

## LA-ICPMS 時間分解分析に関するデータ処理法の検討 Improvement of data processing for Time-Resolved-Analyses (TRA) using LA-ICPMS

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Laser-Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICPMS) is commonly used for in-situ analyses of isotope ratios and elemental abundance. Laser-ablation sample introduction is destructive method, and the spatial resolution of an analysis is inversely related to total signal-intensity. It means that observed signal-intensity is never satisfied and unstable, because space-resolution of the analyses is always optimized as high as possible. Furthermore, a natural rock sample often contains mineral inclusions, and signal-intensities can be disturbed by them. Therefore, Time-Resolved-Analysis (TRA) mode is commonly used for most LA-ICPMS analyses.

Using TRA mode, we can estimate the preciseness of each run. However, the way of data processing has not been made enough discussions yet. For the data processing, most researchers regard flatness of the signal intensity as important. Integration time of each runs were decided based on flatten signal and/or signal ratio. Signals of the beginning and the end of ablation were not used for the calculation. However, this processing method has several problems. One of the problems was, signal intensity was not always flatten shape, because analyzed samples were usually limited. Furthermore, flatness of the signal was not commonly determined and different researchers use different criteria. In this study, we applied several calculation method for the same TRA dataset, and estimate the preciseness for each calculation method.

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Keywords: LA-ICPMS, time resolved analyses, TRA, femtosecond laser, data processing

## LAL-MC-ICPMS 法による普通コンドライトに含まれる Fe-Ni 相の鉄同位体比測定 Fe isotopic study of Fe-Ni metal in ordinary chondrite using LAL-MC-ICPMS

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The ordinary chondrite is the most abundant and primitive meteorite in the solar system. It is widely believed that the formation sequence of the ordinary chondrites tell us details of the early solar system history. Among the various minerals or components found in the ordinary chondrites, the Fe-Ni metal is one of the characteristic materials of ordinary chondrite. Despite the major components, the formation processes of Fe-Ni metals have still been veiled. The Fe isotopic signature is one of the key information to unveil the formation processes of Fe-Ni metals in the ordinary chondrites, because (a) Fe is ubiquitously distributed in various minerals or phases in the meteorites, and (b) Fe isotope composition can vary through the formation processes. Standing on this view point, some previous studies measured the Fe isotopic ratios of Fe-Ni metals in the ordinary chondrites [1, 2]. In those studies, the ordinary chondrites were crushed in the mortar and Fe-Ni metals were sampled through handpicking or micro-mill technique to collect Fe-Ni metals. It should be noted that these techniques have the risk of the contamination from the equipments or apparatus used for the sample handling although these techniques have been widely accepted as the sampling methods of the solid materials for the isotopic analysis.

In this study, we applied a new sampling technique, LAL (laser ablation in liquid) [3, 4], to collect Fe-Ni metals from the ordinary chondrites for the Fe isotopic measurement using MC-ICPMS. For the LAL sampling, the sample surface was polished and the metal phase was ablated in the deionized water using the femtosecond laser (wavelength 780 nm). Unlike with the conventional sampling techniques applied in the previous studies, the LAL technique can provide minimum risk of contamination of Fe from equipments. After the LAL sampling procedure, the resulting sample suspension was collected using micropipette and was then subsized to acid digestion using conc. HCl and conc. H<sub>2</sub>O<sub>2</sub>. The sample solution was heated until dryness and the resulting sample cake was re-dissolved in 0.1% HCl, and then used for the isotopic analysis of Fe using MC-ICPMS connected to the desolvating nebulizer system.

Total 15 ordinary chondrite metals were analyzed in this study. The delta <sup>56</sup>Fe data for L chondrites did not vary with the delta <sup>56</sup>Fe data for LL chondrites. In contrast, Fe in the H chondrites was isotopically slightly lighter than those for L or LL chondrites. These Fe isotopic variations among H, L and LL chondrites are consistent with the data obtained by Theis et al. (2008) [1]. These Fe isotopic ratios within the metallic phase in the H, L and LL chondrites is possibly related to the formation processes of them, however, cannot be explained by the simple redox reaction suggested by Theis et al. (2008). Possible cause of the present variation of Fe isotopic ratios will be discussed in this presentation.

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Keywords: laser ablation, laser ablation in liquid, ordinary chondrite, iron isotope

## ウダチナヤキンパーライトマグマに含まれる起源の異なる二つの希ガス成分 Two noble gas components in the Udachnaya kimberlite magma, Siberia

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キンパーライトはダイヤモンドを地表にもたらした火山岩であり、その起源はダイヤモンドが生成しうる地下 150km (e.g., Haggerty, 1994) で深と考えられているが、その起源物質については十分明らかにされていない (e.g., Smith, 1983)。

我々はキンパーライト中のオリビンに含まれる希ガスの同位体分析を通してその起源に迫ることを試みてきた。Sumino et al. (2006) ではロシア・シベリア地方のウダチナヤキンパーライトに含まれるオリビン斑晶に、プルーム起源のネオンが含まれることを報告した。このことはウダチナヤキンパーライトの起源がマントル深部、おそらく下部マントルがコア・マントル境界であることを強く示唆する。

本研究ではウダチナヤキンパーライトマグマの希ガス組成の特徴や進化について考察を深めるため、複数の原岩から新たに分離した 7 フラクションのオリビン斑晶を分析した。内 1 つは斑晶サイズによる希ガス組成の差異を調べるため、粒径 250 ~ 500  $\mu\text{m}$  (他は 200  $\mu\text{m}$  ~ 2 mm) のオリビンのみとした。また、同キンパーライトに含まれる 2 つの捕獲岩試料も分析した。一般にマグマ起源の希ガスは斑晶中の流体包有物に濃集しているため、本研究では包有物中から選択的に希ガスを抽出できる段階破砕法を用いた。

$^3\text{He}/^4\text{He}$  比は破砕が進むにつれ、結晶格子や固相の包有物に含まれる放射壊変起源  $^4\text{He}$  の寄与の増大により低下した。 $^3\text{He}/^4\text{He}$  比がほぼ一定の最初の数ステップのみが放射壊変起源成分の影響がない、キンパーライトマグマ本来の同位体比を示していると考えられる。このステップでは多くの試料が  $^3\text{He}/^4\text{He}=5.4 \sim 6.5R_A$  という値だったのに対し、粒径の小さな試料は  $3.8R_A$  と低い、捕獲岩 ( $2.5 \sim 3.2R_A$ ) に近い同位体比を示した。

ネオンの同位体比は大きく 2 つのトレンドに分かれた。一方は Sumino et al. (2006) で報告された、ウダチナヤキンパーライトマグマ本来の組成を反映していると考えられるトレンドであり、他方は MORB 源より核反応起源  $^{21}\text{Ne}$  に富んだ端成分の存在を示唆するトレンドである。後者は Buikin et al. (2005) で報告されたヨーロッパの大陸下マントルのトレンドに類似しており、捕獲岩のデータも併せて考えると、シベリア大陸下マントルの組成を反映している可能性がある。なお、粒径の小さな斑晶は後者に属し、ヘリウム同様大陸下マントル起源希ガスの強い寄与を示唆する。

Kamenetsky et al. (2008) は鉱物学的見地から、ウダチナヤキンパーライトマグマ中で純粋に斑晶として成長したオリビンのほとんどは粒径が 200  $\mu\text{m}$  以下に限られ、粒径の大きな斑晶は中心部に捕獲結晶のコアを持つことを報告している。粒径の小さな斑晶がより大陸下マントル的な希ガス組成を持つ事実は、その結晶化した時期が粒径の大きな斑晶に比べて遅く、大陸下マントルからの希ガスによるキンパーライトマグマの汚染が進み、同位体比がより大陸下マントル的に変化した希ガスを取り込みつつ斑晶が成長した事を示唆する。一方、サイズの大きな斑晶はガス量の乏しいコアを持ち、粒径の小さな斑晶より成長開始が早かったためリムの部分に大陸下マントルの影響が少ない希ガスを保持していると考えられる。

本研究はウダチナヤキンパーライトマグマに、マグマ本来のものと、大陸下マントルからの混染によるものの、起源の異なる二つの希ガス成分が含まれていたことを見出した。サイズの異なるオリビン試料を段階破砕法によって分析することで、大陸下マントルによるキンパーライトマグマの汚染の進行具合が異なる希ガスを結晶化の過程で捕獲したことを反映して、斑晶ごとに異なる希ガス組成を持つことを明らかにした。

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Keywords: noble gas, kimberlite, olivine, Udachnaya, Siberia, plume, subcontinental lithospheric mantle

## シベリア・ウダチナヤキンバーライト産ダイヤモンドの希ガス同位体組成 Noble gas isotopic compositions of diamonds in the Udachnaya kimberlite pipe, Siberia

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Noble gas isotopes trapped in fluid/melt inclusions in diamonds can constrain the origin of such deep-mantle-derived materials because they show completely different values between the more primordial source, which contributes OIBs and which is possibly stored in the deep mantle, and the depleted MORB source in the convecting mantle. In contrast, in situ radiogenic/cosmogenic noble gas isotopes might be distributed homogeneously in the diamond lattices. In vacuo sequential dynamic crushing extraction-by which diamond stones are crushed mechanically in vacuum-is a powerful tool for selective noble gas extraction from the inclusions. This report presents a noble gas study, conducted using a combination of several non-destructive micro-spectroscopic methods, of inclusions in diamonds in Udachnaya kimberlite (Siberia).

Sumino et al. (2006) [1] analyzed noble gases in olivine phenocrysts in the Udachnaya kimberlite and obtained <sup>3</sup>He/<sup>4</sup>He of kimberlite magma of ca. 5.7 R<sub>A</sub> which resembles that of subcontinental lithospheric mantle (SCLM) and a less-nucleogenic feature in neon isotopes of the magma than in the MORB source. The He/Ne systematics revealed that helium and neon in the Udachnaya kimberlite magma are explainable by a mixing between a plume-like and the SCLM-like components. The results indicate that the source of the Udachnaya kimberlite has similar noble gas characteristics to those of OIBs, and constrain a depth of its origin to be deeper than the MORB source mantle. To clarify the origin of the Udachnaya diamonds and their genetic relation to the host kimberlite, diamond crystals of cubic habit with abundant micro-inclusions and of 1-3 mm were investigated in this study.

