論文内容の要旨

Lithium isotopic analyses of ophiolites, peridotite xenoliths and ocean island basalts: constraints on cycling and isotopic heterogeneity of Li in the mantle

マントル内のリチウムの循環と同位体不均質の解明のためのオフィオライト，マントル捕獲岩，海洋島玄武岩のリチウム同位体比の研究

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The large relative mass difference of Li between ^{6}Li and ^{7}Li leads to the significant isotopic fractionation in nature, ranging from – 20 to + 40 ‰ in the δ^7Li values. Hence, Li isotopes have been widely utilized in investigation of various geological processes as an effective geochemical tracer, especially in the processes involving the fluid/water-solid interaction from the Earth's surface to the deep mantle. In spite of recent studies on Li isotope geochemistry, the behavior of Li isotopes in the deep crust and mantle, as well as the crust-mantle cycling of Li still remains controversial. Here, Li isotopic analyses of the ophiolites, peridotite xenoliths and OIBs were carried out with MC-ICP-MS in order to elucidate the behavior of Li during crust-mantle cycling. Those samples are expected to provide constraints on such individual processes in the crust-mantle cycling as hydrothermal alteration for the ophiolites, subduction for peridotite xenoliths, and recycled Li product for OIBs.

The procedure of two-step chemical separation with cation exchange resin was established for Li purification. The first-step separation using methanol-HNO_3 eluent enhanced the separation of lithium with other matrix ions especially sodium. To remove organic materials and to purify Li further, sample solution from the first-step separation was purified by the second-step separation with HCl eluent. The long-term reproducibility of Li isotopic analysis in this study is within ±0.55‰ (2σ, n=8) for in-house Li standard solution (AAS). The δ^7Li value of JB-2 was also determined and its average is + 4.13 ‰ ± 0.51 (2σ).

The ophiolites of the Wadi Fizh area, Oman, which are considered as the ancient oceanic crust, were analyzed for Li isotopic composition. The oceanic crust as the starting material of crust-mantle cycling is modified in its composition by hydrothermal alteration. The upper parts (~ 1000 m) of the oceanic crust have heavy Li signatures by seawater alteration with a high water-rock ratio. The δ^7Li values of the Oman ophiolite range from + 2.9 to + 22.0 ‰ and are heavier than the normal MORB even in the deep part of the oceanic crust. It is likely that the water-rock ratios in the Oman ophiolite were high during hydrothermal alteration, compared with those in the oceanic crust collected from ODP site 504B. This result suggests that the subducting slab varies in its Li isotopic ratios of from the normal MORB to heavy ones, and even the slab consisting of the lower oceanic crust can have heavy Li isotopic signatures.

Peridotite xenoliths from Avacha volcano, Kamchatka derived from the sub-arc mantle wedge, were analyzed for trace elements and Li isotopic ratios. The δ^7Li values of mantle xenoliths range from + 3.5 to + 5.6 ‰, which falls within the range of the normal MORB mantle (+ 3 ~ + 5 ‰), and the Li contents represent little variation about 1.2 ppm (1.13 ppm to 1.25 ppm), indicating that metasomatic agents of aqueous fluid and hydrous melt also have similar Li isotopic compositions with the normal mantle. The metasomatic fluid derived from subducting slab is likely to be similar in Li isotopic composition with the normal mantle or buffered in the mantle, and no heterogeneity in Li isotopes in the mantle wedge by the fluid released from the slab was observed.

Basalts from Logudoro, Sardinia (Italy) with geochemical features similar to EM1 source, were analyzed. The Li abundances of the Logudoro basalts vary between 7.7 and 10.8 ppm, which falls within the common range of Li abundances in OIB. The model calculation of partial melting using the *pMelt* program supports that their elevated Li/Dy ratios are ascribed to partial melting processes occurred at higher pressure than those of ordinary OIB by the increasing amount of residual garnet during partial melting. The Li isotopic compositions of Logudoro basalts range from δ^7Li = + 1.5 to + 3.6 ‰. The diffusion calculations suggest that the fast diffusion of Li prevents the recycled materials from preserving their original Li isotopic compositions.

Although the Li isotopic ratios of subducting slab are variable, the mantle wedge and OIB have Li isotopic ratios similar with the normal mantle, ranging within a few permil scale. When the fast diffusion of Li in high temperature is considered, Li isotopes are difficult to constrain the crust-mantle cycling from subduction to OIB-eruption with long residence time. Nevertheless, it is suggestive that the Li isotopes have a potential as geochemical tracer for geological processes occurring at low temperature and in relatively short time-scale.