



## Hydrogen isotope evidence for loss of water from Mars through time

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[1] The high D/H of the Martian atmosphere ( $\sim 5\text{--}6 \times$  terrestrial) is considered strong evidence for the loss of Martian water to space. The timing and magnitude of the loss of water from Mars can be constrained by measurements of D/H in Martian meteorites. Previous studies of Martian meteorites have shown a large range in D/H, from terrestrial values to as high as the current Martian atmosphere. Here we show that the ancient ( $\sim 4$  Ga) Mars meteorite ALH84001 has a D/H  $4 \times$  terrestrial and that the young ( $\sim 0.17$  Ga) Shergotty meteorite has a D/H  $5.6 \times$  terrestrial. We also find that the young Los Angeles shergottite has zoning in D/H that can be correlated to igneous growth zoning, strongly suggesting assimilation of D-enriched water during igneous crystallization near the Martian surface. In contrast to previous studies, we find higher and less variable D/H ratios in these three meteorites. Our results suggest a two-stage evolution for Martian water—a significant early loss of water to space (prior to 3.9 Ga) followed by only modest loss to space in the last 4 billion years. The current Martian atmospheric D/H has remained essentially unchanged for the last 165 Ma. **Citation:** Greenwood, J. P., S. Itoh, N. Sakamoto, E. P. Vicenzi, and H. Yurimoto (2008), Hydrogen isotope evidence for loss of water from Mars through time, *Geophys. Res. Lett.*, 35, L05203, doi:10.1029/2007GL032721.

### 1. Introduction

[2] The large range of D/H measured in Martian meteorites ( $\delta D$ :  $-150\text{‰}$  to  $+4300\text{‰}$ ) [Watson *et al.*, 1994; Gillet *et al.*, 2002]; natural abundances of D/H are defined as  $\delta D = \{[(D/H)_{\text{sample}}/(D/H)_{\text{standard}}] - 1\} \times 1000$ , where the standard is Standard Mean Ocean Water (SMOW) is much larger than the range of  $\delta D$  for water on Earth ( $-480$  to  $+130\text{‰}$ , [Hoefs, 2004]) and has been ascribed to a mixture of Martian atmospheric water with either Martian magmatic water [Watson *et al.*, 1994; Leshin *et al.*, 1996; Leshin, 2000; Gillet *et al.*, 2002] or terrestrial water from contamination during analysis [Sugiura and Hoshino, 2000; Boctor *et al.*, 2003]. Another model invokes shock-induced fractionation of D/H to explain the heterogeneity found in Martian meteorites [Minitti *et al.*, 2007a, 2007b]. We used

an isotope microscope at Hokkaido University consisting of a Cameca ims 1270 ion microscope with a newly developed stacked CMOS-type active pixel sensor (SCAPS) detector [Yurimoto *et al.*, 2003] which allows unparalleled imaging (called isotopography) of hydrogen and deuterium within mineral grains with a spatial resolution of  $\sim 1$  micron to determine the hydrogen isotope distribution in the hydrous phosphate mineral apatite in Martian meteorites ALH84001, Shergotty, and Los Angeles. This 2-D ion imaging technique allowed us to find areas for spot analysis free of micro-fractures in these highly shocked materials; we found that the micro-fractures have significant terrestrial contamination and may be responsible for the lower and more variable D/H of previous studies [Watson *et al.*, 1994; Leshin *et al.*, 1996; Leshin, 2000; Sugiura and Hoshino, 2000; Gillet *et al.*, 2002; Boctor *et al.*, 2003]. We undertook this study with the goal of unraveling the origin of the highly variable D/H in Martian meteorites so that better constraints for D/H of Martian water reservoirs could be estimated. We also sought to evaluate the recent hypothesis that the young ages of Martian shergottites represent an acidic alteration event involving crustal fluids during recent warming events rather than igneous crystallization [Bouvier *et al.*, 2005].

