

**A MODERATE D/H RATIO FOR A SURFICIAL WATER RESERVOIR ON MARS.** T. Usui<sup>1,2</sup>, C. M. O'D. Alexander<sup>3</sup>, J. Wang<sup>3</sup>, J. I. Simon<sup>4</sup>, and J. H. Jones<sup>4</sup>, <sup>1</sup>Dept. of Earth & Planet. Sci., Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152-8551, Japan ([tomohirusui@geo.titech.ac.jp](mailto:tomohirusui@geo.titech.ac.jp)), <sup>2</sup>Lunar Planetary Institute, USRA, <sup>3</sup>Dept. of Terrestrial Magnetism, Carnegie Institute of Washington, <sup>4</sup>KR, NASA Johnson Space Center.

**Introduction:** Martian surface morphology implies that Mars was once warm enough to maintain persistent liquid water on its surface and that water played a significant role in the formation of weathered/altered terrains [e.g., 1, 2, 3]. Volatiles exhaled by volcanic activity would have been the dominant greenhouse gases and would have significantly affected the Martian climate. The enrichment of some volatile elements in the atmosphere, which would have dissolved in surface water, could also have influenced water chemistry (e.g., acidity) and played a significant role in weathering and aqueous alteration processes. While much of this picture is qualitative, Martian meteorites contain records of major Martian volatile reservoirs.

This study characterizes Martian surficial volatile reservoirs based on *in situ* ion microprobe analyses of volatile abundances and H-isotopes of glassy phases (groundmass glass [GG] and impact melt [IM]) in Martian basalts (shergottites). Although these meteorites are of igneous origin, some glassy phases underwent impact-induced modification that trapped surficial and atmospheric volatile components [4, 5]; e.g., inert gases contained in IMs from EETA79001 (EETA79) match the relative abundances of modern Martian atmosphere [6]. Analyses of these glassy phases demonstrate that surficial volatile reservoirs have distinct D/H ratios from their magmatic volatiles.

**Samples:** This study employs three olivine-phyric shergottites: Y-980459 (Y98), LAR 06319 (LAR06), and Lithology-A of EETA79. These meteorites are petrographically similar, but are geochemically distinct in terms of their radiogenic isotopes and incompatible trace elements. The composition of Y98 closely approximates a Martian primary melt that was directly derived from a geochemically depleted mantle reservoir [7]. In contrast, LAR06 represents a melt that has assimilated a geochemically enriched Martian crust [4]. EETA79 shows an intermediate geochemical signature, which is interpreted to reflect mixing of the depleted and enriched sources represented by Y98 and LAR06, respectively [e.g., 8].

**Method:** We have employed a low-volatile contamination sample preparation method without using epoxy [4]. Epoxy penetrates into fractures of Martian meteorites and becomes a ubiquitous and unavoidable contamination source. We have greatly reduced potential contamination by embedding our samples in liquid indium metal while under vacuum. The potential ef-

fects of contamination were further assessed by detailed SEM/microprobe petrographic observations and by checking C and H secondary ion images.

Hydrogen isotope compositions and the abundances of volatile elements (H<sub>2</sub>O, CO<sub>2</sub>, S, Cl, F) of IMs and GGs have been measured using an ion microprobe (Cameca ims-6f) at DTM-CIW, following the techniques of [9, 10].

**Results and Discussions:** IM occurs in maskelynite (shocked plagioclase) in both LAR06 and EETA79. They are characterized by high Al<sub>2</sub>O<sub>3</sub> (~20 wt%) and Na<sub>2</sub>O (~4 wt%) contents, as well as moderate mafic mineral components (e.g., ~5-10 wt% FeO and ~0.5-0.7 wt% TiO<sub>2</sub>). This suggests that the IMs are derived by melting of primary plagioclase and pyroxene. The distinction between IMs in LAR06 and EETA79 is P content; the former has higher P<sub>2</sub>O<sub>5</sub> (~1.5 wt%) content than the latter (~0.2 wt% P<sub>2</sub>O<sub>5</sub>).

