

Lithium and boron isotopic ratio analyses using laser ablation-multiple Faraday collector-ICPMS

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We report the origin of isotope fractionation induced by laser parameters, and instruments optimization for accurate *in situ* measurement of lithium (d7Li) and boron (d11B) isotope ratios in glasses and minerals using laser ablation multiple Faraday collector ICP-MS. Laser ablation parameters were examined using 266 nm femtosecond (266 fsLA) and 193 nm nanosecond excimer (193 exLA) laser ablation systems for crater diameters of 30–200 μm . We found that higher laser repetition rates and larger crater diameters have led to enhanced fractionation of lighter isotopes, as much as -8 permil for both d7Li and d11B. Fractionation was primarily affected by the ICP aerosol loading and secondly by the thermal fractionation at the LA site. The former was accounted for by mass loading effects, which lowered the plasma temperature and led to insufficient aerosol vaporisation. The latter was related to the molten layer on the crater walls, which resulted in coarser and heavier d7Li and d11B aerosols that did not reach the ICP. Both processes can result in Rayleigh fractionation during aerosol formation and vaporisation. Controlled ablation using a constant crater size, repetition rate, and high laser fluence of 193ExLA enabled reproducible ablation for the standard NIST SRM 61x glasses and unknown basalt glasses. Based on the principles of isotopic fractionation deduced from our experiments, we propose a novel ablation volume correction (AVC) protocol for accurate isotopic analyses of various samples with different matrices. Both the repeatability and the laboratory bias of the d7Li and d11B measurements using the new AVC protocol were better than 1 permil for samples containing a few tens to a few tens of thousands ppm Li and B. We also report significant local heterogeneity of up to several permil found in some basalt glasses, but not in NIST SRM 612 and 610.

キーワード : LA-MFC-ICPMS、 isotope fractionation、 Li isotopic ratio、 B isotopic ratio、 glass and mineral
Keywords: LA-MFC-ICPMS, isotope fractionation, Li isotopic ratio, B isotopic ratio, glass and mineral

Setting up of oxygen extraction system for stable isotope analysis of silicate minerals.

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The mass spectrometers at Niigata University (Finnigan MAT-251 and Thermo MAT-253) are capable of measuring stable isotope composition of carbon dioxide for ultra-small volume (<0.1 micro moles) and with high precision (<0.1 ‰). In this study, we developed a system for high precision analysis of oxygen isotope composition of small volume silicate minerals. The new sample preparation line was installed that comprises of three main parts. 1) the reaction chamber; 2) the gas purification line, and 3) O₂-CO₂ converter.

The reaction chamber separate oxygen from silicate minerals by reacting with the fluorine released from CoF₃ at 700°C. After purification of the released oxygen with liquid nitrogen, the gas is passed through KBr trap to remove the excess fluorine. Pure oxygen gas is then allowed to react with graphite at 750°C, to form carbon dioxide, which is used to measure oxygen isotopes using mass spectrometer.

A technique has been developed in which CoF₃ is used as a reagent for quantitative liberation of oxygen from oxides and silicates. By doing several trial experiments, the background in the reaction line was reduced by preheating of KBr trap, the converter and respective filters. For the converter, it was found that good reproducibility can be obtained at 750 °C and 30 minutes of reaction time. Analysis and measurement of NBS-28 quartz standard reference material were performed, but in this study it was unable to get good reproducibility. The possible reasons and remedies are discussed in detail. The possible candidates that contaminate oxygen are water vapor that instantaneously react with CoF₃, reaction of fluorine gas with adsorbed water inside the vacuum line or fractionation of oxygen during transportation inside the line. Further improvements in preparation procedure are being carried out.

