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WATER ON MARS: INSIGHTS FROM APATITE IN REGOLITH BRECCIA NORTHWEST AFRICA 7034.

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Introduction: Determining the source of planetary water from the hydrogen isotope compositions of crustal samples is complicated by overprinting of geologic and atmospheric processes. As Mars has no plate tectonics, crustal material, which has likely exchanged water with the martian atmosphere, is not recycled into the mantle keeping the water reservoirs in the mantle and atmosphere mostly isolated, buffered by the crust. As the only known martian samples that are regolith breccias with a composition representative of the average crust of Mars, and with ~6000 ppm bulk water [1], Northwest Africa (NWA) 7034 and its paired stones provide an important opportunity to investigate the water content and hydrogen isotopic composition of the martian crust.

The majority of NWA 7034's bulk water may be located in hydrous Fe-oxide phases and phyllosilicates, with apatite contributing a maximum of 150 ± 50 ppm bulk water [2]. However, hydrous Fe-oxides and phyllosilicates are secondary alteration minerals while apatite is a primary igneous mineral. Apatite occurs in all four types of clastic igneous lithology recognized in NWA 7034: basalt, basaltic andesite, trachyandesite, and an Fe-, Ti-, and P-rich (FTP) lithology [3]. Apatite differs between the clasts, with varying size, morphology, and abundance providing the opportunity to compare the H-isotopic composition and water contents of different lithologies within the breccia, two of which (trachyandesite and FTP clasts) were previously unsampled in martian meteorites [1,3].

Analytical Methods: Chips of anhydrously-prepared NWA 7034 and terrestrial standards were co-mounted in indium in aluminum discs. Backscattered electron (BSE) images, X-ray element maps, and quantitative compositional analyses were obtained with the Cameca SX-100 electron probe microanalyzer (EPMA) at the University of Arizona's Lunar and Planetary Laboratory. High resolution images of phases identified for quantitative analysis were obtained on the JEOL JXA-8530F EPMA at ASU (operating conditions: 20 kV and 15 nA) both before and after isotopic analysis.

Secondary ion mass spectrometry (SIMS) measurements of H-isotopic compositions and H_2O concentrations were performed on the Cameca IMS-6f at ASU using analytical protocols similar to those described in [4]. A Cs^+ primary beam (~15 nA) was ras-

tered over a ~40×40 µm^2 area (a field aperture limited the analyzed area to the central 15 µm to reduce background H counts associated with crater edges). Each measurement consisted of 50 consecutive cycles each of H^- and D^- with counting times of 1 s and 10 s, respectively. The $^{16}O^-$ peak was measured at the end of each analysis in order to determine the $H^-/^{16}O^-$ ratio used for determination of H_2O content. The H_2O concentrations were estimated using a $H^-/^{16}O^-$ vs. H_2O calibration curve on terrestrial standards via the method of [5]. The amount of H_2O background was determined by analyses of nominally anhydrous San Carlos olivine and dry PMR 53 pyroxene. Instrumental mass fractionation was monitored throughout the analytical sessions on terrestrial apatite and basaltic glass standards.
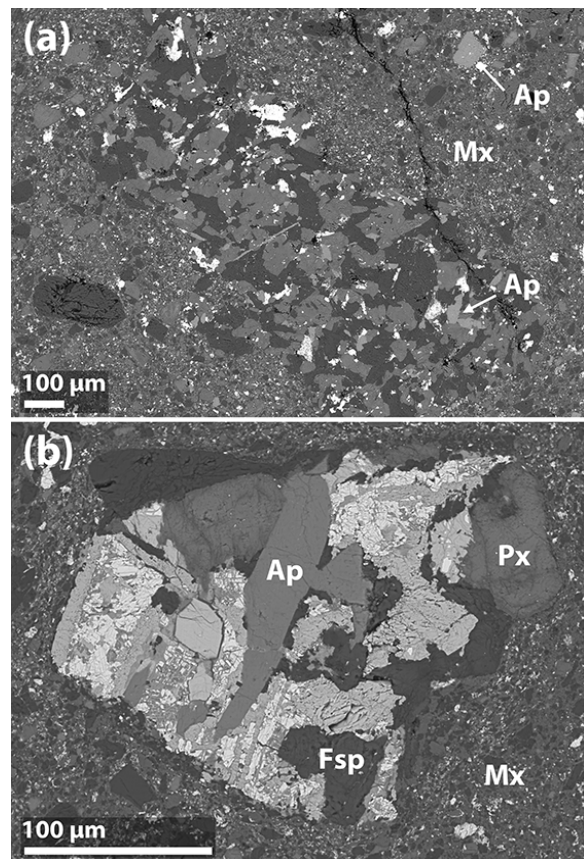

