

WATER IN THE CRUST: IMPLICATIONS FOR THE EVOLUTION OF MARS. J. J. Barnes^{1,2}, F. M. McCubbin², A. R. Santos³, J. M. D. Day⁴, J. W. Boyce², S. P. Schwenzer⁵, U. Ott^{6,7}, I. A. Franchi⁵, S. R. Messenger, M. Anand^{5,8}, and C. Agee⁹. ¹Lunar and Planetary Laboratory, University of Arizona, 1629 E University Blvd, Tucson, AZ 85721, USA (jjbarnes@lpl.arizona.edu), ²NASA Johnson Space Center, mailcode XI, 2101 E NASA Parkway, Houston, TX 77058, USA, ³NASA Glenn Research Center, 21000 Brookpark Rd, Cleveland, OH 44135, USA, ⁴Scripps Institution of Oceanography, 9500 Gilman Drive, La Jolla, CA 92093, USA, ⁵The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK, ⁶Max-Planck-Institut für Chemie, Hahn-Meitner-Weg 1, 55128 Mainz, Germany, ⁷MTA Atomki, Bem tér 18/c, 4026 Debrecen, Hungary, ⁸The Natural History Museum, Cromwell Road, Kensington, London, SW7 5BD, UK, ⁹Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA.

Introduction: In the absence of a magnetosphere, the martian atmosphere has been stripped of the light hydrogen (¹H) over billions of years by the solar wind [1]. This process has resulted in a heavily fractionated atmosphere [2-4]. To understand the origin(s) of water inside Mars and the interaction between different water reservoirs on the planet (i.e., the atmosphere, crust, and interior), the H-isotopic composition of water measured in samples can be used to provide important insights. While numerous martian meteorites have been investigated for the water content and H-isotopic compositions of constituent minerals/phases [5-7], the H inventory of the martian crust remains poorly understood. This is surprising since the crust is reported to be the most water-rich reservoir on Mars [8].

Here, we investigated the H-isotopic composition of water in two martian meteorites that are expected to have interacted with crustal fluids. The results allow us to constrain the isotopic composition of H in the crust over martian geological time.

Samples: Northwest Africa (NWA) 7034 and its pairings represent a regolith breccia of a basaltic bulk composition, the fine-grained matrix of which bears a strong resemblance to the major and trace element composition estimated for the ancient southern highlands crust on Mars. Clasts in NWA 7034 have ages as old as 4.4 Ga with phosphates recording a Pb-loss event at 1.5 Ga [9]. On the other hand, Allan Hills (ALH) 84001 is a coarse-grained, orthopyroxenite and is the oldest unbrecciated igneous sample we have from Mars, dated at ~4.1 Ga [10]. A younger age for phosphates (~3.9-4.0 Ga, [11]) and the presence of carbonates indicate crustal alteration of ALH 84001. Together, these samples provide an opportunity to investigate the evolution of H in the martian crust at two end points separated by ~2.4 Ga.

Methods: We studied apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$] grains in thin sections of each of NWA 7034 and ALH 84001 for their texture, chemistry, and H-isotopic composition. Our analytical approach followed coordinated analyses of phosphates by scanning electron microscopy (SEM), electron probe

microanalysis (EPMA), and nanoscale secondary ion mass spectrometry (NanoSIMS).

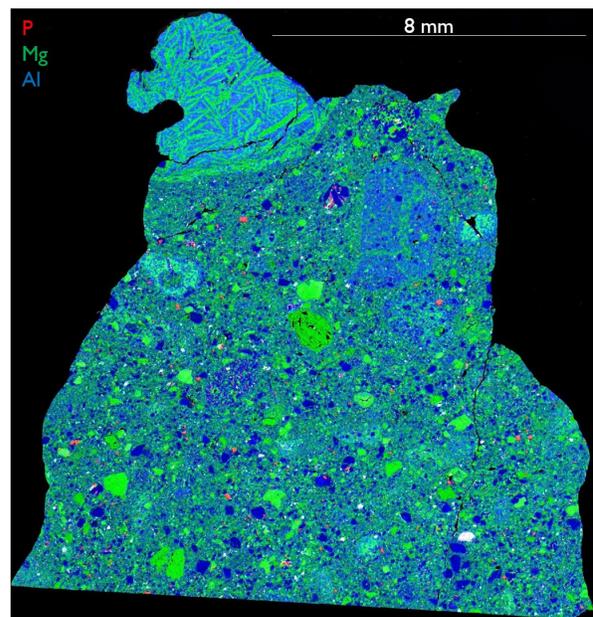


Figure 1. False color X-ray composite map of thin section NWA 7034 1B,2 (UNM number) [12] studied in this work. Note that phosphates appear in red. Fe-Ti oxides and sulfides are white to gray.

