HYDROGEN ISOTOPE ANALYSES OF APATITE IN MARTIAN POLYMICT BRECCIA NORTHWEST AFRICA 11522 (PAIRED WITH NORTHWEST AFRICA 7034). A. Smith[1], L. J. Hallis[2], K. Nagashima[3] and G. R. Huss[3]. [1]School of Earth and Environmental Sciences, The University of Manchester, UK (aimee.smith@manchester.ac.uk), [2]School of Geographical and Earth Sciences, University of Glasgow, UK. [3]Hawai'i Institute of Geophysics and Planetology, University of Hawai'i, 1680 East-West Road, Honolulu, HI 96822, United States.

Introduction: Northwest Africa (NWA) 7034 and its pairings are amongst the most unique and diverse of the martian meteorites, and are reported to have formed via impact melting and welding of an area of martian regolithic soil [1-3]. As a result, these meteorites are polymict breccias, containing a diverse set of lithologies including igneous, protobreccia, and melt clasts. The clastic nature of these rocks has resulted in a range of age dates between ~1.5 Ga to 4.4 Ga, representative of various crystallisation and resetting events [1, 4-5].

NWA 7034 is water-rich compared to the other known martian meteorites, with ~6000 ppm of extraterrestrial H_2O released during stepped heating [1]. NWA 7533 (a paired stone of NWA 7034) is also estimated to contain a high concentration of water (~8000 ppm) [6]. These high water contents may be partly due to the presence of hydrous apatite, as NWA 7034 and pairings contain numerous apatite grains within various lithological clasts, as well as free apatite grains within the groundmass [2].

In this study, we report volatile ratios and hydrogen isotope data from apatites in North West Africa (NWA) 11522 - a paired stone to NWA 7034. In-situ hydrogen isotope data can indicate the source of water in each grain (e.g., parental melt water sourced from the martian interior, water sourced from the cryosphere, or atmospheric water).

Methods: The composition of NWA 11522 apatite grains was determined using SEM-EDS analyses at the University of Glasgow. SEM-EDS analysis cannot directly measure OH, but by measuring F and Cl accurately, the missing component (assumed to be 100 % OH) can be inferred via stoichiometry.

Apatite grains >25μm diameter, with minimal fractures and inclusions, were selected for hydrogen isotope analysis. Eight apatite grains from two NWA 11522 samples were analyzed, four grains from an indium mounted sample and four from an epoxy mounted sample. Three of these apatite grains were contained within protobreccia clasts, the remainder were free within the matrix.

The Cameca ims 1280 ion microprobe at the University of Hawai'i was used to collect *in situ* hydrogen isotope data from apatites in NWA 11522. A focused Cs+ primary ion beam with a current of 4 nA was used to produce negative ions of H, D, and ^{18}O. The primary beam was rastered over an area of 25x25 μm for 200 seconds to remove surface contamination and the 15 nm carbon coat. The raster was then reduced to 15x15 μm for analysis, and an electronic gate was used to limit data collection to the innermost 8 x 8 μm. For abundance determination, we constructed a $^{1}H/^{18}O$ vs H_2O calibration curve using terrestrial standards [7-8]. The same standards were used to correct for instrumental mass fractionation of D/H. Our H_2O detection limit was <10 ppm.

Results: *Apatite F, Cl and OH abundances.* Based on 13 anions, stoichiometric calculations were made to determine the ratio of F:Cl:OH in the apatite X-site. Despite the fact that NWA 11522 is a polymict breccia, apatite volatile ratios are closely clustered, with Cl-rich and F-poor compositions (Figure 1).

