Insights into martian water reservoirs from analyses of martian meteorite QUE94201

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Abstract. The martian atmospheric D/H value of 5.2 times terrestrial is significantly higher than any found on Earth, and has been ascribed to preferential loss of H relative to D from the atmosphere through Jeans escape over time. Here, based on ion microprobe analyses of apatite grains from martian meteorite QUE94201, it is shown that the pre-Jeans escape martian water reservoir has a D/H value twice that of terrestrial water, rather than the "terrestrial" value that has been assumed in prior work. The data support a two-stage history for martian volatiles in which early hydrodynamic escape enriched martian water to ~2x terrestrial D/H values. Subsequent Jeans escape to produce the current atmospheric values has thus been responsible for less D-enrichment than previously thought. A martian crust containing 2-3 times more water than previously proposed is implied by the results.

Introduction

The presence of valley networks, most plausibly produced by flowing water, provides compelling evidence for a significant crustal water reservoir on Mars early in its history. However, few constraints on the abundance of water in modern martian reservoirs other than the atmosphere are available. One clue to deciphering the history of water on Mars is the deuterium-to-hydrogen ratio (D/H) in water in the current martian atmosphere which shows an enrichment in D over H by a factor of 5.2 relative to terrestrial values [Bjoraker et al., 1989] (δD = +4200‰; δD notation expresses the deviation of a measured D/H ratio from that of standard mean ocean water on Earth in parts per thousand; the range of δD values on Earth is about +100 to -300 ‰; [Hoefs, 1997]). The martian atmospheric D/H value has been ascribed to preferential loss of H relative to D through Jeans (thermal) escape over time [Owen et al., 1988; Yang et al., 1988; Donahue, 1995].

Assuming the rate of loss of H and D from the martian atmosphere has not been constant through time (a very likely scenario [Yang et al., 1988; Donahue, 1995]), in order to translate the measured atmospheric D/H value into the amount of water that has been lost from Mars, two quantities must be known: (1) the size of the water reservoir affected by the loss process (i.e., the amount of D-enriched "exchangeable" water remaining on Mars), and (2) the initial D/H value of martian water from which the atmospheric escape takes place. Determining the inventory of D-enriched water is difficult without direct samples of martian groundwater and ice from the polar caps. However, previous studies of isotopic systematics of volatiles in martian meteorites imply that a significant reservoir of exchangeable crustal water may exist on Mars [Karlsson et al., 1992; Watson et al., 1994; Leshin et al., 1996; Fanghler et al., 1998]. The initial D/H value of the water on Mars from which the atmospheric enrichment takes place has previously been widely assumed to be approximately identical to the terrestrial value (δD = 0 ‰). However, there are reasons to doubt this assumption. Although more meteorites appear to have water with a D/H value similar to terrestrial water (δD = 100; e.g., Robert and Epstein, 1982) recent data on the D/H of water from comets [Balsiger et al., 1995; Fehrenbacher et al., 1995; Boeckele-Morvan et al., 1998; Meier et al., 1998] and some meteorites [Deloule and Robert, 1995] show significantly higher D/H values than terrestrial, indicating that inhomogeneities in the D/H of water accreted by the terrestrial planets are possible. Additionally, differences in the accretional histories of Mars and Earth (e.g., homogeneous vs. heterogeneous accretion [Dreibus and Wanke, 1981]) could have given rise to different D/H values for water on the two planets at the end of accretion.

It should be possible to test the assumption that the D/H value of water on Mars had δD ~ 0 ‰ prior to modification by Jeans escape of hydrogen. Mars, unlike Earth, probably has not experienced significant crustal recycling through the action of plate tectonics. Thus, the isotopic composition of magmatic water on Mars should accurately reflect the isotopic composition of water in the mantle (the source of the basaltic magmas), which presumably has remained unchanged since the planet's earliest history. Magmatic hydrous minerals in the martian meteorites provide the best opportunity to study magmatic water on Mars. Unfortunately, such minerals are extremely rare in the 14 known martian meteorites, samples widely believed to have been blasted off of Mars in several events in the past ~15 Ma [McSween, 1994]. They are all igneous rocks, ranging from the 180 Ma basaltic shergottites [Shih et al., 1982; Jones, 1986] to the ancient (4.5 Ga) orthopyroxenite ALH84001 [Nyquist et al., 1995].

