

**EVOLUTION OF WATER ON MARS: MARS SAMPLE RETURN CONSIDERATIONS FOR HYDROGEN ISOTOPE MEASUREMENTS.** J. P. Greenwood, Dept. of Earth & Environmental Sciences, Wesleyan University, Middletown, CT 06459 USA ([jgreenwood@wesleyan.edu](mailto:jgreenwood@wesleyan.edu)).

**Introduction:** The history of water on Mars, from accretion to an early, putatively warm and wet climate, and then to the present cold and dry epoch, is of the utmost importance for our overall understanding of the Martian climate, prospects for the evolution of life, an understanding of silicate melt generation, and the water content of the mantle. Hydrogen isotopes of water in returned samples from Mars will shed light on this question and must be considered a high priority measurement in the returned samples. Here I outline a simple plan to maximize the scientific return of MSR for hydrogen isotopes.

**What we know and don't know regarding D/H of Mars:**

*D/H and Martian meteorites.* Martian meteorites allow us to make measurements under the best possible circumstances in our terrestrial laboratories. They allow us develop instrumentation and methodologies for the measurement of returned Martian samples. New research measuring D/H in Martian meteorites has led to a revolution in our understanding of the evolution of water on Mars [1]. Previous studies found an enormous range in  $\delta D$  in the Martian meteorites [2-8] from terrestrial-like values (as low as  $\sim -150\text{‰}$  [5]) up to values measured remotely for the Martian atmosphere ( $\sim +4300\text{‰}$  [2]).  $\delta D$  values for ALH 84001, the only sample of ancient Mars, ranged from  $\sim 0$  to  $+2000\text{‰}$  [6,7], suggesting a gradual enrichment of D/H of the Martian atmosphere over time, dominated by thermal escape from the top of the Martian atmosphere.

New research on D/H of Martian meteorites upends the current paradigm. A new measurement of  $\delta D$  in apatite of ALH 84001 of  $+3000\text{‰}$ ,  $1000\text{‰}$  higher than any previous measurement in ALH 84001, suggests an early fractionation of D/H and loss of water from Mars, by at least 3.9 Ga, and possibly by 4.5 Ga [1]. The role of thermal escape of water from Mars is thus greatly diminished, with a fractionation of  $\delta D$  of only  $\sim 1500\text{‰}$  in the last 4 Ga. Hydrodynamic escape of hydrogen during accretion and an early magma ocean stage is the most likely candidate for enriching D/H on early Mars [9,10].

New measurements of D/H in basaltic shergottites significantly change our understanding of D/H in more recent epochs. As stated above, all previous work on Martian meteorites found a range from terrestrial to Martian atmospheric values for D/H. The new results are higher in D/H with much less variability [1]. The

$\delta D$  range in basaltic shergottites Los Angeles and Shergotty has a low of  $+3500\text{‰}$  with high values for Shergotty of  $+4600\text{‰}$ . The addition of a Stacked CMOS-type Active Pixel Sensor (SCAPS) detector to a Cameca ims 1270 ion microscope allowed imaging of D/H zonation in mineral grains, and showed a correlation of igneous zonation of fluorine and chlorine with D/H in one apatite grain of Los Angeles (Fig. 1, modified from [1]). This strongly suggests assimilation of a D-enriched component to the Los Angeles magma during apatite crystallization [1]. The D/H zonation is clearly Martian in character (opposite to what would be expected for terrestrial contamination), and its coupling with igneous zonation suggests the preservation of Martian hydrogen isotope zonation in apatite.

The value of D/H of the Martian mantle is also in doubt now. Previous work suggested a  $\delta D$  of  $\sim +900\text{‰}$  for the Martian mantle, based on a correlation of  $\delta D$  with  $H_2O$  content in Martian meteorite QUE94201 [8]. The new study of D/H in basaltic shergottites [1] sees no correlation between  $\delta D$  and  $H_2O$  content, suggesting that this method is inappropriate for determination of Martian mantle  $\delta D$ . The lowest  $\delta D$  value in the new work is  $+3000\text{‰}$  for ALH 84001, suggesting that the Martian mantle could have this high value as well [1].

*D/H of the Martian atmosphere.* Remote measurements of atmospheric D/H on Mars are much more imprecise than measurements made on samples in our terrestrial labs. Modeling results suggest Martian atmospheric D/H can vary by a factor of 2 locally on an annual scale due to current climactic conditions [11], suggesting that significant variation may be found in returned samples able to equilibrate with Martian atmospheric D/H in the present epoch.