For Y98, we have analyzed GGs instead of IMs because IMs are rare in Y98 [7] and are not present in our Y98 sections. Y98 GGs exhibit quenched textures as a result of rapid cooling during the eruption. The major element compositions (e.g., high Al<sub>2</sub>O<sub>3</sub>) suggest that they represent a fractionated liquid after the crystallization of olivine and pyroxene [4].

IMs in LAR06 contain lower H<sub>2</sub>O (~150 ppm), CO<sub>2</sub> (~20 ppm) and S (100-400 ppm), but higher F (10-30 ppm) and Cl (40-80 ppm), than IMs in EETA79 (~300 ppm H<sub>2</sub>O, ~300 ppm CO<sub>2</sub>, 3200 ppm S, <3 ppm F, ~30 ppm Cl). The halogen abundances could possibly reflect the incorporation of primary phosphates, which is consistent with higher P<sub>2</sub>O<sub>5</sub> in LAR06 IMs than those in EETA79. IMs in both samples have much higher H<sub>2</sub>O/CO<sub>2</sub> ratios than that of the Martian atmosphere (<10<sup>-3</sup>), implying the presence of another water source. Y98 GGs contain low H<sub>2</sub>O (20-50 ppm) contents relative to F (15-30 ppm) and Cl (30-50 ppm). The high halogen/H<sub>2</sub>O ratios in Y98 GGs, compared to those of Y98 primary magma [4], indicates degassing of magmatic water during eruption.

A [ $\delta$ D-1/H<sub>2</sub>O] mixing diagram (Fig. 1) shows that the glassy phases in all three shergottites have a relatively limited range of  $\delta$ D values regardless of the distinct  $\delta$ D of their magmatic sources. In a previous study [4] using olivine-hosted melt inclusions, we showed that the Y98 primary magma had a chondritic, low- $\delta$ D value of  $\leq 275$  ‰, whereas that of LAR06 had a very high- $\delta$ D value of 5079 ‰. In contrast, the glassy phas-

es in Y98 and LAR06 both have moderate  $\delta D$  values. The Y98 GGs exhibit a slightly greater  $\delta D$  variation of 200-1600‰, but still much less extreme than the range exhibited by the melt inclusions (squares; Fig. 1a). LAR06 IMs exhibit lower  $\delta D$  values of ~2000-3000 ‰ than the primary LAR06 melt (5079 ‰). IMs in EETA79 also have intermediate  $\delta D$  values of ~1600 ‰. Mixing calculations indicate that contamination of terrestrial water during the ion microprobe analyses does not significantly affect these glass  $\delta D$  values (Fig. 1b).

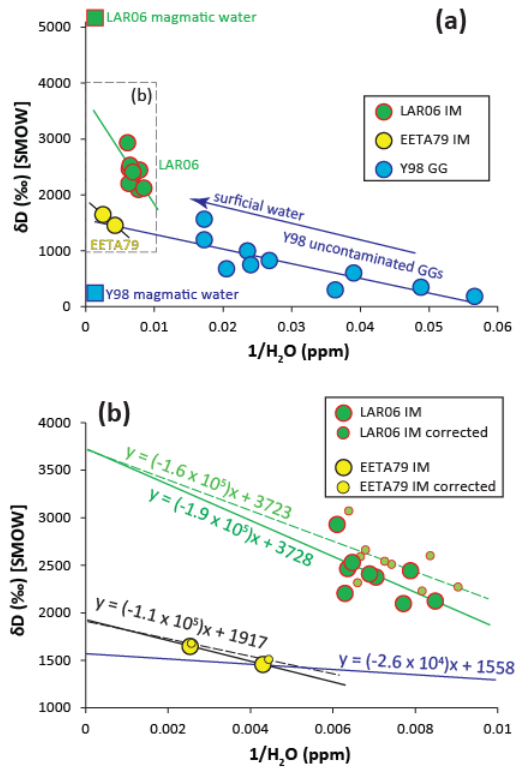


Fig. 1:  $\delta D$ - $1/H_2O$  mixing diagram. Hatched area in (a) is enlarged in (b). For Y98, only uncontaminated GGs are shown (see [4]). For EETA79 and LAR06, IM data with/without analytical blank correction for terrestrial water (7 ppm  $H_2O$  with  $\delta D = -200$ ‰, [4]) are plotted. The corrected and uncorrected IM data have similar regression lines with almost identical intercepts. The  $\delta D$  values of Y98 and LAR06 magmatic water (filled squares) are obtained from their melt inclusions [4].