### 2. Materials and Methods

[3] Polished thin-sections of meteorites Los Angeles (UCLA 748 and UCLA 750), Shergotty (USNM 321-1), and ALH84001 (ALH84001, 6) were carbon-coated for electron and ion microbeam analysis. Quantitative electron microprobe analyses were conducted at Yale University using established methods for the analysis of phosphates in Martian meteorites [Greenwood *et al.*, 2003]. Cathodoluminescence (CL) was conducted under high vacuum in a FEI Nova NanoSEM600 field emission scanning electron microscope at the Smithsonian Institution. Panchromatic CL imagery was obtained using a Gatan MonoCL3+/XiCLone system with an electron beam energy of 12 kV and a working distance of 7 mm, and a high-sensitivity photomultiplier tube detector.

[4] The Hokudai isotope microscope system (Cameca ims 1270 secondary ion mass spectrometer (SIMS) instrument and SCAPS ion imager) was applied to determine D/H ratios and H<sub>2</sub>O contents of apatite. For isotopography of hydrogen, the sample surface was homogeneously irradiated over an  $\sim 80$   $\mu\text{m}$  diameter area with a Cs<sup>+</sup> primary beam of 20 keV and a beam current of  $\sim 1$  nA. The negative secondary ion images of <sup>1</sup>H and <sup>2</sup>D on the sample surface were collected sequentially in a SCAPS for one analytical sequence with exposure times of 20 s for <sup>1</sup>H and 1600 s for <sup>2</sup>D (with a second <sup>1</sup>H image taken after the <sup>2</sup>D image to assess analytical stability). For spot analysis, a Cs<sup>+</sup> primary

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**Table 1.** Summary of Ion Microbeam Spot Analyses for D/H and Water Contents in Martian Apatites<sup>a</sup>

Sample	$\delta D$ (SMOW), ‰	$2\sigma$ Error, ‰	H <sub>2</sub> O, wt %
<i>Los Angeles</i>			
748-4core	4120	71	0.26
748-4rim	4340	54	0.24
748-4rim	4348	62	0.18
748-4crack	2876	106	0.42
748-3,54	4122	53	0.57
748-3,80	3947	73	0.46
750-11,1	3475	71	n.d.
750-11,2	3468	59	0.62
750-11,2crack	2794	65	0.44
<i>Shergotty</i>			
Sh7	4606	50	0.30
Sh8	4590	67	0.45
<i>ALH84001</i>			
Gr6	2998	138	0.08

<sup>a</sup>Two analyses on cracks show significantly lower  $\delta D$  than other analyses in the same grain.  $2\sigma$  error for  $\delta D$  includes error from counting statistics and reproducibility of the standard during the same analytical session. Relative error ( $1\sigma$ ) for H<sub>2</sub>O (wt %) is  $\sim 5\%$  for all. n.d., not determined.

