore (1) the fractions of peridotite and pyroxenite, (2) mantle potential temperature, (3) pressure of termination of melting, (4) degree of melting, and (5) residual mode of the sources. In order to constrain these parameters, the model calculates a mass balance for 26 incompatible trace elements in the sources and in the generated basalt/picrite. OBS1 is coded in an Excel spreadsheet and runs with VBA macros. Using OBS1, we examine the source compositions and conditions of the mid-oceanic ridge basalts, Loihi/Koolau basalts in the Hawaiian hotspot, and Jurassic Shatsky Rise and Mikabu oceanic plateau basalts and picrites. The OBS1 model shows the physical conditions, chemical mass balance, and amount of pyroxenite in the source peridotite, which are keys to global mantle recycling.

キーワード: かんらん岩, 輝石岩, 断熱融解, 微量元素, マスバランス
Keywords: Peridotite, Pyroxenite, Adiabatic melting, Trace element, Mass balance

Geochemical Composition of Dykes along the Cameroon Volcanic Line (CVL): Constraints on CVL magmatism and tectonism

Geochemical Composition of Dykes along the Cameroon Volcanic Line (CVL): Constraints on CVL magmatism and tectonism

ASAAH, Asobo nkengmatia elvis^{1*}; YOKOYAMA, Tetsuya¹; AKA, Festus tongwa²; USUI, Tomohiro¹; KURITANI, Takeshi³; WIRMVEM, Mengnjo jude⁴; IWAMORI, Hikaru¹; OHBA, Takeshi⁴
ASAAH, Asobo nkengmatia elvis^{1*}; YOKOYAMA, Tetsuya¹; AKA, Festus tongwa²; USUI, Tomohiro¹; KURITANI, Takeshi³; WIRMVEM, Mengnjo jude⁴; IWAMORI, Hikaru¹; OHBA, Takeshi⁴

¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-, ²Institute of Mining and Geological Research, P.O. Box 4110, Yaounde, Cameroon, ³Graduate school of Science, Osaka City University, 3-3-138 Sugimoto, Sumi Yoshi-ku, Osaka 558-8585,, ⁴Department of Chemistry, School of Science, Tokai University, Hiratsuka, 259-1211, Japan

¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-, ²Institute of Mining and Geological Research, P.O. Box 4110, Yaounde, Cameroon, ³Graduate school of Science, Osaka City University, 3-3-138 Sugimoto, Sumi Yoshi-ku, Osaka 558-8585,, ⁴Department of Chemistry, School of Science, Tokai University, Hiratsuka, 259-1211, Japan

Mafic dykes along the Cameroon Volcanic Line (CVL) align in a general N 30?? - N 70?? direction. These alignments are consistent with the tectonic lineaments and the orientation of the CVL, indicative of a time and space relationship between the dykes and CVL lavas with the tectonic activities of the African plate. However, sub-alkaline volcanic rocks studied in some areas along the CVL are thought to be older than and not related to the CVL magmatism. Mafic dykes outcrop in the Oku Volcanic Group (OVG) but have not been studied. The aim of this study is to 1) characterize volcanic dykes in the OVG and Mt. Bambouto, 2) constrain the geochemical relationship between the dykes and CVL alkaline lavas, and 3) establish a tectonic history of emplacement of these dykes. Three dykes in the OVG and two along the Dschang-Santcho escarpment (flank of Mt. Bambouto) were systematically studied. An alkaline dyke is observed intruding a sub-alkaline dyke for the first time along the CVL, indicating a time and space relation between the two series. The dykes are weathered and show chemical evidence of crustal contamination. Contamination of less than 20 % for the alkaline dykes (BD2 and BDS alkaline) and 30 - 40% (BDS sub alkaline, BD3 and DS), can explain the varying degrees of crustal signatures in the samples. Geochemical characteristics suggest that the Batibo alkaline intrusions and the sub-alkaline intrusions were derived from a similar mantle source with OVG lavas. These characteristics are similar to those of the CVL alkaline lavas and OIBs. However, the differences in elemental concentrations and isotope composition of the sub alkaline dykes and the alkaline dykes in the OVG can be ascribed to varying degrees of weathering, assimilation of crustal components and different degrees of partial melting. The Low MgO, Ni, Cr, and V in the Batibo alkaline intrusion are due to the rapid rate of chemical weathering of olivine. The dykes in this study are related to the CVL magmatism in space and time. Fractures cutting through the basement rocks, but not the dykes suggest that the dykes are younger than the tectonic activities. The Sub-alkaline intrusion that is also intruded by the alkaline dyke in the BDS is older (43 - 422 Ma). This indicates that its emplacement was earlier than the surface expression of the alkaline CVL magmatism in the Tertiary (<31 Ma).

キーワード: Oku volcanic group, Dykes, Crustal contamination, Cameroon Volcanic Line, Magmatism, Tectonism
Keywords: Oku volcanic group, Dykes, Crustal contamination, Cameroon Volcanic Line, Magmatism, Tectonism

地球全ケイ酸塩のハフニウム同位体進化：隕石ジルコンからの証拠 The Hf isotope evolution of the bulk silicate Earth: Evidence from meteorite zircon

飯塚 毅^{1*}; 山口 能央¹; 日比谷 由紀¹; アメリン ユーリー²
IIZUKA, Tsuyoshi^{1*}; YAMAGUCHI, Takao¹; HIBIYA, Yuki¹; AMELIN, Yuri²

¹ 東京大学, ² オーストラリア国立大学

¹The University of Tokyo, ²The Australian National University

¹⁷⁶Lu-¹⁷⁶Hf 放射壊変系列は、地球の地殻-マントル分化の時間スケールやメカニズムを制約するのに広く用いられている。しかし、Lu-Hf 同位体データを正確に解釈するには、地球のケイ酸塩部分全体 (Bulk Silicate Earth: BSE) の Hf 同位体進化を知る必要がある。Lu と Hf は共に難揮発性かつ親石性元素であるため、BSE の Hf 同位体進化曲線は、未分化隕石コンドライトの現在の ¹⁷⁶Hf/¹⁷⁷Hf 及び ¹⁷⁶Lu/¹⁷⁷Hf から推定されてきた。しかし、変成作用時の Lu と Hf の再分配により、コンドライト中のこれらの同位体比は非常に大きな変動を示すため、現在用いられている BSE モデルの ¹⁷⁶Hf/¹⁷⁷Hf 及び ¹⁷⁶Lu/¹⁷⁷ の値の妥当性を検証する必要がある。さらに近年、太陽系初期に光励起を介した ¹⁷⁶Lu 壊変の加速がコンドライト中で進んだとする仮説が提唱されており、この仮説が正しければコンドライト隕石の Lu-Hf 同位体組成は BSE のそれを反映しない。