The individual micro-inclusions are usually smaller than several micrometers, with some exceptions reaching 10-15 micrometers [2]. According to the distribution of carbonates (i.e., inclusions) obtained by FT-IR investigation, doubly polished plates of the samples were cut into several pieces. Noble gases in the sample pieces (less 0.5-1 mg each) were extracted using in-vacuo stepwise heating or crushing. Although the samples released helium that was dominated by radiogenic <sup>4</sup>He at their graphitization (2000 degree C) during stepwise heating, the crush-released helium exhibited <sup>3</sup>He/<sup>4</sup>He of 3.5-7.4 R<sub>A</sub>, indicating that the inclusion-hosted helium has similar <sup>3</sup>He/<sup>4</sup>He to that of the host kimberlite magma. This similarity implies diamond formation in a SCLM environment. A correlation between CO<sub>3</sub><sup>2-</sup> content and <sup>3</sup>He suggests that mantle-derived noble gases are trapped in the carbonate-rich inclusions. In contrast, diamond-lattice-hosted helium is dominated by radiogenic <sup>4</sup>He, possibly produced in situ from trace amounts of U and Th after diamond formation.

Because the scarcity of neon released by stepwise heating and crushing of the sample pieces made it impossible to determine neon isotope ratios precisely, we extracted noble gases by crushing several diamond stones together which exhibits similar volatile compositions each other based on FT-IR investigation. The result showed that crush-released inclusion-hosted neon isotope ratios form a trend in a neon three-isotope plot which is almost identical to that of the host kimberlite magma reported by [1], suggesting a common source of the diamonds and host kimberlite magma. The diamond-forming fluids and incipient carbonatitic fluids/melts of the kimberlite magma may originate from partial melting of SCLM peridotite previously metasomatised by a plume.

[1] Sumino et al. (2006) *Geophys. Res. Lett.* 33, L16318. [2] Zedgenizov et al. (2004) *Mineral. Mag.* 68, 61-73.

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Keywords: noble gas, diamond, kimberlite, mantle plume, subcontinental lithospheric mantle, Udachnaya, Siberia

## キンバーライト中の I/Br 比とそれらの産出地域による系統的分類 Systematic differences of I/Br ratios in kimberlites related to their origin

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キンバーライトはマントル起源の火山岩で、超塩基性でありながら H<sub>2</sub>O や CO<sub>2</sub> などの揮発性成分に富む特異的な特徴を持つ。ダイヤモンドを含むことから、そのマグマ源は少なくとも 150km より深いところにあると推定されている (e.g., Dawson, 1980)。また、希ガス同位体組成の研究から、キンバーライトはマントル由来の希ガスを保持していることが報告されている (e.g., Sumino et al., 2006)。さらに、マントル起源の鉱物中には地球生成時から存在していたと推定される同位体組成をもつ希ガスが見つかっており (e.g., Craig and Lupton, 1976; Kaneoka et al., 1978)、地球内部には現在も地球生成時に取り込まれた揮発性元素が存在すると予想される。このことから、キンバーライト中のハロゲン元素組成やその特徴を調べることで、地球形成時に保持された始源的なハロゲン元素に関する情報も得られる可能性がある。また、ハロゲン元素は様々な酸化状態をとることから、ハロゲン元素組成と産出地や噴出年代を比較することでマグマの起源に関する情報を知る手掛かりになる可能性がある。そこで、我々は 6 地域のキンバーライトの Cl, Br, I を測定し、各産出地域の特徴やその起源を考察した。

試料は南アフリカ産キンバーライト 11 個と、中国産キンバーライト 10 個、グリーンランド産キンバーライト 8 個、ブラジル産キンバーライト 2 個、ロシア産キンバーライト 2 個、カナダ産キンバーライト 1 個の計 34 個である。試料から Cl, Br, I を分離する方法は Pyrohydrolysis 法 (Muramatsu and Wedepohl 1998) を改良したものをを用いた。水蒸気を含んだ酸素ガスを送りながら、試料を約 1100 °C で加熱し、揮発性ガスを揮発させ、超純水でトラップする方法である。その後、トラップした溶液中の Br, I 濃度を ICP-MS で、Cl 濃度をイオンクロマトグラフィーで測定した。

分析の結果、キンバーライトは I/Br 比において 2 つのグループに分類できることが分かった。そこで、本研究では南アフリカ (South Africa) のように I/Br 比が高いキンバーライトを Group S (I/Br 比:  $1 \times 10^{-1}$ )、中国 (China) のように I/Br 比が低いものを Group C (I/Br 比:  $6 \times 10^{-3}$ ) と分類した。これらの結果と様々な物質の I/Br 比を比較したところ、前者の Group S は、玄武岩や橄欖岩などの地殻やマントルを構成する岩石と同様の I/Br 比を持っていることが分かった。このことから、Group S の I/Br 比は一般的な地球内部 (マントルや地殻) の値を示していると考えられる。また、Group S の I/Br 比は CI コンドライトの値 (I/Br 比:  $1 \times 10^{-1}$  [Anders and Ebihara, 1982]) とほぼ一致することから、地球形成時に保持された始源的な I や Br がマントルに存在する可能性が考えられる。さらに、南アフリカ、グリーンランド、ブラジル、カナダ産キンバーライトの地域や噴出年代が異なるにも関わらず、似た I/Br 比を示すことから、マントルの I/Br 比はこれらのキンバーライトが噴出した数億年の間は変化していないと考えられる。

一方、後者の Group C は I/Br 比の低い物質との mixing の可能性が考えられる。同様の I/Br 比は海水の影響を受けているとされるエクログャイト中の流体包有物 (Svensen et al., 2001) で見られ、海水を蒸発させた時の海水の I/Br 比が似た変動トレンドを示すことが報告されている (Zherebtsova and Volkova, 1996)。このことから、これらのキンバーライトは分別した海水起源のハロゲン元素の影響を受けていると考えられる。そのハロゲン元素がキンバーライトの起源物質に取り込まれた詳しいプロセスについては不明であるが、I/Br 比によって分類されたグループとそれぞれのキンバーライトマグマが噴出した時代の大陸配置図 (Torsvik et al., 2010) とを比較した結果、Group C のキンバーライトマグマが噴出した時代では、その近くに沈み込み帯が存在した可能性があり、このことも沈み込んだ物質の影響を示唆していると考えられる。

キーワード: キンバーライト, ハロゲン元素, I/Br 比, 南アフリカ, 中国, ロシア

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

## 中央海嶺からの硫黄、フッ素、塩素、臭素のフラックスの見積もり Estimation of S, F, Cl and Br fluxes at Mid Ocean Ridges

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地球表層の揮発性元素の大部分は、固体地球内部からの脱ガスによって蓄積してきたことが知られている。その一つである希ガスは、脱ガスの様式に制約を与えるためのトレーサーとして利用されてきた。大気中のアルゴンの同位体組成から脱ガス史に関する推定が行われ、地球形成初期(40億年以上前)における固体地球内部からのカタストロフィク脱ガスによって現在の地球の大気が形成されたというモデルが示された [1, 2]。また、マントル起源が自明である希ガスのヘリウム3 (<sup>3</sup>He) との比較によって炭素や窒素の中央海嶺や島弧からのフラックスが求められ、大気形成史に制約条件を与えた [3, 4]。

しかし、反応性が高いため多様な化学形で地球表層に存在する硫黄・ハロゲンに関しては、大気形成史に関する知見が十分に示されていない。加えて、中央海嶺におけるハロゲンのフラックスは、CO<sub>2</sub> との濃度比とそのフラックスから間接的に計算されてきたが [5]、CO<sub>2</sub> のフラックス自体 <sup>3</sup>He との比較で求められたものである。よって、これらの元素を <sup>3</sup>He と直接比較した方が良い。本研究では、中央海嶺玄武岩 (MORB) と背弧海盆玄武岩 (BABB) に含まれる硫黄、ハロゲン、<sup>3</sup>He の濃度を分析し、硫黄・ハロゲンのマントルからのフラックスを <sup>3</sup>He と比較することによって見積もった。

### 【分析】

MORB と BABB のフレッシュなガラス部分を約 1 g 選び、それをステンレス製のクラッシャーに入れ、水酸化ナトリウム水溶液 (1-4mol/L) を 1-2cm<sup>3</sup> 滴下した。そして、クラッシャーを液体窒素 (77K) に浸けて水溶液を凍結させてから上下に振り、ステンレス球を玄武岩ガラスと凍った溶液に衝突させることでそれらを破碎した。これにより、玄武岩ガラスの気泡に含まれていた硫黄、フッ素、塩素、臭素を含む反応性の高い元素を、衝撃で部分的に融解したアルカリ溶液中へと抽出した。一方、同時に気泡から抽出した不活性なヘリウムのガスを真空ラインに導入し精製してから、希ガス用の質量分析計 (VG5400) へと導入してヘリウム4 (<sup>4</sup>He) の強度とヘリウムの同位体比 (<sup>3</sup>He/<sup>4</sup>He) を測定した。また、溶液中に含まれる硫黄、フッ素、塩素、臭素の濃度をイオンクロマトグラフィ (Dionex-320) で測定した。

### 【結果と考察】

玄武岩ガラスの気泡中の <sup>3</sup>He、硫黄、フッ素、塩素、臭素の濃度はそれぞれ、(4-31) × 10<sup>-15</sup> mol/g, (20-430) × 10<sup>-9</sup> mol/g, (60-5000) × 10<sup>-9</sup> mol/g, (160-450) × 10<sup>-9</sup> mol/g, (5-1300) × 10<sup>-9</sup> mol/g であった。実験で扱ったサンプルが典型的な MORB との仮定のもと、硫黄、フッ素、塩素、臭素の中央海嶺からのグローバルフラックスを、各元素の <sup>3</sup>He との濃度比と <sup>3</sup>He のグローバルフラックス ((527 ± 102) mol/yr [6]) から見積もった。その値は、MORB と BABB 全体の揮発性元素が放出されるとした場合、それぞれ (1-26) × 10<sup>10</sup> mol/yr, (2-120) × 10<sup>11</sup> mol/yr, (2-120) × 10<sup>10</sup> mol/yr, (4-230) × 10<sup>10</sup> mol/yr となる。さらに、我々は得られた硫黄、フッ素、塩素の中央海嶺からのフラックスを、それらの島弧からのフラックスや沈み込み帯においてリサイクルする速度、そして地殻に付加する速度と比較し、現在の地球表層存在度を満たすのに必要な集積時間を見積もった。結果は、硫黄が 92 Myr 以上、フッ素が 11 kyr 以上、塩素が 1.0 Gyr 以上となり、これらは地球年齢 (4.55 Gyr) よりも短くなり得ることが分かった。これは、硫黄やハロゲンの反応性がアルゴンよりも高いため、異なるプロセスで地球表層に蓄積した可能性を示す。