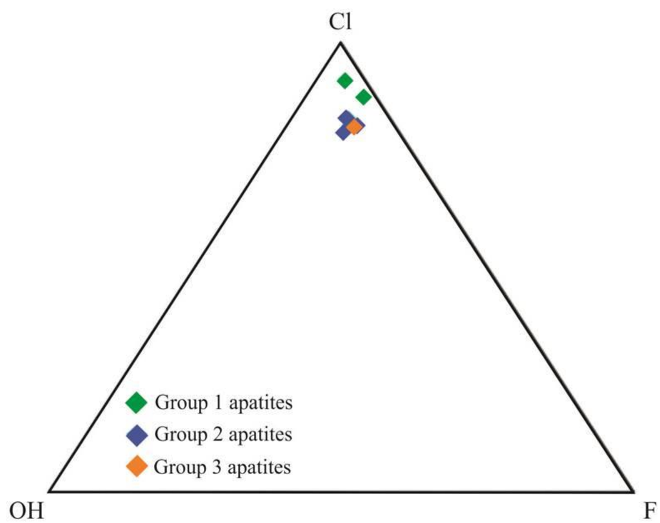

Figure 1: F:Cl:OH ratios within NWA 11522 apatite X-sites**.**

Deuterium/Hydrogen isotope ratios. Apatite grains in NWA 11522 show δD values between 52‰ and 782‰, with water contents between 1380±30ppm and 5098±100ppm (Figure 2). Three distinct groups are evident based on these values. Group 1 is characterized by high δD values (557-782‰) and low water contents (1380-1842 ppm). Group 2 has intermediate δD values (264-512 ‰) and high water contents (4083-5097 ppm). Group 3 is characterized by low δD values (51-

52 ‰) and high water contents (4308-4677 ppm). Apatite in groups 1 and 3 is predominantly euhedral, whereas group 2 apatite has a mostly spongey texture.

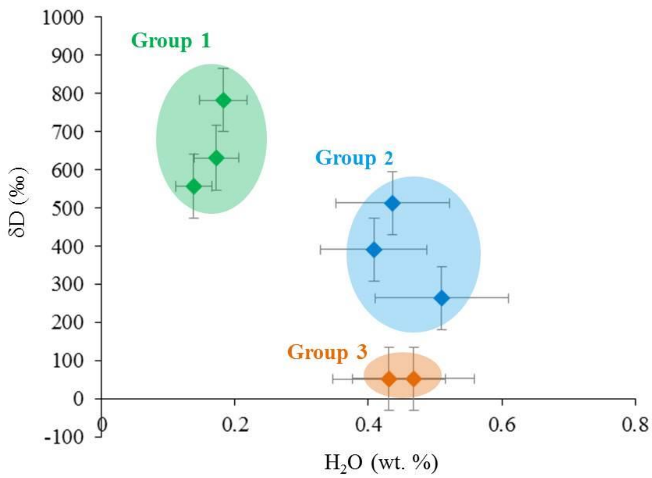

Figure 2: Groupings of apatite based on D/H ratio (δD) versus water content (H_2O wt.%). Group 1 is contained within the green region, group 2 in the blue region, and group 3 in the orange region. Uncertainties are 2σ.

Discussion: *Apatite composition.* The similarity of F:Cl:OH ratios in NWA 11522 apatite grains, irrespective of texture, or mineralogical and lithological associations, indicates overprinting of the original volatile compositions. This overprinting could have occurred as a result of the formation of the polymict breccia on Mars. [5] report that groundmass texture, along with the concordance of ~1.5 Ga dates for bulk rock K-Ar, U-Pb in apatite, and U-Pb in metamict zircons, indicates a single pervasive thermal event occurred at this time within NWA 7034.

Apatite D/H ratios. Based on D/H ratios, three distinct groups of apatite are evident in NWA 11522.

Group 1, characterized by a high δD and a low water content, could be the result of shock effects. During shock, H is lost as a result of devolatilisation [9-10]. Therefore, loss of H would decrease the water content. It would also increase the D/H ratio of the apatites, due to the preferential loss of the lighter hydrogen isotope, resulting in the high δD values recorded in this study. Alternatively, devolatilization may have occurred as a result of thermal alteration (possibly the thermal event inferred by [5] at ~1.5 Ga. Evidently, devolatilization has occurred in Group 1. The mechanism that caused this devolatilization is hard to constrain since NWA 11522 has experienced both shock and thermal heating. A combination of both shock and thermal heating is also possible.

Group 2 is characterized by intermediate δD values and high water contents, possibly as a result of hydrothermal alteration. In addition, the dominant apatite texture of group 2 is spongey, whereas the texture of apatite in groups 1 and 3 is predominantly euhedral. The spongey texture of group 2 apatite grains suggests alteration by, or direct deposition from, a fluid with an intermediate δD value. On Mars intermediate □D values are characteristic of the cryosphere [11]. This hydrothermal alteration must have occurred after the thermal event that lithified the polymict breccia, possibly as a result of related cryospheric ice melt.

Group 3 is dominated by low δD values and high water contents, possibly diagnostic of terrestrial contamination [9].

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