Fig. 1: *BSE images of apatite (Ap) in (a) a basaltic clast and interclastic matrix (Mx), and (b) an FTP clast; Fsp = feldspar, Px = pyroxene.*

Results: Apatite grains in multiple basalt and FTP clasts (Fig. 1), one impact melt clast, and interclastic matrix were analyzed; all are Cl-rich. The largest apatite grains are located in the interclastic matrix (up to ~190 μm diameter); apatite grains in FTP clasts were generally larger than in basaltic clasts (up to ~100 μm diameter vs. up to ~40 μm diameter).
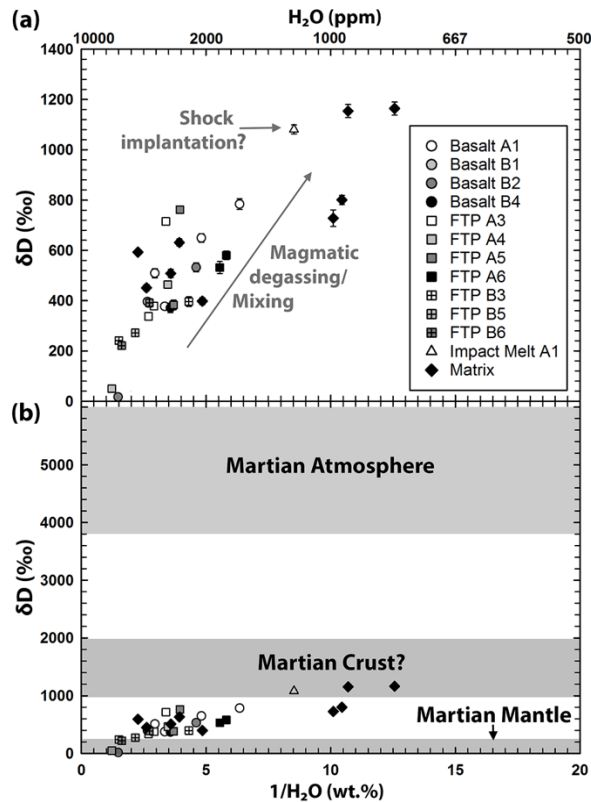

Fig. 2: *H-isotopic composition versus reciprocal of water concentration in apatite from NWA 7034. (a) Data from anhydrously-prepared samples are grouped by lithological setting (clast type or interclastic matrix). (b) The same data shown with fields representing the mantle (<275 ‰ [6–8]), proposed crustal reservoir (δD = 1000–2000‰ [9]), and the atmosphere (4950 ± 1080 ‰ [10]).*

Apatite grains analyzed here show a range of δD values between 17 and 1164 ‰ (Fig. 2). Apatite grains in the interclastic matrix (i.e., mineral fragments) and from the impact melt clast have the highest δD, on the order of ~1100 ‰. The apatite from an impact melt clast has a heavy isotopic composition (δD = 1081 ± 18 ‰) and relatively low H_2O concentration (1173 ± 235 ppm) compared to other clastic apatite. There is no significant systematic difference between the isotopic compositions of apatite grains from basalt clasts and FTP clasts. However, there is

variability in the hydrogen isotope composition between apatite grains within the same clast.

The H_2O concentrations for NWA 7034 apatite range from 796 to 8201 ppm; the average H_2O concentration (3110 ± 1800 ppm; 2SD) agrees with that estimated by [2] (3000 ± 1000 ppm) via quantitative electron microprobe analysis.

Discussion: The δD values determined here for NWA 7034 apatite are lower, and H_2O concentrations are higher, than those estimated via NanoSIMS (δD = 453–2564 ‰; 238–1343 ppm H_2O; [11]). However, it is unlikely that the higher water concentrations measured here are due to terrestrial contamination since samples were prepared anhydrously and apatite chemistry is stoichiometric.

To test for effects of impact processing, apatite from an impact melt clast was analyzed; this yielded a δD value of 1081 ± 18 ‰ and H_2O concentration of 1173 ± 235 ppm (Fig. 2). While these results suggest shock implantation and dehydration during impacts (e.g., [11]), such an interpretation should be considered with caution as it is based on only one data point.

With the exception of the FTP clasts, all igneous lithologies (basalt, basaltic andesite, and trachyandesite clasts) in NWA 7034 exhibit apparent fractional crystallization behavior [3]. Degassing via dehydrogenation (i.e., H_2 loss) typically leads to isotopically heavier δD and a negative relationship between δD and H_2O concentrations (e.g., [12]), such as seen here for NWA 7034 apatites. Alternatively, it may be possible that the relationship seen in NWA 7034 apatite could be the result of crustal assimilation and/or mixing with fluids in a crustal reservoir (e.g., [13]).

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