

WATER ON MARS: CORRELATED MICROSCALE ANALYSES OF HYDROGEN ISOTOPES, WATER CONTENTS, AND REDOX STATE IN MARTIAN PYROXENES

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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, the water reservoirs in the mantle and atmosphere are mostly isolated, and likely buffered by a third reservoir in the crust [2]. The nakhlites Nakhla and Lafayette potentially originate from the same lava flow [3] and may contain magmatic water in their igneous minerals (e.g., [4]). The regolith breccia Northwest Africa (NWA) 7034 and its pairing group are the only known samples with compositions representative of the average martian crust [5], and contain lithologies not identified in other martian meteorites [6]. Nakhla, Lafayette, and NWA 7034 are some of the least-shocked martian samples available for study (all <20 GPa [7,8]), and so may have preserved primary magmatic signatures to a greater extent than more shocked martian meteorites. Collectively, they provide the opportunity to investigate the hydrogen (isotopic composition, δD in per mil, and water concentration, H₂O in ppm) and Fe redox (Fe³⁺/ΣFe) systematics of a variety of geologic settings at different times in martian history. Here we present correlated δD -H₂O-Fe³⁺/ΣFe systematics for the early-formed primary igneous mineral pyroxene, which may be one of the most reliable phases for determining the nature and abundance of primary water (e.g., [10–12]), in the martian meteorites Nakhla, Lafayette, and NWA 7034.

Analytical Methods: Interior, fusion-crust free meteorite chips (one Nakhla, one Lafayette, two NWA 7034) were co-mounted with terrestrial standards in indium metal in four Al discs; 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). Measurements of H isotope compositions and H₂O contents of pyroxenes were performed on the Cameca IMS-6f SIMS at ASU [11,12]. The Fe K X-ray Absorption Near-Edge Structure (XANES) spectra were collected on spots adjacent to the SIMS pits using station 13-ID-E at the GSECARS X-ray microprobe at the Advanced Photon Source at Argonne National Lab, following the method of [13] and [14]. These analytical methods are described in more detail in [11,12].

Results: *Nakhlites.* Pyroxenes in Nakhla have heavy H isotope compositions ($\delta D = 310 \pm 170$ ‰ to 1440 ± 120 ‰), low H₂O contents ($<10 \pm 2$ ppm to 90 ± 17 ppm) [15], and average Fe valence values of 2.139 to 2.171 [11]. Pyroxenes in Lafayette have similarly heavy H isotope compositions ($\delta D = 840 \pm 60$ ‰ to 1630 ± 120 ‰), low H₂O contents ($\sim 10 \pm 2$ ppm to 30 ± 6 ppm) [15], and Fe valence values from 2.115 to 2.175 [10].

Regolith breccia. Phenocrystic groundmass-hosted pyroxenes in NWA 7034 have lighter H isotope compositions ($\delta D = -160 \pm 12$ ‰ to 275 ± 220 ‰) and higher H₂O concentrations (40 ± 8 ppm to $\sim 2240 \pm 500$ ppm) than nakhlite pyroxenes. Pyroxenes from Fe-, Ti-, and P-rich (FTP) clasts have generally heavier H isotope compositions ($\delta D = 130 \pm 110$ ‰ to 330 ± 110 ‰) and lower H₂O concentrations ($\sim 100 \pm 20$ ppm to 900 ± 180 ppm) than groundmass pyroxenes. Pyroxenes in FTP clasts have systematically higher Fe valence values (average = 2.144 ± 0.045) than the pyroxene phenocrysts (average = 2.079 ± 0.022), similar to nakhlite pyroxenes (average = 2.153 ± 0.016).

Discussion: Pyroxenes from both nakhlites and the regolith breccia exhibit overall inverse relationships between δD and water concentrations. This may result from degassing via dehydrogenation (i.e., H₂ loss), which typically leads to isotopically heavier δD and an inverse relationship between δD and water concentrations (e.g., [16]). 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). Combined δD -H₂O-Fe³⁺/ΣFe systematics suggest that pyroxenes in both the nakhlites and NWA 7034 experienced a mix of dehydration (i.e., H₂O loss) and dehydrogenation (H₂ loss). Overall, some NWA 7034 pyroxenes contain more water than nakhlite pyroxenes, perhaps due to post-eruption addition of water on Mars (as seen in apatites from NWA 7034 [9]). These differences likely reflect the different environments on Mars in which the igneous components of the martian crust were formed and later altered.

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