

WATER ON MARS: INSIGHTS FROM CORRELATED MICROSCALE INVESTIGATIONS OF HYDROGEN ISOTOPES, WATER ABUNDANCES, AND IRON VALENCE OF PYROXENE IN THE REGOLITH BRECCIA NORTHWEST AFRICA 7034. J. Davidson^{1,2,*}, 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: jda-vidson@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 ($Fe^{3+}/\Sigma Fe$) 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 H₂O- δD - $Fe^{3+}/\Sigma Fe$ 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 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 (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 + ($Fe^{3+}/\Sigma Fe$)”; precision of the Fe valence values is estimated to be ± 0.006 (1 σ).

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 (F_{S16-44}). These pyroxenes have lighter H isotope compositions ($\delta D = -160 \pm 12$ ‰ to 275 ± 220 ‰) and higher H₂O contents (40 ± 8 ppm to $\sim 2240 \pm 500$ ppm) relative to nakhilite 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 $\sim 300 \mu\text{m}$ 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 (F_{S10-52}) than the phenocrysts, do not exhibit exsolution lamellae, and have heavier H-isotopic compositions ($\delta D = 130 \pm 110 \text{‰}$ to $330 \pm 110 \text{‰}$) and generally lower water contents ($\sim 100 \pm 20 \text{ ppm}$ to $900 \pm 180 \text{ ppm H}_2\text{O}$) [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.

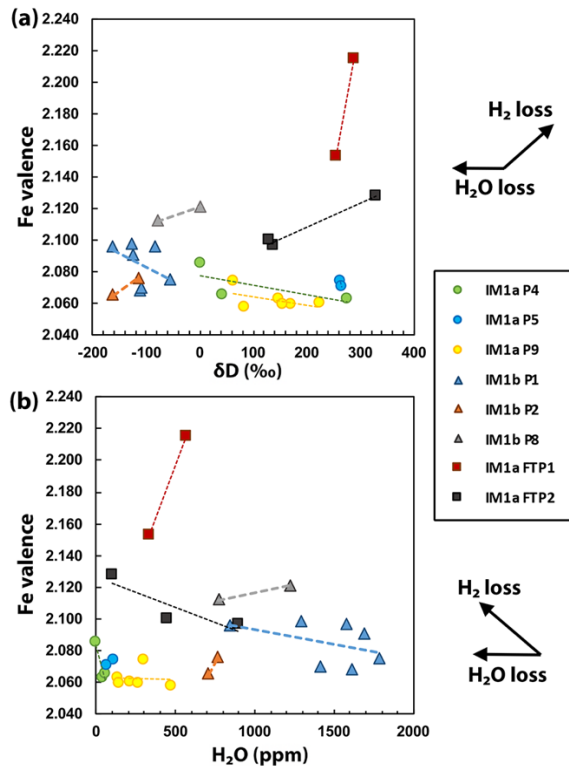


Fig. 1: Fe valences of pyroxenes from NWA 7034 versus (a) H isotope compositions (δD in per mil), and (b) water concentrations (H_2O in ppm). Linear colored trendlines are linear fits to intra-grain data. Trends for H_2 and H_2O loss [10] are shown to the right.

Discussion: The H_2O 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 H_2O 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., 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).

The Fe valences of pyroxenes from the FTP clasts show an increase in valence with increasing δD , consistent with H_2 release (i.e., dehydrogenation), while phenocryst valences generally show a slight decrease with increasing δD , consistent with H_2O loss (i.e., dehydration) (Fig. 1a). The pyroxene in clast FTP2 exhibits a clear increase in valence with decreasing water content, consistent with H_2 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 H_2O loss superimposed on the H_2 loss suggested by the H-isotope compositional data. The pyroxene phenocrysts generally exhibit evidence for H_2O loss.

Summary: These results suggest that the pyroxenes in NWA 7034 experienced a combination of dehydration (i.e., H_2O loss) and dehydrogenation (H_2 loss). The pyroxenes in the FTP clasts experienced predominantly dehydrogenation (H_2 loss) while the phenocrysts in the groundmass experienced predominantly dehydration (H_2O 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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