

# Development of high precision Li isotope analysis for olivine with High Resolution Secondary Ion Mass Spectrometry, and its application to the Horoman Peridotite Complex: Implications for mantle metasomatism.

学籍番号: 41415222 渡辺昌樹

The author reports on a new analytical procedure for Li isotope analysis by a High mass Resolution Secondary Ion Mass Spectrometer (HR-SIMS), Cameca ims 1270, and its applications to the Horoman Peridotite Complex. The Li isotope system might provide the potential to understand the geochemical evolution of the Earth's mantle, because 1) Li is a moderately incompatible constituent of minerals in peridotite, 2) Li isotopes show large variation in the terrestrial system, caused by low-temperature fractionation and mixing, 3) Li is a fluid-mobile element. The Li isotopes, combined with existing geochemical information, therefore, could be powerful geochemical tracers, especially for fluid related mantle processes, such as mantle metasomatism. In this study, the author developed the following analytical procedure to accomplish the accurate Li isotope analysis at high spatial resolution, and confirmed its potential to investigate complex mantle process in terms of large Li isotopic variation recorded in olivine from Horoman Peridotite Complex.

The key to high precision Li isotope analysis is to correct the time drift of energy distribution and obtain a high transmission efficiency from olivine (Li: 1~2 ppm), keeping sufficient mass resolution ( $M/\Delta M \sim 1600$ ) to discriminate the interferences (e.g.  ${}^6\text{LiH}^+$ ). Initially, the drift of energy distribution was calibrated in each run using the Sample HV Control Program of CAMECA; next the width of energy window and the size of the field aperture were determined to obtain the optimized conditions. As a result, the internal precision of Li isotopic ratio was typically  $\pm 0.6\%$  ( $1\sigma_m$ ) on  $\sim 10^5$  cps for  ${}^7\text{Li}^+$  using an O<sup>-</sup> primary beam of 20 nA intensity for sputtering; the reproducibility based on repeated measurements on standards was  $\pm 0.5$  to  $0.8\%$  ( $1\sigma$ ). These analytical conditions were of sufficient spatial resolution (beam size:  $\sim 50 \mu\text{m}$ ) to extract the Li isotopic zoning profile from mantle olivine.

In order to determine an accurate Li isotopic composition by HR-SIMS, it is necessary to calibrate instrumental mass fractionation. In this study, therefore, the author applied a calibration curve method using the reliable standards. For this purpose, two olivines in mantle xenoliths from San Carlos, Arizona, and from Malaita, Solomon Islands, were prepared. The homogeneity of Mg# and Li isotope composition of these olivine standards was confirmed by EPMA and HR-SIMS respectively. Absolute Li isotope compositions of these olivine standards were determined by TIMS (Moriguti & Nakamura, 1993; 1998).

The Horoman Peridotite complex, which is one of the freshest orogenic peridotite complexes, has been investigated to understand mantle processes. Yoshikawa and Nakamura (2000) suggested that the Horoman peridotite was metasomatized by aqueous fluid presumably derived from a subducted slab. However, the nature of the metasomatic agent itself is still unclear. For further constraint of metasomatic process, Li isotope systematics were applied to olivine from the Horoman Peridotite.

In order to investigate Li isotopic signature in olivine related to mantle metasomatism, three representative samples, plagioclase lherzolite (PL), spinel lherzolite (SL) and dunite (DU) were selected from Horoman Peridotite Complex. Yoshikawa & Nakamura (2000) reported imprinting of the metasomatic effect increased with depletion of melt component based on Sr-Nd isotopes and trace element geochemistry. The polished thin sections were prepared for the Li isotope analysis by HR-SIMS. The  $\delta^7\text{Li}$  ( $= [{}^7\text{Li}/{}^6\text{Li}]_{\text{sample}}/[{}^7\text{Li}/{}^6\text{Li}]_{\text{standard}} - 1 \times 1000$ ) values of PL and SL are from  $-0.5$  to  $+3.7 \text{‰}$  ( $n=6$ ), and from  $+2.7$  to  $+7.4 \text{‰}$  ( $n=9$ ), respectively. DU shows  $\delta^7\text{Li}$  ranges of  $-32.8$  to  $+6.2 \text{‰}$  ( $n=29$ ), which include extremely light values. The variation of Li isotope from PL is consistent with that of MORB, and SL shows a heavier Li signature than that from PL. These heavy  $\delta^7\text{Li}$  signatures may reflect the composition of aqueous fluid presumably derived from a subducted slab. However, it is difficult to explain the extremely light signature of Li isotope in DU by such a fluid. If the metasomatic process for DU occurred at low-temperature conditions, it is possible that the in-situ isotopic fractionation was induced by reaction between olivine and metasomatic fluid. This hypothesis could explain the extremely light isotopic signature ( $\delta^7\text{Li} = \sim -30\%$ ) in DU.