WATER ON MARS: INSIGHTS FROM CORRELATED MICROSCALE INVESTIGATIONS OF HYDROGEN ISOTOPES, WATER ABUNDANCES, AND IRON VALENCE OF NOMINALLY ANHYDROUS PYROXENE IN NAKHLITES.

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Introduction: Determining the nature of water in planetary materials is a critical endeavor in aiding our understanding of the source(s), abundance, and evolution of planetary water [1]. As Mars has no plate tectonics, crustal material is not recycled into the mantle, keeping the water reservoirs in the mantle and atmosphere mostly isolated, buffered by a potential third reservoir in the crust [2]. The nakhlites Nakhla and Lafayette provide the opportunity to investigate martian meteorites that potentially originate from the same lava flow [3] and whose igneous minerals may contain magmatic water (e.g., [4]). Furthermore, they are two of the least-shocked martian samples available for study (<20 GPa and <15 GPa, respectively [5]), and so may have preserved magmatic signatures to a greater extent than other more highly shocked martian meteorites.

Many previous studies of volatiles in martian meteorites have focused on determining the H isotope ratios (expressed as δD) and H_2O contents (in parts per million; ppm) of the late-forming mineral apatite (e.g., [1,4,6]). However, earlier-formed primary igneous minerals, such as pyroxene, may be more reliable for determining the δD–H_2O systematics of their parent magmas (e.g., [7]). As such, we target nominally anhydrous pyroxenes, which are abundant in the clinopyroxenites Nakhla and Lafayette [7,8]. Combining H isotope compositions and water abundances with spatially correlated analyses of iron valence ($Fe^{3+}/\Sigma Fe$) can provide insights into the petrogenetic processes experienced by a sample (e.g., assimilation, dehydrogenation, and subsolidus diffusion) [9,10]. Here we report the combined H_2O–δD–$Fe^{3+}/\Sigma Fe$ systematics of nakhlite pyroxenes. The goal of this work is to understand the variability in hydrogen isotope compositions and redox within martian nakhlites; the H_2O–δD data were previously reported [11].

Analytical Methods: Interior, fusion-crust free chips of Nakhla and Lafayette were each co-mounted with terrestrial standards in indium metal in two aluminum discs; no water was used to prepare samples. Quantitative compositional analyses of pyroxene were obtained with a Cameca SX-100 electron probe microanalyzer (EPMA) at the University of Arizona (20 kV, 20 nA) while high-resolution secondary and backscattered electron (BSE) imaging was undertaken on ASU's JEOL JXA-8530F EPMA (20 kV, 15 nA).

Secondary Ion Mass Spectrometry (SIMS): Measurements of H isotope compositions and H_2O contents of pyroxenes were performed on the Cameca IMS-6f SIMS at ASU using analytical protocols described in more detail in [6, 11]. Background H_2O concentrations during each analytical session (10 and 18 ppm for Nakhla; 7 ppm for Lafayette), determined by analyses of nominally anhydrous San Carlos olivine and dry PMR53 pyroxene, were corrected for via the method of [12].

X-ray Absorption Near-Edge Structure (XANES): C-coats and SIMS analysis debris were removed prior to spectral analysis. The Fe K XANES spectra were collected on spots adjacent to the SIMS pits on each pyroxene studied here (five from Nakhla, seven from Lafayette) using station 13-ID-E at the GSECARS X-ray microprobe at the Advanced Photon Source at Argonne National Lab, following the method of [9]. For each analysis spot (~1 μm diameter), spectra were collected at four different orientations, accomplished by rotating the sample mount through 90 degree increments, and were merged to form a single spectrum. Previous work on Dish Hill kaersutite amphiboles demonstrated that the Lasso method produces Fe valences with the least orientation effects [9]; results are reported here using this method [13]. The Lasso method (Devas software; http://nemo.mtholyoke.edu) was trained using spectra of three pyroxene standards that have been previously measured via Mössbauer spectroscopy: Harcourt augite, Dish Hill 227 clinopyroxene, and Dish Hill 101B orthopyroxene. Multiple analyses were performed on all pyroxenes (with the exception of Px14 in Lafayette on which a single analysis was conducted). Average Fe valences are reported as "2 + ($Fe^{3+}/\Sigma Fe$)"; precision of the Fe valence values is estimated to be ± 0.003 (1σ).

Results: *Nakhla.* Pyroxenes in Nakhla occur as minimally fractured, large crystals (up to ~900 μm diameter), with a narrow range of Fe-contents (Fs_{22-34}), heavy H isotope compositions ($\delta D = 310 \pm 170$ ‰ to 1440 ± 120 ‰), and low H_2O contents (<10 ± 2 ppm to 90 ± 17 ppm) [11]. Nakhla Fe average valence values, range from 2.139 to 2.171 (Fig. 1).

Lafayette. Pyroxenes in Lafayette are similar in appearance to those in Nakhla (up to ~800 μm diameter), with a limited range of Fe-contents (Fs_{22-25}), heavy H isotope compositions ($\delta D = 840 \pm 60$ ‰ to

1630 ± 120 ‰), and low H_2O contents (~10 ± 2 ppm to 30 ± 6 ppm) [11]. Lafayette Fe valence values range from 2.115 to 2.175 (Fig. 2), which is slightly wider than, but overlapping with, those of Nakhla.