Results: In NWA 7034, apatite occurs in a number of different lithic clasts, including iron-titanium-phosphorous-rich clasts, basalt clasts, and trachyandesite clasts. All the apatites in NWA 7034 have similar chemistries, regardless of textural setting, and all of them yield similar 1.5 Ga ages [9]. Chlorine is more hydrophilic than F, which promotes formation of Cl-rich apatite compositions in fluid-rich systems [14-17]. Equilibration of apatite with crustal fluids is supported by the Cl-rich compositions exhibited by apatites in NWA 7034 in comparison to apatites from most other martian meteorites (Figure 2; [8]).

There are at least two compositional types of apatite in ALH 84001. One population is igneous and the other

has textures (Figure 3) and Cl-rich compositions (Figure 2) indicating formation through secondary hydrothermal processes from interaction with crustal fluids.

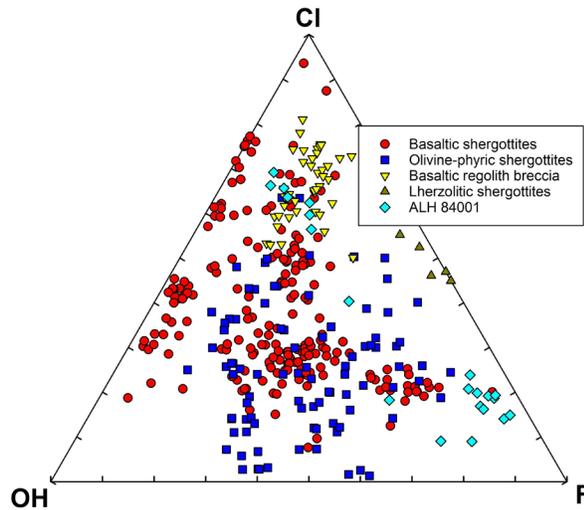


Figure 2. Ternary plot of apatite X-site occupancy (mol%) from all martian meteorites. Data from ALH 84001 from this study, basaltic regolith breccia (NWA 7034) from [8,12], and data for all other martian meteorites are compiled in [8]. Note that OH was not directly measured, so it was calculated assuming $1 - F - Cl = OH$. EPMA data yielding $(F + Cl) > 1$ atom are plotted along the OH-free join assuming $1 - Cl = F$.

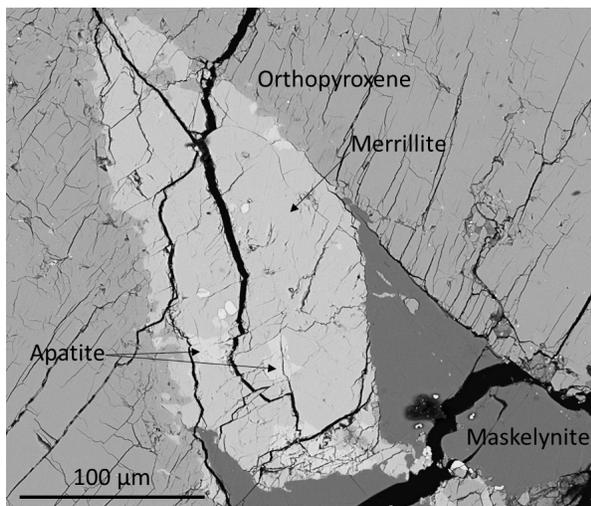


Figure 3. Backscattered electron image of apatite and merrillite grains in ALH 84001.

Apatite grains within both NWA 7034 and ALH 84001 display a similar spread in D/H ratios (between ~ 3.1 and 4.7×10^{-4}) over a wide range of water and Cl contents and textural settings. The data for both samples are in agreement with H-isotopic data on other lithic

clasts in NWA 7034 and its pair NWA 7533 [7,18] and intercumulus apatite in ALH 84001 [19]. The results are also consistent with D/H values reported for the martian crust within the time span of ~ 0.7 to 470 Ma before the present [20] and analyses of Hesperian (~ 3 Ga old) clays by the Sample Analysis at Mars (SAM) instrument onboard the Mars Science Laboratory rover (D/H ratio of $4.67 \pm 0.31 \times 10^{-4}$) [21]. The combination of these results indicates that the martian crust is characterized by D/H ratios that are depleted in deuterium relative to the current martian atmosphere [2–4] and this has been the case for at least the last 3.9 Ga. The crust is the largest reservoir of water per unit mass on Mars with an estimated abundance of 1410 ppm H₂O [8]. Therefore, characterizing the H-isotopic composition of the martian crust is an important step towards understanding the origin and evolution of water in the interior of Mars.

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