WATER CONTENT AND δD OF THE MARTIAN MANTLE FROM FTIR AND SIMS ANALYSES OF NAKHLITES.

A. H. Peslier[1], R. Hervig[2], S. Yang[3], J. J. Barnes[4], M. Humayun[3], A.J. Irving[5], and A.D. Brandon[6], [1]Jacobs, NASA-Johnson Space Center, Mail Code X13, Houston TX 77058, USA, anne.h.peslier@nasa.gov, [2]School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA (richard.hervig@asu.edu), [3]National High Magnetic Field Lab, Florida State University, Tallahassee, FL 32310, USA (humayun@magnet.fsu.edu; syang@magnet.fsu.edu), [4]ARES, NASA-Johnson Space Center, Houston TX 77058, USA (jessica.j.barnes@nasa.gov), [5]Dept. of Earth & Space Sciences, University of Washington, Seattle, WA, USA (irvingaj@uw.edu), [6]Dept. of Earth and Atmospheric Sciences, University of Houston, Houston, TX 77204, USA (abrandon@Central.uh.edu).

Introduction: Our models of solar system formation and of the evolution of inner solar system planets depend on knowing the amount of water they contain [e.g. 1,2]. Moreover, hydrogen (H) isotopes can help pinpoint the source material that brought volatiles to these planets [e.g. 1]. Finally, water influences key chemical and physical properties of rocks, such as melting temperature, viscosity and thermal conductivity [3-6], which are crucial parameters used to understand the long-term evolution of differentiated planets and their volcanism. The content and origin of water are of course best known for Earth [e.g. 7], but we need to determine that of other differentiated planets, and the present work targets Mars.

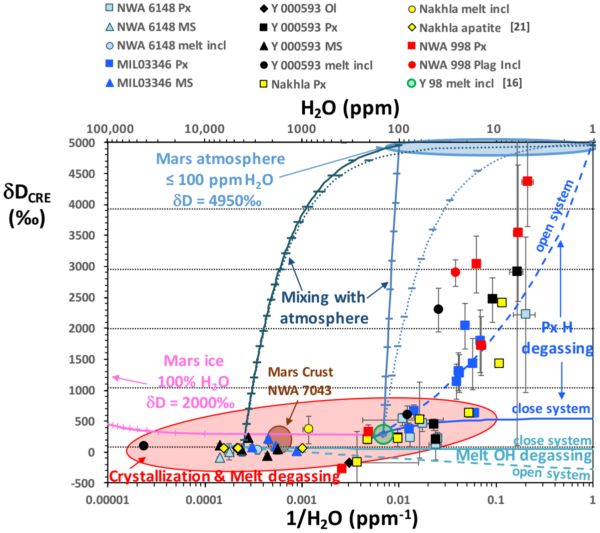
To determine how much water the interior of Mars contains and what its D/H ratio is, we can analyze Martian meteorites. There are two caveats to this type of study: 1) they all come from the crust [8], and thus extrapolations are needed to calculate the water content of the mantle, and they could have been affected by degassing and surface processes (hydrothermal or alteration), 2) they are meteorites and thus their H content or δD could have been disturbed during shock and during their transit in space between Mars and Earth.

Here, nakhlites, clinopyroxenites from Mars, are targeted because this suite of meteorites may derive from the same lava flow or shallow magma chamber on Mars and may have been ejected from the planet by one impact event, as evidenced by their similar compositions, crystallization (~1.3 Ga) and space exposure (~11 My) ages [e.g. 9-11]. Also, nakhlites are the least shocked martian meteorites [12]. Five well-characterized nakhlites were analyzed for water content and H isotopes: Northwest Africa (NWA) 998, Nakhla, Yamato (Y) 000593, Miller Range (MIL) 03346 and NWA 6148.

Methods: Hand-picked pyroxene, olivine and mesostasis pieces were polished without glue or lubricant. They were analyzed by FTIR (water content and speciation), electron microprobe (major elements), SIMS (water content and H isotopes), SEM (SIMS crater examination) and LA-ICPMS (trace elements). Traverses across pyroxenes were made with all these in situ techniques.

Results and interpretation: In all nakhlites, the SIMS data exhibit a trend from high water content (thousands of ppm H_2O) and low δD (< 200 ‰), mainly in the mesostasis and mixed-phase melt inclusions but also in a few pyroxene grains with hundreds of ppm H_2O, to low water contents (< 10 ppm H_2O) and high δD (≥1000 ‰), in most pyroxenes and a couple of inclusions (Fig. 1). The low-water content, high-δD side of the correlation appears to be best explained by water loss (as H and D) from already crystallized pyroxenes during degassing, after eliminating other processes such as interaction with the martian atmosphere, alteration by low temperature or hydrothermal fluids, shock, surface alteration, and hydrothermal processes. Degassing is consistent with the observation that pyroxenes with < 20 ppm H_2O have lower water content at their edge compared to their interior, independently of content variations of slower diffusing major elements. The high-water, low-δD side of the correlation is consistent with melt OH degassing.