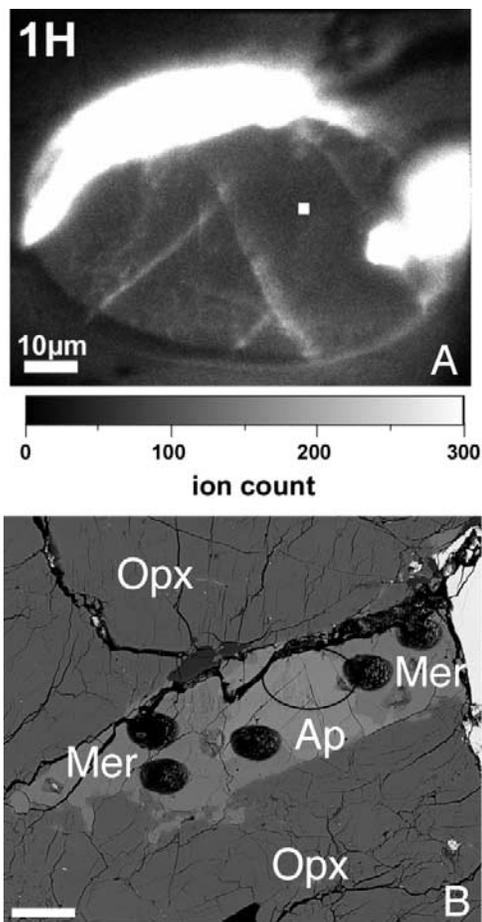
beam of 20 keV and  $\sim 3$  nA was focused to a beam spot of  $\sim 10$   $\mu\text{m}$  on the surface. In order to remove the signal of adsorbed water from the crater edge of the primary beam, secondary ions generated from the center of the primary beam irradiation area of 2  $\mu\text{m}$  square were collected using a field aperture of 200  $\mu\text{m}$  square. The negative secondary ions of <sup>1</sup>H and <sup>2</sup>D were collected sequentially in an electron multiplier at  $M/\Delta M$  of  $\sim 2300$ . After the hydrogen isotope analysis, H<sub>2</sub>O contents were immediately analyzed at the same spot under the same SIMS setting. The negative secondary ions of <sup>1</sup>H and <sup>18</sup>O were collected sequentially in an electron multiplier to calculate a <sup>1</sup>H/<sup>18</sup>O ratio. The H<sub>2</sub>O contents were corrected according to a calibration curve method against <sup>1</sup>H/<sup>18</sup>O ratios [Boctor *et al.*, 2003] using two terrestrial apatite standards of known composition determined by conventional gas mass spectrometry in the stable isotope facility at Yale University. One is 0.048 wt% H<sub>2</sub>O (Durango Apatite); another is 1.24 wt% H<sub>2</sub>O and  $\delta D = -116 \pm 4$  ( $1\sigma$ ) ‰ (Linopolis Apatite). D/H ratio was corrected with Linopolis apatite. The reproducibility of H<sub>2</sub>O contents was estimated to be about 5% relative error ( $1\sigma$ ). Typical reproducibility of D/H ratio for the standard measurements was  $\sim 10\%$  ( $1\sigma$ ).

### 3. Results

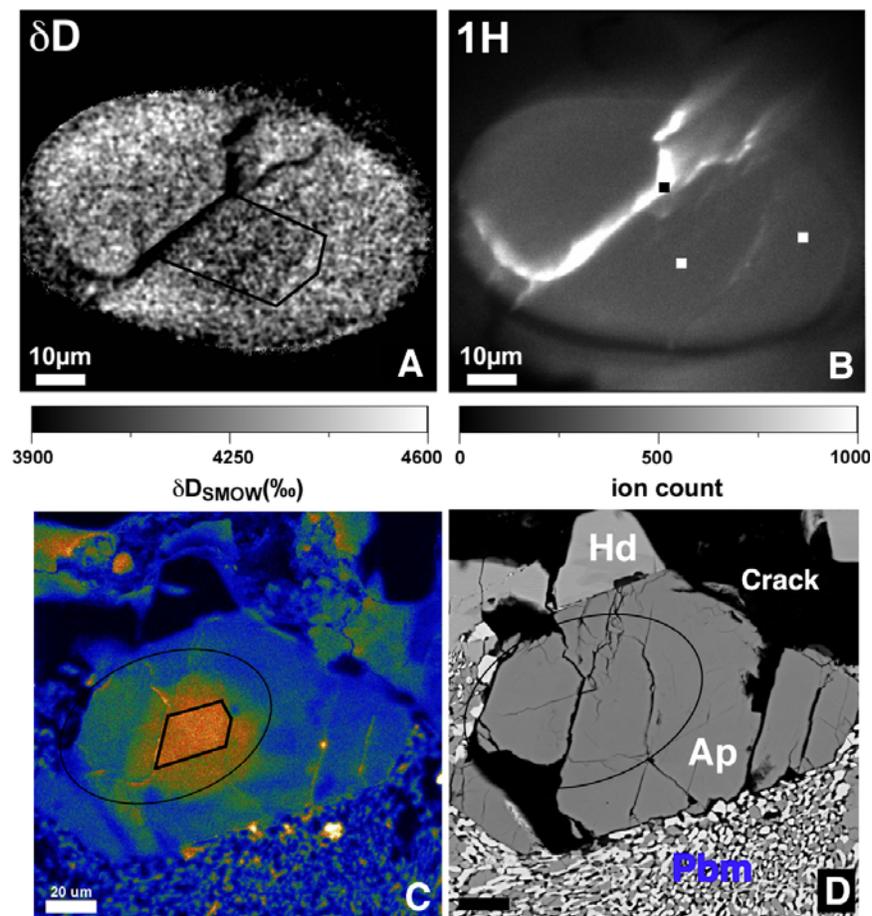
[5] We measured D/H in one chlorapatite grain in the ALH84001 meteorite (Table 1). The  $\delta D = +2998 \pm 138\%$  ( $2\sigma$ ) from a spot analysis is more than 900% higher than the highest previous measurements of D/H in this meteorite [Leshin *et al.*, 1996; Sugiura and Hoshino, 2000; Boctor *et al.*, 2003] and  $>2200\%$  higher than a previous measurement of D/H in this same mineral grain [Boctor *et al.*, 2003], illustrating the difficulties with measuring hydrogen isotopes in these highly shocked and fractured meteorites. The <sup>1</sup>H image shows abundant hydrogen, likely due to terrestrial contamination, in micro-fractures in the apatite grain (Figure 1). This apatite grain is included within a larger merrillite grain and associated with chromite and minor plagioclase glass [Greenwood *et al.*, 2003].

