FTIR ANALYSIS OF WATER IN PYROXENE AND PLAGIOCLASE IN ALH 84001 AND NAKHLITES.

A. H. Peslier[1] M. J. Cintala[2], R Montes[1] and F. Cardenas[1], [1]Jacobs, NASA Johnson Space Center (JSC), Mail Code XI3, Houston, TX 77058, USA; anne.h.peslier@nasa.gov, [2]NASA JSC, Mail Code XI3, Houston, TX 77058, USA.

Introduction: Determining the volatile budget of the interior of Mars is crucial for our understanding of that planet's formation, geodynamics, cooling history and the origin of its volcanism and atmosphere as well as its potential for life. Surficial water is evident from spacecraft and rover data in polar caps and the atmosphere, in the presence of river channels, and in the detection of water-bearing minerals [e.g., [1-5]]. Meteorites, however, are our best candidates for estimating the amount of water present at depth, even if all are crustal samples. The last 10 years have seen a blooming of studies measuring water and halogens in Martian meteorites. The bulk of these studies target phosphates [e.g. [6-8], a typically late-stage phase in the igneous Martian meteorites that potentially would concentrate incompatible element hydrogen (H quantified traditionally as "water", i.e., H_2O concentrations in weight) near the end of the crystallization sequence. However, determining the amount of water, F, and Cl in the magma from which a phosphate crystallized from is not straightforward and in most instances not possible [9,10]. On the other hand, phosphates have turned out to be very useful in identifying hydrothermal processes that could have added water while or after the magma flowed and crystallized [8]. Another caveat of analyzing Martian meteorite phases for water is that shocked phases such as maskelynite and impact melts appear to have incorporated water from the Martian atmosphere, as evidenced by high H isotope (δD) signatures [11,12], and therefore their water concentrations cannot be interpreted in terms of deep planetary processes. The best candidates for estimating the water content of the Martian interior have been melt inclusions (glass or amphibole-bearing) which the enclosing mineral (usually olivine) would have prevented from exchanging volatiles with the surroundings after crystallization [6,13,14]. Even some of these, however, have high δD, meaning they were affected by H exchange via impact events or with crustal reservoirs or hydrothermal fluids [12,14-16].

Here, nominally anhydrous minerals (pyroxene, olivine, plagioclase, or maskelynite) in orthopyroxenite ALH 84001 and selected nakhlites are analyzed for water and major elements, in order to determine 1) whether they contain any water; 2) if they do, what controls its distribution (crystallization, degassing, hydrothermal or impact processes); and 3) if any of these measurements can be used to infer the water contents of the parent magma and their mantle sources. A shock-reverberation experiment was also performed on terrestrial orthopyroxenes (opx) to simulate the heavily shocked conditions of ALH 84001 (> 31 GPa [17]).

Methods: Nakhlite pyroxene, olivine and plagioclase mineral separates were doubly polished using crystal bond. ALH 84001 opx and maskelynite grains and opx shocked in the impact experiment were unprocessed; i.e., relatively flat pieces were analyzed as is (no glue to avoid glue interference in the OH region of the FTIR spectra in these heavily fractured minerals). The shock experiment was performed at ~40 GPa at the Experimental Impact Laboratory at NASA-JSC. Grains from two major element compositions of opx from terrestrial peridotite xenoliths were placed next to each other in the stainless-steel sample container, one having been dehydrated, the other containing 187 ppm H_2O. The Hyperion microscope of a Bruker FTIR and a Cameca SX100 electron microprobe at NASA-JSC were used to analyze the minerals. Mineral specific absorption coefficients [18,19] were applied to polarized transmission spectra to calculate water contents.

Results for nakhlites: Spectra of pyroxenes are characterized by small pleochroic OH bands at 3450, 3520 and 3625 cm^{-1}, characteristic of intrinsic H in augite [18]. Olivine in NWA 998 has no detectable water. Pyroxene water contents are ≥ 9 ppm H_2O in NWA 998, 0-4 ppm H_2O in MIL 03346 and 1-19 ppm H_2O in NWA 6148. FTIR and electron-microprobe traverses were possible for two pyroxene grains from NWA 6148. Water contents are lower at the edges compared to the cores but these variations are not correlated with the zonation of major elements (Figure). This is best explained by H loss via degassing from the pyroxenes.

