Isotopography of hydrogen in apatite of Martian meteorites: Constraints on their petrogenesis and the history of water on Mars

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Ion and electron microscope analyses of apatite in Martian meteorites Shergotty, Los Angeles, and ALH84001 reveal that the apatite grains preserve a record of late-stage magmatic assimilation of a deuterium-rich and chlorine-rich component. 2-D ion imaging using the Hokudai Cosmochemistry Cameca ims 1270 with SCAPS detector show isotope zoning from deuterium-poor core to deuterium-rich rim in a Los Angeles apatite. This same grain is also zoned from a fluorine-rich core to a chlorine-rich rim and spans the compositional range from fluor-apatite to chlorapatite. The apatites are believed to represent late-stage crystallization of the parent magmas (more than 95% total crystallization), thus the late addition of a deuterium-rich and chlorine-rich component is indicated. A plausible scenario would be crustal assimilation by the magma upon emplacement near the Martian surface. This argues against hydrogen isotope alteration of the apatites during the waning stages of the igneous hydrothermal system, or low-temperature acidic alteration of the apatites during periodic warming commensurate with obliquity cycles. The apatites have significant terrestrial hydrogen associated with the many micro-fractures of these shocked meteorites, and the about 1 micrometer spatial resolution of hydrogen isotope imaging via SCAPS was found necessary to find crack-free areas for spot analyses.

The apatites appear to preserve an excellent record of atmospheric D/H on Mars. The values we measure for apatites in Shergotty in two separate analytical sessions (delta D=+4606 (24) permil; +4590 (31) permil (1sigma)) are the highest values reported for a Martian meteorite, and higher than more imprecise telescopic measurements of Martian atmospheric D/H. It is unlikely that the Martian atmospheric D/H has been decreasing since 185 Ma (the crystallization age of Shergotty), thus we suggest that the Martian atmospheric D/H is similar to the value we measure in Shergotty, and that the D/H of the Martian atmosphere has remained essentially constant in the recent epoch.

A D/H analysis for apatite in the ancient ALH84001 (delta D=+2998 (68) permil (1sigma)) is higher than previous measurements of this meteorite by more than 900 permil. The crystallization age of ALH84001 is 4.5 Ga, but shock event(s) at 3.9 Ga are also recorded in radiogenic isotopes. This suggests that the Martian atmospheric delta D was likely about +3000 by either 4.5 or 3.9 Ga (depending on whether or not the shock event at 3.9 Ga was capable of leading to hydrogen isotope exchange of apatite). This result suggests that the majority of Martian water was lost to space by at least 3.9 Ga. Early loss of hydrogen (and water) by hydrodynamic escape is indicated. This work also suggests that the loss of hydrogen from the Martian atmosphere by Jeans escape has been less efficient than previously hypothesized. It appears that the Martian delta D has only increased by about 1500 permil in the last 4 billion years.