[6] Even though Shergotty is a fall, significant and pervasive terrestrial contamination was observed along intragrain micro-fractures. We measured D/H in two apatite grains that had areas large enough for a micro-fracture-free spot analysis. Our two spot measurements [ $\delta D = +4590 \pm 67\%$ ;  $+4606 \pm 50\%$  ( $2\sigma$ )] (Table 1) were obtained during different analytical sessions. These measurements are  $\sim 250\%$  higher than any previous measurements of D/H in a Martian meteorite [Watson *et al.*, 1994; Leshin *et al.*, 1996; Leshin, 2000; Sugiura and Hoshino, 2000; Gillet *et al.*, 2002; Boctor *et al.*, 2003]. The two chlorapatite grains analyzed are both associated with late-stage crystallization features, such as K-,Si-rich glass, Fe-Ti oxides and iron-rich pyroxenes.

[7] Three apatite grains were measured for D/H in the Los Angeles meteorite in two thin-sections (Table 1). Two of the apatite grains are adjacent to one another in thin-section UCLA 748. All three grains are zoned from fluo-



**Figure 1.** Ion and electron images of chlorapatite grain in ALH84001. (a) <sup>1</sup>H image. High hydrogen content can be seen on micro-fractures. The two large bright areas are a crack and an ion probe spot from a prior study. A white square (2  $\mu\text{m}$  across) corresponds to the spot analysis area of Gr6 in Table 1. (b) Backscatter electron image (BSE). The area of (A) is shown with a black ellipse. Five ion probe spots from another study [Boctor *et al.*, 2003] are seen as dark ovals in the phosphate grains. Scale bar is 50  $\mu\text{m}$ . Ap: apatite; Opx: orthopyroxene; Mer: merrillite.



**Figure 2.** Ion and electron images of Los Angeles apatite grain 748-4. (a)  $\delta D$  image. Area of high CL intensity is outlined with black lines. (b)  $^1H$  image. A black and two white (left and right) squares ( $2 \mu m$  across) correspond to the spot analysis areas of 748-4crack, 748-4core and 748-4rim in Table 1, respectively. (c) Panchromatic CL image with the area of Figures 2a and 2b outlined with the black ellipse. The area of highest CL intensity is outlined with black lines. (d) BSE image showing area of Figures 2a and 2b outlined with black ellipse. Scale bar is  $20 \mu m$ . Ap: apatite; Hd: hedenbergite; Pbm: pyroxferroite breakdown material.

