

Lithium and oxygen isotope compositions of chondrule constituents in the Allende meteorite. T. Kunihiro¹, T. Ota¹, and E. Nakamura¹, ¹The Pheasant Memorial Laboratory, Institute for Planetary Materials, Okayama University, Misasa, Tottori 682-0193, Japan (tkk@misasa.okayama-u.ac.jp).

Introduction: Carbonaceous and ordinary chondrites have long been considered as primordial materials, relatively unchanged since their formation; however, most have been altered by interaction with aqueous fluid on their parent asteroids [1–3]. The unique geochemical characteristics of Li make it possible to trace processes on asteroids. Lithium is highly soluble in aqueous fluids [4] and Li isotopes exhibit significant fractionation in geologic materials ($\delta^7\text{Li}$ ranges from -20 to 40%) because of the large mass difference between ^6Li and ^7Li (e.g., [5]). The Li is preferentially retained in solid phases while ^7Li preferentially enters solution. To understand the behavior of Li during nebular and asteroidal processes, we report Li isotope compositions together with O isotope compositions of chondrule constituents in the main and at igneous rim of chondrules, with examination of formation and alteration of the phases.

Experimental Methods: Oxygen-isotope compositions were determined by SIMS. A Cs⁺ primary beam (200 pA) of 20 keV was focused and scanned on the sample surface by $5 \times 5 \mu\text{m}^2$, yielding a $6 \times 6 \mu\text{m}^2$ crater. Secondary O⁻ was accelerated to -10 kV and a normal incident electron gun was used to compensate positive charging on the sputtered area.

Lithium isotope compositions were also determined by SIMS. O and Li isotope measurements were carried out onto the same spots. As well as the O isotope analysis, instrumental mass fractionation is one of the major difficulties in high-precision Li isotope analysis by SIMS (e.g., [6]). Isotope compositions were determined by a formula $\delta^7\text{Li} = \delta^7\text{Li}^{\oplus} - \Delta^7\text{Li}$, where $\delta^7\text{Li}^{\oplus}$ is the ion-intensity ratio that the instrumental mass fractionation was corrected ($\delta^7\text{Li}^{\oplus} \equiv \delta^7\text{Li}^+ - f_{\text{IMF}}$), and $\Delta^7\text{Li}$ is the relative matrix effect of particular phase relative to a working standard. Note that f_{IMF} is estimated using the working standard. To evaluate the matrix effects relative to working standards, we analyzed reference olivine (F_{01–99}), low-Ca pyroxene (W₀₀), high-Ca pyroxene (W_{031–39}), and plagioclase (ab_{42–72}). As a result, significant matrix effects were recognized in olivines with F_{01–99}, and between the working standards and the other reference materials; thus, we estimated $\Delta^7\text{Li}$ for olivine, pyroxene, and plagioclase, based on linear correlations between the matrix-related bias and chemical varieties of those phases. As for olivine (F_{052–100}) in chondrules, matrix effects

were estimated based on a linear correlation with chemical varieties, and the matrix effects were corrected. The estimated matrix effects of low-Ca and high-Ca pyroxenes (W_{01–7} and W_{040–49}) and plagioclase (ab_{15–37}) in chondrules relative to the working standard en-sl were negligibly small, being within or comparable to analytical reproducibilities for the working standards. Thus, we did not apply the matrix effect correction on the pyroxenes and the plagioclase.

Results: A total of nine chondrules were measured. $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values for minerals (olivine, low-Ca pyroxene, high-Ca pyroxene, and plagioclase) scatter between the CCAM line defined from data on Allende (slope of 0.94 ± 0.02 and intercept of -4.2% [7]) and Y&R line (slope of 1.00 ± 0.03 and intercept of -1.04 [8]). These O isotope compositions are in good agreement with those previously obtained by bulk analyses of CV chondrules [9–11]. Based on the O isotope composition of olivines, nine chondrules were divided into three groups. Averages of $\Delta^{17}\text{O}$ of olivines (F_{0>65}) in chondrules BOP-2 (Fig. 1), PO-6, and BO-4 are -5.3 , -5.2 , and -5.4% . Averages of $\Delta^{17}\text{O}$ of olivines (F_{0>65}) in chondrules PO-7, PO-1, PO-3c, and PO-3s are -6.1 , -6.5 , -6.3 , and -6.0% . Average of former and latter chondrules are $\Delta^{17}\text{O} -5.3 \pm 0.4\%$ and $-6.2 \pm 0.4\%$, respectively, and former and latter chondrules were classified as group 1 and 2 chondrules. Olivines in chondrules PO-8 and PO-3n show variation in $\Delta^{17}\text{O}$ from -23.7 to -6.2% and the chondrules were classified as group 3 chondrules.

On group 1, all the isotope compositions for olivine are similar and range from $\delta^{18}\text{O} -6$ to -3% , pyroxene is similar but slightly more $\delta^{18}\text{O}$ -rich, and plagioclase in BOP-2 and FeO-rich olivines in PO-6, are a lot more $\delta^{18}\text{O}$ -rich. For group 2, all the isotope composition for olivine, low-Ca pyroxene, and high-Ca pyroxenes are similar and around -6% , and FeO-rich olivines in PO-1 and PO-3c are a lot more $\delta^{18}\text{O}$ -rich. For group 3, the isotope composition for olivine are in the range from $\delta^{18}\text{O} -50\%$ to -10% .