本研究では、隕石中に含まれるジルコン鉱物の高精度 Lu-Hf 同位体分析を行った。ジルコンは変成作用の影響を受けづらく、非常に低い Lu/Hf をもつために、結晶化時の Hf 同位体組成を保持できる。そこで本研究では、ユークライト隕石に含まれる初期太陽系に結晶化したジルコンを用いて、太陽系の初生 ¹⁷⁶Hf/¹⁷⁷Hf を決定した。また我々は、この太陽系初生 ¹⁷⁶Hf/¹⁷⁷Hf を用いて、コンドライト中の ¹⁷⁶Lu 壊変率が太陽系史を通して一定であったことを示し、さらに、太陽系形成時の Lu-Hf 同位体組成を保持している最も初生的なコンドライト隕石を同定することに成功した。本研究で得られた新しい BSE の Lu-Hf 組成 (¹⁷⁶Hf/¹⁷⁷Hf = 0.282793 +/- 11; ¹⁷⁶Lu/¹⁷⁷Hf = 0.0338 +/- 1) から、地球の冥王代ジルコンの Hf 同位体組成は 45 億年前以前の地球ケイ酸塩分化イベントを反映していることが明らかになった。

キーワード: 地球全ケイ酸塩, ジルコン, ハフニウム同位体, 地殻-マントル分化, ユークライト, 初期太陽系
Keywords: bulk silicate Earth, zircon, hafnium isotopes, crust-mantle differentiation, eucrite, early solar system

金属-硫化物メルト間の元素分配挙動 Partitioning behavior of elements between metal and sulfide melt

鈴木 敏弘^{1*}; 平田 岳史²; 高橋 栄一¹
SUZUKI, Toshihiro^{1*}; HIRATA, Takafumi²; TAKAHASHI, Eiichi¹

¹ 東京工業大学 地球惑星科学科, ² 京都大学 地球惑星科学
¹Earth and Planet. Sci., Tokyo Tech., ²Earth and Planet. Sci., Kyoto Univ.

金属の固相-液相間の元素分配挙動は、地球型惑星の核の進化を解明するための重要な情報である。珪酸塩系の研究では、分配係数がイオン半径や結晶構造と密接に関連している事が知られている事から、金属系においても原子半径との関連性が議論されている。例えば、Van Orman et al. (2008) は高圧下で Fe-S 系での Re, Os, Pt の分配係数を測定し、原子半径を用いればこれらの結果を Lattice Strain Model (Blundy & Wood, 1994) で説明できるとした。一方、Stewart et al. (2009) は原子半径ではなく、Neutral Atom Radius (Clementi et al. 1967) を用いる事により、説明できると主張した。しかしながら、固相の基本構造を形成する Fe よりもかなり大きな Os が最大の分配係数を示す事は奇妙であった。金属系の元素分配係数は、液相中の軽元素濃度（硫黄、リン、炭素）に大きく依存している事が知られており、分配係数が化学的親和性と関連している事が考えられる。本研究では異なる硫黄濃度で FeNi-S 系の高圧融解実験を行い、分配挙動の変化を観察した。

白金属などの 14 元素をそれぞれ約 150ppm 添加した Fe-Ni(95:5) 合金を、アーク放電法を用いて合成した。この合金を少量の FeS 粉末とともに MgO カプセルに入れ、東京工業大学の川井型マルチアンビルを用いて高圧融解実験を行った。回収した試料の主成分元素組成は EPMA で測定し、微量元素濃度は京都大学の LA-ICP-MS で測定した。

得られた分配係数は、これまでの研究と同様に、液相中の硫黄濃度に大きく依存していた。このため、化学的親和性を排除して原子半径と分配係数の関係のみを観察するためには、純粋な金属だけの系での分配係数から議論する必要がある。本研究では、硫黄濃度が減少するとともに、元素間の分配係数の差が減少する事が観察された。このため、硫黄を含まない系では、Au や W のように Fe よりも非常に大きな元素でも、その分配係数に大きな差は無いと推定される。

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キーワード: 元素分配, 金属, 硫化物, 超高压
Keywords: element partitioning, metal, sulfide, high pressure

シングルショットレーザーアブレーション多重検出器型 ICP 質量分析法を用いたジルコンの U-Pb 年代分析 Single shot laser ablation-multiple collection-ICP-mass spectrometry for U-Pb age

服部 健太郎^{1*}; 坂田 周平¹; 平田 岳史¹
HATTORI, Kentaro^{1*}; SAKATA, Shuhei¹; HIRATA, Takafumi¹

¹ 京都大学 大学院 理学研究科 地球惑星科学専攻

¹ Division of Earth and Planetary Sciences, Graduate School of Science, Kyoto University

Combination of laser ablation sample introduction technique and ICP-mass spectrometry (LA-ICPMS) has been widely used for element and isotopic analyses for solid samples¹⁾. One of the great advantages of LA-ICPMS is high quantitative capability achieved by the "post ionization" configuration. With the post ionization, ionization and atomization of the analytes in the plasma source will be independently carried out, and therefore, the optimization of the operational conditions for both the sampling and ionization can be made. This suggests that the hard ionization can be carried out even under the "soft" laser sampling. One of the major source of the analytical error is an elemental fractionation during the laser ablation (down-hole fractionation)²⁾. In fact, the measured Pb/U ratio can change with time when the larger ablation was made with ablation spots of higher aspect ratios³⁾. To overcome this, we have tried to measure U-Pb ages from the ablation spots of smaller aspect ratio (i.e., shallower pit).