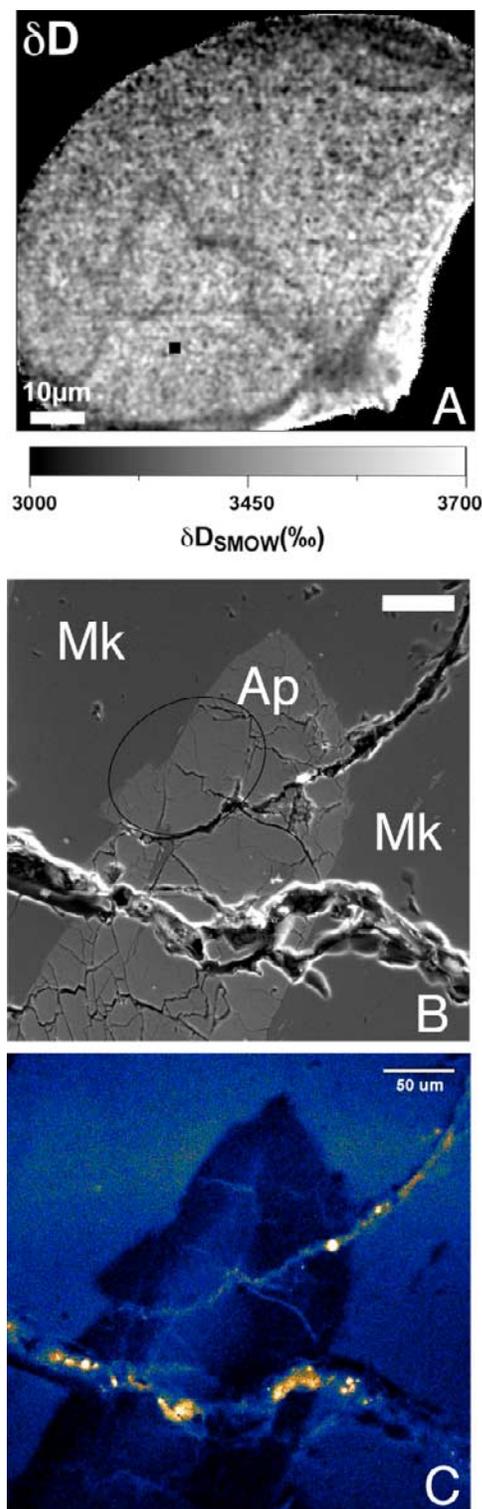
rapatite cores to chlorapatite rims, and are associated with K-,Si-rich glass, Fe-Ti oxides and pyroxferroite-breakdown material [Warren *et al.*, 2004]. In sample UCLA 748, one small apatite grain (748-4) with pronounced core-to-rim zoning shows a correlation between CL intensity and  $\delta D$  by isotopography (Figure 2). High CL intensity is correlated with high F in these apatites. The CL image is best interpreted as igneous normal growth zoning of this grain from early crystallizing fluorapatite to late-crystallizing chlorapatite. The isotopography shows that  $\delta D$  was increasing during crystallization of this grain with a range of  $\sim 300\%$  from the fluorapatite core to the chlorapatite portion of the grain. Three ion probe spot analyses confirm the isotopographic results. One ion probe spot analysis [ $\delta D = +4120 \pm 71\%$  ( $2\sigma$ )] is within the boxed area of Figures 2a and 2c, and is in the fluorine-rich core of this grain. Two other spot analyses are from the rim area of this grain and have significantly higher  $\delta D$  [ $\delta D = +4348 \pm 62\%$  and  $+4340 \pm 54\%$  ( $2\sigma$ )] than the core region of this apatite grain. The fracture in the center of Figures 2a and 2b shows high hydrogen and low  $\delta D$ . A spot analysis that overlaps onto this fracture is significantly lower in D/H [ $\delta D = +2876 \pm 106\%$  ( $2\sigma$ )]. A larger apatite grain (748-3)

next to this small apatite grain has a similar hydrogen isotope signature [ $\delta D = +4122 \pm 53\%$ ;  $+3947 \pm 73\%$  ( $2\sigma$ )] (Table 1).

