

EVOLUTION OF WATER ON MARS THROUGH TIME: NEW CONSTRAINTS ON MARTIAN WATER RESERVOIRS FROM HYDROGEN ISOTOPES IN YOUNG AND OLD MARTIAN METEORITES.

James. P. Greenwood¹, Shoichi Itoh², Naoya Sakamoto², Edward P. Vicenzi³ and Hisayoshi Yurimoto², ¹Dept. of Earth & Environmental Sciences, Wesleyan University, Middletown, CT 06459 (jgreenwood@wesleyan.edu),

²Dept. of Natural History Sciences, Hokkaido University, Sapporo 060-0810, Japan, ³Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, Washington, DC 20560-0119.

Introduction: The hydrogen isotope ratio (D/H) of the various water reservoirs on Mars and their evolution through time is of paramount importance to our understanding of water on Mars. Conceivably, the D/H ratio can be used as a tracer for the temporal evolution of water reservoirs on Mars (polar caps and seasonal ice, regolith ice, atmospheric water vapor and mantle water) if the initial and current D/H values are known. We have recently measured D/H in Martian meteorites ALH84001, Los Angeles, and Shergotty and have found the highest values yet reported for these meteorites (Fig. 1; [1]). Here we review these measurements and model possible evolution of Martian water reservoirs using these new D/H values. We suggest our measurements of D/H in Shergotty apatite may be representative of the largest reservoir of surface water, regolith ice. Our measurements of ALH84001 appear to represent the D/H of Mars at 4.5 Ga or 3.9 Ga, and suggest that early hydrodynamic escape of hydrogen (i.e. loss of water during accretion) left the Martian water inventory much more fractionated with respect to hydrogen isotopes than previously thought. Our work on Los Angeles using 2D hydrogen isotope mapping sheds light on the mechanism of crust/regolith ice exchange, which suggests assimilation during emplacement of the basaltic shergottite magmas in the uppermost crust.

Hydrogen isotopes through time on Mars:

Ancient Mars. Our results for D/H in ALH84001 (see Appendix) suggest that the Martian mantle achieved a highly fractionated D/H ratio of 4 x terrestrial (SMOW) by 4.5 Ga or 3.9 Ga. A δD value of $\sim +3000\text{\textperthousand}$ for a Martian water reservoir by 4.5 Ga would strongly suggest that the majority of water was lost from Mars by this time. A plausible mechanism for the loss of the majority of Martian water by 4.5 Ga (crystallization age from Sm-Nd [2]) would be hydrodynamic escape of hydrogen during accretion [3,4]. This is much earlier than estimates for the loss of the majority of Martian water from those obtained from geomorphology [5]. To reconcile these two results would require that Mars accreted significantly more water than currently envisioned (i.e. Mars could lose a great deal of water by 4.5 Ga, but there was still enough water left to create the fluvial features seen on the Martian surface). Alternatively, the D/H we measured in ALH84001 was set during later hydrothermal

activity (such as that which formed the carbonates in ALH84001 [6]) and that the D/H was recorded by 3.9 Ga (Ar-Ar age for ALH84001 interpreted to be due to shock [7]).

Younger Mars. Our values for δD of $\sim +4600\text{\textperthousand}$ in Shergotty (see Appendix) are 400% higher than spectroscopic measurements of the current Martian atmosphere [7]. Several possible reasons for this can be postulated: (1) it is possible that the current Martian atmosphere is $+4600\text{\textperthousand}$, since our results are within 2σ of the spectroscopic measurement [8]; (2) the atmosphere has become lower in D/H since the Shergotty magma crystallized 165 Ma [9]; 3) the crustal water incorporated by the Shergotty magma was not from the atmosphere, but from another water reservoir, such as regolith ice, which is heavier than the current Martian atmosphere. We cannot rule out scenario (1) at this time. Scenario (2) might require input of juvenile water since 165 Ma to the Martian atmosphere, but D/H fractionations between ice and vapor are large at Martian temperatures [10], thus 400% or greater differences in δD might not be that rare on Mars.