In previous work, the D/H values of magmatic, hydrous minerals apatite, Ti-rich amphibole, and biotite were analyzed in three martian meteorites by ion microprobe [Watson et al., 1994]. The elevated and variable D/H values of water discovered in the minerals (δD~+500 to +4300) were interpreted qualitatively as representing a mixture of magmatic water in the minerals with a D-enriched component derived from the martian atmosphere (with a D/H value ~5x terrestrial), through isotopic exchange with D-enriched groundwaters introduced after the phases crystallized [Watson et al., 1994]. The isotopic composition of the magmatic water end member was not well constrained by the data, an upper limit was stated to be in the range of δD = +500 to +1000 ‰, the lowest δD values measured in the minerals. The single apatite grain studied had a higher water content and δD than any of the amphiboles studied, making this mineral an ideal target for further work.
Figure 1. Scanning electron microscope backscattered electron image of apatite grain 1 in thin section QUE94201.5. Scale bar is 30 μm across. Four ion microprobe analysis pits are visible in the image. The apatite is surrounded by mesostasis rich in fayalitic olivine (brighter) and silica (darker), with a pyroxene grain on the far right (medium grey).

Methods

Analyses of ΔD and water content of magmatic, hydrated apatite [Ca₅(PO₄)₃(OH,F,F,Cl)] from shergottite QUE94201 (hereafter called QUE) were performed with the Cameca IMS1270 ion microprobe at UCLA. QUE was collected in the Queen Alexandria Range, Antarctica in the 1994 field season and comprises a single 12 gram stone. This sample represents a fractionated basaltic liquid composition, and is composed predominantly of pyroxene (pigeonite and augite) and maskelynite (shocked plagioclase feldspar), opaque oxides, phosphates (merrillite and apatite) and mesostasis [McSween et al., 1996]. Probably because of its evolved bulk composition, it contains a high abundance of apatite compared to the other martian meteorites. However, apatite is still present at the <1% level, highlighting the importance of the use of a microbe analysis technique.

ΔD measurements were performed on five apatite grains from polished thin section (PTS) QUE38 (Fig. 1) and on one grain from PTS QUE38. The primary 18O beam was focused to a diameter of 8-15 μm, beam currents ranged from 0.75 to 1.3 nA. H+, D+ and H2+ secondary ions were measured by ion counting at a mass resolving power of ~1800. Correction for instrumental mass fractionation utilized a terrestrial apatite standard. In addition, water contents in most spots analyzed for ΔD were determined by measuring 18O/16O and applying a sensitivity factor determined from analyses of the standard apatite. Count rates of H+ were 6 × 10⁴ to 2 × 10⁵ cps.

Results and Discussion

Eleven apatite ΔD measurements range from +1680 to +3570‰ with a typical uncertainty of ±140‰ (2σ) (Table 1). The isotopic data show a striking enrichment of O17 content of the apatite (Fig. 2). The data fall within the range of values observed in other martian meteorites by Watson et al. [1994], however the previous study analyzed water contents in only a few selected areas, thus it is not possible to compare the QUE data with the Watson et al. [1994] data in Fig. 2. Although the largest variations in ΔD and water content are observed between different apatite grains, in the cases where multiple analyses could be performed, slight intergrain variations are observed (Table 1). Any zoning patterns, if present, could not be accurately detected due to the small size of the grains compared to the spatial resolution of the analyses.

Because of the rapid diffusion and equilibration of hydrogen in high-temperature magmas, it is most reasonable to approach the interpretation of the data assuming the QUE magma initially contained water with a constant ΔD value, and that some process altered this magmatic ΔD to result in the variable ΔD/H values observed. The data are suggestive of mixing between two isotopically distinct hydrogen reservoirs because most physical processes (e.g., degassing) are incapable of producing the ~2000‰ isotopic variation observed. One physical process that has been proposed to explain the ΔD variation reported by Watson et al. [1994] is shock devolatilization imposed by the impact event that ejected the rocks from Mars [Minitti et al., 1997; Minitti and Rutherford, 1998]. However, experimental data to date do not demonstrate that this mechanism is capable of producing the observed large ΔD-enrichments [Minitti and Rutherford, 1998].

