

WATER ON MARS: INSIGHTS FROM NOMINALLY ANHYDROUS PYROXENE IN NAKHLA AND NORTHWEST AFRICA 7034.

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Introduction: Determining the source of planetary water from the hydrogen isotopic compositions of martian meteorites is complicated by overprinting of geologic and atmospheric processes on Mars, shock metamorphism during ejection, and terrestrial weathering on Earth. As the only known samples with compositions representative of the average martian crust [1], the regolith breccia Northwest Africa (NWA) 7034 and its paired samples provide an important opportunity to investigate the water content and hydrogen isotopic composition of the martian crust. Moreover, the clinopyroxenite Nakhla provides the opportunity to investigate the H systematics of a martian sample whose igneous minerals are thought to contain magmatic water [2]. Nakhla and NWA 7034 are the least-shocked martian samples available for study (<20 GPa [3] and 5 to 15 GPa [4], respectively).

While other studies of the martian meteorites have largely concentrated on determining D/H ratios (expressed as δD) and H₂O contents of the hydrated mineral apatite [e.g., 2,5], earlier-formed primary igneous minerals, such as pyroxene, may be more reliable for determining the δD -H₂O systematics of their parent magmas. This is because later-formed apatite crystallizes from highly fractionated melt that may additionally have undergone other processes such as degassing. As such, we target nominally anhydrous pyroxene in this study. Pyroxene is abundant in the clinopyroxenite Nakhla [2] and occurs in the groundmass and a variety of clastic igneous lithologies in NWA 7034 including Fe-, Ti-, and P-rich (FTP) clasts and basaltic clasts [1,6], providing the opportunity to compare the H isotopic compositions and H₂O contents of different lithologies within the breccia and between different geologic settings on Mars.

Analytical Methods: Interior, fusion-crust free samples of Nakhla (one chip) and NWA 7034 (two chips) were co-mounted with terrestrial standards in indium metal in three aluminum discs; no water was used in any of the sample preparation techniques utilized here. Quantitative compositional analyses of pyroxene were obtained with a Cameca SX-100 electron probe microanalyzer (EPMA) at University of Arizona while high-resolution secondary and backscattered electron imaging was undertaken on a JEOL JXA-8530F EPMA at Arizona State University (ASU) before and after isotopic analysis. Secondary ion mass spectrometry (SIMS) measurements of H isotopic compositions and H₂O contents of pyroxenes were performed on the Cameca IMS-6f at ASU using analytical protocols similar to those described in [5]. The H₂O concentrations were estimated using a H⁻¹⁶O⁻ vs. H₂O calibration curve on terrestrial standards. Background H₂O concentrations (18 ppm for Nakhla; 9 and 19 ppm for NWA 7034), determined by analyses of nominally anhydrous San Carlos olivine, were corrected via the method of [7]. Instrumental mass fractionation was monitored throughout analytical sessions on terrestrial pyroxene and basaltic glass standards.

Results: Pyroxenes in Nakhla, which occur as minimally fractured, large crystals (up to ~900 μm diameter), have heavy H isotopic compositions ($\delta D = 310 \pm 170$ ‰ to 1300 ± 155 ‰), and low H₂O contents (12 ± 2 ppm to 70 ± 15 ppm). Most pyroxenes in NWA 7034 occur as large orthopyroxene phenocrysts in the groundmass (up to 700 μm diameter), and have light H isotopic compositions ($\delta D = -162 \pm 12$ ‰ to 280 ± 220 ‰), and high H₂O contents (40 ± 8 ppm to $\sim 2240 \pm 500$ ppm) compared to Nakhla pyroxenes. Pyroxenes were also analyzed in a basaltic clast (<60 μm diameter; $\delta D = 260 \pm 70$ ‰ to 290 ± 60 ‰; $\sim 330 \pm 65$ ppm to 570 ± 115 ppm H₂O) and an FTP clast (~ 300 μm diameter; $\delta D = 130 \pm 110$ ‰ to 330 ± 110 ‰; $\sim 100 \pm 20$ ppm to 900 ± 180 ppm) in NWA 7034.

Discussion: Pyroxenes in Nakhla and NWA 7034 exhibit an inverse relationship between H₂O contents and H isotopic compositions. Degassing via dehydrogenation (i.e., H₂ loss) typically leads to isotopically heavier δD and an inverse relationship between δD and H₂O concentrations (e.g., [8]), such as seen here for Nakhla and NWA 7034 pyroxenes and previously in NWA 7034 apatites [5]. Data for Nakhla pyroxenes agree with a previous study [9].

The H₂O contents in some NWA 7034 pyroxenes are slightly higher than those reported for clinopyroxene in the shergottite Tissint (1300 ± 200 ppm H₂O) [10]. It is unlikely that the highest H₂O contents in NWA 7034 pyroxenes were incorporated during crystallization; they may, however, be explained by post-eruption addition of water. Since both Nakhla and NWA 7034 were prepared via the same anhydrous method, it seems unlikely that this water was introduced during sample preparation.

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