Scenario (3) is intriguing in that the Shergotty magma probably assimilated crustal material, and that we now know that the regolith is likely the dominant surface reservoir for water on Mars [11]. If regolith ice was assimilated, and we are measuring the hydrogen isotope signature of that ice in Shergotty, then we can possibly theorize on the history of Martian water from this signature in Shergotty. Obviously, a number of assumptions must be realized for this analysis to be valid (such as the signature measured in Shergotty is that of regolith ice and is representative of the planetary inventory of said ice), but it is a useful exercise nonetheless and is considered below.

Constraints on Martian water reservoirs:

Mars Surface Water. By 3.9 Ga, Martian water must have largely been dissipated to space to rationalize the δD of $\sim +3000\text{\textperthousand}$ we measure in ALH84001. A Martian water reservoir sampled by the 165 Ma Shergotty magma had a δD of $+4600\text{\textperthousand}$ (or higher if we are measuring a mixture of magmatic and crustal water).

Mars Mantle Water. It is within the realm of possibility that the Martian mantle is $+3000\text{\textperthousand}$, since this is the lowest value we measure in our study, and the value we measure could be representative of magmatic water at 4.5 Ga during crystallization of the apatite.

The lowest value we measure in Los Angeles (also 165 Ma) is +3500‰, consistent with a Martian mantle of 3000-3500‰. Previous work has suggested that δD is correlated with H₂O content in apatite [12], and this relationship could be used to estimate D/H of the Martian mantle, but we see no such correlation in our measurements of apatite (Fig. 2). The Martian mantle has been suggested to be similar to the terrestrial in D/H [13, 14]; if so, then a mechanism other than hydrodynamic escape is likely needed to explain the elevated D/H we measure in ALH84001.

Evolution of regolith ice D/H through time: We assume here that the majority of the current Martian water inventory has been in the form of ice for the last 4 billion years. We model the loss of Martian water via Rayleigh fractionation using ice-vapor hydrogen isotope fractionation factors at 253K [10]. Results are shown in Figure 3 for initial ice with the terrestrial value, and also with an initial value of $\delta D = +3000\text{‰}$ (4xSMOW). If D/H of ice was originally equivalent to terrestrial, then >99.9999% of Martian ice would need to have sublimated to give the values we measure in Shergotty. A more realistic scenario is that regolith ice originally had a value of +3000‰, set by water loss to space during accretion. Ice with this value ~4 Ga would need to have undergone only 90% sublimation and subsequent loss to space in the last 4 Ga to give the values we measure in Shergotty at 165 Ma. Current inventories of regolith ice are unknown, but could be equivalent to a global layer 500-1500 m of water if surface ice inventories can be extrapolated to the regolith [11].

Conclusions: Our results for ALH84001 strongly suggest that the Martian water reservoir was fractionated to δD of +3000‰ by 3.9 Ga, and possibly by 4.5 Ga. The most likely mechanism to explain this elevated D/H would be via hydrodynamic escape during accretion. Our results for Shergotty suggest that Martian crustal water had a δD value of +4600‰ at 165 Ma. If regolith ice is the source of the crustal water assimilant for Shergotty, then constraints can be placed on the hydrogen isotope evolution of the crustal water reservoir (presumably in the form of regolith ice). We find that if Martian crustal water was +3000‰ by 3.9 Ga, and if the major Martian water reservoir has been regolith ice since that time, then only 90% of the water inventory has been lost from Mars since 3.9 Ga.

APPENDIX:

Mars Meteorite Methods: We studied the hydrous phosphate mineral apatite in these three meteorites by a combination of optical microscopy, FEG-SEM/BSE/EDS (SI/Yale), WDS-EPMA (Yale), and FEG-CL (cathodoluminescence) (SI). We then undertook hydrogen isotope imaging using the Hokudai

Cosmochemistry Cameca ims 1270 w/ SCAPS [15]. This technique allows for 2D ion imaging (called isotopography). We also undertook ion probe spot analyses of hydrogen isotopes.

Mars Meteorite Results and Discussion:

ALH84001. A chlorapatite grain was analyzed by the above methods. A $\delta D = +2998 \pm 68\text{‰}$ (1σ) was obtained from ion probe spot analysis. This value is >900‰ higher than previous measurements of D/H in this ancient meteorite [16-18].