The shallower ablation pit could be obtained when a smaller number of laser shots were adopted. To achieve this, a multiple collector-ICPMS was adopted to the U-Pb age determinations. With the multiple collector system, precision in the isotope ratio measurements can be improved even from the transient signals produced by the smaller number of laser shots. Hence, six isotopes were monitored by the six independent multipliers; ²⁰²Hg (IC), ²⁰⁴Pb (IC), ²⁰⁶Pb (IC), ²⁰⁷Pb (IC), ²⁰⁸Pb (IC), ²³²Th (F) and ²³⁵U or ²³⁸U (IC).

Three natural zircons (OD-3⁴⁾, Plesovice⁵⁾ and GJ-1⁶⁾) were employed to evaluate the reliability of the resulting U-Pb ages. Nancy 91500⁷⁾ zircon was used as a calibration standard for the Pb/U ratio measurements. The glass standard (NIST SRM 610) was used for the calibration in the ²⁰⁷Pb/²⁰⁶Pb isotope ratio measurements. Laser ablation system used in this study was a New Wave Research femto laser ablation system (Fremont, CA 94538, USA), and the ICPMS instrument used in this study was a Nu Instruments (Wrexham, UK) Nu Plasma II multi-collector ICPMS. For comparison, U-Pb ages were also measured by the single collector-ICPMS instrument (Nu Instruments AttoM). In our presentation, we will demonstrate the high analytical capability of the MC-ICPMS technique from the single shot laser sampling.

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キーワード: LA-MC-ICPMS, U-Pb 年代, ジルコン, シングルショット, 元素分別, アスペクト比
Keywords: LA-MC-ICPMS, U-Pb age, zircon, single shot, elemental fractionation, aspect ratio

有孔虫のNd同位体分析を目的とした極微量Nd同位体分析法の開発 Isotope analysis of ng-sized Nd samples: toward the isotopic analysis of foraminifera extracted from deep-sea sediments

若木 重行^{1*}; 吉村 寿紘²; 黒田 潤一郎²; 大河内 直彦²; 石川 剛志¹
WAKAKI, Shigeyuki^{1*}; YOSHIMURA, Toshihiro²; KURODA, Junichiro²; OHKOUCHI, Naohiko²;
ISHIKAWA, Tsuyoshi¹

¹ 海洋研究開発機構 高知コア研究所, ² 海洋研究開発機構 生物地球化学研究分野

¹KOCHI, JAMSTEC, ²Department of Biogeochemistry, JAMSTEC

Modern seawater has heterogeneous Nd isotopic compositions. The source rocks of Nd in the ocean, continental rocks and igneous rocks derived from the mantle, show wide range of variation in their radiogenic ¹⁴³Nd/¹⁴⁴Nd ratios (~5 permil). The short residence time of Nd in the ocean (300-500 yr: Tachikawa et al., 2003; Amakawa et al., 20004; Arouze et al., 2009) compared with the ocean mixing timescale of 1500 yr (Broecker and Peng, 1982) prevents the homogenization of seawater Nd isotopic compositions. The Nd isotopic variation of the seawater has been used to distinguish different water masses, to trace the ocean circulation and to estimate the flow rate and contribution of Nd from various sources (ca. Piepgras and Wassurburg, 1980; Amakawa et al., 2013).

Calcareous shells of foraminifera are now drawing attention as a proxy of seawater Nd in the past, which can be used to trace the changes of the oceanic Nd isotopic composition related with paleoclimate changes (Tachikawa et al., 2014). One of the difficulties in analyzing Nd isotopic composition of foraminifera comes from the low Nd concentration of the foraminiferal shells. The low Nd concentration (up to several ppm) of foraminiferal shells requires quite large sample sizes (several mg) to meet the minimum sample size required for Nd isotope analysis (Nd amount of 2-5 ng). Lowering the sample size limits for Nd isotope analysis may expand the applicability of the technique to foraminifera-poor sediments derived from oceanic drilling sites.

We have developed a new technique to measure isotope ratios of ng to sub-ng sized Nd samples using total evaporation normalization method (Wakaki et al., 2007) together with the low-blank Nd separation chemistry. Isotope ratios of Nd are measured using thermal ionization mass spectrometer (Thermo TRITON) at Kochi Core Center.

The ¹⁴³Nd/¹⁴⁴Nd values of the isotopic reference reagent JNdi-1, measured at sample sizes of 0.5, 1 and 2 ng of Nd, all agreed with the values obtained by large sample measurement (100 ng of Nd) within statistical errors. The reproducibility of ¹⁴³Nd/¹⁴⁴Nd values are 100 ppm (n = 8), 60 ppm (n = 9) and 40 (n = 8) ppm for 0.5, 1 and 2 ng measurements, respectively. The precision and accuracy of the sample analysis, including chemical procedure, is checked by analyses of two GSJ reference rocks, JB-2 (basalt) and JCp-1 (coral). The basalt sample was decomposed by mixed HF-HNO₃-HClO₄, and the coral sample was decomposed by HNO₃. Sample aliquots, containing 0.5 and 1.2 ng of Nd, respectively, were processed by using the low-blank Nd separation chemistry. The measured ¹⁴³Nd/¹⁴⁴Nd ratios of JB-2 (n = 9) and JCp-1 (n = 8) samples all agreed with the values obtained by measurements with large sample sizes within statistical errors. These results demonstrate that our technique gives reliable results even for samples as small as 0.5 ng of Nd. Preliminary results of subsurface-dwelling planktonic foraminifera samples, *Globorotalia tumida*, collected from a Quaternary sediment core from the West Caroline Basin (western equatorial Pacific Ocean) will be presented.

