

## EVIDENCE FROM OLIVINE-HOSTED MELT INCLUSIONS THAT THE MARTIAN MANTLE HAS A CHONDRITIC D/H RATIO AND THAT SOME YOUNG BASALTS HAVE ASSIMILATED OLD CRUST.

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**Introduction:** Magmatic degassing of volatile elements affects the climate and near-surface environment of Mars. Telescopic and meteorite studies have revealed that the Martian atmosphere and near-surface materials have D/H ratios ~5-6 times terrestrial values [e.g., 1, 2]. Such high D/H ratios are interpreted to result from the preferential loss of H relative to heavier D from the Martian atmosphere, assuming that the original Martian water inventory had a D/H ratio similar to terrestrial values and to H in primitive meteorites [e.g., 1, 3]. However, the primordial Martian D/H ratio has, until now, not been well constrained. The uncertainty over the Martian primordial D/H ratio has arisen both from the scarcity of primitive Martian meteorites and as a result of contamination by terrestrial and, perhaps, Martian surface waters that obscure the signature of the Martian mantle.

This study reports a comprehensive dataset of magmatic volatiles and D/H ratios in Martian primary magmas based on low-contamination, *in situ* ion microprobe analyses of olivine-hosted melt inclusions from both depleted [Yamato 980459 (Y98)] and enriched [Larkman Nunatak 06319 (LAR06)] Martian basaltic meteorites. Analyses of these primitive melts provide definitive evidence that the Martian mantle has retained a primordial D/H ratio and that young Martian basalts have assimilated old Martian crust.

**Samples:** Olivine-hosted melt inclusions (MIs) from Y98 and LAR06, are interpreted to represent unfractionated Martian melts [e.g., 4, 5]. Y98 and LAR06 are petrographically similar in that they both contain magnesian olivine phenocrysts in chemical equilibrium with their bulk-rock compositions, but they 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 and not affected by crustal assimilation [e.g., 4]. Unlike other shergottites, Y98 has quenched groundmass glass (GG) and glassy MIs devoid of secondary daughter crystals because of rapid cooling during eruption (>1000°C/hr) [6]. In contrast, LAR06 is interpreted to represent a melt from a geochemically enriched source [e.g., 5]. Note that the origin of the enriched source is controversial. Either a geochemically-enriched mantle source or crustal assimilation by a basalt from a depleted

mantle source are both plausible. In contrast to Y98, LAR06 has MIs that are mostly filled with secondary daughter crystals, such as pyroxenes.

**Methods:** We have developed a sample preparation method without using epoxy. Epoxy penetrates into fractures of Martian meteorites and becomes an ubiquitous and unavoidable contamination source. We greatly reduced contamination by embedding our samples in liquid indium metal while under vacuum. The potential effects of contamination were further assessed by detailed petrographic observations and by checking C and H secondary ion images.

Hydrogen isotope compositions and the abundances of volatile elements of MIs and GGs in indium-mounted samples of Y98 and LAR06 have been measured using an ion microprobe (Cameca ims-6f) at DTM-CIW, following the techniques of [7, 8].

**Results and Discussions:** Y98 MIs contain distinctly higher H<sub>2</sub>O and CO<sub>2</sub> contents than Y98 GGs that were quenched near the surface [6], and yet, both have similar F concentrations (Fig. 1). Such differences are best explained by loss of H<sub>2</sub>O and CO<sub>2</sub> during eruption, whereas F was not significantly degassed. Therefore, fluorine can be used as an indicator of the degree of crystal fractionation (primarily olivine + pyroxene), and the consistency of F/H<sub>2</sub>O ratios in the Y98 MIs (Fig. 1b) suggests that the Y98 MIs contain their original volatile contents. The maximum CO<sub>2</sub> concentration (1600 ppm) in the Y98 MIs implies the depth of MI-entrapment to be ~3 kbar, which translates to ~30 km, in the mid to lower crust.

A MI in LAR06 has considerably higher F and H<sub>2</sub>O but lower CO<sub>2</sub> (240 ppm) contents than the Y98 MIs (Fig. 1a). These volatile abundances are partly attributable to post-entrapment crystallization of daughter crystals and/or inward growth of host olivine within the MI. But, the lower-CO<sub>2</sub> implies that the LAR06 MI was likely trapped at considerably shallower depth than the Y98 MIs. It is also likely that a higher F/H<sub>2</sub>O ratio in the LAR06 MI than in the Y98 MIs reflects the incompatible-element-rich nature of the primary LAR06 melt.

The MI measured in LAR06 has a high  $\delta D$  value (5079±11‰) (Fig. 2). The high- $\delta D$  water in the LAR06 MI represents a D-enriched, near-surface or atmospheric component on Mars. Previous estimates of the D-enriched component in shergottites

(>~3000‰) were obtained from late-stage magmatic phases (e.g., apatite) [e.g., 2], whereas our high- $\delta D$  value records an early-stage LAR06 melt that has sampled a geochemically enriched reservoir. Our study, therefore, demonstrates that the LAR06 parent melt assimilated crustal materials that had interacted with the Martian atmosphere, rather than originating in an enriched mantle in the deep interior.