Overall, the Fe valence ranges are narrow and the percent ferric Fe contents are low in pyroxene from both nakhlites; average Fe valences are also similar between the two samples.
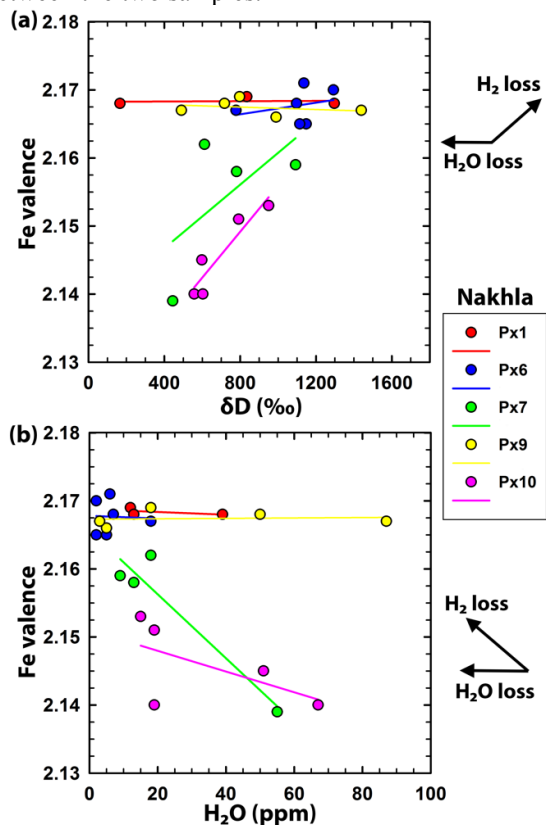

Fig. 1: *Fe valences of pyroxenes from Nakhla versus (a) H isotope compositions (δD in per mil), and (b) water concentrations (H_2O in ppm). Linear colored trendlines are fits to intra-grain data. Trends for H_2 and H_2O loss [10] are shown to the right.*

Discussion: Pyroxenes in Lafayette and Nakhla exhibit an overall inverse relationship between H isotope compositions and H_2O contents [11], consistent with the trend seen previously in nakhlite pyroxenes [7]. Such a trend may result from degassing via dehydrogenation (i.e., H_2 loss), which typically leads to isotopically heavier δD and an inverse relationship between δD and H_2O concentrations (e.g., [10]). Alternatively, this trend may result from mixing between two distinct reservoirs (one with high δD and low H_2O content, and the other with low δD and high H_2O content).

Based on the slopes of the intra-grain valence trendlines, three of five Nakhla grains exhibit evidence for H_2O loss (i.e., dehydration; Px1, Px6, Px9) whereas the other two suggest some degree of H_2 loss (i.e., dehydrogenation) (Px7, Px10; Fig. 1). In Lafayette, grains also show possible evidence of both H_2 and H_2O loss (Fig. 2). These results suggest that these pyroxenes experienced a combination of dehydration (i.e., H_2O loss) and dehydrogenation (H_2 loss).
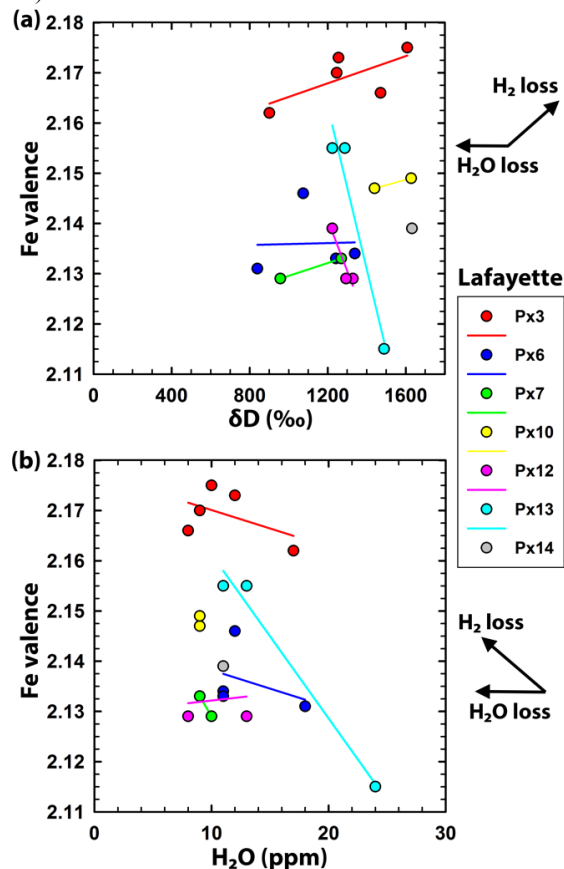

Fig. 2: *Fe valences of pyroxenes from Lafayette versus (a) H isotope compositions (δD in ‰), and (b) water concentrations (H_2O in ppm). Linear colored trendlines are fits to intra-grain data. Trends for H_2 and H_2O loss [10] are shown to the right.*

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