**Mars Sample Return Strategy:** In order to understand the temporal evolution of water on Mars using D/H, we need samples from the different geologic epochs of Mars. We will need sample return from at least two sites on Mars, the ancient heavily cratered terrain, and the younger northern plains. Basaltic samples from these two sites would allow us the possibility to measure D/H in hydrous magmatic minerals, such as apatite, the most common hydrous mineral in the Martian meteorites. This would allow us a chance to determine D/H of the Martian mantle and the temporal evolution of magmatic water on Mars. Of course, conclusive measurement of D/H of the Martian mantle has

yet to be realized in the Martian meteorites, so this a serious caveat [1].

Sedimentary and/or alteration minerals in returned samples from a young and ancient locale on Mars will likely also shed light on the temporal evolution of Martian surface water, as well as the range of D/H possible in the current climactic regime. Highly labile hydrated magnesium sulfates can equilibrate D/H with the Martian atmosphere, apparently on a daily basis [12]. Thus four samples from 2 sites would be considered a minimum for detailed examination of D/H from returned samples from Mars.

**Preservation of Martian D/H in returned samples from Mars:** We have measured D/H in apatite in the Mojave(?) desert find Martian meteorite Los Angeles, as well as Martian D/H zonation in an apatite grain from this meteorite. Martian D/H systematics have been exquisitely preserved in apatite, even though this meteorite had terrestrial carbonate deposition in rock fractures, which suggests significant interaction with terrestrial water. Thus apatite, a common igneous phosphate mineral on Earth and Mars, will likely preserve its D/H signature during sample return and handling.

Hydrous sulfates present another challenge. D/H of jarosite in Martian meteorite MIL 03346 shows that Martian D/H can be preserved in jarosite from a Martian meteorite [13] but jarosite is a relatively stable sulfate mineral on Mars [14]. Hydrous magnesium sulfates and their ability to exchange D/H during a sample return mission will need careful consideration. Sheet silicates, zeolites, and Martian ice have the same problem, though if samples can be kept frozen and isolated from terrestrial water, measurement of D/H in these phases could be undertaken.

**Instrumentation concerns for Mars Sample Return:** Secondary Ion Mass Spectrometry (SIMS) will be an important technique for the measurement of trace elements and isotopes in returned samples from Mars. A dedicated ion microscope with a next generation SCAPS detector would be considered essential to Mars sample return, not just for D/H measurement. The power of the SCAPS detector, to visualize 2-D isotope or trace element zonation in a thin-section, will allow us to assess the effects of terrestrial contamination or alteration occurring during the sample return and handling here on Earth for a variety of elements and isotopes. A NanoSims for the measurement of D/H at higher spatial resolution than is capable with a Cameca ims 1280 ion microscope would also be an essential instrument for Mars sample return as well, especially for fine-grained hydrous alteration minerals.

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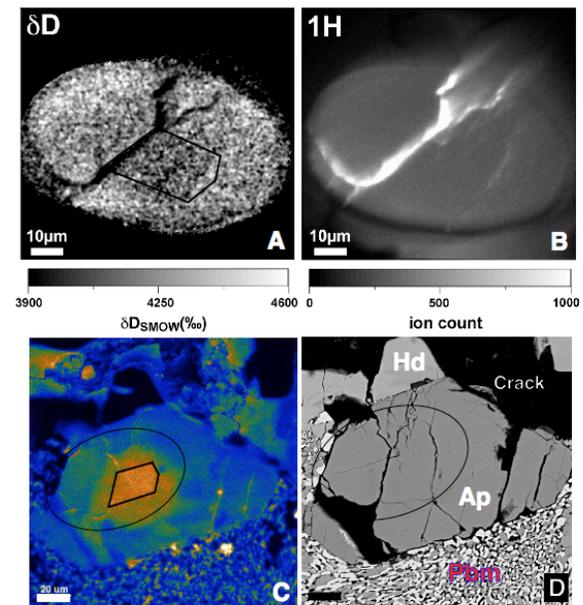


Fig. 1. (A)  $\delta D$  SCAPS image of  $\delta D$  zonation in Los Angeles apatite grain 748-4. Black box outlines area of high fluorine seen in (C). (B)  $^1H$  SCAPS image of same grain. (C) Panchromatic CL image of same grain showing igneous zonation pattern. The high CL intensity correlates with high fluorine. Black box outlines highest fluorine intensity and is also shown in (A) The black oval denotes area of SCAPS analysis shown in (A) and (B). (D) BSE image of apatite grain 748-4 showing late-stage crystallization features, such as pyroxferroite breakdown material (PBM), and hedenbergite (Hd). Modified from [1].