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キーワード: 大気形成, 硫黄, ハロゲン, ヘリウム, グローバルフラックス, 中央海嶺玄武岩

Keywords: atmospheric formation, sulfur, halogen, helium, global flux, mid ocean ridge basalt

## ストロンチウムの安定同位体地球化学 Stable isotope geochemistry of strontium

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Strontium has four naturally occurring isotopes ( $^{84}\text{Sr}$ ,  $^{86}\text{Sr}$ ,  $^{87}\text{Sr}$  and  $^{88}\text{Sr}$ ). Among them,  $^{87}\text{Sr}$  is a daughter nuclide of radiogenic  $^{87}\text{Rb}$ , and its abundance changes due to the contribution of the radiogenic growth of  $^{87}\text{Sr}$  produced by the beta-decay of  $^{87}\text{Rb}$ ; the radiogenic growth of  $^{87}\text{Sr}$  has provided important constraints of the age and sources in cosmochemical and geochemical materials. Moreover, the isotopic composition of other Sr isotopes, such as  $^{84}\text{Sr}$ ,  $^{86}\text{Sr}$  and  $^{88}\text{Sr}$  may also vary due to mass-dependent isotopic fractionation through various physicochemical reactions in nature. This mass-dependent isotopic fractionation can provide key information about the sequence and/or mechanism of sample formation. The field of science that deals with them is widely known as stable isotope geochemistry. However, the application of stable isotopes of Sr has been retarded, mainly due to difficulty in obtaining an accurate and precise  $^{88}\text{Sr}/^{86}\text{Sr}$  isotopic ratio. In the conventional isotopic analysis of  $^{87}\text{Sr}/^{86}\text{Sr}$ , the  $^{88}\text{Sr}/^{86}\text{Sr}$  isotopic ratio has been normalized to 1/0.1194 to correct the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for the mass-discrimination effect; the natural variation in the  $^{88}\text{Sr}/^{86}\text{Sr}$  ratio has been neglected.

In this study, we present a method to determine  $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  simultaneously. The former variation reflects the mass-dependent isotopic fractionation through the physico-chemical processes, and the latter originates from decay of the parent nuclide  $^{87}\text{Rb}$  as well as the mass-dependent isotopic fractionation. In order to determine the mass-dependent isotopic fractionation, the mass-discrimination effect on  $^{88}\text{Sr}/^{86}\text{Sr}$  was externally corrected by an exponential law using Zr. For the radiogenic growth of  $^{87}\text{Sr}/^{86}\text{Sr}$ , the mass-dependent isotopic fractionation effect on  $^{87}\text{Sr}/^{86}\text{Sr}$  was corrected by a conventional correction technique using the  $^{88}\text{Sr}/^{86}\text{Sr}$  ratio. The reproducibility of the  $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  measurements for a high-purity Sr chemical reagent was 0.006% (2SD,  $n = 20$ ) and 0.007% (2SD,  $n = 20$ ), respectively. Strontium isotopic ratios ( $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ) were measured on geochemical reference materials (igneous rock: JB-1a, JA-2 and JG-2; carbonate mineral: JLS-1, JDO-1, JCP-1 and JCT-1) and one seawater sample. The resulting  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios obtained here were consistent with previously published data within the analytical uncertainties. The resulting  $^{88}\text{Sr}/^{86}\text{Sr}$  ratios for igneous rocks and carbonate minerals showed enrichments of the lighter Sr isotopes over the seawater sample. The  $^{88}\text{Sr}/^{86}\text{Sr}$  ratio of geochemical samples could reflect the physico-chemical processes for the sample formation. Also, a combined discussion of  $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  of samples will render multi-dimensional information on geochemical processes.

キーワード: 安定同位体地球化学, ストロンチウム, 同位体分別

Keywords: Stable isotope geochemistry, Strontium, Isotopic fractionation

## オスmium同位体組成から見たボニナイトマグマの起源

### Contribution of anciently depleted mantle and slab derived components to boninite magma genesis

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Boninite is a volcanic rock derived from highly depleted hydrous mantle that melted at a shallower depth with water derived from the subducted slab. Boninite occurred at the inception stage of the Izu-Bonin-Mariana arc (~48-45 Ma), and thus, may record less modified upper mantle composition with the subducted slab components. In order to improve the understanding of Os recycling in the subduction setting, Cr-spinels from boninites, Cr-spinel/magnetite mixtures from tholeiites which erupted subsequently after boninites (<45 Ma), and the whole rock of those lavas were analyzed for Os isotopes. The initial Os isotope ratios of the Cr-spinel from the boninites show highly unradiogenic to unradiogenic values ( $^{187}\text{Os}/^{188}\text{Os}(i) = 0.1179\sim 0.1256$ ), whereas those in the Cr-spinel/magnetite mixtures from the tholeiites ( $^{187}\text{Os}/^{188}\text{Os}(i) = 0.1270$  and  $0.1369$ ) are slightly radiogenic. The initial Os isotope ratios of the whole rock samples are more radiogenic and have larger variety than those of Cr-spinel and Cr-spinel/magnetite mixtures, possibly because of contamination with the crustal materials during magma ascent or alteration after emplacement. Based on highly unradiogenic initial Os isotope ratios of the Cr-spinels from boninites, the source of the boninites should be highly depleted mantle with a small amount of the slab flux composed of altered oceanic crust (AOC) and unradiogenic components such as oceanic island basalt (OIB) volcanoclastics or very young mid-oceanic ridge basalt (MORB). In contrast, the Os isotopic compositions of Cr-spinel/magnetite mixtures of tholeiites are clearly higher than those of Cr-spinels of boninites and slightly higher or similar to chondrites and primitive upper mantle (PUM) values. They were possibly affected by radiogenic slab components such as pelagic sediments and AOC with depleted mantle.

キーワード: オスmium同位体比, ボニナイト

Keywords: Os isotope ratio, boninite



## スタグナントスラブの融解：中国東部新生代アルカリ玄武岩からの制約 Melting of a stagnant slab in the mantle transition zone: Constraints from Cenozoic alkaline basalts in eastern China

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The feasibility of the melting of oceanic igneous crust in stagnant slabs has been proposed by studies on experimental petrology, however, relevant geochemical evidence of melting has not yet been found from igneous rocks. We present evidence that proves that melts from the igneous layer in the stagnant Pacific slab have contributed to the source composition of basalts from eruption in eastern China. Fe-rich (>13 wt%), Si-poor (<43 wt%) basalts only occur above the leading edge of the stagnant Pacific slab in eastern China. Their source has Nd-Hf isotope compositions akin to the igneous layer in the Pacific slab, while they have Sr-Nd-Pb isotope compositions similar to those of mid-oceanic-ridge basalt. The extremely low Rb and Pb (Ce/Pb > 30) contents of these basalts suggest that this source material was modified by a subduction process. Together, these geochemical characteristics help us to conclude that these basalts have received a significant contribution from the melts derived from dehydrated carbonate-bearing oceanic crust, without a long time-integrated ingrowth of Sr-Nd-Hf-Pb isotope systems at the leading edge of the stagnant Pacific slab.

キーワード: プレート内アルカリ玄武岩, 中国東部, 山東半島, HIMU 玄武岩, スタグナント太平洋スラブ, 海洋地殻リサイクル

Keywords: Intraplate alkaline basalt, eastern China, Shandong Peninsula, HIMU basalt, stagnant Pacific slab, oceanic crust recycling

## マントル捕獲岩から推定する中国東北部の温度構造 Thermal structure beneath Northeast China recorded in mantle xenoliths

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中国東北部は、太平洋プレートの沈み込みに対する背弧であり、これまで火成活動という点では島弧に比べ重要視されてこなかった。しかし、中国東北部には新生代の火山地帯が複数存在し、一般に考えられているよりも活発な火成活動が引き起こされている可能性がある。長期間または大規模な火成活動が起こっていれば、マグマによるリソスフェアの温度擾乱が予想される。そこで我々は当該地域におけるマグマの存在を探る方途の一つとして、リソスフェアの温度構造を調べた。

我々は中国遼寧省寛甸火山地域のマントル捕獲岩（スピネルレールゾライト）の由来温度、圧力を決定した。二酸化炭素流体包有物の残留流体密度を圧力指標として用いることで、従来の地質圧力計では求めることができなかったスピネルレールゾライトの由来圧力を求めることができた。5個の捕獲岩試料から得られた由来温度および由来深度はそれぞれ 1000 °C、30-40 km 程度であり、およそ 110-140 mW/m<sup>2</sup> の熱流量に相応する。一方、Huang and Xu (2010, Journal of Earth Science) によって同地域のざくろ石輝岩捕獲岩（由来深度 50-60 km 程度）から 70 mW/m<sup>2</sup> 程度の熱流量が推定されているため、これら二つを勘案するとモホ面付近における高温領域を想定せざるを得ない。これは、マントル最上部における長期間にわたるマグマの存在を示しているのではなからうか。このような継続的な火成活動が背弧の普遍的な特徴であるならば、これまで考えられてきた地球全体の熱収支や熱史において、背弧は無視できない影響力を持つ可能性がある。

キーワード: 背弧, 温度構造, 熱流量, 中国東北部, マントル捕獲岩, 流体包有物

Keywords: back-arc, geotherm, heat flow, Northeast China, mantle xenolith, fluid inclusion

## 10GPaにおけるガーネット、カンラン石/含水メルト間の元素分配実験 Element partitioning between garnet, olivine and hydrous melt at 10GPa

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It is thought that the bottom depth of Earth's magma-ocean would be more than 1000km. In order to understand chemical differentiation of magma-ocean, it is important to estimate pressure dependence of element partition coefficients quantitatively. PC-IR diagram is modeled by strain energy of lattice site in crystal by Blundy and Wood (1994). We aim to expand the model to various conditions pertinent to the Earth's magma ocean (pressure, temperature, amount of water etc.). We determined PC-IR diagram of olivine / dry melt between 1 atm. and 10GPa, and found that the parabolic curve for trivalent cations becomes wider with pressure (Imai et al., Goldschmidt Conference 2009). The widening of parabola means that Young's modulus of crystal site decreases with pressure, but it is unreasonable because lattice site is compressed by pressure (Imai et al., JpGU 2010). The widening parabola can be explained with adopting Young's modulus of 'melt' which was not considered in Blundy and Wood's model. In other words, we propose that melt becomes 'harder' with pressure. In this study, we focus on element partitioning and PC-IR diagram for hydrous magma ocean.