[8] The third apatite grain analyzed in Los Angeles thin-section UCLA 750 is a large composite grain (750-11), is zoned from fluorapatite cores to chlorapatite rims (Figure 3c), and is associated with late-stage crystallization features. An isotopographic analysis covered the complete F/Cl core-to-rim zoning sequence, but did not show significant variation in hydrogen isotopes (Figure 3a and Table 1). Two spot analyses in this grain from separate areas were very similar [ $\delta D = +3475 \pm 71\%$ ;  $+3468 \pm 59\%$  ( $2\sigma$ )], but lower than the other two petrographically related apatite grains in UCLA 748 (748-3, 748-4). This suggests significant heterogeneity in hydrogen isotopes on the  $\mu m$  to cm scale in these two separate areas of the Los Angeles meteorite.

#### 4. Discussion

[9] The correlation between hydrogen isotope zoning and igneous zoning in one apatite grain of Los Angeles (748-4) suggests a model in which late-stage assimilation of Martian crustal material occurred by the parent magma of this



**Figure 3.** Ion and electron images of Los Angeles apatite grain 750-11. (a)  $\delta D$  image. Bright artifact signals due to large cracks can be seen in the extreme lower right edge of the image. A black square ( $2 \mu\text{m}$  across) corresponds to the spot analysis area of 750-11,1 in Table 1. (b) Secondary electron image showing area of Figure 3a outlined with black ellipse. Scale bar is  $50 \mu\text{m}$ . Mk: maskelynite; Ap: apatite. (c) Panchromatic CL image.

meteorite. The intergrain and intragrain heterogeneity of hydrogen isotopes in Los Angeles suggests that this high-temperature assimilation occurred rapidly, as hydrogen isotopes did not completely equilibrate within or between different areas of the Los Angeles shergottite protolith. The correlation of D/H with apparent igneous growth zoning suggests this process occurred during crystallization of the magma, and not by later secondary alteration via crustal fluids at high temperature [Watson *et al.*, 1994] or low temperature [Bouvier *et al.*, 2005]. Given the strong coupling of the H isotope geochemistry and micro-textural evidence for magmatic zonation in Los Angeles apatite grain 748-4, it is likely that the young age estimates of the shergottites reflect igneous crystallization [Nyquist *et al.*, 1979], as hydrogen isotopes do not appear to have been reset in this grain. The large apatite grain in UCLA 750 does not show hydrogen isotope zoning, but is much lower in  $\delta D$  ( $500\text{--}800\text{‰}$ ) than the two grains in UCLA 748, suggesting that this grain has not been isotopically reset by later D-enriched crustal fluids. This observation is inconsistent with the recent suggestion that acidic crustal fluids have reset the radiogenic isotope ‘clocks’ of most Martian meteorites [Bouvier *et al.*, 2005]. The apatite grains that we analyzed are associated with late-stage crystallization features, such as the most iron-rich silicate minerals and K-rich, Si-rich glasses [Warren *et al.*, 2004]. Apatite in the Zagami basaltic shergottite does not crystallize until 95% crystallization and is found in mm- to cm-sized crystallized melt pockets [McCoy *et al.*, 1999]. If the results on the petrology of Zagami can be extended to Los Angeles, then late-crystallizing and isolated melt pockets underwent variable assimilation of a deuterium-rich, and possibly chlorine-rich, crustal component.