キーワード: 古環境, Nd 同位体, 有孔虫

Keywords: paleoclimate, Nd isotopes, foraminifera

ベーリング海、Bowers Ridge の起源と漸新世島弧火成作用：IODP exp. 323, Hole U1342 から得られた結果
Origin of Bowers Ridge and its Oligocene arc magmatism: Results from the IODP Expedition 323, Hole U1342

川畑 博^{1*}; 佐藤 佳子²; 木村 純一²; 常 青²; 仙田 量子²; 高橋 俊郎³; 平原 由香⁴; 宮崎 隆²; Scholl David W.⁵
KAWABATA, Hiroshi^{1*}; SATO, Keiko²; KIMURA, Jun-ichi²; CHANG, Qing²; SENDA, Ryoko²; TAKAHASHI, Toshiro³; HIRAHARA, Yuka⁴; MIYAZAKI, Takashi²; SCHOLL, David W.⁵

¹ 高知大学, ² 海洋研究開発機構, ³ 新潟大学, ⁴ 愛知教育大, ⁵ U.S. Geological Survey,
¹ Faculty of Science, Kochi University, ² Japan Agency for Marine-Earth Science and Technology (JAMSTEC), ³ Faculty of Science, Niigata University, ⁴ Aichi University of Education, ⁵ U.S. Geological Survey,

The Bowers Ridge is an 800 km-long arcuate aseismic ridge extending northward from the Central Aleutian Ridge. IODP Expedition 323 drilled a total of 41.54 m of igneous basement at site U1342 in the northwestern Bowers Ridge, where an 800 m-deep wave-eroded platform exist. The recovered basement, composed of andesitic lavas and basaltic to andesitic volcanoclastic rocks (Kawabata et al., 2011), provide an opportunity to explore temporal change in magma composition at Bowers Ridge just before the cessation of arc magmatism in the Oligocene.

The recovered volcanic samples yield 26-34 Ma ⁴⁰Ar-³⁹Ar ages (Sato et al., 2015) and have arc signature characterized by depletion of HFSE and enrichment of LILE on the multi-element diagrams normalized to NMORB. The trace element features, with the presence of anorthitic plagioclase phenocrysts (An₉₃), confirm the arc-origin of the ridge that was deduced from dredge samples around Site U1342 (Cooper et al. 1987; Wanke et al., 2012). In arc magmatism, flux from subducted oceanic crust played an important role as suggested by high Ce/Pb and unradiogenic ²⁰⁶Pb/²⁰⁴Pb.

Temporal change of magma chemistry was examined from both the core and reported dredge samples. Lower units of core samples exhibit low to middle-K series, whereas both the upper units of core and dredge samples show middle to high-K series. In addition, the dredge samples are more enriched in LREE, Rb, and Ba, and show higher (LREE, MREE)/HREE ratios than the core samples. The dredge basalts and andesites fall within the adakite field on the discrimination diagrams of Sr/Y vs Y and La/Yb vs Yb (Wanke et al., 2012), whereas all the core samples are non-adakitic basalts and andesites. These geochemical results suggest that the difference in magma compositions between the core and dredge samples could mainly reflect the difference in the amount of slab-derived flux and/or the flux compositions. In this context, the inferred slab melting event (Wanke et al., 2012) may not be a unique scenario for producing the adakitic dredge basalts and andesites. Larger amount of slab-derived flux and higher melting pressure can also explain the change in magma compositions from the non-adakitic core samples to the adakitic dredge samples. Thus, more careful examination is required to determine whether or not the already inferred extraordinary high geothermal gradient is essential for the Oligocene magmatism at the Bowers Ridge.

キーワード: アダカイト, バウアーズリッジ, 残存島弧
Keywords: adakite, Bowers Ridge, remnant arc

フッ素含有量から明らかにするチリ南部火山帯の島弧火成活動への新たな知見 Fluorine content reveals new insight into arc magmatism of Southern Volcanic Zone, Chile.

遠山 知亜紀^{1*}; 折橋 裕二²; 新正 裕尚³; 角野 浩史⁴; 村松 康行⁵

TOYAMA, Chiaki^{1*}; ORIHASHI, Yuji²; SHINJOE, Hironao³; SUMINO, Hirochika⁴; MURAMATSU, Yasuyuki⁵

¹ 海洋研究開発機構, ² 東京大学地震研究所, ³ 東京経済大学, ⁴ 東大院理, ⁵ 学習院大学

¹JAMSTEC, ²ERI, Univ. of Tokyo, ³Tokyo Keizai Univ., ⁴Univ. of Tokyo, ⁵Gakushuin University

The halogen elements have high partition coefficients in aqueous fluid (Bureau et al., 2000), but the difference in their partition coefficients for aqueous fluid/silicate melt/silicate minerals/organic matter results in distinct elemental ratios in seawater, pore fluid, sediment, oceanic crust and mantle (e.g., Johnson et al., 2000; Burgess et al., 2002; Palme and O'Neil, 2004). For instance, fluorine is incorporated into apatite, amphibole and phengite (Svensen et al., 2001) while iodine has a high abundance in organic-rich marine sediments because it is an essential element for life. These characteristics make halogens useful to trace water cycling in subduction zones (e.g., Fehn et al., 2003; Muramatsu et al., 2007; Sumino et al., 2010). Recently, subduction of marine pore fluid into the mantle has been suggested based on noble gas isotopes in the mantle (Holland and Ballentine, 2006) and halogen compositions of exhumed mantle wedge peridotites (Sumino et al., 2010). However, only a little is known about the behavior of halogen elements during subduction processes and their fate in the earth's mantle. Therefore, we newly analyzed halogen concentrations in regional representative lavas obtained from 13 volcanoes on the Quaternary volcanic front of the Southern Volcanic Zone (SVZ) of Andean arc in Chile. In this presentation, we focus on fluorine content that has least influence of degassing on volcanism.

Fluorine contents of most analyzed samples are 100-300 ppm. To understand behavior of fluorine on fractional crystallization, the correlations of SiO₂ and FeO*/MgO with fluorine data from a volcano are plotted. This result indicates that the fluorine dependency with these parameters changes at SiO₂ = 55 wt% and FeO*/MgO = 4.2, resulting from apatite crystallization and removal from the magma. Thus, the evolved rock samples from which apatite crystallized were excluded from further discussion.

We compared fluorine with major and trace element data obtained by previous study (Shinjoe et al., 2013) and newly revealed that the fluorine concentrations of selected samples were not correlated with boron concentrations. This means that fluorine shows different behavior in the subduction zone magmatism though both fluorine and boron are fluid-mobile elements. The basaltic samples from Hudson, the southernmost volcano of SVZ, show very high fluorine concentration (~1000 ppm). Similar anomalies were confirmed also with Nb and Ta. The chemical characteristics suggest that the magma source of this region has been derived from the metasomatized mantle wedge by influence of slab-derived melt (Kilian and Behrmann 2003; Shinjoe et al., 2013). The fluorine concentration possibly becomes new sensitive detector of slab-derived melt in arc volcanism.