Climatic and Tectonic Evolution during about 27-13 Ma of the northeastern part of the Qinghai–Tibetan Plateau evidenced by geochemical and mineralogical records in the Xunhua Basin

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The Xunhua Basin which located at the northeastern part of the Qinghai–Tibetan Plateau provides a valuable opportunity to understand the climatic and tectonic evolution of Qinghai–Tibetan Plateau. Here we present a synthesis of clay mineralogy, bulk mineral composition and bulk-rock geochemistry of sediments during about 28-14 Ma in the Xunhua Basin. Climate changes during the episode were documented in the sediments and were expressed by the proportion of clay species (Smectite, illite, chlorite) and clay indices, the proportion of non-clay minerals (calcite, quartz, gypsum, orthoclase, and plagioclase), as well as chemical weathering indices, Rb/Sr and Ba/Sr ratios. The results suggest that a warm and seasonally dry and humid climate prevailed over the period ~27-25 Ma, followed by a relatively cold and dry climate in the period ~25-23 Ma. During the period ~23-17Ma, the climate is colder and drier than the previous period and a subsequently warm and humid climate in the period ~17-13 Ma. The dramatic reduction of chlorite proportion at 23 Ma suggested that the source materials changed because of the uplift of mountains around such as Laji mountain. The climate in Xunhua Basin could have been controlled by global climate and the climate cycles of the East Asian monsoon might add additional influence.

Keywords: paleoclimate, geochemistry, clay mineral

冥王代地殻の主成分元素組成：高圧融解実験からの制約

Major element composition of the Hadean crust: constraint from high-pressure melting experiments

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冥王代 (>4.6 Ga) にマントルと地殻がどのように分化していたか、そして地殻がどのような組成であったかを知ることは、地殻の抽出とリサイクルによるマントル化学組成進化の初めの様相を理解する上で必要不可欠である。これまで、冥王代ジルコンや太古代初期の泥質片麻岩の分析から、冥王代花崗岩質-安山岩質地殻の存在が活発に議論されてきた (Hopkins et al. 2010; Kemp et al. 2010; Iizuka et al. 2015; Komiya et al. 2015; Reimink et al. 2016)。しかし、冥王代に地殻がどのように形成され、どのような定量的組成であったのかはいまだによくわかっていない。本研究では、冥王代地殻の主成分元素組成を決定し、冥王代におけるマントル-地殻分化の初めの段階を制約することを目的とした。

先行研究によると、冥王代にはマントルのポテンシャル温度 (MPT) が高かったと考えられる (Korenaga 2013)。そしてMPTが高い場合、マントルカンラン岩の融解によって生成される地殻はコマチアイト質となる (Takahashi & Scaillet 1985)。冥王代ジルコンの酸素同位体比から液体の水の存在が示唆されている (Mojzsis et al. 2001) ことと、冥王代の高温のマントルによって地殻の地温勾配は急であった可能性があることを鑑みると、冥王代の苦鉄質-超苦鉄質地殻は沈み込む際に含水融解し、花崗岩質-安山岩質のメルトを生成した可能性がある。

我々はまず、先行研究の高MPTにおけるマントル対流モデル (Korenaga 2009; Foley et al. 2014) を参考に、冥王代の火成活動様式と未分化カンラン岩の融解によって生成される地殻の組成を推定した。プレートテクトニクス開始以前においては、カンラン岩がソリダス至近の温度で極わずかに融解して生成されたメルトが、厚い (~200 km) リソスフェアの底で分離して地殻を形成し、プレートテクトニクス開始以降は、カンラン岩が海嶺下で大規模に部分融解して生成されたメルトが地殻を形成していたと考えられる。そして我々は、プレートテクトニクス開始以前における地殻の組成を高圧融解実験 (Kondo et al. 2016) から推定し、プレートテクトニクス開始以降の地殻組成はpMELTS (Ghiorso et al. 2002) を用いた計算によって推定した。どちらの場合でもメルト組成はコマチアイト質と推定されたが、プレートテクトニクス以前の方がFeOやTiO₂、Na₂O、K₂O含有量が高くなることがわかった。このFeとTi、アルカリ元素に富んだコマチアイト組成をS (solidus) -コマチアイト質と呼ぶ。