According to two component model, early earth might contain about 2 wt. % H<sub>2</sub>O. Ikoma and Genda (2006) suggested that hydrogen atmosphere covered early earth and might coexist with magma-ocean. Thus, we may not ignore the effect of water for chemical differentiation of magma-ocean.

In present study, we investigated partition coefficients between garnet, olivine and melt which contain various amounts of water at 10 GPa using a Kawai-type multi-anvil apparatus and compared with previous studies at dry and hydrous conditions (dry: Suzuki et al., in prep.; Imai et al., in prep, hydrous: Inoue et al., 2000; Mibe et al., 2006). We prepared two mafic starting materials (45 and 39 wt. % SiO<sub>2</sub>), doped with 26 trace elements and added 5 to 13 wt. % H<sub>2</sub>O. Platinum was used as sample container. Major, minor and trace elements analysis of garnet, olivine and coexisting hydrous melt were performed with EPMA and LA-ICP-MS. After experiment, some amount of iron in samples reacted with capsule, and alkali ions escaped with aqueous fluid when it was quenched.

Partition coefficients (D) between garnet, olivine and hydrous melt were calculated using obtained elements concentrations in each phase, and were compared with previous experimental results at dry conditions. For major elements in garnet, D values for divalent ions (Mg<sup>2+</sup>, Fe<sup>2+</sup>, Ca<sup>2+</sup>) at hydrous conditions are smaller and those of Al<sup>3+</sup> and Si<sup>4+</sup> are higher than those at dry conditions. For trace elements in garnet, D values of other ions (REE<sub>3+</sub>, Sc<sup>3+</sup>, Y<sup>3+</sup>) are the same between dry and hydrous conditions. D values for divalent cations in olivine at hydrous conditions are slightly smaller, and that for Si<sup>4+</sup> is larger than at dry condition. All D values for trivalent cations in present study are obviously smaller than those at dry condition (Imai et al., in prep.). When PC-IR diagrams at 5 GPa are compared between hydrous and dry condition (Mibe et al., 2006; Imai et al., in prep., respectively), similar features are present.

We fitted our results using lattice strain model (Blundy and Wood, 1994) on PC-IR diagram and obtained three parameters, optimum ionic radius in lattice site (r<sub>0</sub>), the partition coefficients of host cation (D<sub>0</sub>) whose ionic radius is r<sub>0</sub>, and apparent Young's modulus of lattice site for crystal and melt (E). The change in partition coefficients between dry and hydrous can be explained by the effect of only D<sub>0</sub> and temperature. The r<sub>0</sub> and E remains constant for both dry and hydrous conditions. The change of D<sub>0</sub> is explained by the variation in composition of melt. Although absolute value of partition coefficients decrease dramatically from dry to hydrous conditions, our analysis can predict the changing value with limited information (i.e., temperature and concentration of some key elements in melt, Takahashi and Irvine, 1981).

キーワード: 元素分配, 含水, カンラン石, ガーネット, 高圧, 微量元素

Keywords: element partitioning, hydrous, olivine, garnet, high pressure, trace element

## 高圧下における Fe-Ni 合金と硫化物メルト間の微量元素分配 Trace element partitioning between Fe-Ni Alloy and sulfide melt under high pressure

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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に重要な情報である。今回は Fe-Ni-S 系の高圧融解実験を 10、15GPa で行い、元素分配係数を測定した。14 元素 (Co, Cu, Ge, Mo, Ru, Ph, Pd, W, Re, Os, Ir, Pt, Au, Pb) 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 で測定した。微量元素濃度は、京都大学のセクター型 ICP-MS にフェムト秒レーザーを組み合わせた装置で測定した。

測定した元素の中で、Ru, Re, Os, Ir, Pt は固相の金属へ分配し、Mo, Pd, Au は硫化物である液相に濃集する傾向が見られ、分配挙動には硫黄の影響がある事を示唆している。珪酸塩の鉱物とメルト間の場合、元素分配挙動は結晶構造とイオン半径が深く関連している事が知られている (例えば Onuma et al., 1968)。同様に、金属の固相 - 液相間の分配挙動についても、原子半径と関連している可能性が指摘されていた (例えば Orman et al., 2008)。しかし、今回の結果では原子半径との関連性は見られなかった。金属の固相 - 液相間の分配挙動に関する規則性を導き出すためには、さらなる研究が必要である。

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キーワード: 高圧, 元素分配, 金属, 硫化物

Keywords: High pressure, Element partitioning, Metal, Sulfide

## エコンドライトのニオブ-ジルコニウム同位体学 Nb-Zr systematics of U-Pb dated achondrites

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The short-lived radionuclide  $^{92}\text{Nb}$  decays to  $^{92}\text{Zr}$  with a half-life of 36 Ma [1]. Nb and Zr are both refractory lithophile elements and can fractionate from each other during partial melting of the mantle. Thus, Nb-Zr isotope systematics can potentially place chronological constraints on early planetary silicate differentiation. This application requires the initial abundance of  $^{92}\text{Nb}$  (or  $^{92}\text{Nb}/^{93}\text{Nb}$ ) and its homogeneity in the solar system to be unambiguously defined. Yet previously reported initial  $^{92}\text{Nb}/^{93}\text{Nb}$  values range from  $\sim 10^{-5}$  to  $>10^{-3}$  [2-6], and remain to be further constrained. All but one of the previous studies estimated the initial  $^{92}\text{Nb}/^{93}\text{Nb}$  using Zr isotope data for single phases with fractionated Nb/Zr in meteorites such as zircons and CAIs, under the assumption that their source materials and bulk chondrites had had identical initial  $^{92}\text{Nb}/^{93}\text{Nb}$  and Zr isotopic compositions [2-5]. To evaluate the homogeneity of the initial  $^{92}\text{Nb}$  abundance, however, it is desirable to define internal mineral isochrons for meteorites with known absolute ages. Although Schonbachler et al. [6] defined Nb-Zr internal isochrons for two meteorites (Estacado and Vaca Muerta), their absolute crystallization (or possibly recrystallization) ages are not precisely constrained, leading to uncertainties in the resultant estimate for the initial  $^{92}\text{Nb}/^{93}\text{Nb}$  of the solar system.

To establish the solar system initial  $^{92}\text{Nb}/^{93}\text{Nb}$  and its homogeneity, we are studying the Nb-Zr systematics of minerals from achondrites whose absolute crystallization ages were precisely determined with the U-Pb chronometer. Abundances of trace elements including Nb and Zr were determined by LA-ICPMS for pyroxene, plagioclase, pyrite, spinel and/or opaque minerals from 3 eucrites (Agoult, Ibitira and A-881394), 5 angrites (SAH99555, D'Orbigny, NWA2999, NWA4590 and NWA4801) and Acapulco. The results reveal that Agoult, Ibitira and NWA4590 contain phases with reasonably high Zr contents and a good spread in Nb/Zr ( $<0.01$  for pyroxene and  $\sim 3$  for opaque minerals and spinel) to define precise internal isochrons. These minerals and whole rock samples were further processed for Zr separation and analyzed for Zr isotopes by MC-ICPMS. We found that the spinel and opaque mineral fractions have restricted positive  $^{92}\text{Zr}$  anomalies up to 30 ppm relative to the terrestrial standard samples. We are still in the process of determining their Nb/Zr isotopic ratios, but preliminary results of Zr isotope analyses, combined with the approximate Nb/Zr of minerals estimated by LA-ICPMS, suggest that the initial  $^{92}\text{Nb}/^{93}\text{Nb}$  is in the order of  $\sim 10^{-5}$ , consistent with the results of previous work using the internal isochron approach [6].

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キーワード: 初期地球分化, 消滅核種, 太陽系年代学

Keywords: early Earth differentiation, short-lived radionuclide, solar system chronology

## シャツキー海台のマグマ組成とその成因 Magma variety and its origin for Shatsky Rise

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日本から約 1500km 東の太平洋に存在するシャツキー海台は、ジュラ紀と白亜紀境界に形成された巨大海台である。地磁気の縞模様を基に、海台は海嶺の 3 重会合点のトレースに沿って南から北へむかって順次形成されたことが分かっている。海台は南から北へ向かってタム山塊・オリ山塊・シルシヨフ山塊という主に 3 つの高地からなり、南のタム山塊が最大であり、北へ行くほど山塊の規模が小さくなる。

統合国際深海掘削計画 (IODP) 第 324 次航海はシャツキー海台の 5 サイトで基盤岩を採取すること試みた。海台の全体像を知るため、タム山塊で 2 サイト、オリ山塊で 2 サイト、シルシヨフ山塊で 1 サイトの掘削が行われた。そして 4 サイトで合計 471m のコアが回収された。採取された新鮮ガラス組成および全岩化学組成を基にシャツキー海台マグマは 4 タイプ (normal, low-Ti, high-Nb, U1349) に分類できることが分かった。normal タイプは中央海嶺玄武岩 (N-MORB) に似た組成を持つが、HREE に少し枯渇している。low-Ti タイプは同 Mg 含有量で比較した場合、normal タイプに比べて低い Ti, Fe, Mn 組成を持つ。high-Nb タイプは normal タイプに比べて液層濃集元素 (K, Nb, REEs 等) に富む enrich したマグマである。U1349 は normal タイプに比べて未分化で枯渇した組成が特徴である。これら 4 タイプの産状を調べたところ、タム山塊およびシルシヨフ山塊の大部分は normal タイプから形成されているのに対し、オリ山塊は層序全体の半分程度を normal タイプ以外の 3 タイプで占められていることが分かった。そして normal タイプ以外の 3 タイプは海台全体の約 1/3 を構成していることが判明した。発表では主に normal タイプのマグマ成因と分化に関する議論について話を行う。なお、この研究は IODP 乗船後研究の一環で行った。

キーワード: 統合国際深海掘削計画, 第 324 次研究航海, 大規模火成区, 巨大海台, プルーム

Keywords: Integrated Ocean Drilling Program, Expedition 324, Large Igneous Province, Oceanic Plateau, Plume

## 海台定置に伴う強親鉄性元素の挙動

## Highly siderophile element behavior during oceanic LIP emplacement

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Causal mechanisms and ultimate trigger for the global environmental catastrophes, such as mass extinction and oceanic anoxia events are long-standing matter of debates. Since the discovery of global Ir anomaly in Cretaceous-Tertiary boundary layer and the Chichxulub crater, the highly siderophile elements (HSEs) in sedimentary sequences have been recognized as useful geochemical tracers for identifying extraterrestrial impacts. However, an important question remains as to whether enormous supply of HSEs to the surface environment is also caused by massive volcanism leading to the formation of large igneous provinces (LIPs). This classic idea has been recently revived by the Cenozoic-Mesozoic marine Os isotope record that displays frequent negative excursions over the time intervals of LIP eruption. In this contribution, we present HSE concentration data of oceanic LIP basalts recovered from Hole U1349A on summit site of Ori massif of the Shatsky Rise. The drillcore provides an ideal opportunity to evaluate the possibility of HSE loss due to volcanic degassing and/or contrasting alteration styles because it is separated into subaerial and submarine portions from a single magma type of narrow compositional range. The results demonstrate that Os, Ir, Ru and Pt values are nearly uniform throughout the core, whereas Pd and Re values in subaerial portions are systematically lower than those in deeper submarine portion. Current dataset may therefore lend no support to the notion that degassing and alteration processes are responsible for significant release of HSEs except for Pd and Re.