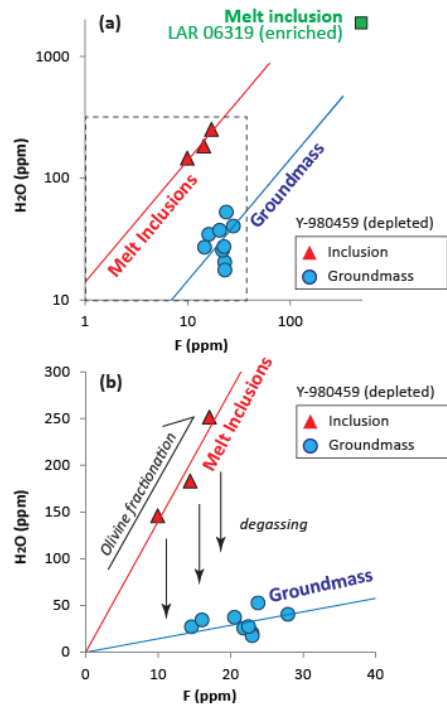


Fig. 1:  $H_2O$  and  $F$  contents in Y98 MI, Y98 GG, and LAR06 MI. Hatched area in (a) is enlarged in (b). Red and blue lines are linear regression lines of Y98 MIs and GGs, respectively.

In contrast to LAR06, the MIs from Y98 have nearly chondritic  $\delta D$  values ( $275 \pm 10\%$ ) (Fig. 2). Since the volatiles contents in Y98 MIs are high and appear to have been undegassed with constant  $F/H_2O$  ratios, it is unlikely that the  $\delta D$  values of the Y98 MIs are disturbed by terrestrial water contamination. Spallation effects on H isotopes by galactic cosmic rays during the meteorite transport to Earth are also expected to be insignificant because cosmic-ray exposure ages are short (typically <2 Ma). Kinetic processes of isotope fractionation, such as diffusive loss through host-olivine crystals, increase D/H ratios of water left behind, so that the measured  $\delta D$  values ( $275 \pm 10\%$ ) yield upper limits for the initial hydrogen isotope compositions of the MIs. Thus, the low- $\delta D$  values of primary magmatic water in the Y98 MIs represent an upper limit for the geochemically depleted mantle source.

The Y98 GGs exhibit a large  $\delta D$  range of ~200-800‰ and a linear negative correlation between  $\delta D$  and  $F/H_2O$  (Fig. 2). This correlation with such a large  $\delta D$  variation cannot be produced by degassing or magmatic crystal fractionation processes. Kinetic fractionation would produce increased D/H values with decreasing water contents [i.e., in contrast to Fig. 2] and magmatic processes do not fractionate  $F/H_2O$  values to this degree. Alternatively, the data may reflect two component mixing on Mars: i.e., near-surface high- $\delta D$  and magmatic low- $\delta D$  (~200‰, similar to the Y98 MIs) components. The lowest  $F/H_2O$  GGs appear to have formed by a two-stage process where magmatic degassing increased the  $F/H_2O$  ratio and then assimilation of crustal water both lowered the  $F/H_2O$  ratio and increased D/H.

The origin of water in the terrestrial planets has been debated. Two extreme cases are envisioned: wet accretion of chondrite-like materials vs. dry accretion followed by the addition of volatile-rich materials (e.g., comets) [9]. The near-chondritic  $\delta D$  value determined herein for the Martian mantle is not consistent with a cometary origin [ $\delta D = \sim 1000\%$ , cf., [10]], but rather indicates that carbonaceous chondrite-like materials were the likely source of primordial Martian water.

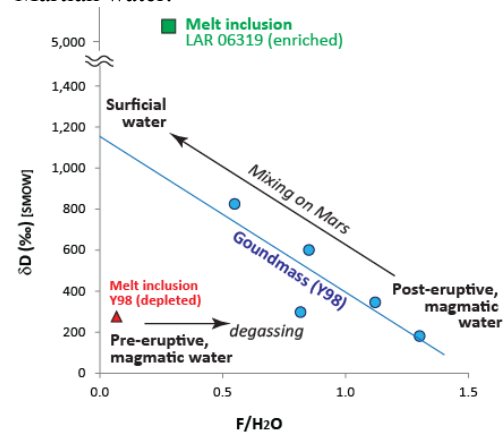


Fig. 2:  $\delta D$  versus  $F/H_2O$  diagram. Symbols as in Fig. 1.  $\delta D = [(D/H)_{\text{sample}}/(D/H)_{\text{reference}} - 1] \times 1000$ , where the reference is Standard Mean Ocean Water (SMOW).

**References:** [1] Owen, T., et al. (1988) *Science*, 240, 1767-1770. [2] Greenwood, J.P., et al. (2008) *GRL*, 35, doi: 10.1029/2007GL032721. [3] Jakosky, B.M. and Phillips, R.J. (2001) *Nature*, 412, 237-244. [4] Usui, T., et al. (2008) *GCA*, 72, 1711-1730. [5] Basu Sarbadhikari, A., et al. (2009) *GCA*, 73, 2190-2214. [6] Greshake, A., et al. (2004) *GCA*, 68, 2359-2377. [7] Hauri, E., et al. (2002) *Chem. Geol.*, 183, 99-114. [8] Hauri, E.H., et al. (2006) *EPSL*, 248, 715-734. [9] Albarede, F. (2009) *Nature*, 461, 1227-1233. [10] Hartogh, P., et al. (2011) *Nature*, 478, 218-220.