我々は、プレートテクトニクス以前の間歇的かつ滴り落ちるような沈み込みのある状況 (Foley et al. 2014) で、このS-コマチアイト質地殻が含水融解することを想定した。これまでに、コマチアイトの含水融解はほとんど研究されてきていない。我々は、S-コマチアイト組成の出発物質を酸化物と炭酸塩の粉末から合成し、ピストンシリンダー型高圧発生装置を用いて、1-3 GPaの圧力、1000-1300 °Cの温度でS-コマチアイトの含水融解実験を行った。この実験において、我々は特に酸素フガシティを注意深く調整、評価した。実験結果として、S-コマチアイトの含水融解によって生成されるメルトの主成分元素組成はピクライト質となり、出発物質の組成を反映して、Tiとアルカリ元素に富むことがわかった。したがって、冥王代のプレートテクトニクス以前の状況では、まず未分化マントルカンラン岩の融解からS-コマチアイト質地殻が形成され、そして沈み込みに伴うS-コマチアイトの含水融解によって、Tiとアルカリ元素に富んだピクライト質地殻が形成されていたと考えられる。

キーワード：冥王代、地殻、主成分元素組成、高圧融解実験

Keywords: Hadean, crust, major element composition, high-pressure melting experiment

Highly siderophile elements in Hawaiian xenoliths: Implications for the origin of low $^{187}\text{Os}/^{188}\text{Os}$ signatures in oceanic mantle

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Mantle xenoliths in ocean islands basalts (OIB) are generally regarded as fragments of shallow oceanic lithosphere accidentally brought by deeply-derived magmas en-route to the surface, and are genetically unrelated to the hot spot magmas which embed them and their mantle sources. However, it has been proposed that peridotite xenoliths from Salt Lake Crater in Oahu Island (Hawaii) and a high-temperature group of peridotite xenoliths in Malaita, Solomon Islands (Ontong Java Plateau) may represent the pieces of subcreted plume material which cause the primary volcanic activity on their regions (Bizimis et al., 2009 EPSL; Ishikawa et al., 2011 EPSL). This idea is largely based on characteristic contrast of the frequency distribution of whole-rock $^{187}\text{Os}/^{188}\text{Os}$ compositions between these xenolithic peridotites and Pacific uppermost mantle deduced from abyssal peridotites and mantle tectonites in ophiolites.

In this study, we investigated whole-rock abundances of highly siderophile elements (HSE: Os, Ir, Ru, Pt, Pd and Re) together with other major-trace lithophile elements in peridotites from Salt Lake Crater in Oahu Island (Hawaii) with the aim of examining whether peridotite xenoliths having low $^{187}\text{Os}/^{188}\text{Os}$ compositions ($^{187}\text{Os}/^{188}\text{Os} < 0.120$) represent (1) ancient depleted mantle domain produced by shallow melting, subsequently recycled back into deep mantle by subduction processes, or (2) lowermost mantle domain associated with ancient Re-depletion, possibly due to chemical interaction with metallic outer core and/or segregation of metallic materials. Our results demonstrate that refertilisation and melt-rock interaction are predominant mechanisms creating the observed major-trace element variations in Salt Lake Crater peridotites. By contrast, their HSE patterns are characterised by strong depletions in the Re, Pd and Pt relative to Ir-group platinum group elements (IPGE: Os, Ir, Ru), suggesting that refertilisation processes involving silicate melts can have little overall effect on the HSE compositions. This supports the idea that their Os isotope records are strongly influenced by past melt depletion processes, and such ancient depleted materials are commonly embedded in deeply-derived mantle plumes.

キーワード：強親鉄性元素、オスミウム同位体、マントル捕獲岩、かんらん岩、ハワイ

Keywords: Highly siderophile elements, Os isotopes, mantle xenoliths, peridotite, Hawaii