This research was supported by IODP After Cruise Research Program, JAMSTEC.

キーワード: 強親鉄性元素, 大規模火成作用区, 巨大海台, 統合国際深海掘削計画, 第 324 次研究航海

Keywords: highly siderophile elements, large igneous provinces, oceanic plateau, Integrated Ocean Drilling Program, Expedition 324

## A comparative geochemical and petrological study of the Siberian and Ethiopian large igneous provinces (LIPs)

## A comparative geochemical and petrological study of the Siberian and Ethiopian large igneous provinces (LIPs)

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This study is mainly targeted to find the possible eastern marginal extension of Siberian LIP and to compare them with the central Siberian LIP and is also aimed to compare and contrast the geochemical and petrological characteristics of Siberian LIP (~ 250 Ma) with the Ethiopian LIP (~ 30 Ma) to consider the mantle and crustal processes in view of magmatic diversity among those LIPs. A review of previous geochemical data from the Siberian and Ethiopian LIP confirms notable differences in their major and trace element compositions. Siberian LIP comprises a variety of rocks (such as basalts, andesitic basalts, picrites and meimechites) with a wide range of SiO<sub>2</sub> (40-62 wt.%). In contrast, Ethiopian LIP is characterized by bimodal volcanism with the absence of intermediate rock. The Ethiopian high-Ti basalts and picrites have higher TiO<sub>2</sub> (3-6 wt.%), lower CaO/Al<sub>2</sub>O<sub>3</sub> (0.5-1.5) and MgO (5-26 wt.%) than the Siberian high-Ti picrites and meimechites (2-4, 1.8-2.3 and 13-36 wt.% respectively). Siberian LIP shows more significant depletion in HFSE (mainly Nb) and higher La/Sm ratios than Ethiopian LIP. This may suggest contamination of Siberian LIP magma by continental crustal rocks. Triassic volcanic and intrusive rock samples are collected from the Chukotka province (Northeast Russia), which is geographically far to the east from the central Siberian flood basalt province. The petrography of the studied samples includes basaltic rocks (i.e. hornblende basalt, lamprophyre, pyroxene phyric basalt, and ankaramite) and gabbroic rocks (i.e. hornblende gabbro, pyroxene-hornblende gabbro, pyroxene gabbro, and quartz diorite). Basaltic rocks exhibit porphyritic texture with phenocrysts of plagioclase+ clinopyroxene+ hornblende, whereas gabbroic rocks show granular, ophitic and poikilitic textures with a crystals of hornblende+ clinopyroxene+ plagioclase and rare phlogopites. Opaque minerals are usually magnetite with a size reaching about 7 mm in hornblende gabbro and also iron sulphides in pyroxene-phyric basalt. The chemical composition of clinopyroxene phenocrysts from basalts are in the range of Wo<sub>29-51</sub>En<sub>38-49</sub>Fs<sub>4-33</sub> with a general ferrosilite (Fs) increase from core to rim, but a few phenocrysts in the pyroxene-phyric basalt show a reverse zoning. The clinopyroxene phenocrysts from the pyroxene phyric basalt have a range of Mg# (0.72- 0.91), whereas those from hornblende basalt, ankaramite and lamprophyre units have 0.54-0.76, 0.83-0.92, and 0.83-0.93 respectively. Clinopyroxene phenocrysts from hornblende basalt are highly differentiated and richer in FeO (average ~ 16.4 wt.%) than clinopyroxenes from the high-Ti and alkaline meimechite (Siberian LIP) and Ethiopian High-Ti basalt. Clinopyroxenes both from basalts and gabbros show only low-Ti (<1 wt.%) characteristics. Hornblendes both from basalts and gabbros have tschermakitic composition with alkali content ranges from 3.41 to 4.39 wt.%. Phlogopites occurring as a minor phase in the pyroxene-hornblende gabbro with Mg# ranges from 0.64 to 0.66. The groundmass plagioclases from the lamprophyre includes the three feldspar end members, i.e. An<sub>8-73</sub>Ab<sub>2-85</sub>Or<sub>1-89</sub>. This suggests relatively high alkali content of the magma. The Triassic basalts and gabbros of Chukotka province may represent the easternmost portion of the Siberian LIP characterized by a low-Ti, HFSE depleted and hydrous basic magma.

キーワード: Siberia, Chukotka, Ethiopia, LIPs, hornblende basalt, meimechites

Keywords: Siberia, Chukotka, Ethiopia, LIPs, hornblende basalt, meimechites



SGC55-16

会場:101B

時間:5月23日 14:30-14:45

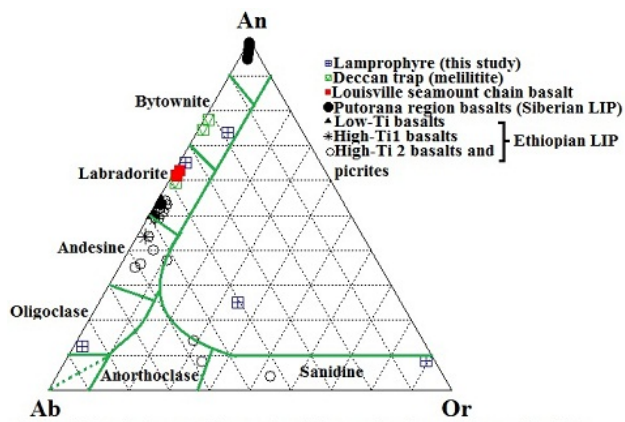


Fig. 1 Ab-An-Or ternary diagram for feldspars from lamprophyre. Ab, albite; An, anorthite; Or, orthoclase.

## マンツルの地球化学的な東西半球の存在とその意味 East-west geochemical mantle hemispheres and their implications on mantle dynamics

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Oceanic basalts, including mid-ocean ridge basalts (MORB) and ocean island basalts (OIB), have been extensively studied as geochemical messages from the mantle to decipher differentiation and convection within the Earth [Hofmann, 2003]. However, the spatial coverage of MORB and OIB is insufficient for resolving even a global feature of the compositional variability. We analyze the oceanic basalts together with the arc basalts in subduction zones that extend over a long distance comparable to mid-ocean ridges and cover the areas with a few mid-ocean ridges or hotspots. Combining the arc data with those from oceanic basalts, and by using Independent Component Analysis [Iwamori and Albarede, 2008; Iwamori et al., 2010] to remove influences from the subducted materials, global geochemical domains appear primarily as east-west hemispheres, rather than north-south hemispheres as has been long argued for [Hart, 1984]. The eastern hemisphere, ranging roughly from the Mid-Atlantic Ridge to Eastern Eurasia and Australia, is underlain by a subducted component-rich mantle being created possibly by extensive subduction beneath the supercontinent Pangea. The primary feature of this spatial pattern and relationships is that the geochemical domains have been anchored to asthenosphere for at least 300 m.y. in the past, and the continents dispersed without significantly disturbing the asthenospheric structure, possibly due to mechanical decoupling between lithosphere and asthenosphere. The second (thus less obvious but important) feature is as follows: distribution of a subducted component-poor domain beneath the western hemisphere, including the American Plates that had been a part of the supercontinent, suggests eastward flow of asthenosphere once located under the Panthalassic Ocean, i.e., migration over several thousands km during the last ~300 million years. The flow pattern and velocity seem consistent with the westward lithospheric rotation against the asthenosphere [Ricard et al., 1991] that exhibits internal deformation.

Keywords: mantle, isotope, hemisphere, supercontinent, lithosphere, subduction

## 200nm フェムト秒レーザーアブレーション SF-ICPMS 元素分析法によるマトリクス効果の低減

### Origin of Suppressed Matrix Effect by 200Fs-SF-ICPMS Elemental Analysis

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We have tested an ultraviolet 200nm femtosecond laser ablation (200FsLA) sector-field inductively coupled plasma mass spectrometry (SF-ICPMS) system for major and trace element analyses in silicate glasses and minerals. By optimizing the 200FsLA optics and the analytical protocol and employing a modified ion sampling interface in the SF-ICPMS, the sensitivity of the system has been improved with reduced backgrounds, achieving accurate spot analyses of 44 elements from ppb to wt.% levels at a crater diameter of 30 microns. Corrections for differences in the laser sampling efficiency between samples and the standards were performed by 100% normalization of the sum of the oxides of all the elements analyzed. Use of 200FsLA minimized the matrix effect by 50% compared to that by a 193-nm nanosecond excimer LA. The origin of this improvement was identified as the suppression of melting point-induced element fractionation at the laser ablation site due to a decreased thermal effect by 200FsLA. Sensitivity enhancement in some elements with high first ionization energy still remained in the basalt aerosols relative to silica-rich aerosols. This is inferred to be due to the higher thermal conductivity of the basalt aerosols in the inductively coupled plasma enhancing ionization. Accurate determination of trace elements (within 5% of the accepted values) was achieved for glasses ranging from MPI-DING komatiite to rhyolite, using single basalt glass BHVO-2G as the calibration standard. This method is also applicable to various anhydrous silicate minerals such as plagioclase, pyroxenes, and garnet. However, SRM610 glass, which has a very different matrix than BHVO-2G, is preferred for zircon. Apart from this exception, the proposed method does not require any external analytical techniques when the amounts of unmeasured elements such as halogens or water in the materials are negligibly low, which is the case for many geological materials.