Neither mixing (with atmosphere-derived, ΔD-enriched waters) or shock would tend to increase the ΔD of the minerals, making the magmatic water the low-ΔD end-member of the trend in Fig. 2. A best fit mixing model to account for the variation of the data gives a value of +200 ± 250‰ for the H isotopic composition for the low-ΔD end member. This fit assumes only that the low-ΔD end member has a constant ΔD value. In the context of the previously proposed model for ΔD isotopic variability in martian magmatic minerals [Watson et al., 1994], the apatite crystallized with initially variable water content and uniform ΔD of ~900‰. The possibility that the

<table>
<thead>
<tr>
<th>Analysys spot</th>
<th>ΔD (‰) ± 2σ ¹</th>
<th>water content (wl. ‰) ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>QUE5, grain 1, spot 1</td>
<td>1683 ± 134</td>
<td>0.53</td>
</tr>
<tr>
<td>QUE5, grain 1, spot 2</td>
<td>1778 ± 136</td>
<td>0.64</td>
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<tr>
<td>QUE5, grain 1, spot 3</td>
<td>2058 ± 114</td>
<td>0.55</td>
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<tr>
<td>QUE5, grain 1, spot 4</td>
<td>2138 ± 124</td>
<td>0.42</td>
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<tr>
<td>QUE5, grain 2, spot 1</td>
<td>1818 ± 146</td>
<td>nd ³</td>
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<tr>
<td>QUE5, grain 2, spot 2</td>
<td>2356 ± 166</td>
<td>0.42</td>
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<tr>
<td>QUE5, grain 3, spot 1</td>
<td>2778 ± 190</td>
<td>0.38</td>
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<td>2701 ± 188</td>
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<td>3565 ± 728</td>
<td>0.22</td>
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<tr>
<td>QUE38, grain 1, spot 1</td>
<td>7288 ± 130</td>
<td>nd</td>
</tr>
<tr>
<td>QUE38, grain 1, spot 1 ¹</td>
<td>2147 ± 136</td>
<td>nd</td>
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* Analyses were performed in two different polished thin sections: QUE94201 and QUE38. Where multiple analyses locations in a single grain were measured, a new spot number is given.
† replicate analysis in same spot
‡ Uncertainties reflect the internal measurement precision within a spot and the standard deviation of multiple analyses of the same sample over the course of the analysis session.
§ Based on repeated analysis of standards, uncertainties on water content measurements are ±10% relative.
³ nd = not determined
Figure 2. δD values and water contents ofapatite grains from martian meteorite QUE94201. δD values are expressed relative to standard mean ocean water (SMOW). Uncertainties are discussed in Table 1. Only the D/H data for which water content determinations were made are plotted here (see Table 1 for all D/H data). The data are interpreted to represent a mixture of at least two end members, and most plausibly represent addition (or exchange) of water with an atmospheric D/H signature (δD ~+4200‰) to minerals which initially uniformly contained water with δD of ~-900 ± 250‰, or ~twice the D/H value commonly assumed for magmatic water on Mars. The curve shows the mixing model from which the initial D/H of the minerals was calculated.

The water content of the grains was initially variable is supported by variable F and Cl abundances in the same minerals [McSween et al., 1996]. Exchange of a fixed amount of the H in the minerals (i.e., a fixed water:rock ratio over this 12 gram sample) with H from crustal water (with a D/H value similar to the atmosphere) can produce the observed variation in δD. The δD values of the apatites with the lowest initial water contents are affected by exchange, and the highest water content apatites are affected the least. The amount of exchanged water is dependent on the choice of δD value for the high-δD end member. If δD = +4200‰ is chosen, 0.17 wt. % water in each grain is exchanged in this model.

Another possibility to explain the isotopic variations is that the magma assimilated crustal material containing D-enriched water during crystallization [Jakosky and Jones, 1997], and the minerals crystallized with variable δD values from the isotopically variable magma. The anti-correlation of δD and water content would seem to argue against this since assimilation should increase both δD and the water content of the magma, opposite to the observed trend in Fig. 2. It is important to note that regardless of which mechanism is ultimately shown to be responsible for the production of the high and variable D/H values observed here, the isotopic composition of the low-δD end member remains the same. Thus, the implications for the accretional and early history of water on Mars, and the fraction of hydrogen lost by Jeans escape (discussed below) remain unchanged.

