

LITHIUM AND LEAD ISOTOPIC SIGNATURES OF MARTIAN SUB-SURFACE COMPONENTS RECORDED IN SHERGOTTITES PHOSPHATES. M. Koike¹, N. Takahata¹, Y. Sano¹, K. Nagaishi² and T. Ishikawa³, ¹Atmosphere and Ocean Research Institute (AORI), The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8564, Japan (mizuho_k@aori.u-tokyo.ac.jp), ²Marine Works Japan Ltd., 200 Monobe Otsu, Nankoku, Kochi 783-8502, Japan, ³Kochi Institute for Core Sample Research, JAMSTEC, 200 Monobe Otsu, Nankoku, Kochi 783-8502, Japan.

Introduction: The existence of liquid water on past and probably current Mars has been almost conclusive by recent intensive studies (e.g. [1]). Since water plays key roles in the near-surface environmental evolutions of terrestrial planets, it is important to elucidate the potential sources, the amounts and behaviors of water at past and current Mars. Lithium is one of the light lithophile elements and may be a useful tracer for hydrous activities. It is known that Li isotopes are not significantly fractionated by simple magmatic differentiations. On the other hand, large fractionation of $\delta^7\text{Li}$ can be occurred by H_2O -degassing from magma, subsolidus diffusion in minerals or secondary processes such as weathering (e.g. [2]).

Previous studies of shergottites reported core-to-rim variations of $\delta^7\text{Li}$ and Li concentrations (hereafter [Li]) in large olivine and pyroxene crystals, which are associated with H_2O -degassing from the shergottites parental magma [3][4]. Diffusions in silicates were also reported for shergottites and nakhlites [4][5]. While those studies concern magmatic Li isotopes and their fractionation processes, late-stage minerals, such as phosphates (as well as impact-induced glasses) might have incorporated additional Li from the martian crust. Mixing of additional components, presumably the crustal materials, to the shergottite magma has also been indicated from Pb isotopic systematics [6]. If such components had been incorporated into the phosphates before their crystallization, their $\delta^7\text{Li}$ and [Li] might reflect water-mineral interactions at the martian near-surface system.

In order to understand the near-surface hydrous environments on Mars, we focus on the isotopic signatures of Li and U-Pb system recorded in shergottites phosphates. Here, we present our preliminary reports of Tissint.

Sample: Tissint is the fall, depleted olivine-phyric shergottite. It has numerous glassy components enclosing bubbles. These glasses showed LREE-enrichment, indicating the contaminations of martian crustal materials [7]. The U-Th-Pb systems of acid leaching were well documented [6].

Analytical Conditions: Small bulk sample of Tissint was embedded in epoxy resin, polished and cleaned using ultrasonic bath with ethanol, and gold-coated after $\sim 100^\circ\text{C}$ baking overnight. The section

was then observed by SEM-EDS to identify phosphate with enough size ($>20\mu\text{m}$ in diameter; Fig. 1). The isotopic analyses of Li and U-Pb were conducted in different sessions using a NanoSIMS at AORI, University of Tokyo. For Li analyses, a primary InA O^- ion with beam size of $\sim 7\mu\text{m}$ was scanned over $10\mu\text{m}$ square area. Secondary ions of $^6\text{Li}^+$, $^7\text{Li}^+$, $^{29}\text{Si}^+$, $^{31}\text{P}^+$ were collected with multi-collectors and peak-jumping. The sensitivity of $^7\text{Li}^+$ and the instrumental mass fractionation factor of $^7\text{Li}^+/^6\text{Li}^+$ for apatite are determined with standard as 230 cps/nA/ppm and $(^7\text{Li}^+/^6\text{Li}^+)_{\text{meas}}/(^7\text{Li}^+/^6\text{Li}^+)_{\text{ref}} = 1.005$, respectively. A Natural apatite from Morocco ([Li]=3.1 ppm, $\delta^7\text{Li}=6.8\pm 0.3\text{‰}$) was used as standard. The bulk [Li] and $\delta^7\text{Li}$ of the standard were analyzed by MC-ICP-MS at Kochi Institute for Core Sample Research, JAMSTEC. For U-Pb, a 5nA O^- ion beam with $\sim 15\mu\text{m}$ in diameter was focused. Both ^{238}U - ^{206}Pb and ^{207}Pb - ^{206}Pb were obtained on the same spots. Detailed analytical protocols were shown in elsewhere [8].

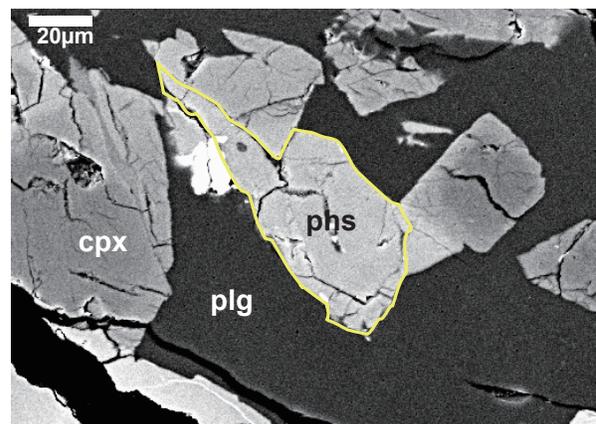


Fig. 1. SEM image of a phosphate (Phs-5) in Tissint.

Table 1. $\delta^7\text{Li}$ and [Li] of the Tissint phosphates.