Results from the impact experiment: The opx grains appear heavily crushed, resembling those observed in ALH 84001 [20]. The original shape of the mm-sized opx is retained and lined with black interstitial material (glass, melt?). The baseline of the opx spectra in the OH region is humpback-shaped, likely due to IR light scattering on the multiple fractures in the grains. Only one grain out of the two analyzed had the recognizable intrinsic pleochroic OH bands of opx at 3586, 3566, 3515 and 3500 cm^{-1}, totaling ~ 38 ppm H_2O. This low concentration is best explained by the H leaving the water-bearing opx and probably entering the glassy material (not analyzed).

Results for ALH 84001: FTIR spectra of the four opx grains analyzed resemble those of the experimentally shocked opx with a humpback baseline in the OH region. Again, the texture of ALH 84001 opx described in [20] as "coarse, deformed opx cut by numerous crushed zones of fine-grained opx and chromite" likely caused IR light scattering. No OH was detected. If any water was present in the parent melt of ALH 84001, it likely was lost from the opx during impact events. The two analyzed maskelynite grains ($An_{34}Ab_{62}$ [20]), however, were clear optically and showed non pleichroic OH bands at 3540 (main), 3359 and 3250 cm^{-1}. For comparison, terrestrial plagioclase GRR1389 ($An_{32}Ab_{66}$) has pleochroic OH bands at 3690 (small), 3368 and 3238 cm^{-1}. The fact that the OH bands in maskelynite are not pleochroic and the relative heights of the OH bands differ from those of GRR1389 may be due to the transformation of the plagioclase into glass by shock. Maskelynite water contents vary from 22 to 84 ppm H_2O.

Conclusions: Water concentrations in nakhlite (<20 ppm H_2O) and ALH 84001 (0 ppm H_2O) pyroxenes are low compared to those of terrestrial pyroxenes (59-576 in cpx and 9-267 in opx from oceanic pyroxenites [21,22]). Degassing (NWA 6148) or shock (ALH 84001) likely caused H loss. Maskelynite in ALH 84001 contains variable amounts of water but H isotopic analyses will be necessary to determine its origin (mantle source versus contamination by Martian atmosphere contamination during shock).

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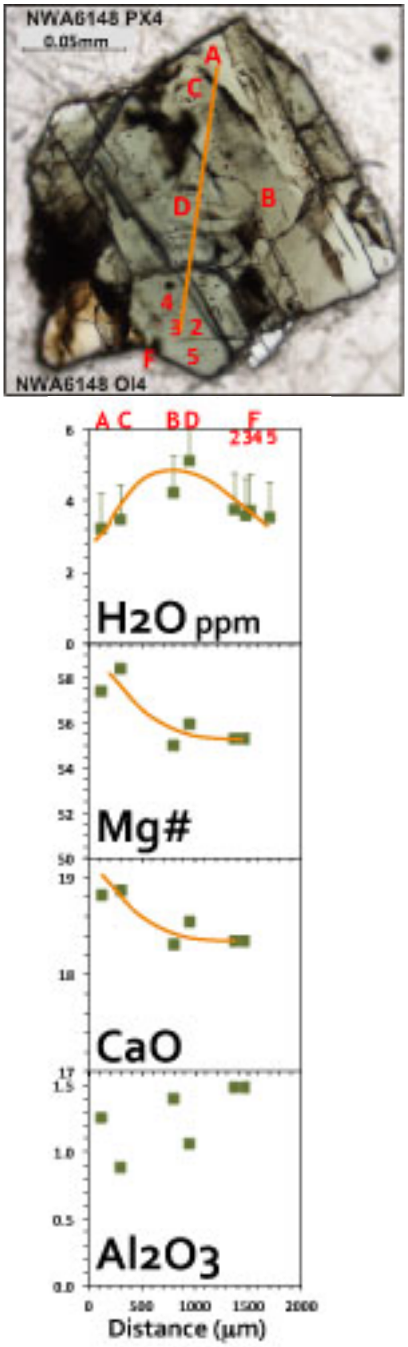

Figure: Plane-polarized photo of a pyroxene from nakhlite NWA 6148 and cross-section analyses for water and major elements. Major elements do not correlate with water contents, likely indicating degassing. Orange lines emphasize trends.