ALH84001 has been dated at 4.50 ± 0.13 Ga via Sm-Nd [2] and a shock event is recorded at 3.9 Ga in Ar-Ar [7]. Paleotemperature calculations suggest that ALH84001 has likely not been heated above ambient Mars conditions since the 3.9 Ga shock event [19]. The lack of heating of ALH84001 argues that hydrogen isotopes have not been reset in this apatite grain since 3.9 Ga. It is unknown if the D/H value we measure represents the D/H value during igneous crystallization, or whether D/H has been exchanged during the hydrothermal activity that formed the carbonate globules [6]. The D/H value we measure in ALH84001 suggests that either the Martian mantle water or the atmospheric/crustal water reservoirs had become highly fractionated by 3.9 Ga, and that most of the water on Mars was lost by this time. It is also possible that D/H in this apatite represents the Martian mantle value at 4.5 Ga, which would suggest that a significant fraction of Martian water was lost to space during hydrodynamic escape as a consequence of accretion.

Shergotty. Two apatite grains were measured for D/H in separate analytical sessions. The values were identical within analytical error ($\delta D = +4606 \pm 25\text{‰}$; $+4590 \pm 31\text{‰}$ (1σ)). These values are 300‰ higher than any previously reported D/H in Martian meteorites [12-14, 16-18, 20], and 400‰ higher than spectroscopic measurements of the current Martian atmosphere [8].

Shergotty was likely emplaced as a magma into the Martian crust at shallow depths. The value for D/H we measure in Shergotty likely represents a sample of a Martian crustal water reservoir incorporated during crystallization of the magma at 165 Ma [9].

Los Angeles. More extensive work was undertaken on this meteorite due to less fracturing than Shergotty, and also having a number of large apatite grains (unlike ALH84001, where only one apatite grain was found in 13 thin-sections that JPG has studied since 1996). Three grains of apatite in two thin-sections were studied. In UCLA 750, one large apatite grain was studied. In UCLA 748, two petrographically related apatite grains were studied.

UCLA 750: This large apatite grain was found to be zoned from core-to-rim in fluorine and chlorine. A

monotonic increase in chlorine with a concomitant decrease in fluorine is seen in electron microprobe traverses from core-to-rim of this grain. This F/Cl zoning is readily apparent in cathodoluminescence imaging. Two SCAPS measurements were made on separate portions of this grain, which encompassed the entire range of core-to-rim variation. The SCAPS image shows no hydrogen isotope zoning. Two ion probe spot analyses from these two SCAPS spots are identical within error ($\delta D = +3468 \pm 26\%$; $+3475 \pm 33\%$ (1σ)). Thus, for this grain, no hydrogen isotope zoning or variation is seen, despite a large change in F/Cl composition. The F/Cl zoning appears to be due to igneous growth.

UCLA 748: A very different scenario is seen in this section. We performed SCAPS on a small apatite grain with apparent F/Cl zoning. In this grain, we find that hydrogen isotopes are zoned, and that they appear to be correlated with the F/Cl igneous growth zoning. An $\sim 500\%$ difference in δD is seen within the SCAPS spot. Two ion probe spots were undertaken in this SCAPS spot: one in the fluorine-rich core, and another that overlapped onto the prominent fracture in the image. The fluorine-rich core had a $\delta D = +4120 \pm 35\%$ (1σ). The spot analysis that overlapped onto the crack was significantly lower with a $\delta D = +2876 \pm 53\%$ (1σ). The fractures in the Martian meteorites are a significant source of terrestrial contamination, and will yield a mixture of Martian hydrogen and terrestrial hydrogen from contamination when measured. The SCAPS technique allowed for us to make fracture-free spot analyses in apatite grains. An apatite grain next to this grain had similar values to the fluorine-rich core analysis ($\delta D = +4122 \pm 26\%$; $+3947 \pm 34\%$), but we did not perform SCAPS on this grain, and cannot be certain that these analyses were free from terrestrial contamination.