キーワード: フッ素, 沈み込み帯, スラブメルト, スラブ流体

Keywords: fluorine, subduction zone, slab melt, slab fluid

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 components of apatite grains from pyroclastic flow deposits of Aso volcano

道久 真理絵^{1*}; 佐野 有司²; 高畑 直人²; 石田 章純²; 小池 みずほ²; 吉田 健太³; 東野 文子³;
小木 曾 哲¹

DOKYU, Marie^{1*}; SANO, Yuji²; TAKAHATA, Naoto²; ISHIDA, Akizumi²; KOIKE, Mizuho²;
YOSHIDA, Kenta³; HIGASHINO, Fumiko³; KOGISO, Tetsu¹

¹ 京都大学人間・環境学研究所, ² 東京大学大気海洋研究所, ³ 京都大学理学研究科

¹Graduate School of Human and Environmental Studies, Kyoto University, ²Atmosphere and Ocean Research Institute, The University of Tokyo, ³Graduate School of Science, Kyoto University

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。そのような水の起源の解明のためには、初期地球内部の水の量や、地球の材料物質と考えられている隕石中の揮発性成分量を明らかにすることが重要である。この手がかりの1つに、地球最古のジルコンが含有する初生的なアパタイトがある(山本 他, 2013)。アパタイトは結晶中に揮発性成分(F, Cl, OH)を持つため、このアパタイトから初期地球内部の水、さらにはF, Clについての情報を得ることが期待される。また、隕石中のアパタイトから地球の材料物質の水やF, Clについて推測することも可能であると考えられる。

しかしながら、アパタイト-メルト間の揮発性成分量に関する知識は不十分であり、特にアパタイト中の水についての先行研究は多くない。Mathez and Webster (2002) や Webster et al. (2009) では、高温高压実験によってアパタイト-メルト-フルイド間のF, Clの分配について明らかにしようとしているが、アパタイト中のOHや揮発性元素サイト(Xサイト)中でのOH-F-Clの交換関係については議論されていない。また、Pan and Fleet (2002) では、アパタイト中の揮発性元素の組成は揮発性元素以外の元素の影響を受けると述べられている。よって本研究では、阿蘇火山火砕流堆積物中のアパタイトと、斜長石中のメルトインクルージョンの揮発性成分を分析し、水も考慮に入れたXサイトでの交換関係や、揮発性元素組成について影響を与え得るその他の元素について調べることで、アパタイト-メルト間で揮発性成分がどのように分配されるかを明らかにすることを目的とする。

本研究では、Aso-3 と Aso-4 それぞれの安山岩質軽石と流紋岩質軽石の計4試料を用いた。岩石試料からアパタイトを取り出し、EPMA(京大理学研究科)で主成分元素とF, Cl量を、nano-SIMS(東大大気海洋研)ではOH量を組成分析した。斜長石中のメルトインクルージョンは小豆畑(2009)の試料を用い、EPMAで主成分元素とF, Cl量を組成分析した。分析の結果、1試料中のアパタイトのCl量はほぼ一定である一方、F量に幅があった。これはFとOHが交換関係にあることを示す。また、F, Clは流紋岩質試料の方に、OHは安山岩質試料の方に多いことがわかった。メルトインクルージョンとアパタイトの間にF, Clの相関性は見られなかったが、温度・圧力・斜長石組成等から見積もられたホストマグマ中のH₂O量(Kaneko et al., 2007)とアパタイト中のOH量との間には正の相関がみられた。

また、アパタイト中のOH濃度とCaO, P₂O₅, MgO各濃度に正の相関が見られたことから、FまたはOHの挙動に影響を与える要因としてCa, P, Mgの存在が考えられる。例えば、アパタイト中のCaがその他の元素(Na, K, REEなど)や空孔に置換されることに伴ってXサイトでOHがFに置換される可能性がある。さらに、アパタイト族はM₅(ZO₄)₃Xで表されるが、アパタイトのMサイトに入る陽イオン量は酸素13に対し5と期待されるどころ、本試料では4.66-4.88と少なかった。そのため、希土類元素などMサイトに入る可能性のある元素についてさらなる分析が必要である。

キーワード: アパタイト, 揮発性元素, 水

Keywords: apatite, volatile component, water

先小御岳火山のマグマの分化にかかわるザクロ石・角閃石の分別作用 Garnet-amphibole fractionation generating basalt to dacite magmas of Pre-Komitake volcano, Japan

柴田 知之^{1*}; 吉本 充宏²; 藤井 敏嗣²; 中田 節也³

SHIBATA, Tomoyuki^{1*}; YOSHIMOTO, Mitsuhiko²; FUJII, Toshitsugu²; NAKADA, Setsuya³

¹ 京都大学大学院理学研究科附属地球熱学研究施設, ² 山梨県富士山科学研究所, ³ 東京大学地震研究所

¹Beppu Geothermal Research Laboratory, Kyoto University, ²Mount Fuji Research Institute, Yamanashi Prefectural Government, ³Earthquake Research Institute, University of Tokyo

The Pre-Komitake volcano, which was discovered by scientific drilling into Mt. Fuji, is an older volcanic body than Fuji and Komitake volcanoes buried beneath the NE flank of Fuji volcano (Nakada et al., 2004; Yoshimoto et al., 2010). The Fuji, Komitake, and Pre-Komitake volcanoes are situated in a complex tectonic setting near the junction of three plates: the North American Plate in the east, the Eurasian Plate in the west, and the Philippine Sea Plate in the south, under two of which the Pacific Plate subducts from east to west. The magmas of Pre-Komitake are different from those of Fuji and Komitake (Yoshimoto et al., 2010). According to Yoshimoto et al. (2010), the Pre-Komitake lavas are characterized by hornblende-bearing andesites and dacites, in contrast to the hornblende-free basaltic rocks of Fuji and Komitake. These authors also suggested that the concentrations of incompatible elements increase with increasing SiO₂ in the magmas of Pre-Komitake, whereas those of Fuji increase despite SiO₂ remaining fairly constant (Fujii, 2007). They suggested that the variations in magma chemistry in this area between 250 ka and recent times might have occurred as a result of a change in regional tectonics that occurred ~150 ka, although this remains unproven. To our knowledge, no detailed research has yet been carried out into Pre-Komitake magma genesis on the basis of comprehensive major and trace elements, and isotopic compositional data sets. Therefore, we analyzed the trace element and Sr-Nd isotopic compositions of the Pre-Komitake magmas in order to better understand their genesis.