The Y98 GGs exhibit a strong negative correlation between  $\delta D$  and Cl contents (Fig. 2); a similar trend is observed in a  $\delta D$ -F diagram. Our previous study [4] suggested that the  $\delta D$  variation in Y98 GGs reflects mixing of two components: near-surface moderate- $\delta D$  (~1500‰) and magmatic low- $\delta D$  (~275‰) components. The  $\delta D$ -Cl diagram further implies that the surficial water component in Y98 GGs has a lower halogen content than the Y98 magma.

In contrast, the IMs exhibit a positive correlation in the  $\delta D$ -Cl diagram (Fig. 2). The Cl (and F) variation is greater in LAR06 than EETA79, although the latter has only two data points. Such halogen variations in the IMs are interpreted to reflect the incorporation of magmatic phosphates. Note that no phosphate is present in Y98 [7]. Considering the high  $\delta D$  value (~5000‰) of LAR06 magmatic water (Fig. 1), IMs with higher  $\delta D$  values (~3000‰) presumably reflect more magmatic phosphate contribution. The lower- $\delta D$  ends of the IM variations (~2000‰ for LAR06 and ~1500‰ for EETA79) may represent a near-surface hydrous reservoir (Fig. 2).

Figs. 1 and 2 show a convergence among the glass  $\delta D$  values, which could be attributable to the impact-induced addition of a common near-surface water with a moderate  $\delta D$  value (~1500-2000 ‰). The origin of this surficial hydrous reservoir remains unresolved: (1) it may be derived from the Martian atmosphere, but its moderate  $\delta D$  is distinctly lower than the widely-accepted atmospheric  $\delta D$  value of ~4000-5000 ‰, and/or (2) it could originate from the addition of a weathered soil/dust component enriched in volatile elements. It is also interesting that the enriched (LAR06), intermediate (EETA79), and depleted (Y98) characterizations, based on REE elements, appear to also be reflected in  $\delta D$ .

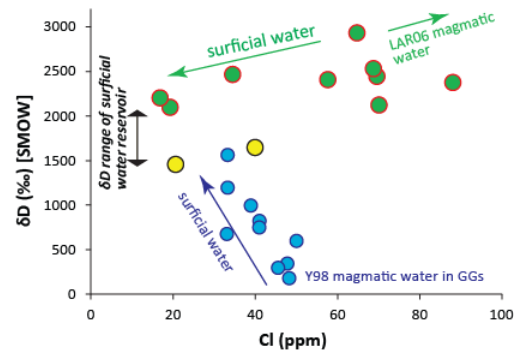


Fig. 2: Correlations between  $\delta D$  and Cl. Symbols as Fig. 1. Distinct trends of IMs (LAR06 and EETA79) and Y98 GGs converge on a moderate  $\delta D$  range (~1500-2000‰) regardless of the distinct  $\delta D$  of their magmatic sources.

**References:** [1] Malin, M.C. and Edgett, K.S. (2000) *Science*, 288, 2330-2335. [2] Baker, V.R. (2001) *Nature*, 412, 228-236. [3] Jakosky, B.M. and Phillips, R.J. (2001) *Nature*, 412, 237-244. [4] Usui, T., et al. (2012) *EPSL*, 357-358, 119-129. [5] Rao, M.N., et al. (2011) *JGR*, 116, E08006. [6] Treiman, A.H., et al. (2000) *Planet. Space Sci.*, 48, 1213-1230. [7] Usui, T., et al. (2008) *GCA*, 72, 1711-1730. [8] Symes, S.J.K., et al. (2008) *GCA*, 72, 1696-1710. [9] Hauri, E., et al. (2002) *Chem. Geol.*, 183, 99-114. [10] Hauri, E.H., et al. (2006) *EPSL*, 248, 715-734.