WATER ON MARS: INSIGHTS FROM CORRELATED MICROSCALE INVESTIGATIONS OF HYDROGEN ISOTOPE, WATER ABUNDANCES, AND IRON VALENCE OF PYROXENE IN THE REGOLITH BRECCIA NORTHWEST AFRICA 7034. J. Davidson1,2,*, M. Wadhwa2, S. Sutton3, and R. L. Hervig2, 1Buseck Center for Meteorite Studies, Arizona State University (ASU), Tempe, AZ 85287, USA. 2School of Earth and Space Exploration, ASU, Tempe, AZ 85287, USA. 3Department of the Geophysical Sciences and Center for Advanced Radiation Sources (CARS), University of Chicago, Chicago, IL 60637, USA. *Email: jdhavidson@asu.edu

Introduction: Determining the nature of water in planetary materials aids 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 regolith breccia Northwest Africa (NWA) 7034 and its pairing group are the only known samples with compositions representative of the average martian crust [3] and are among the least-shocked martian samples available for study (<5 to 15 GPa [4]). They provide the opportunity to investigate the water content and hydrogen isotopic composition of the bulk of the martian crust (e.g., [5]).

Many previous studies of volatiles in martian meteorites have focused on determining the H isotope ratios (expressed as δD) and H2O contents (in parts per million; ppm) of the late-forming mineral apatite (e.g., [1,5]). However, earlier-formed primary igneous minerals, such as pyroxene, may be more reliable for determining the δD–H2O systematics of their parent magmas (e.g., [6,7]). As such, we target nominally anhydrous pyroxenes, which are found in igneous clasts and groundmass within NWA 7034 [3,8]. Combining H isotope compositions and water abundances with spatially correlated analyses of iron valence (Fe3+/ΣFe) 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 H2O–δD–Fe3+/ΣFe systematics of pyroxenes from a variety of petrographic settings in NWA 7034. The goal of this work is to understand the variability in hydrogen isotope compositions and redox within martian meteorites; the H2O–δD data were previously reported [7].

Analytical Methods: Two interior, fusion-crust free chips of NWA 7034 were co-mounted with terrestrial standards in indium metal in two Al discs (IM1a and IM1b); no water was used in sample preparation. Quantitative compositional analyses of pyroxene were obtained with a Cammea 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 (15 kV, 15 nA).

Secondary Ion Mass Spectrometry (SIMS): Measurements of H isotope compositions and H2O contents of pyroxenes were performed on the Cameca IMS-6f SIMS at ASU using analytical protocols described in more detail in [5, 7]. Background H2O concentrations during each analytical session (9 and 19 ppm H2O), determined by analyses of nominally anhydrous San Carlos olivine and dehydrated PMR53 pyroxene, were corrected for via the method of [11].

X-ray Absorption Near-Edge Structure (XANES): Carbon 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 of eight pyroxene grains studied here 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 [12]. 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. Average Fe valences are reported as “2 + (Fe3+/ΣFe)”; precision of the Fe valence values is estimated to be ± 0.006 (1σ).

Results: Most pyroxenes in NWA 7034 occur as large, exsolution lamellae-bearing orthopyroxene phenocrysts in the groundmass (up to 700 μm diameter) [7]; six such pyroxenes were analyzed here (P4, P5, and P9 in the IM1a mount, and P1, P2, and P8 in the IM1b mount) and these orthopyroxenes and lamellae exhibit a range of Fe-contents (Fs16-44). These pyroxenes have lighter H isotope compositions (δD = −160 ± 12 ‰ to 275 ± 220 ‰) and higher H2O contents (40 ± 8 ppm to ~2240 ± 500 ppm) relative to nakhlite pyroxenes [7]. The Fe valence values of phenocrystic pyroxenes range from 2.058 to 2.145 (Fig. 1), are similar for the two different sample mounts, and have an average of 2.079 ± 0.022.
The two pyroxenes (each ~300 µm diameter) analyzed here from two different Fe-, Ti-, and P-rich (FTP) clasts in one of the mounts (IM1aFTP1 and IM1aFTP2) have a wider range of Fe-contents (Fe10.52) than the phenocrysts, do not exhibit exsolution lamellae, and have heavier H-isotopic compositions (δD = 130 ±110 ‰ to 330 ± 110 ‰) and generally lower water contents (~100 ± 20 ppm to 900 ± 180 ppm H2O) [7]. The pyroxenes in the FTP clasts have systematically higher Fe valence values than the pyroxene phenocrysts (FTP1 = 2.180 ± 0.032, FTP2 = 2.108 ± 0.017) (Fig. 1), with an average value of 2.144 ± 0.045.

The Fe valences for the pyroxene phenocrysts in NWA 7034 (average = 2.079 ± 0.022) are systematically lower compared to those we previously reported for Nakhla and Lafayette (averages = 2.161 and 2.145, respectively) [13]. In contrast, the average valence for the FTP clast pyroxene (2.144) is consistent with the nakhlite data.

![Fig. 1: Fe valences of pyroxenes from NWA 7034 versus (a) H isotope compositions (δD in per mil), and (b) water concentrations (H2O in ppm). Linear colored trendlines are linear fits to intra-grain data. Trends for H2 and H2O loss [10] are shown to the right.](image)

**Discussion:** The H2O contents of some NWA 7034 pyroxenes are higher than those reported for pyroxenes in other martian meteorites (e.g., [6, 13]), perhaps due to post-eruption addition of water on Mars. Pyroxenes in NWA 7034 exhibit an inverse relationship between H isotope compositions and H2O contents. This is consistent with the trend seen previously in NWA 7034 apatites [7] and Nakhla pyroxenes [6,13]. Such a trend may result from degassing via dehydrogenation (i.e., H2 loss), which typically leads to isotopically heavier δD and an inverse relationship between δD and H2O concentrations (e.g., [10]). Alternatively, this trend may result from mixing between two distinct reservoirs (one with high δD and low H2O content, and the other with low δD and high H2O content).

The Fe valences of pyroxenes from the FTP clasts show an increase in valence with increasing δD, consistent with H2 release (i.e., dehydrogenation), while phenocryst valences generally show a slight decrease with increasing δD, consistent with H2O loss (i.e., dehydration) (Fig. 1a). The pyroxene in clast FTP2 exhibits a clear increase in valence with decreasing water content, consistent with H2 release (i.e., dehydrogenation) (Fig. 1b). However, the FTP1 clast shows an apparent decrease in valence with decreasing water content. This may be the result of H2O loss superimposed on the H2 loss suggested by the H-isotope compositional data. The pyroxene phenocrysts generally exhibit evidence for H2O loss.

**Summary:** These results suggest that the pyroxenes in NWA 7034 experienced a combination of dehydration (i.e., H2O loss) and dehydrogenation (H2 loss). The pyroxenes in the FTP clasts experienced predominantly dehydrogenation (H2 loss) while the phenocrysts in the groundmass experienced predominantly dehydration (H2O loss). This difference likely reflects the magmatic environments on Mars in which the igneous components of the martian crust were formed and evolved.

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