The Sr and Nd isotope ratios ranged from 0.703320±0.703476, and 0.512885±0.513087, respectively, which are very similar to those of the lavas from Fuji and Komitake volcanoes (Nagai et al., 2004) that erupted subsequently. Enrichment of large ion lithophile elements, Pb and Sr, can be seen in the primitive mantle-normalized multi-element diagram of the Pre-Komitake, Komitake, and Fuji lavas. These collectively show island arc lava signatures, however, the middle to heavy rare earth elements are more depleted in the Pre-Komitake lavas, compared to those from Fuji. Positive Eu anomalies are observed, although the extents of these anomalies decrease with increasing SiO₂ in the Pre-Komitake lavas, whereas this is not observed in Fuji lavas. The Sr/Y ratios of Pre-Komitake lavas increase from basalt to basaltic andesite, but decrease through andesite to dacite. This occurs in combination with a rapid increase in La/Yb ratios, followed by a more gradual increase. A gradual decrease in Dy/Yb ratios is also seen over the entire compositional range. These data suggest deep (>12 kbar) fractionation of garnet and amphibole followed by shallow (i.e., ~5 kbar) fractionation of amphibole and plagioclase. Such variations are not observed in the Komitake and Fuji lavas, for which deep fractionation of clinopyroxene and shallow fractionation of plagioclase have been suggested. All three lavas, including those from the Pre-Komitake volcano, show similar isotopic, major, and trace element compositions in the unfractionated basalts. The differing geochemical trends found in the Pre-Komitake lavas are likely to be due to different mineral fractionations occurring in the hydrous Pre-Komitake basalts compared to the dry Fuji and Komitake basalts.

キーワード: 先小御岳火山, 富士山, 微量元素, Sr-Nd 同位体, ザクロ石の結晶分化

Keywords: Pre-Komitake volcano, Fuji volcano, Trace elements, Sr-Nd isotope ratios, Garnet fractionation

小笠原ボニナイト中のCrスピネルへの白金族元素の分配
Partition of the platinum group elements between Cr spinels and whole rocks in boninites
from Ogasawara islands

仙田 量子^{1*}
SENDA, Ryoko^{1*}

¹ 独立行政法人海洋研究開発機構
¹ JAMSTEC

Abundance of the platinum group elements (PGEs) in volcanic rocks are expected to have some information about source mantle or magma genesis as other elements. Sulfides and Cr spinel are known to important host of PGEs, for example, enrichment of PGEs are reported in chromitites from layered intrusions, ophiolites and alpine-type peridotites (Ahmed and Arai, 2002, Buchl et al., 2004). Among volcanic rocks, however, Cr spinel can be observed in mafic-ultramafic magmas as komatiite and boninite. The correlation between whole rock Cr and PGEs in magmatic rocks are observed (Hamlyn et al., 1985), whether PGEs status in Cr spinels unresolved. Experimental studies on partitioning of PGEs between spinels and silicate melts are reported and showed significant amounts of IPGEs (Iridium-group PGE; Ru, Os, Ir) can be held in solid solution in spinel species as Cr spinels with high partition coefficient under oxidized conditions ($fO_2 > QFM + 2$). In empirical studies, the partitioning of Rh, Ru and Ir into Cr spinels increases with increasing oxygen fugacity are shown in komatiites by Jung-Woo et al. (2012). Here newly PGE data of Cr spinels and whole rocks from boninites Ogasawara and Guam islands are shown and have a discussion about PGE partitioning in boninite and tholeiite magma.

Keywords: platinum group element, boninite, partition

捕獲岩を用いた日本島弧深部地殻の組成推定 Determining the deep crustal composition of Japan island arc using xenoliths

長尾 潤^{1*}; 小澤 一仁²
NAGAO, Jun^{1*}; OZAWA, Kazuhito²

¹ 東京大学大学院理学系研究科地球惑星科学専攻, ² 東京大学大学院理学系研究科地球惑星科学専攻
¹Department of Earth and Planetary Science Graduate School of Science, The University of Tokyo, ²Department of Earth and Planetary Science Graduate School of Science, The University of Tokyo

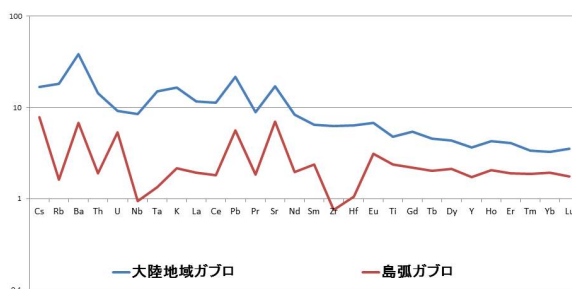
大陸地殻の進化過程を理解する上で、大陸地殻組成を正確に決定することは必要不可欠である。大陸深部地殻の試料を直接入手することは困難なため、その組成は地震波データと変成岩や捕獲岩といった岩石試料から推定される。地震波の速度は密度に左右されるため、地震波データからは大陸地殻の構造や主要元素の情報が得られるが、微量元素については調べられない。一方、変成岩や捕獲岩といった岩石試料からは主要元素だけでなく微量元素についても調べられるが、これらの岩石試料を採取できる地域は非常に限られている。したがって、幅広い範囲の大陸深部地殻の主要元素及び微量元素組成を推定するためには、地震波データと岩石試料から得られた化学的データを併せて解釈する必要がある。

これまでに大陸深部地殻の組成は大陸地域については詳細に調べられてきたが、日本の様な島弧については詳しく調べられていない。地震波データによれば、大陸地域と島弧とでは地殻の厚さ・主要元素組成が異なるので、島弧の深部地殻の組成を推定する必要がある。そのため、今回は秋田県一ノ目潟と佐賀県高島の捕獲岩合わせて約100個について主要元素をXRFで、微量元素をLA-ICPMSを用いて測定した。

