MAGMATIC WATER IN MARTIAN METEORITES. L. J. Hallis[1,2], G. J. Taylor[1,2], K. Nagashima[1] and G. R. Huss[1,2], [1]Hawai'i Institute of Geophysics and Planetology, Pacific Ocean Science and Technology (POST) Building, University of Hawai'i, 1680 East-West Road, Honolulu, HI 96822, United States. lydh@higp.hawaii.edu. [2]UH, NAI Astrobiology program.

Introduction: Certain primary igneous minerals, such as apatite, within the martian meteorites contain water in their crystal structure. Providing these minerals have not been altered by terrestrial or Martian weathering, or shock processes after crystallization, this water should represent a direct sample of the water reservoir of Mars mantle. As the planetary accretion process does not appear to fractionate hydrogen isotopes[1], and as Mars does not recycle crustal materials via plate tectonics, the D/H ratio of the water in these minerals represents the primordial ratio of the Martian globe. Therefore, this ratio could be used to assess the origin of Mars' water, and that of the other terrestrial planets.

Finding martian apatites that have not been contaminated by terrestrial water is no trivial matter. The martian meteorite Nakhla was seen to fall in Egypt in 1911, and was removed to the British Museum shortly after. However, Nakhla did not fall as a single stone, but as a meteor shower, and a number of samples may not have been collected from the field until as late as 1913. In addition to these possible two years of terrestrial exposure, contamination during sample storage and preparation must be considered.

As a way of checking each sample for terrestrial contamination we measured the D/H ratio of iddingsite-like alteration veins as well as the D/H ratio of apatite grains. As the minerals in these veins are the product of secondary alteration on the martian surface[2-5], they should contain water with an elevated D/H ratio relative to terrestrial minerals – reflecting the deutirium enrichment in the martain atmosphere[6]. This ratio could be easily lowered by terrestrial contamination, as the alteration veins consist of clays and amorphous phases with very loosely bound water[5], in contrast the the structurally bound water in apatite. Therefore, if a sample contains iddingsite-like alteration with elevated D/H ratios it can be concluded that the D/H ratio in the apatite of this sample has not been significantly altered by terrestrial water.

Methodology: *Sample preparation:* Our sample set included eight UH polished thin-sections of Nakhla (20a-h), sourced from rock chip 20 of parent BM 1913,25, allocated by the NASA Johnson Space Center. These thin-sections were newly prepared at the University of Hawaii without the use of water (using polishing oil and petroleum ether to clean). Each sample was placed in a vacuum oven at 60 °C as soon as it was prepared to minimize atmospheric contamination, they were only removed for analysis.

Measurement protocol: We utilized the JEOL JSM-5900LV scanning electron microscope at the University of Hawaiʻi (UH) to produce backscatter electron images and elemental X-ray images at × 250 magnification (20 µm pixel size) for each thin-section, in order to locate areas of interest. These areas were subsequently imaged at higher resolutions, with various pixel sizes (approximately 1–5 µm), to pick out the individual apatite grains and Fe-rich clay-like veins for ion microprobe analysis.

Deuterium and hydrogen isotopic compositions were analyzed in situ with the UH Cameca ims 1280 ion microprobe. A 2 nA focused Cs^+ primary ion beam was used to produce negative ions of H, D, and ^{18}O for apatites. For Fe-rich clay-like veins, H, D, and ^{30}Si were measured with ~80 pA primary beam. The secondary ion mass spectrometer was operated at 10 keV with a 50 eV energy window. Isotopes were detected using an electron multiplier. The mass resolving power was 1900, sufficient to separate any interfering molecules. A normal-incidence electron flood gun was used for charge compensation.

Prior to each measurement, the 2nA primary beam was rastered over a 25 × 25 µm area for 200 s to remove the carbon coat and surface contamination. The raster was then reduced to a 15 × 15 µm analysis area. An electronic gate was used to reject the signal from all but the inner ~8 × 8 µm of the rastered area. This eliminates signal from the edges of the sputtered crater and minimizes the contribution of hydrogen creeping across the surface. The data were collected of 40 cycles, with H measured for 3 seconds, D for 40 seconds, and ^{18}O for 2 seconds in each cycle. The beam was turned off for the first 10 cycles of the measurement, as well as for the last 5 cycles, to measure the background hydrogen and deuterium counts per second.