キーワード: フェムト秒レーザーアブレーション, ICP-MS, 元素分析, マトリクス効果

Keywords: Femtosecond laser ablation, ICP-MS, Elemental analysis, Matrix effect

## 地球内部物質大循環と希ガス同位体

## Global recycling of materials in the Earth's interior and noble gas isotopes

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海嶺におけるプレートの生成や火山噴火を含むさまざまな形態の火成作用、島弧周辺におけるスラブの沈み込みなどを通じて、地表物質が地球内部にもちこまれた後、またその一部が地表に表出する大規模な循環が生じていることが、放射性起源同位体を含む各種の同位体比などの結果から推測されている。また地震波トモグラフィーなどの結果から、スラブがマントル内に沈み込んでいく様子が示されている。

しかし地表物質が実際に循環する深さや状況についての詳細は、不明なところが多い。例えばスラブの沈み込みにより、そのスラブ表層部から放出された水などの効果で島弧マグマの形成などが議論されている。しかしその関与する程度や残りのスラブの地球深部への影響などについては、研究者によって見方が大きく異なっている。

希ガスは化学的に不活性なうえ、その挙動に関しては物理的な性質のみに支配されていると見なしてよい。また大気と地球内部では、その元素・同位体組成が大きく異なっていることも知られている。さらに揮発性元素であるので、地表付近で形成された物質の大部分はマグマ中に存在していた希ガスと大気中の希ガスが交換していることも分かっている。そのため、地表物質の希ガスは放射性起源同位体以外では大気組成の同位体比をもっていることで識別できる。さらに放射性起源同位体を含む  $3\text{He}/4\text{He}$ ,  $40\text{Ar}/36\text{Ar}$  などの同位体比を組み合わせることで、異なるマグマ源の性質も推定できる。

このような希ガスを用いて地球内部の状態を調べる試みは非常に多く行われてきており、 $3\text{He}/4\text{He}$ ,  $40\text{Ar}/36\text{Ar}$  などの系統的な違いから、MORB のマグマ源より OIB のマグマ源は、より深い部分に存在することが推定されてきている。また一般的に He については、地表から地球内部に循環することはないとされている。希ガスのもつ性質を利用すると、地球内部における物質循環に関する情報を得る有力な手段となる。例えば、Ar, Kr, Xe などの重希ガス水などとともに地球内部に循環し、大気成分の希ガスが海水などとともに特に OIB のマグマ源に大きく寄与しているとの報告もある。その説に従うと、循環物質は OIB や島弧玄武岩などへの影響は大きい、MORB のマグマ源への影響は相対的に小さいことになる。また大気成分は OIB のマグマ源に広がり、その影響が OIB の希ガス同位体比に反映されていることになる。しかしその影響の程度と固体元素同位体比などの間には特に相関は見られない。一方、これらの重希ガスなどよりもはるかに移動度が高いと見なされている He で、地殻循環物質が関与していると思なされるような MORB より低い  $3\text{He}/4\text{He}$  を示す OIB は、固体元素同位体比などでもやはり地殻物質の関与を示している。 $3\text{He}/4\text{He}$  がマントル内で特有の値を示すことは、循環物質の影響が限られていることを示唆する。一方、マントル内で、移動しやすい He の影響が地域的に限られていることは、OIB における重希ガスの大気成分の源は、He が示す循環物質の影響とは異なった要因による影響も含んでいることを示唆している。この例に見られるように、希ガス同位体比から循環物質の影響について論じるためには、それぞれの試料が示している情報の意味を明らかにすることが重要であり、それらの再検討を必要とする。

キーワード: 物質大循環, 地球内部, 希ガス, 同位体

Keywords: Global recycling, Earth's interior, Noble gas, Isotope

## FOZO と HIMU の成因の違いは何か？

### FOZO-HIMU connection: link to chemical heterogeneity of MORB

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One of fundamental concepts of the mantle geochemistry is a hypothesis called 'mantle reservoir model' (White, 1985; Zindler and Hart, 1986), in which isotopic composition of the ocean island basalts (OIBs) are explained by mixing of distinct and isolated reservoirs in the Earth's interior. In early research on the mantle reservoirs, the isotopic compositions of OIBs were mainly explained by the mixing of depleted MORB mantle (DMM) and three enriched reservoirs (HIMU, EM1, and EM2) whose isotopic compositions are enriched extremes. In addition to these 'extreme reservoirs', the importance of reservoirs whose isotopic compositions are common and intermediate has been pointed out, such as FOZO (Focal Zone, Hart et al., 1992), C (common component; Hanan and Graham, 1996), PREMA (Prevalent Mantle, Zindler and Hart, 1986) and PHEM (Primitive Helium Mantle, Farley et al., 1992). Although the existence of these 'intermediate reservoirs' is still in debate, the isotopic compositions of these reservoirs, in particular FOZO, have been commonly used to describe the isotopic distribution of OIBs.

The origin of mantle reservoirs is considered to be recycling of oceanic crust with/without sediments. Thus recycling of pure oceanic crust is important because the oceanic crust is the major constituent of recycled material. As the recycling of pure oceanic crust is inferred to produce HIMU and FOZO components, elucidating the origin of these reservoirs should be important from the perspective of production of mantle heterogeneity (e.g., Stracke et al. 2005). A major question about the origin of these reservoirs would be the process that made the difference between HIMU and FOZO. Additional question about their origin is the process that can explain the rare occurrence of HIMU and ubiquitous presence of FOZO.

In the present study, we have conducted geochemical modeling for understanding the origin of HIMU and FOZO. For the model, MORB compositions from East Pacific rise and Mid-Atlantic ridge are compiled from published data. The results suggest that oceanic crust with various stages of magmatic evolution can produce U and Th enrichment that is suitable for the origin of HIMU and FOZO, i.e., less evolved common MORB can be the source for FOZO and strongly evolved rare MORB can be the source for HIMU. Although the magmatic evolution processes also produce high Pb concentration that is inappropriate for the origin of HIMU, sulfur enrichment during the evolution can erase the effect of Pb enrichment due to desulfurization and Pb loss beneath subduction zones. Depleted Sr isotopic composition of HIMU seems to contradict high Rb concentration of evolved MORB magmas. However, high degree of dehydration and Rb loss beneath subduction zones can produce depleted Sr isotopic composition of recycled crust. In this context, magma evolution at mid-ocean ridges and variable degree of dehydration beneath subduction zones play an essential role in producing the isotopic variations between HIMU and FOZO.

キーワード: FOZO, HIMU, マントル貯蔵庫, MORB, リサイクルリング, 海洋島玄武岩

Keywords: FOZO, HIMU, Mantle reservoirs, MORB, recycling, OIBs

## カンラン岩部分融解時の白金族元素の挙動について Behavior of platinum-group elements during peridotite partial melting

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Platinum-group elements (PGE) are key tracers for the chemical differentiation of the early Earth and the subsequent chemical evolution of the Earth's interior. PGE abundances in the mantle are much higher than expected from core-mantle equilibration, which is often attributed to late meteorite bombardment (so called "late veneer") on the Earth after core formation, although alternative hypotheses have also been proposed. A critical point to testify the models for the excess PGE in the mantle is accurate estimation of the PGE abundances in the primordial mantle. Many peridotite samples with relatively primitive composition have broadly chondritic relative abundances of PGE, which is in favor of the late veneer hypothesis. However, absolute concentrations of PGE are strongly variable among rock types and sample locations, because PGE concentrations in peridotite samples are likely to be modified by partial melting processes the samples experienced. Thus it is highly required to understand the PGE behavior during partial melting processes in order to accurately estimate the PGE abundances in the mantle. Since PGE in peridotite samples are dominantly concentrated in base metal sulfides (BMS) and platinum-group minerals (PGM), it is necessary to know the phase relations of BMS and PGM in partially molten peridotite minerals. I will review the experimental studies on the stability of PGM and BMS during partial melting of peridotite, and discuss the role of these minerals for the generation of the diversity of PGE concentrations in peridotite samples.

キーワード: 白金族元素, 白金族鉱物, マントル, 部分融解

Keywords: platinum-group element, platinum-group mineral, mantle, partial melting

## イタリア・フィネロかんらん岩体の Sr-Nd 同位体・微量元素組成 Sr-Nd isotopic and trace element geochemistry of the Finero peridotite massif, southwestern Alps, Italy

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The Finero mafic-ultramafic complex is one of the orogenic peridotite massifs emplaced into granulite facies metabasites of the Ivrea-Verbano Zone of Northern Italy. The Finero mafic-ultramafic complex is an antiformal body that comprises four main units from core to rim: a Phlogopite Peridotite, an layered Internal Gabbro, an Amphibole Peridotite, and an External Gabbro (e.g. Cawthorn, 1975, JG; Coltorti & Siena, F, 1984, N. Jb.Mineral. Ab). The Phlogopite Peridotite and other units have been interpreted as residual mantle left after extraction of 18 % mid-ocean ridge basalt (MORB) and a crustal cumulate body, respectively (Coltorti & Siena, 1984, N. Jb.Mineral. Ab.; Siena & Coltorti, 1989, N. Jb.Mineral. Ab. Hartmann & Wedepohl 1993, GCA). The Phlogopite Peridotite unit consists of dunite and harzburgite with minor pyroxenites and chromitite. Amphibole and phlogopite are remarkable in the phlogopite peridotites of the Finero Phlogopite Peridotite massif than other Ivrea-Verbano peridotite massifs (Balmuccia and Baldissero, Hartman & Wedepohl, 1993, GCA). Amphibole ubiquitously occurs, and amphibole and/or phlogopite-bearing segregations and veins are locally abundant of the Finero Phlogopite Peridotite unit (e.g., Selverstone & Sharp, 2011, EPSL). These hydrous minerals were believed to be formed by interaction with residual peridotite and slab derived fluid/melt (e.g. Zanetti et al., 1999, CMP). Apatite and carbonate also founded in the phlogopite peridotite as sporadic region and thin layer (e.g. Zanetti et al., 1999, CMP; Morishita et al., 2003, Lithos). The sporadic region seems to be influenced by mantle derived melt (Raffone et al., 2006, MCA) or slab-derived CO<sub>2</sub> bearing hydrous agent (Morishita et al., 2008, CG), whereas the thin layers was expected to result from passage of evolved slab-derived CO<sub>2</sub> bearing hydrous agent (Morishita et al., 2003, Lithos; Matsumoto et al., 2005, EPSL; Morishita et al., 2008, CG). In recent, Selverstone and Sharp (2011, EPSL) divided the Finero phlogopite peridotites into the four groups (from type 1 to type 4) based on the petrographic feature of hydrous minerals and suggested at least two chemically distinct metasomatic fluids from the Cl, H, and O stable isotope geochemistry with petrologic and major and trace element data.

