

HIGH D/H RATIOS OF WATER IN MAGMATIC AMPHIBOLES IN CHASSIGNY: POSSIBLE CONSTRAINTS ON THE ISOTOPIC COMPOSITION OF MAGMATIC WATER ON MARS; L.L. Watson, I.D. Hutcheon, S. Epstein, and E.M. Stolper, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125.

Abstract. We have measured the D/H ratios of kaersutitic amphiboles contained in magmatic inclusions in the SNC meteorite Chassigny using the ion microprobe. A lower limit on the δD_{SMOW} of the amphiboles is $+1420 \pm 47$ ‰. Assuming Chassigny comes from Mars and the amphiboles have not been subject to alteration after their crystallization, this result implies either that recycling of D-enriched martian atmosphere-derived waters into the planetary interior has taken place, or that the primordial hydrogen isotopic composition of the interior of Mars differs significantly from that of the Earth ($\delta D_{SMOW} \sim 0$ ‰). In addition, the measurements indicate that the amphiboles contain < 0.3 wt. % water. This is much lower than published estimates, and indicates a less-hydrous Chassigny parent magma than previously suggested.

Introduction. The D/H ratio of water in the martian atmosphere is enriched by a factor of 5.15 relative to the Earth [1] and weathering products in the nakhlite meteorites ("N" of the SNC group, thought to be possibly martian samples [2,3]) have also been shown to contain water significantly enriched in deuterium [4,5]. These D enrichments are thought to result from massive escape of hydrogen (relative to the heavier deuterium) from the martian upper atmosphere throughout its history [6,7]. A measurement of the D/H ratio of magmatic (interior) water would provide important constraints on the extent of such hydrogen loss because the D/H ratio of the martian interior likely reflects its original value (which has been assumed to be near the terrestrial value of 1.5×10^{-4} [8]) since unlike the Earth with its subduction zones, recycling of near-surface and atmosphere-derived waters to the martian deep interior is generally considered to be an unimportant process.

The SNC meteorite Chassigny ("C" of the acronym SNC) contains cumulus olivine crystals that trapped small (up to ~ 150 μm in diameter) pockets of melt during growth [9,10]. After entrapment, the inclusions partially crystallized, and the residual melt became progressively enriched in water. This led ultimately to the stabilization of kaersutite, a titanium-rich amphibole. Based on the crystal chemistry of the amphibole group and analyses of the Chassigny kaersutites with the electron microprobe and qualitative ion microprobe analyses, these kaersutite crystals have previously been suggested to contain hydroxyl as a major constituent [9,10]; Johnson et al. [10] estimated that they contain 1.5 wt.% water as hydroxyl groups. The amphiboles occur *only* in the interiors of the melt inclusions and are 10-30 μm in size. Thus, although the bulk meteorite is very poor in water, the amphiboles in the inclusions are thought to have concentrated magmatic water in structural sites. The goal of this work has been to measure the D/H ratio of the water in these amphiboles as a means of constraining the D/H ratio of magmatic water on another planet, possibly Mars.

Measurements. The D/H ratio of the kaersutites cannot be determined by conventional heating/extraction techniques since they are much too small and few in number to separate from the bulk meteorite. We have measured the D/H ratio of four single crystal kaersutites, ranging in size from 15 to 30 μm , in thin section USNM 624-1 on the PANURGE ion microprobe at Caltech. A large instrumental fractionation of the two hydrogen isotopes makes these measurements difficult [11]. This fractionation is strongly dependent upon the major element composition of the material being studied, requiring D/H standards with chemical compositions similar to that of the Chassigny kaersutite. Since no suitable terrestrial standard was available because the meteoritic kaersutites are outside of the range of common terrestrial amphibole compositions, we synthesized three glasses of the same bulk composition as the kaersutite (from [10]) containing dissolved water of various hydrogen isotopic compositions. The hydrous glasses were synthesized in a piston-cylinder apparatus at 10 kbar and 1550°C. Small chips of each glass were mounted and polished for ion microprobe analysis and the remaining sample was heated on a conventional extraction line to determine the δD of the dissolved water. Ion microprobe measurements of D/H ratios were made using a mass resolving power of ~ 1200 , sufficient to resolve D^+ and H_2^+ , and a $^{16}\text{O}^-$ primary beam of ~ 1.5 nA focused to a diameter of 3 to 5 μm .