All chondrules measured for O-isotope compositions were also measured for Li-isotope compositions. Analyses for chondrule BOP-2 are shown in Fig. 2 as a representative chondrule. The negative correlation is consistent with [12]. Low-Ca pyroxene and plagioclase are the most Li enriched and depleted phases, respectively. Li isotope compositions range from $\delta^7\text{Li} -30\%$ to $+30\%$. There is no obvious correlation between Li concentration and isotope composition (Fig. 2).

Discussion: Plagioclase is significantly depleted in ^{16}O than other silicates. On the parent body metamorphism, O-isotope composition in 10 μm -sized plagioclase could be completely exchanged [13]. Plagioclase can be either of chondrule formation or of asteroidal process, and even when former is the case, the ^{16}O -poor composition was resulted from the asteroidal process. Li concentration and isotope composition of plagioclase were resulted from those of asteroidal reservoir.

Low-Ca pyroxene is the most Li-enriched phase (Fig. 2). Low-Ca pyroxene on Fig. 2 forms array with significant range determined by two components of ([Li], $\delta^7\text{Li}$) to be (0.5 $\mu\text{g/g}$, +33‰) and (5 $\mu\text{g/g}$, -10‰). Krot et al. [14] suggested that igneous rim formed either by gas-solid condensation of silica-normative materials onto chondrule surfaces and subsequent incomplete melting, or by direct SiO (gas) condensation into chondrule melt, occurred in gas enriched in alkalines and Si. If latter is the case, the Li isotope composition of the gaseous reservoir is estimated to be $\delta^7\text{Li}$ -10‰.

References: [1] Krot A. N. et al. (1995) *Meteoritics*, **30**, 748. [2] Zolensky M. E. et al. (2008) *Review in Mineralogy and Geochemistry*, **68**, 429. [3] Brearley A. (2014) *Treatise on Geochemistry*, pp. 309 [4] Brenan J. M. et al. (1998) *GCA*, **62**, 3337. [5] Tomascak P. B. et al. (2016) *Advances in Lithium Isotope Geochemistry*, pp. 47. [6] Bell D. R. et al. (2009) *Chemical Geology*, **258**, 5. [7] Clayton R. N. et al. (1977) *EPSL*, **34**, 209. [8] Young E. D. and Russell S. S. (1998) *Science*, **282**, 452. [9] Clayton R. N. (1981) *Phil. Trans. R. Soc. Lond. A*, **303**, 339. [10] Rubin A. E. et al. (1990) *GCA*, **96**, 247. [11] Jones R. H. et al. (2000) *Meteor. Planet. Sci.*, **35**, 849–857. [12] Liu M. -C. and Chaussidon M. (2019) *LPSC*, 1979 [13] Rudraswami N. et al. (2011) *GCA*, **75**, 7596. [14] Krot A. N. et al. (2004) *Meteor. Planet. Sci.*, **39**, 1931.

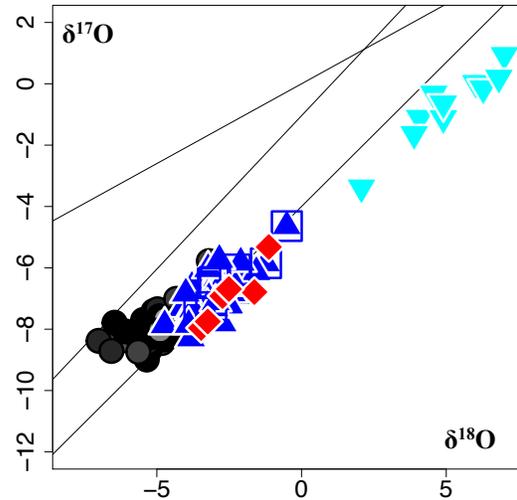


Figure 1: O isotope composition of chondrule BOP-2. Olivines are shown by circle. Low-Ca pyroxenes, high-Ca pyroxenes, and plagioclases are shown by triangle (blue), diamond (red), and inverted triangle (cyan). Low-Ca pyroxenes in igneous-rim regions are shown with symbols of square.

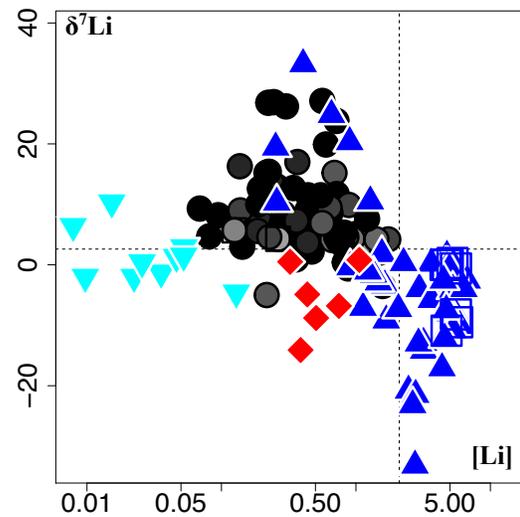


Figure 2: Li element-and-isotope composition of chondrule BOP-2.