The ratio of deuterium (^2H or D) to hydrogen (^1H) in water is commonly quoted relative to Vienna Standard Mean Ocean Water (VSMOW), and is given as $\delta D = [((D/H)_{sample}/(D/H)_{VSMOW})-1]*1000$, with units of per mil (‰). Hence, VSMOW has a δD value of 0 ‰. On Earth, ice and rocks have negative δD values, with meteoric water varying from ~0 ‰ (oceans) to -400 ‰

(ice sheets), while the Earth's mantle has values of -80 to -40 ‰[1].

Results: Our hydrogen isotopic measurements of apatite in Nakhla 20b and 20c show δD values of between approximately -111 and +155 ‰, (Table 1). These values are in line with those of terrestrial meteoric water and the Earth's mantle. The iddingsite-like alteration veins in our samples contain δD values between -105 and +800 ‰, indicating, at the very least, incomplete hydrogen isotope exchange with the terrestrial atmosphere. This second dataset proves that the low δD values in Nakhla apatite grains are related to the true hydrogen isotope ratio of primordial Martian water.

Conclusions: The similarity of the Nakhla apatite δD values to those of the Earth's oceans, rocks and mantle suggests that the Earth and Mars, and possibly the other terrestrial planets, accreted water from the same source, or from more than one source with similar D/H ratios. Carbonaceous chondrites have been considered a likely source because of the similarity in their D/H to terrestrial ocean water[7]. Jupiter-family comets may also be a source; comet 103P/Hartley 2 has a D/H ratio indistinguishable from that of Earth[8]. A significant contribution from the long-period comets of the Oort Cloud seems to be ruled out by the elevated D/H ratios of their water (δD > +800 ‰)[9-11]. Therefore, it appears that water in inner solar system materials may have similar D/H ratios, whereas materials from further out in the solar system may be deuterium enriched.

The most recent dynamical models suggest that the region of terrestrial planet formation was limited to a zone within ~1 AU, because of the inward and outward migration of Jupiter[12]. These models could explain the lack of mixing between the inner and outer solar system hydrogen isotope reservoirs and, thus, the similarity between D/H in Mars and Earth.

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Table 1: δD (‰) and water estimated content of Nakhla apatite grains, along with the δD (‰) of iddingsite-like veins. Known major terrestrial, martian and cometary reservoir values are shown for comparison.

Sample	δD (‰)	2s (‰)	H_2O (wt %)	2s (wt %)
Nakhla 20b apatite 2	155	62	0.47	0.02
Nakhla 20b apatite 3	-111	62	0.46	0.02
Nakhla 20b apatite 4	-14	62	0.10	0.02
Nakhla 20c apatite 1	118	62	0.64	0.02
Nakhla 20c Fe-vein 1	856	44		
Nakhla 20c Fe-vein 2	-2	23		
Nakhla 20c Fe-vein 3	1170	45		
Nakhla 20c Fe-vein 4	707	62		
Nakhla 20c Fe-vein 5	-12	32		
Nakhla 20c Fe-vein 6	-62	16		
Nakhla 20c Fe-vein 7	-93	30		
Nakhla 20c Fe-vein 8	-37	19		
Nakhla 20e Fe-vein 1	-105	25		
Nakhla 20e Fe-vein 2	113	28		
Nakhla 20e Fe-vein 3	234	36		
Nakhla 20e Fe-vein 4	241	24		
Nakhla 20e Fe-vein 5	-30	26		
Terrestrial Oceans[1]	0			
Terrestrial Mantle[1]	-80 to -40			
Terrestrial Ice Sheets[1]	-300 to -400			
Comet Hartley 2[8]	6.25	300		
Comet P/Halley[9]	888	92		
Comet Hyakutake[10]	813	625		
Comet Hale-Bopp[11]	1063	1000		
Martian Atmosphere[6]	4200			