Our purpose of this study is to confirm the relationship between the petrographic features and other geochemical signatures such as trace element and Sr-Nd isotopic compositions. Sr-Nd isotopic compositions of acid washed amphibole separates from the spinel harzburgite with minor amphibole and/or phlogopite (type 1), harzburgite with segregation phlogopite and/or amphibole (type 2) and amphibole-rich segregations (type 3) are significantly enriched character (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.7075 - 0.7091, <sup>143</sup>Nd/<sup>144</sup>Nd = 0.51232 - 0.51237) similar to those of the continental crust as suggested by previous studies (Voshage et al., 1987, CMP; Lu et al., 1997, CG; Zanetti et al., 1999, CMP; Matsumoto et al., 2005, EPSL). Such enriched isotopic feature is common for the peridotite xenoliths from cratonic subcontinental lithospheric mantle (e.g. Pearson et al., 1995, GCA). Amphibole of type 1 spinel harzburgite has most enriched Sr-Nd isotopic compositions. Amphibole of the type 2 and type 3 spinel harzburgites have similar Sr-Nd isotopic compositions with each other. Selverstone and Sharp (2011, EPSL) inferred that these segregations had originated hydrous melt induced by H<sub>2</sub>O-CO<sub>2</sub> fluid derived subducting slab. Our results combined with previous studies, therefore, suggest that hydrous silicate melt formed amphibole-rich segregation has relatively depleted Sr-Nd isotopic compositions.

キーワード: 金雲母かんらん岩, フィネロ苦鉄質 - 超苦鉄質岩体, Sr-Nd 同位体組成, 微量元素組成

Keywords: phlogopite peridotite, Finero mafic-ultramafic massif, Sr-Nd isotopic compositions, trace element compositions

## 小笠原諸島の浜砂から採取したクロムスピネルのOsから明らかになった沈み込み帯での酸化還元環境 Redox condition in subduction system elucidated from Os in Cr-spinel from Bonin Island beachsands

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The Os isotopic system is a potential tracer of a recycled crustal component in mantle or volcanic rocks because of the significant contrast between Os isotope ratios of crust and mantle. It is because, fractionation between Re and Os during mantle partial melting leads to a significant contrast in  $^{187}\text{Os}/^{188}\text{Os}$  between high values ( $^{187}\text{Os}/^{188}\text{Os} > 0.5$ ) in crustal rocks and low values ( $^{187}\text{Os}/^{188}\text{Os} < 0.13$ ) in mantle rocks. For instance, a recycled ancient crustal component with high  $^{187}\text{Os}/^{188}\text{Os}$  is involved in the production of hotspot volcanic rocks in Polynesia (Hofmann, 1997). However, the potential for crustal contamination overprinting this possible signal has hampered the utility of Os isotopic ratios.

We explored the use of Os isotopes in chromian spinel (Cr-spinel) as a discriminator of primitive magma Os compositions in the Izu-Bonin arc, using beach sands as composite samples of the boninite and tholeiite magmas in three different islands. Cr-spinel is an early-stage crystal that preserves its isotopic composition even during later crustal contamination of the bulk rock. We found highly unradiogenic Os isotopic compositions in Cr-spinels from boninites, suggesting that they represent primitive magmas with slight or no Os contribution from the subducting slab during the generation of boninites in the infant arc stage (48-46 Ma). Conversely, the radiogenic Os isotopic ratios in Cr-spinels from tholeiites most likely reflect the contribution from a slab-derived component, because more oxidative conditions in the subarc mantle probably allowed Os to mobilize from the subducting slab during the transitional arc stage (45-41 Ma). Although shallow-level assimilation of crustal components with radiogenic Os may overprint the original Os signature of tholeiite magma during its ascent, Cr-spinel allows us to compensate such possibilities.

Possible mechanism for the difference in Os transfer from the subducted slab between the early stage and transitional stage of the Izu-Bonin arc system is redox condition in the wedge mantle. We suggest that during boninite formation in the infant arc stage, the mantle beneath the Izu-Bonin arc was not strongly oxidized, resulting in less mobile Os in the subduction system. This leads to minimal input of radiogenic Os derived from the subducting slab to the primitive boninite magma. During formation of the Mukoojima tholeiites, the mantle was well oxidized by continuous input of slab-derived fluid and/or melt, providing mobile Os to the source mantle. This may account for the oxidative chemical compositions of Cr-spinel and the elevated Os isotopic compositions in the mantle source of the Mukoojima tholeiites.

Keywords: osmium isotope, Cr-spinel, Bonin Islands, redox condition



## Mineralogy and petrology of the basalts from the Erdenetsogt Formation, Hangay-Hentey fold belt of central Mongolia Mineralogy and petrology of the basalts from the Erdenetsogt Formation, Hangay-Hentey fold belt of central Mongolia

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This paper deals with the first mineralogical and petrological study of the basaltic rocks from the Erdenetsogt Formation (EF) in middle Paleozoic accretionary complex hosted by Tsetserleg terrane, which is westernmost part of the Hangay-Hentey fold belt (HHFB) of central Mongolia. EF is mainly made up of intensively deformed oceanic plate stratigraphy (OPS): pelagic radiolarian/ribbon chert, red and green quartzites (metachert), fine to medium-grained sandstone, siltstone with minor amount of limestone, and some basaltic rocks which have been discovered lately during geological mapping in the south Hangay region. The basaltic rocks exhibit mostly metabasalts, dolerites, microgabbros, and occasional meta-picrites composition with subophitic, intersertal, and partly intergranular textures. The phenocryst assemblage is composed of olivine (completely altered by chlorite, carbonate and serpentine and is only observed in meta-picrite) and clinopyroxene (well-preserved in all basaltic rocks) and smaller matrix plagioclase (replaced by albite). Accessory minerals include chromian-spinel, titanomagnetite and pyrite. Here, we present preliminary major element data for phenocryst and groundmass clinopyroxene (Ca-rich augite/diopside) and chromian-spinel measured by electron microprobe from the north and south of Uyanga Soum (village), where these basaltic rocks are exposed. There was no chemical variation in relict minerals observed from the basaltic rocks from these two parts. The preserved clinopyroxenes in basaltic rocks have a Mg# between 78-85, and follow a typical tholeiitic trend in the Ca-Mg-Fe diagram with rims slightly enriched in Fe relative to the cores. On the basis of Ca +Na vs. Ti and Ca vs. Ti+Cr discrimination diagrams, our results are consistent with tholeiitic magma of non-orogenic origin. The relict chromian-spinels (up to 0.25 mm in size) are found only in completely altered olivine phenocrysts of meta-picrite and its chemistry exhibits very limited in composition with Cr# of 55-68 numbers, which consistent with intraplate tholeiite. Spinel plot of Al<sub>2</sub>O<sub>3</sub> wt.% vs. TiO<sub>2</sub> wt.% (range from 0.9 to 1.8 wt.%) ratio suggests OIB rather than MORB. In the Cr-Al-Fe+3 diagram, along with the Cr-Al line with low ferric iron content, resembling spinel among spinel peridotite xenoliths. In Mg# vs. Cr# diagram, it implies more fractionated magma than MORB. From this fact it is concluded that the chromian spinel of meta-picrite may have been derived from a mantle plume source. Our review of previous limited geochemical studies suggests enriched OIB for these basalts. In general, the mineral chemistry of the basalts from EF indicates tholeiitic OIB (hot spot/seamount) affinity in agreement with previous suggestions by some researchers. The OIB have been developed within Paleo-Pacific Ocean plate located between the Siberian and the North China Cratons, and then accreted to the active continental margin of Siberian Craton during middle to late Paleozoic.

キーワード: Hangay-Hentey fold belt, Erdenetsogt Formation, mineral chemistry, basaltic rock, clinopyroxene, chromian spinel  
Keywords: Hangay-Hentey fold belt, Erdenetsogt Formation, mineral chemistry, basaltic rock, clinopyroxene, chromian spinel

## 室生火砕流堆積物とその類似凝灰岩の全岩化学組成

## Whole-rock chemical compositions and REE analyses of the Muro pyroclastic flow deposit and related tuffs

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The Muro pyroclastic flow deposit is the rhyolitic tuffs that are distributed from the central part of Nara prefecture to the western part of Mie prefecture, southwestern Japan. It consists of a 15 km (north-south) x 28 km (east-west) body. The tuff is classified into two main lithologies. One is a glassy dense welded tuff called "black lava" and the other is a cryptocrystalline tuff "white lava" that have suffered devitrification<sup>1</sup>). Both FT and K-Ar dating methods indicate that the age of the tuffs is about 15 Ma<sup>2</sup>). Several studies have been done for the Muro pyroclastic flow deposit (Shinjoe.H. et al, 2002; Iwano.H et al, 2007), however, the source is less well understood. In this study, we present newly obtained whole rock major, trace and rare earth element compositions of the Muro pyroclastic flow deposit and related tuffs. The related tuffs we analyzed are the Tamateyama tuff and the Sekibutsu tuff in Kii peninsula, and the Kn-1 tuff in Boso peninsula. A total of 15 samples were analyzed for chemical compositions. The whole-rock major-trace element compositions and REE compositions were analyzed by XRF and ICP-MS, respectively. Most of the samples except the Kn-1 tuff indicate that the SiO<sub>2</sub> contents vary from 73.0 to 75.5 wt% and the alumina-saturation index (A.S.I.) are more than 1.1 which shows those rocks are peraluminous. However, the Kn-1 tuff indicates especially low values of SiO<sub>2</sub> (SiO<sub>2</sub> = 59.9 wt%) and A.S.I. (c. 0.3). It shows that the Kn-1 tuff is metaluminous. Furthermore, the Kn-1 tuff has higher value of CaO, MnO, and P<sub>2</sub>O<sub>5</sub> than the other samples. The Kn-1 tuff might have different type of source from the Muro pyroclastic flow deposits. When compared with the chemical compositions between the white and black lavas, SiO<sub>2</sub> content of the white lava is higher than the black lava, whereas the CaO, MnO, FeO\*, MgO and Na<sub>2</sub>O content of the black lava is higher than the white lava. However, both white and black lavas show similar chemical trends on the Harker's variation diagrams. Most of the samples show nearly same pattern on the REE composition diagrams normalized by CI-chondrite. They are LREE-rich, mid-to HREE flat and negative Eu anomaly pattern. The chemical compositions of the Muro pyroclastic flow deposits have relevance to the related tuffs (Tamateyama and Sekibutsu) except the Kn-1 tuff.