In Los Angeles, we find very different results in two areas of the meteorite, which suggests that hydrogen isotopes are variable on the μm to cm scale. The correlation of increasing chlorine and increasing D/H in what appears to be igneous growth zoning seen in one apatite grain of Los Angeles, coupled with the spatial heterogeneity between thin-sections suggests a model involving variable assimilation of water with a high D/H during crystallization of the apatite. A petrographic model developed for Zagami suggests that apatite crystallizes very late in the basaltic shergottites (>95% crystallization) and that apatite crystallizes in isolated late-stage melt along with other late-stage minerals [21]. We use this model to explain our observations. We propose a model for the incorporation of water into the basaltic shergottites that involves assimilation of a Cl-enriched and D-enriched compo-

ment during the latest stages of magmatic crystallization of the basaltic shergottites, upon emplacement in the uppermost crust. This assimilation was rapid and variable. In one region of Los Angeles (UCLA 750), hydrogen isotopes were able to be homogenized before growth of this large apatite grain, while chlorine was not, likely due to higher diffusivity of chlorine relative to hydrogen in silicate melts. In another region of Los Angeles (UCLA 748), crystallization of apatite occurred coincident with assimilation, which led to water being incorporated by apatite before hydrogen isotopes were equilibrated in this late-stage melt pocket. Thus, in this grain, D/H and Cl increased during crystallization.

References: [1] Greenwood J. P., Itoh S., Sakamoto N., Vicenzi E. P. and Yurimoto H. (2007) *LPSC XXXVIII*, abst. #2134. [2] Nyquist L. E. et al. (2005) *LPSC XXVI*, 1065. [3] Zahnle K. et al. (1990) *Icarus*, 84, 502. [4] Dreibus G. and Wänke H. (1985) *Icarus*, 71, 225. [5] Carr M. H. (1996) *Water on Mars*, Oxford. [6] Valley J. W. et al. (1997) *Science*, 275, 1633. [7] Turner G. et al. *GCA*, 61, 3835. [8] Bjoraker G. L. et al. (1989) *Bull. Amer. Astron. Soc.* 21, 991 (abstract). [9] Nyquist L. E. et al. (1979) *GCA*, 43, 1057. [10] Friedman I. and O'Neil J. R. (1977) *USGS Prof. Paper* 440-KK. [11] Boynton W. V. et al. (2002) *Science*, 297, 81. [12] Leshin L. A. (2000) *GRL*, 27, 2017. [13] Gillet P. et al. (2002) *EPSL*, 203, 431. [14] Boctor N. Z. and Alexander C. M. O'D. *LPSC XXXVIII*, abst. #1801. [15] Yurimoto H. et al. (2003) *Appl. Surf. Sci.* 203-204, 793. [16] Boctor N. Z. et al. (2003) *GCA*, 67, 3971. [17] Leshin L. A. et al. (1996) *GCA*, 60, 2635. [18] Sugiura N. and Hoshino H. (2000) *Met. Planet. Sci.* 35, 373. [19] Shuster D. L. and Weiss B. P. (2005) *Science*, 309, 594. [20] Watson L. L. et al. (1994) *Science*, 265, 86. [21] McCoy T. J. et al. (1999) *GCA*, 63, 1249.

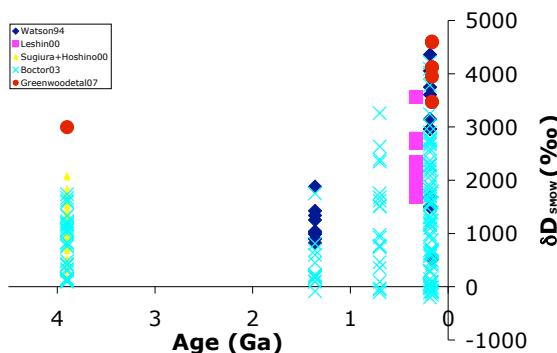


Figure 1. Ion microprobe data for Martian meteorites. Our data (red circles) are higher in dD than previous studies of these same meteorites. The most striking difference in the 3.9-4.5 Ga ALH84001 where our data are >900‰ than prior measurements [16, 18].