主要元素組成から一ノ目潟の捕獲岩は超塩基性岩から中性岩に、高島の捕獲岩は超塩基性岩から酸性岩に分類された。また微量元素組成からは両地域の捕獲岩は、Nb, Ta, Zr, HfといったHFSEに欠如し、PbといったLILEに富むことがわかった。このことからマンテルウェッジでのマンテルの部分融解の際に流体が関与し、日本島弧深部地殻が形成されたと考えられる。こうした日本島弧の深部地殻の組成と大陸地域の成変岩や捕獲岩から推定されている大陸地域の深部地殻の組成とを比較すると(図1)、SiO₂濃度は変わらないにも関わらず、ほぼすべての液相濃集元素について大陸地域に比べて島弧の方では濃度が低いことがわかった。またHFSEについては、日本島弧の方がより顕著に欠如していることがわかった。これらのことは、日本の沈み込み帯において流体の影響が強く、マンテルの部分融解度が大きかったことを反映していると考えられる。Uについては島弧と大陸地域とで濃度に差は見られなかった。Uには酸化的環境下だと流体に溶けやすくなり、還元的环境下だと溶けにくくなるという性質がある。また、約22億年前に地球表層は還元的环境から酸化的環境になったことが知られていることから、大陸地域の古い大陸地殻形成時には還元的环境下でUはHFSE同様、流体に溶けにくかったが、日本島弧の若い大陸地殻形成時には酸化的環境下でLILE同様、流体に溶けやすくなったと考えられる。今回用いた捕獲岩の主要元素・微量元素間に弱い相関があることが確認された。今後別の地域の捕獲岩でも同様の相関が見られるか調べる必要があるが、こうした相関から地震波データと組み合わせることで日本島弧深部地殻の広範囲の組成を推定できることが期待される。

キーワード: 捕獲岩, 一ノ目潟, 高島, ニュートリノ, 島弧, 地殻組成

Keywords: Xenolith, Ichinomegata, Takashima, Neutrino, island arc, crustal composition



COHを含むかんらん岩の融解によるカーボナタイトメルト生成の可能性 Genesis of carbonatite melt by partial melting of COH-bearing peridotite

小澤 亜耶^{1*}; 小木曾 哲¹
OZAWA, Aya^{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

生命体を構成する必須元素（炭素、酸素、窒素、リンなど）の持続的供給は、生命の誕生とその発展を支える重要な条件のひとつと考えられる。だとすれば、初期生命発生時の地球上にはそれら必須元素が豊富に濃集している場所が存在し、その場所こそが初期生命誕生のゆりかごとなった可能性が考えられる。では、必須元素が濃集するような場とはどのようにして形成され得るのだろうか。特にリンに関して言えば、有機体が存在しない場合、地殻あるいはマントルから供給するしかない。地殻はマントルの部分融解によって形成されるので、マントルこそがリンの供給源のはずである。従って、マントルからどのようにしてリンに濃集する岩石が形成されたかを検討することが必要である。

現在地球上に見られるカーボナタイトにはリンが多く含まれており、中には他の火成岩と比較して桁違いにリンを濃集しているものも発見されている。従って、カーボナタイトの生成過程のなかにマントルからリンを濃集させる重要な鍵がある可能性がある。

カーボナタイトの成因について近年有力視されているのは、CO₂を含むマントル物質の部分融解メルトから液相不混和によってカーボナタイトメルトとアルカリ玄武岩質メルトの二相が離溶するというものである。現在噴出しているカーボナタイトとその周辺のアルカリ玄武岩組成を用いて元素の分配を調べた先行研究には Veksler et al. (2011) や Brooker (1998) がある。Veksler et al. (2011) では、同じ出発組成でも無水の場合にはリンは珪酸塩メルトへ濃集し、含水条件ではリンはカーボナタイトメルトへ濃集することが示されている。Brooker (1998) では CO₂ に飽和した実験でより不混和領域が広がり、カーボナタイトメルトへのリンの濃集がより顕著となることが示唆されている。しかし、これらの実験で示された不混和現象が、マントル由来のメルトで起こり得るのかどうかについては明らかではない。

よって本研究では、出発組成として始原的マントル組成 + CO₂ + H₂O を用い、マントル由来のメルトにおいてリンがカーボナタイトメルトに濃集するような液相不混和現象が起こる可能性を検討した。出発組成として、始原的マントル組成に近い KLB-1 組成にシュウ酸二水和物を 10wt.% 加えたものを用い、ピストンシリンダー装置で 2.5GPa・1100℃ の条件下で 26 時間保持し部分融解を起こさせたところ、非常に MgO に富み SiO₂ に乏しいメルトが得られた。

このメルト組成は、Brooker (1998) が実験で決定した (SiO₂+Al₂O₃+TiO₂) - (Na₂O+K₂O) - (CaO+MgO+FeO) 疑似三成分系における珪酸塩メルト - カーボナタイトメルト不混和領域にはプロットされない。従って、このメルトがそのままマントルを上昇しても、そこからカーボナタイトメルトが離溶する可能性は小さい。しかし、このメルトの中でカンラン石等が結晶分化することによってメルト中のアルカリ濃度が上昇すれば、メルト組成は不混和領域に近づいていく可能性がある。

以上のように、マントル由来のメルトからカーボナタイトメルトが生成される可能性はあると言える。こうしたカーボナタイトメルトを離溶する液相不混和現象が、初期地球において起こるためにはどのような条件が必要か、今後の検討が必要である。

キーワード: リン, カーボナタイト, 部分融解, 液相不混和, 初期地球

Keywords: phosphorus, carbonatites, partial melting, liquid immiscibility, the early Earth

ライババエ海洋島玄武岩から分離したCPXの正確な年代補正 Sr-Nd-Pb-Hf 同位体比の測定 Determination of precise age corrected Sr-Nd-Pb-Hf isotope ratios of the clinopyroxene from Raivave OIB samples

宮崎 隆^{1*}; 羽生 毅¹; 仙田 量子¹; 木村 純一¹; 常 青¹; 平原 由香²; 高橋 俊郎³
MIYAZAKI, Takashi^{1*}; HANYU, Takeshi¹; SENDA, Ryoko¹; KIMURA, Jun-ichi¹; CHANG, Qing¹;
HIRAHARA, Yuka²; TAKAHASHI, Toshiro³

¹ 海洋研究開発機構地球内部物質循環研究分野, ² 千葉工業大学, ³ 新潟大学
¹D-SEG, JAMSTEC, ²Chiba Institute of Technology, ³Niigata University

In Sr-Nd-Pb-Hf isotope analyses of whole rock samples, the leaching technique is used for removing the effect of secondary alteration and contamination from outside environments. Especially for the rock samples collected from sea area, the leaching is indispensable to eliminate the effect of seawater alteration. However, even if the strong leaching condition is applied, it is difficult to remove the altered components completely. In order to overcome this problem, clinopyroxene (CPX) was paid attention because of its early crystallization phase and its high resistibility against alteration. It is expected that the CPX preserve more primitive isotope signature than the leached whole rock samples. Using the CPX sample from ocean island basalt (OIB), Hanyu and Nakamura (2000) and Jackson et al. (2009) revealed the Sr and Nd isotope signature of OIB source mantle. Hanyu et al. (2011; 2014) also analyzed Sr and Nd isotopes as well as Pb and Hf isotopes of CPX to investigate the mantle end-members in the OIB samples from Polynesia and St. Helena.