[10] Modeling of the evolution of Martian water through time is dependent on the D/H of primordial Martian water and the present Martian atmosphere [Owen *et al.*, 1988; Yung *et al.*, 1988; Leshin, 2000; Krasnopolsky and Feldman, 2001]. It has been suggested that correlation between D/H and water content of apatite in Martian basaltic shergottite QUE94201 can be used to infer the D/H of the Martian mantle [Leshin, 2000] (which has been assumed to represent the D/H of accreted water). Our results suggest that apatite in basaltic shergottites cannot be used to infer the Martian mantle D/H, as we see no correlation between water content and D/H in apatite grains (Table 1). The lowest D/H value we measure is in the orthopyroxenite ALH84001, which could suggest that the Martian mantle  $\delta D$  is  $\sim 3000\text{‰}$ . The highest  $\delta D$  values ( $\sim 4600\text{‰}$ ) are measured in Shergotty suggesting this composition as a minimum  $\delta D$  for Martian crustal water that was assimilated by this shergottite magma. The high  $\delta D$  of the shergottites ( $\delta D \sim +3500$  to  $+4600\text{‰}$ ) may suggest mixing of magmatic ( $\sim +3000\text{‰}$ ) and crustal water ( $\sim +4600\text{‰}$ ) during crystallization of the shergottite apatites.

[11] ALH84001 has a crystallization age from Sm-Nd isotopes of  $4.50 \pm 0.13$  Ga [Nyquist *et al.*, 1995], but a shock age of 3.9 Ga from Ar-Ar dating [Turner *et al.*, 1997]. The chlorapatite grain analyzed in this study may have been melted during the 3.9 Ga shock event [Greenwood *et al.*, 2003], but it is uncertain if hydrogen isotopes were exchanged in this event [Minitti *et al.*, 2007a, 2007b], or whether they represent the D/H at the time of crystallization

at 4.5 Ga. Hydrogen isotopes may also have been exchanged prior to 3.9 Ga with aqueous fluids associated with carbonate deposition in this meteorite [Valley et al., 1997]. Hydrogen isotopes have likely not been exchanged since 3.9 Ga, as a calculated paleotemperature history for ALH84001 suggests that it has not been heated above 0°C for any significant time in the last 4 billion years [Shuster and Weiss, 2005]. The lack of resetting of the Sm-Nd isotope system (of which phosphates are the main host of Sm and Nd in these meteorites [Wadhwa et al., 1994]) suggests that  $\delta D$  may record conditions at 4.5 Ga.

[12] Three possibilities present themselves for the interpretation of D/H in ALH84001. Firstly, if this  $\delta D$  is representative of the Martian mantle, this large enrichment in deuterium would suggest that the majority of Martian water was lost from the Martian mantle to space during an early magma ocean stage [Owen et al., 1988; Zahnle et al., 1990; Dreibus and Wänke, 1987]. Alternatively, a second possibility is that D/H we measure in ALH84001 represents that of a crustal assimilate that was in equilibrium with the Martian atmosphere during crystallization of the ALH84001 magma at 4.5 Ga. This would suggest that the majority of Martian water was lost from the Martian atmosphere by 4.5 Ga. The third scenario is that the D/H of ALH84001 may have been reset during a shock event at 3.9 Ga or during hydrothermal activity that led to carbonate formation at 3.9 Ga [Borg et al., 1999], and the value measured in this study represents the D/H of the Martian atmosphere at this later time.

[13] All three scenarios imply that the Martian atmosphere was highly fractionated in hydrogen isotopes by at least 3.9 Ga, and suggest that the majority of Martian water was lost by this time. These results call for a two-stage history for the evolution of Martian water—significant, early fractionation and escape prior to 3.9 Ga to evolve Martian crustal water to a  $\delta D$  of  $\sim 3000\%$ , followed by a relatively small additional fractionation from modest hydrogen escape in the last  $\sim 4$  billion years to increase the  $\delta D$  of the crustal water inventory to  $\sim +4600\%$ .

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