キーワード: 室生火砕流堆積物, 希土類元素, 凝灰岩

Keywords: Muro Pyroclastic Flow Deposit, rare earth elements (REE), Tuff

## 東北日本只見川古期花崗岩類の全岩化学組成および希土類組成 Whole-rock chemical compositions and rare earth element compositions of the Paleogene Tadamigawa granitic rocks, northeast

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The Paleogene Tadamigawa granitic rocks are located at the border between Fukushima and Niigata prefectures, northeastern Japan. The granite is divided into two rock types, the Tadamigawa granite and the Hinoematagawa granite. The Tadamigawa granite is coarse-grained biotite granite and it is characterized by the phenocryst of K-feldspar. The Hinoematagawa granite is medium-grained biotite-hornblend granite, and it is intruded by the Tadamigawa granite. In this study, we have analyzed whole-rock chemical compositions including REE of the Tadamigawa granitic rocks, and discuss the petrogenesis of the pluton. 7 samples of the Hinoematagawa granite and 18 samples of the Tadamigawa granite were analyzed for major-minor chemical compositions and REE compositions by XRF and ICP-MS, respectively. SiO<sub>2</sub> contents of the Hinoematagawa granite and the Tadamigawa granite range from 59.6 to 69.4 wt.% and from 62.8 to 74.6 wt.%, respectively. The Tadamigawa granite and the Hinoematagawa granite may be generated from the same magma origin because they show similar trend on the Harker's diagram. The Tadamigawa granitic rocks are plotted within the field of non-alkaline rock on the graph of SiO<sub>2</sub>-(Na<sub>2</sub>O+K<sub>2</sub>O)(Miyashiro, 1978). It is also assumed that the pluton belongs to calc-alkaline rock series because SiO<sub>2</sub> contents increase with increasing FeO/MgO ratio. Additionally, almost all samples were classified into VAG (Volcanic Arc Granite) on the Rb-(Nb+Y) diagram(Pearce et al., 1984). Therefore, the Tadamigawa granitic rocks magma might be originated from the partial melting of the basaltic crust. REE abundance patterns of all samples normalized by chondrite show high-LREE pattern. Many samples show negative Eu anomaly, and the value of Eu anomaly increase with decreasing anorthite content calculated by CIPW norm. The value of Eu anomaly might be concerned with the crystallization differentiation of the original magma. The degree of Eu anomaly of the Tadamigawa granite is higher than that of the Hinoematagawa granite. Whole-rock chemical composition analyses suggest that the Tadamigawa granite is more differentiated than the Hinoematagawa granite.

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キーワード: 只見川, 檜枝岐, 花崗岩, 希土類元素

Keywords: Tadamigawa, Hinoemata, Granite, rare earth elements (REE)

## 希土類元素組成からみた熊野酸性岩類の成因 REE compositions of the Kumano acidic rocks, outer zone of southwestern Japan

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The Kumano Acidic Rocks (KAR) which distributes in south-eastern part of the Kii peninsula, outer zone of southwestern Japan, are igneous rocks that were formed c.15 Ma (Iwano et al., 2007). Around the same time when KAR were formed, many tectonic events occurred in this area (Shinjoe et al., 2007). The formation of KAR may have an important relationship with these tectonic events.

KAR is composed of the Konogi rhyolite, rhyolitic tuff, the Kumano granite porphyry south unit and its north unit. An arc intrusion body that has a characteristic like the Kumano granite porphyry intrudes in the Koza area, southern part of the study area. KAR intrudes into Early Miocene sedimentary rocks of the Kumano Group (KG). In this study, we report the whole rock chemical composition of each rock types of KAR and KG. A total of 19 samples of KAR and KG were analyzed. The major-trace element compositions and REE compositions were measured by XRF and ICP-MS, respectively. The chemical compositions of KAR indicate that KAR is per-aluminous ( $Al_2O_3 / (Na_2O+K_2O+CaO) = 1.10-1.69$ ). It suggests that the original magma melted the wall-rock of KG when it intruded, and/or the original magma was formed by the direct melting of other sediments. Because no whole-rock chemical relationship between KAR and KG was found on the Harker diagram, KAR may have formed by the direct melting of the sediments except KG. REE compositions normalized to CI-chondrite show the high-LREE and flat-HREE pattern. In addition, LREE patterns are divided into two patterns, such as higher and lower value, on the normalized diagram. KAR magma might be differentiated into two types in the magma chamber.

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キーワード: 熊野酸性岩類, 希土類元素, 花崗斑岩

Keywords: Kumano acidic rocks, rare earth elements, granite porphyry

## 斜長石斑晶のSr同位体比分析による鳥海火山のソレイト系列およびカルクアルカリ系列の成因

### Origin of TH and CA suits in Chokai volcanic rocks - examination of Sr isotope ratio in plagioclase phenocrysts

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Tholeiitic (TH) and Calc-alkaline (CA) series lavas is coexisting at Quaternary volcanos in NE Japan arc. Generally, CA lavas have evidence of magma mixing, e.g. disequilibrium phenocrystic assemblage such as olivine and quartz. Therefore, many previous works discussed that the former is evolved from mantle-derived basalt magma by fractional crystallization, and the latter is generated by magma mixing between basic and acidic magmas, both derived from the common TH basalt through fractionation. However, based on Sr isotope micro-analysis of plagioclase phenocrysts in lavas from Zao and Azuma volcanos at central area of NE Japan arc, Tatsumi *et al.* (2008) and Takahashi *et al.* (submitted) argued that isotopically radiogenic TH basalt was formed by melting of the lower-crustal amphibolite and CA was formed by magma mixing of the unradiogenic mantle-derived basalt, the radiogenic crust-derived basalt and the differentiated magma which relates to basalt magmas. Additionally, although estimated primary CA basaltic melt composition at Zao and Azuma volcanos is in frontal-arc, it is medium-K basalt and similar in composition to back-arc side basalt at Chokai volcano. This result is not in agreement with traditional across-arc variation model for mantle-derived basalt magma in island-arc magmatism (e.g. Kuno, 1966), and need reconsideration of the mechanism for geochemical across-arc variation in island-arc volcanic lavas.

The Quaternary Chokai volcano is located at the rear-arc side of NE Japan arc, and this is typical of stratovolcano in Chokai volcanic zone. Chokai volcano activity is divided into Stage1 to Stage3 (Hayashi, 1984; Ban *et al.*, 2001). Stage 1 lavas has not disequilibrium texture or rarely has plagioclase phenocryst which has dimly dusty zone. Stage 2 is composed largely of olivine two-pyroxene andesite with a small amount of olivine two-pyroxene basalt. Most of them contain hornblende as phenocryst. Stage 3 is olivine two-pyroxene andesite and two-pyroxene andesite. The almost plagioclase phenocryst in Stage 2 and 3 lavas has dusty zone and sieve texture. An% of plagioclase phenocrysts core in Stage 1 basalt shows monomodal distribution (An%: 80 to 90), whereas these in Stage 2 and 3 basalts have wide range (An%: 50 to 80). Chokai lavas are plotted on boundary of high-K and medium-K on the SiO<sub>2</sub> vs. K<sub>2</sub>O diagram. On the FeO\*/MgO vs. SiO<sub>2</sub> diagram, trend of Stage 1 and Stage 2 & 3 lavas show the TH and CA, respectively. The range of bulk Sr isotope ratio of TH (Stage 1) and CA (Stage 2 and 3) are very similar (TH: 0.70303 to 0.70341, CA: 0.70297 to 0.70342). But, Sr isotope ratio of TH is constant or look like slightly ascent with increasing SiO<sub>2</sub>, whereas CA is distinctly ascent with increasing SiO<sub>2</sub>. Petrographical and petrological feature of Chokai volcanic lavas indicate that TH is produced by fractional crystallization from basic magma and CA is formed by magma mixing between basic and felsic magma. And, it is thought that a parent magma of TH and the basic end-member magma of CA has different geochemical features.

In this study, we investigated the generation and evolution process of TH and CA suites in Chokai lavas using Sr isotope ratio of whole-rock and plagioclase phenocrysts, and compared them with the frontal-arc volcanic lavas (Zao and Azuma).

キーワード: ソレイト系列, カルクアルカリ系列, ストロンチウム同位体比, 斜長石

Keywords: tholeiitic series, calc-alkaline series, Sr isotope ratio, plagioclase

## Pb isotope analysis of low-Pb geological glasses by femto-second laser ablation-multiple ion counter-ICP-MS Pb isotope analysis of low-Pb geological glasses by femto-second laser ablation-multiple ion counter-ICP-MS

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In-situ analysis of Pb isotopes for the sample with limited size and low Pb content is still great challenging. Such samples include basaltic melt inclusions in olivine ranging from a few ten to one hundred micrometers in size and Pb contents of ~10 ppm. We tested the suitability of femto-second laser ablation sampling coupled to an ICP-MS equipped with multiple Faraday cups (MFC) and ion counters (MIC). Pb isotope ratios of  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  can be precisely determined with MFC for samples with high Pb (> 40 ppm) at large crater size (>100 micrometer in diameter), but this approach is not applicable to small melt inclusions. In contrast to ion current measurement by MFC, direct ion counting using MIC provides ~100 times better signal-to-noise ratio allowing measurement of Pb isotopes with lower intensities (i.e. small ablation crater on low-Pb materials). However, use of MIC detection system is a big challenge due to its poor performance in both linearity and stability. We found that mass bias factor obtained by MIC is signal intensity dependent. Standard bracketing method using similar ion intensities between standard and sample can correct for both the linearity and time dependent decay of MICs. However, control of signal intensity is not always easy for sample with unknown Pb content, especially for melt inclusion with limited sample volume. To overcome this problem, we attempted a dual intensity standard bracketing approach. Different laser repetition rate was utilized for measuring bracketing standard glass in order to cover expected intensity range of Pb signal of unknown sample. Response of each ion counter is calibrated by using linear regression which is then applied to determine the isotope abundance of unknown sample. This method was tested by analyzing Pb isotopes of well characterized reference material BHVO-2G (1.7 ppm Pb). The obtained analytical precision and accuracy of  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  are 0.3-0.4% (2sd) for a spatial resolution of ~30 micrometer. The precision and accuracy are comparable to published works, but spatial resolution is improved.

キーワード: UV-fs laser ablation, Multiple ion counter-ICP-MS, Pb isotope

Keywords: UV-fs laser ablation, Multiple ion counter-ICP-MS, Pb isotope