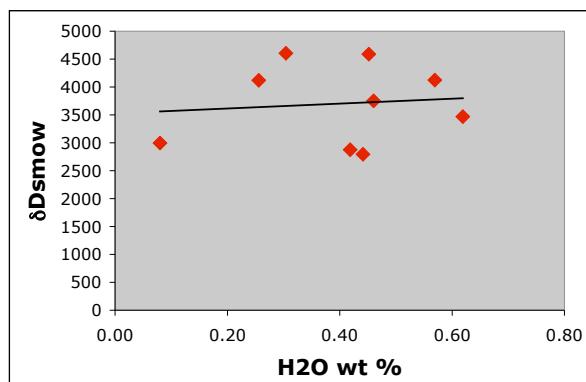


Figure 2. δD vs. H_2O wt % of our analyses of apatite in SNC's. Prior work has suggested that correlation between these parameters could be used to estimate Mars mantle D/H [12]. We see no correlation in these parameters and suggest that this is not a valid method for determining Mars mantle D/H.

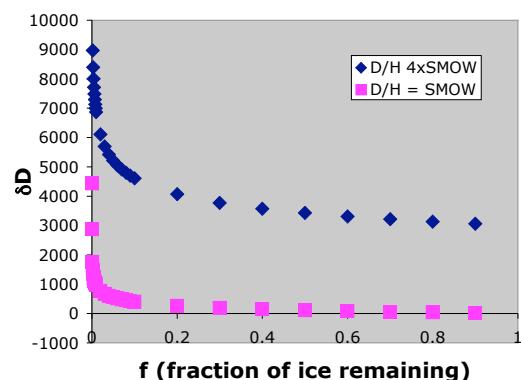


Figure 3. Deuterium enrichment due to Rayleigh fractionation of sublimating ice on Mars is modeled here for 2 initial conditions: Ice with the terrestrial value and ice with $dD = +3000\text{\textperthousand}$. See text for discussion.

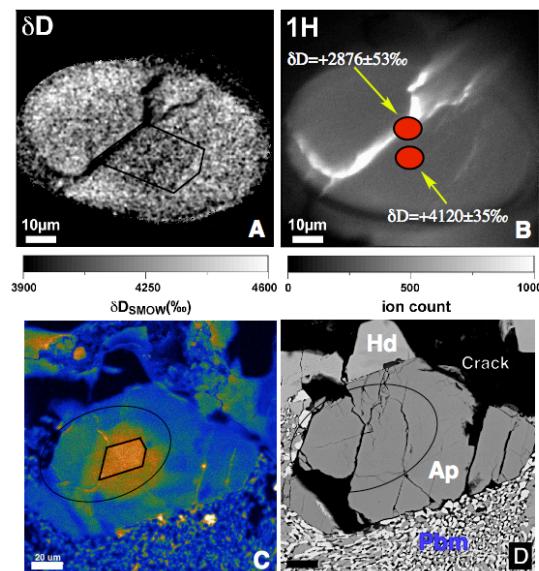


Figure 4. Ion and electron images of zoned apatite grain in UCLA 748. (A) δD image. Black box outlines the fluorine-rich core shown in (C), also as a black box. δD is enriched from core-to-rim in this grain with an ~500‰ variation seen in this image. (B) 1H image showing the two ion probe spot analyses. Spot analyses overlapping onto fractures always show much lower δD than crack-free analyses. (C) Panchromatic cathodoluminescence image. In the shergottitic apatites, we find that high CL intensity is correlated with high fluorine. This grain is zoned from a fluorine-rich core to chlorapatite rim. The characteristics of the zoning appear to be related to igneous growth zoning. Black box denotes the highest fluorine area and is also denoted in (A). Black ellipse shows location of SCAPS of (A) and (B). Scale bar is 20 μm . (D) BSE image of apatite grain, showing petrographic relations with late-stage crystallization materials such as hedenbergite (Hd) and pyroxferroite-breakdown material (Pbm). Black ellipse shows location of SCAPS in (A) and (B). Scale bar is 20 μm .