Results. The H^+ intensity on the standard glasses ranged from 24100 to 65000 counts per second, increasing with the water content of 0.7 to 1.9 wt. %. The H^+ count rate varied from 5300 to 10000 counts per second on the Chassigny kaersutites. The background H^+ intensity measured on anhydrous silicates

was ~2000-3500 cps. No correction for H⁺ or D⁺ arising from adsorbed water was applied due to the large uncertainty in the D/H ratio and absolute abundance of this background component.

The instrumental fractionation factor, α , corresponds to the ratio of the measured D/H ratio to the absolute D/H ratio such that $\alpha = (D/H)_{\text{measured}} / (D/H)_{\text{true}}$. The three standards had δD_{true} values of +48, +592 and +1130 ‰ (where δD is expressed as a per mil difference relative to the D/H ratio of standard mean ocean water). $\delta D_{\text{measured}}$ values for these glasses correlate linearly with δD_{true} and yield $\alpha = 0.607 \pm 0.014$ (2σ) (Fig. 1). Using this fractionation factor, δD_{true} values of four Chassigny kaersutites in three different magmatic inclusions range from $+853 \pm 55$ to $+1420 \pm 47$ ‰ (Fig. 1). The δD values increase with the H⁺ count rate suggesting that the H⁺ and D⁺ signals contain contributions from both adsorbed water and water structurally bound in the kaersutite. A measurement of the isotopic composition of the background gives a δD_{true} value of -127 ± 59 ‰ thus any correction will increase the actual δD values. Thus the δD values reported here should be taken as lower limits.

Discussion. The low count rates for the meteoritic amphiboles compared to the standards suggests that these crystals contain less hydrogen (water) than the 1.5 wt.% previously implied based on electron probe totals and measurement of ~0.5 wt. F [10]. Our data are consistent with a water content of <0.3 wt. %. Estimates of the water content of the parental magmas of Chassigny [10] and of its minimum depth of crystallization (~11 km [10]) will require downward revision since less water is needed in coexisting melt to stabilize an amphibole containing so little water.

The high D/H ratio of the water in the kaersutites is unexpected. Based on models of the origin of the solar system [8] it has been predicted that martian "juvenile" water would have approximately the same D/H ratio as the Earth corresponding to a δD_{SMOW} value of $\sim 0 \pm 100$ ‰. Although we cannot rule out post-crystallization exchange of the hydrogen in the amphibole with heavier surface or atmosphere-derived (meteoric) waters, the facts that the hydrogen is thought to be structurally-bound in the amphibole and that the olivine "containers" show no evidence of alteration make this unlikely. Chassigny differs in this respect from the nakhlites, for example, which contain alteration in the form of reddish-brown "iddingsite" type veins [12,13]. If the measured D/H ratio of the kaersutites is in fact representative of the isotopic composition of the water dissolved in the Chassigny parental magma, either some sort of recycling of heavy atmosphere-derived waters into the magma source region must have taken place or the isotopic composition of the "primordial" water of the mantle of the Chassigny parent body (Mars?) differs significantly from the terrestrial mantle. Moreover, this implies that the deuterium enrichment of the martian atmosphere due to hydrogen escape is less extreme than previously thought.

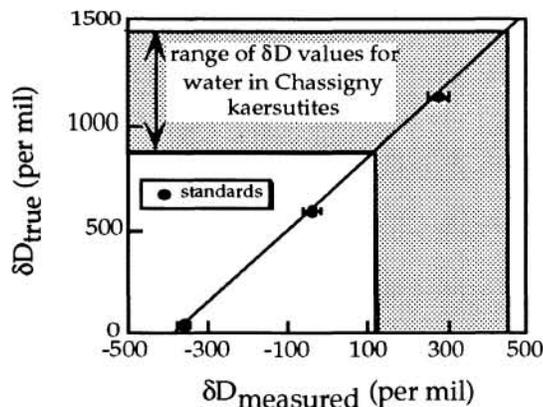


Fig. 1. Corrected hydrogen isotopic composition of water in Chassigny kaersutites (δD_{true}) versus to the values measured by ion microprobe ($\delta D_{\text{measured}}$). The symbols represent the standards used to calibrate the correction factor.

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