Spot#	Li (ppm)	$\delta^7\text{Li}$ (‰)
Phs-1	15.1 ± 4.0	8.0 ± 2.8
Phs-2	18.3 ± 4.8	1.1 ± 3.3
Phs-3	11.1 ± 3.0	-5.1 ± 4.0
Phs-4	16.2 ± 4.3	5.5 ± 3.4
Phs-5	12.3 ± 3.2	8.3 ± 4.0

Errors are at 1-sigma.

Results and Discussion: Five phosphate grains were analyzed for Li and U-Pb. Additional 3 grains were analyzed for U-Pb only.

The concentrations and the isotopic ratios of Li are shown in Table 1. and Fig. 2 (All errors are 1-sigma)., The $\delta^7\text{Li}$ range from -5.1‰ to +8.3‰. Although errors are relatively large, these values are slightly higher than the pyroxene range of -7.1‰ to +5.1‰ [3]. The [Li] of the phosphates (11.2 – 16.2 ppm) are significantly higher than those of the silicates of < 2 ppm [3]. Since Li is moderately incompatible, the higher $\delta^7\text{Li}$ and [Li] can be explained by (a) magmatic differentiation (increase [Li]) along with H_2O -degassing (increase $\delta^7\text{Li}$ and decrease [Li]), or by (b) incorporation of additional high- $\delta^7\text{Li}$ components (crustal materials) at the late stage crystallization. Due to the large uncertainties and limited data, we cannot distinguish above possibilities at this time.

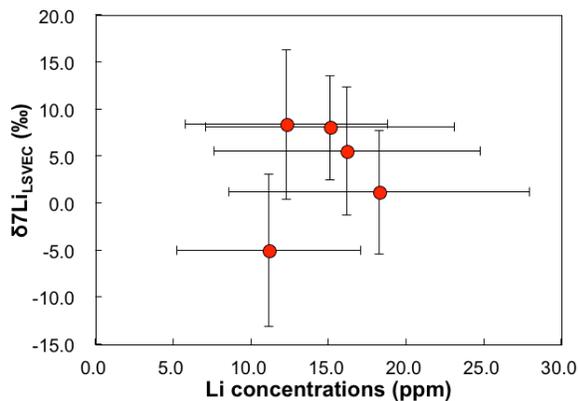


Fig. 2. $\delta^7\text{Li}$ and [Li] of Tissint phosphates.

The ^{238}U - ^{206}Pb analyses of Tissint phosphates did not provide significant age, because of the quite low $^{238}\text{U}/^{206}\text{Pb}$ ratios and the small variations. On the other hand, ^{207}Pb - ^{206}Pb age was unrealistically old as $4820 \pm 330\text{Ma}$. Our Pb isotopic data are similar to the leachates data of the previous acid leaching study [5], suggesting that the phosphates have the most radiogenic Pb in this meteorite. The obtained ^{207}Pb - ^{206}Pb 'age' may be because of the mixing of 2 or more components, possibly martian crustal material. Fig 3 plot our ^{207}Pb - ^{206}Pb results with other literature data of shergottites phosphates (QUE94201, Zagami, LAR06319 and Shergotty). Tissint and QUE94201 are quite similar. While ^{207}Pb - ^{206}Pb age of all shergottites cannot be determined, they might be on the same line. Meanwhile, these shergottites have ^{238}U - ^{206}Pb age as $476 \pm 72\text{Ma}$, although Zagami, Shergotty and LAR06319 may be younger. There is a possibility that

this shows mixing between unradiogenic Pb in the shergottite magma and radiogenic Pb in the martian crust.

In summary, both Li isotopes and U-Pb system in shergottites phosphates indicate the possible incorporation of martian crustal components. For their interpretations and applications to the martian sub-surface hydrological activities, however, further investigations are required.

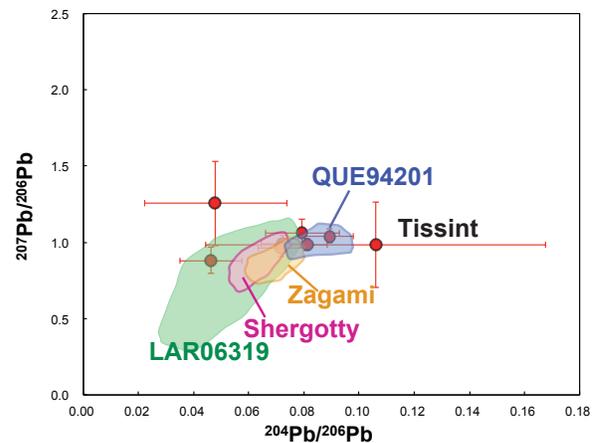


Fig. 3. ^{207}Pb - ^{206}Pb of Tissint and literature values. Literature values of Shergotty [9], LAR06319 (Koike et al., 2014; unpublished data), Zagami and QUE94201 [10] are shown as shaded areas.

References: [1] Ojha L. et al, (2015) *Nature Geosci.* 8, 829-832. [2] Tomascak P. B., (2004) *Rev. in Mineral. Geochem.*, 55, Mineralogical Society of America, Washington DC, pp. 153-195. [3] Beck P. et al. (2004) *GCA*, 68, 2925-2933. [4] Udry A. et al. (2016) *Meteoritics & Planet. Sci.*, 51, 80-104. [5] Beck P. et al. (2006) *GCA*, 70, 4813-4825. [6] Moriwaki R. et al. (2014) *LPS XLV*, Abstract #1773. [7] Chennaoui Aoudjehane H. et al. (2012) *Science*, 338, 785-788. [8] Koike M. et al. (2014) *Geochem. J.*, 48, 423-431. [9] Sano Y. et al. (2000) *Meteoritics & Planet. Sci.*, 35, 341-346. [10] Monde et al. (2001), presented at Annual Meeting of Isotope Geochemistry Division, The Mass Spectrometry Society of Japan.