The most straightforward interpretation of the data presented in Fig. 2 is that magmatic water is the low-δD endmember, and that the D/H value of this water is not the same as terrestrial water but is ~twice the terrestrial D/H value. There are several scenarios that could conceivably produce this factor of 2 enrichment in D over terrestrial values. First, it is possible that the water in the martian mantle reflects accretion of a mixture of components with different D/H values than those that delivered the Earth’s water. In this case, Mars never accreted water with an “Earth-like” D/H. The D/H of terrestrial water is similar to the D/H in the water in most primitive meteorites [Kolodny et al., 1980; Robert and Epstein, 1982; Kerridge, 1985]. The twice terrestrial magmatic D/H value is indistinguishable within uncertainties from the D/H values of comets [Balsiger et al., 1995; Eberhardt et al., 1995; Bockelee-Morvan et al., 1998; Meier et al., 1998], therefore cometary materials would be the best choice for the dominant source of martian water in this scenario.

A more realistic consideration of the accretion history of the terrestrial planets in which materials in the Mars-Earth forming region were relatively well mixed [Chambers and Wetherill, 1998] leads to other, slightly more complex scenarios for explaining the observations. Hydrodynamic escape of H₂, which is effective only very early in martian history during the time of enhanced EUV flux from the young Sun, has the ability to fractionate D from H to produce a wide variety of D-enrichments, depending on the escape flux and the mixing ratio of other atmospheric species such as CO₂ [Zahnle et al., 1990]. Thus, hydrodynamic escape acting upon an early-accreted water reservoir with initially Earth-like D/H, where not all of the accreted water was lost, could leave behind a reservoir enriched in D by a factor of 2 over the accreted water. Alternatively, all originally accreted water could have been lost during homogeneous accretion, a previous model involving accretion of Fe metal and water-bearing materials together, in which reaction with the reduced Fe converts all the water to H₂, which is then lost through hydrodynamic escape [Dreibus and Wanke, 1987]. A subsequent resupply of water, predominantly from a cometary source, could then account for the D/H of martian magmatic water. In either case, the data are consistent with a scenario in which hydrodynamic escape played a significant role in altering the early volatile inventory of Mars, consistent with martian atmosphere noble gas fractionation patterns which are most plausibly explained by an episode of early hydrodynamic escape [Hunten et al., 1987; Zahnle et al., 1990; Pepin, 1991].

In any of the above scenarios, it is still necessary to attain the current atmospheric D/H value of ~5× terrestrial through Jeans escape subsequent to the establishment of the post-hydrodynamic escape water reservoir. The data presented here show that the water reservoir from which the Jeans escape occurs has a higher D/H value than has been considered in previously [Yang et al., 1988; Donahue, 1995]. Thus, in the context of previous models for loss of hydrogen in which an exchangeable reservoir of D-enriched water remains in the crust [Yang et al., 1988; Donahue, 1992], the total amount of water remaining in this exchangeable reservoir must be higher than previously thought.

Using reasonable estimates for the relative loss rates of H and D [Yang et al., 1988; Pathare and Paige, 1995; Krasnopolsky et al., 1998] in order to enrich a reservoir of water to the current atmospheric value from an initially “terrestrial-like” D/H (δD ~ 0 ‰), ~ 80 - 90% of the hydrogen from that reservoir must have been lost (i.e., ~10 - 20% of the water remains on Mars). If, as the data presented here indicate, this reservoir started out with a D/H value of ~2x terrestrial, then the percentage of hydrogen lost from the reservoir would be reduced, resulting in a currently remaining water reservoir.
Acknowledgments: I thank R. Harvey, T. McCoy, K. McKeegan, H. McSween, D. Paige, A. Paturess, J. Tyburczy, and M. Wahdha for helpful discussions and assistance. S. Nadeau provided the apatite standard. I thank the Antarctic Metorozon Curation Facility at JSC for loan of sections and G. Crozaz and H. McSween for use of section QUEL. Helpful reviews from Bruce Jakosky and an anonymous reviewer are appreciated. The ion microprobe facility at IFIA is supported by NSF. This work was supported by NASA.

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(Received December 1, 1999; revised March 1, 2000; accepted March 30, 2000)