Parent/daughter (P/D) ratios such as Rb/Sr, Sm/Nd, U/Pb, Th/Pb, and Lu/Hf were used for determining the age-corrected isotope ratios (initial ratios) of Sr, Nd, Pb, and Hf isotopes. The most suitable method for correction is using P/D ratios determined from the same CPX aliquot used for each of the isotope measurements. However, due to the limitation of the decomposition method used for the Pb isotope analysis in our laboratory, there was difficulty in determining the U/Pb and Th/Pb ratios from the CPX aliquot used for the Pb isotope. Therefore, Hanyu et al. (2011) determined the U/Pb and Th/Pb ratios from the whole rock U, Th, and Pb concentrations and partition coefficients, although the Rb/Sr, Sm/Nd, and Lu/Hf ratios were determined from the same CPX aliquot used for the Sr, Nd, and Hf isotope analyses. To overcome the uncertainty using partition coefficients, Hanyu et al. (2014) determined the U/Pb and Th/Pb ratios using the U, Th, and Pb concentrations of the CPX aliquot used for the Sr, Nd, and Hf isotope measurements, although the uncertainty of inhomogeneity in the CPX separates still remained.

In this study, we reexamined our analytical method, especially for the determination of U/Pb and Th/Pb of the CPX separates. We determined the Rb/Sr, Sm/Nd, and Lu/Hf ratios from the CPX aliquot used for the Sr, Nd, and Hf isotope measurements (Sr-Nd-Hf aliquot) and the U/Pb and Th/Pb ratios from the CPX aliquot used for the Pb isotope measurement (Pb aliquot) to determine the precise age-corrected Sr-Nd-Pb-Hf isotope ratios of the CPX sample from the Raivavae OIB samples. Comparisons between the Sr-Nd-Hf and Pb aliquots showed inhomogeneity in the U, Th, and Pb concentrations and revealed 0.34 and 0.88 of $\Delta U/Pb$ and $\Delta Th/Pb$, in maximum. These $\Delta U/Pb$ and $\Delta Th/Pb$ yielded 1052, 61, and 448 ppm in the $\Delta^{206}Pb/^{204}Pb$, $\Delta^{207}Pb/^{204}Pb$, and $\Delta^{208}Pb/^{204}Pb$ when the age correction used was 6 Ma. These $\Delta^{206}Pb/^{204}Pb$ and $\Delta^{208}Pb/^{204}Pb$ were beyond the analytical uncertainty of the standard samples. Therefore, using P/D ratios determined from the same CPX aliquot used for each of the isotope measurements is an important factor for the determination of precise age-corrected Sr-Nd-Pb-Hf isotope ratios of the Raivavae CPX sample.

キーワード: Sr-Nd-Pb-Hf 同位体, CPX, ライババエ, 年代補正, 親娘比
Keywords: Sr-Nd-Pb-Hf isotopes, CPX, Raivavae, Age correction, P/D ratio

Laser-ablation Sr isotopic analyses of small glass samples using MC-ICPMS Laser-ablation Sr isotopic analyses of small glass samples using MC-ICPMS

常 青^{1*}; 木村 純一¹; ヴァグラロフ ボグダン ステファノフ¹
CHANG, Qing^{1*}; KIMURA, Jun-ichi¹; VAGLAROV, Bogdan stefanov¹

¹ 海洋研究開発機構

¹Japan Agency for Marine-Earth Science and Technology

An analytical protocol was developed for correcting Kr baseline-induced bias and Rb isobaric overlap factors to analyze Sr isotope ratios for small glass samples using laser ablation (LA) with a desolvating nebulizer dual-intake system and MC-ICP-MS. The combined use of a low-oxide interface setup along with high-gain Faraday amplifiers with a $10^{12} \Omega$ resistor enabled precise determination of Sr isotope ratios from 50-100 μm diameter craters using 10 Hz laser repetition rate. Residual analytical biases of $^{84}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios induced from Kr baseline suppressions (Kimura et al., 2013), were found to be nonlinear, but the correction method was applicable to 50-200 $\mu\text{m}/10$ Hz craters. We also found that the $^{85}\text{Rb}/^{87}\text{Rb}$ overlap correction factor changed with time with a change in the surface condition of sampler-skimmer cones. The correction factor of $^{85}\text{Rb}/^{87}\text{Rb}$ was thus determined at least once per five unknown measurements using the nebulizing intake line. We determined $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios from MkAn anorthite (Sr = 305 ppm, Rb = 0.07 ppm), BHVO-2G, KL2-G, ML3B-G (Sr = 312-396 ppm, Rb = 5.8-9.2 ppm), and BCR-2G (Sr = 337 ppm, Rb = 48.5 ppm) basalt glasses using a 50-100 $\mu\text{m}/10$ Hz crater. The results agree well with their reference values determined by thermal ionization mass spectrometry, even with the high Rb/Sr ratio (0.14) in the BCR-2G glass. The internal/intermediate precisions were ± 0.0002 (two-standard deviation: 2SD) for 100 μm craters and ± 0.0005 for 50 μm craters. The new instrument settings and analytical protocol improved the precision by a factor of two compared to the previous report using LA-(sector field)-ICP-MS and enables the analysis of sample volumes that are ten times smaller than those used in previous LA-MC-ICP-MS analyses with equal precision.

キーワード: Sr isotope, geological glasses, LA-MC-ICP-MS, Kr baseline-induced bias, Rb overlap correction
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