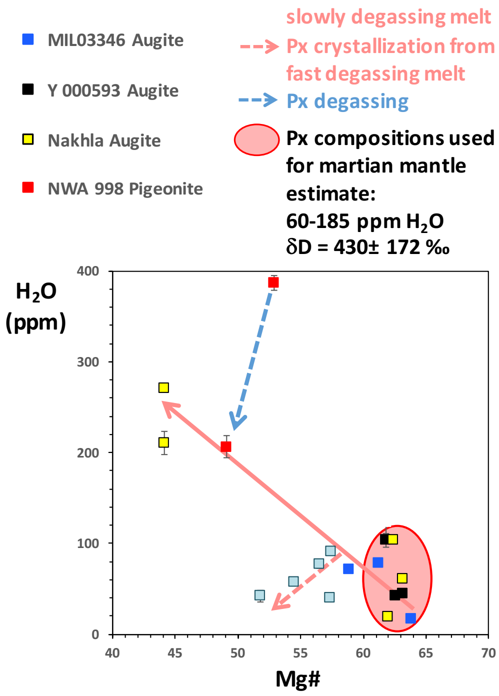
Fig. 1: Water content (ppm H_2O) and δD (‰), blank and cosmic ray exposure (CRE) corrected [13], of nakhlite pyroxene, melt inclusions (melt incl) and mesostasis (MS). Mixing models with martian atmosphere [14] and ice [15], and degassing models are also shown.



Water content and δD of the Martian mantle: Some pyroxenes, however, appear to have preserved their pre-degassing water content and δD, as evidenced in co-correlations of major, trace elements and water contents (Fig. 2). The least degassed, most Mg-rich augites of the nakhlites analyzed here allow us to estimate that the nakhlite mantle source has a δD of 430 ± 172 ‰ and a water content of ~60-185 ppm weight H_2O.

The mantle source of the shergottites, the mafic to ultramafic suite of martian meteorites, is estimated to have a similar δD within uncertainties (275 ± 10 ‰) but a lower water content (15-46 ppm H_2O), making the broad assumption that these values from a melt inclusion in depleted shergottite Yamato (Y) 980459 are representative of the whole suite [16]. The shallow part of the Earth's upper-mantle has similar water contents to the nakhlite and shergottite sources. The δD of the Earth's mantle [7,17-20], however, is significantly lower (-20 to -218 ‰) than that of Mars (Fig. 3). It is difficult to explain the H isotope difference between the two planets by invoking magma ocean degassing processes. Instead, the discrepancy between the δD of Earth and Mars may have arisen from acquiring their water from different proportions of water-rich planetisimals (likely carbonaceous chondrites), with Mars having more CO and Tagish Lake-like material while Earth may have more CM-like material.

Fig. 2: Water contents (ppm H_2O) and Mg# (Mg/(Mg+Fe)) in least degassed nakhlite pyroxenes.



References: [1] Alexander (2017) *PTRS A* **375**.
[2] Sharp (2017) *CG* **448**, 137-150.
[3] Mackwell *et al.* (1985) *JGR* **90**, 11319-11333.
[4] Hofmeister (2004) *PEPI* **146**, 483-495.
[5] Médard & Grove (2006) *JGR* **111**, E11003.
[6] Morschhauser *et al.* (2011) *Icarus* **212**, 541-558.
[7] Peslier *et al.* (2017) *SSR* **212**, 743-811.
[8] McSween Jr. (2015) *AM* **100**, 2380-2395.
[9] Nyquist *et al.* (2001) *SSR* **96**, 105-164.
[10] Treiman (2005) *CE* **65**, 203-270.
[11] McCubbin *et al.* (2013) *MAPS* **48**, 819-853.
[12] Fritz *et al.* (2005) *MAPS* **40**, 1393-1411.
[13] Füri *et al.* (2017) *EPSL* **474**, 76-82.
[14] Owen *et al.* (1988) *Science* **240**, 1767-1767.
[15] Usui *et al.* (2015) *EPSL* **410**, 140-151.
[16] Usui *et al.* (2012) *EPSL* **357-358**, 119-129.
[17] Deloule *et al.* (1991) *EPSL* **105**, 543-553.
[18] Bell & Ihinger (2000) *GCA* **64**, 2109-2118.
[19] Shaw *et al.* (2012) *Nature Geoscience* **5**, 224-228.
[20] Hallis *et al.* (2015) *Science* **350**, 795-797.
[21] Hallis *et al.* (2012) *EPSL* **359-360**, 84-92.
[22] Kerridge (1985) *GCA* **49**, 1707-1714.
[23] Mathew & Marti (2005) *JGR* **110**, E12S05 1-8.
[24] Mathew *et al.* (2003) *EPSL* **214**, 27-42.
[25] Cartigny & Marty (2013) *Elements* **9**, 359-366.
[26] Geiss & Gloeckler (1998) *SSR* **84**, 239-250.
[27] Marty *et al.* (2011) *Science* **332**, 1533-1536.
[28] Altwegg *et al.* (2014) *Science* **347**, Sciencexpress

Fig. 3: Hydrogen (δD in ‰) and nitrogen ($\delta^{15}N$ in ‰) isotopes of the martian mantle compared to those of the Earth's mantle and of carbonaceous chondrites [1,7,16-20,22-25]. The shergottite mantle δD derives from that of a melt inclusion from depleted shergottite (D. sherg.) Y 980459 [16]. Bulk solar and comets δD and $\delta^{15}N$ are also shown [1,26-28 and references therein].