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] (D/D = +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 -500 to +500‰; [Hoefs, 1997]). The martian atmospheric D/H value has thus been responsible for less D-enrichment than previously thought. 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 [Nagoya 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.
predominantly of pyroxene (pigeonite and augite) and a fractionated basaltic liquid composition, and is composed and comprises a single 12 gram stone. This sample represents 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 microbeam analysis technique.

Methods

Analyses of D/H and water content of magmatic, hydrated apatite \([\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})]\) 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 microbeam analysis technique.

D/H measurements were performed on five apatite grains from polished thin section (PTS) QUE,5 (Fig. 1) and on one grain from PTS QUE,38. The primary \(^{19}\)F beam was focused to a diameter of 8 - 15 µm; beam currents ranged from 0.75 to 1.3 nA. \(^{18}\)H, \(^{17}\)H and \(^{17}\)D 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 D/H were determined by measuring \(^{17}\)H/\(^{16}\)O and \(^{18}\)H/\(^{16}\)O ratios. In the context of the previously proposed model for H isotopic variability in martian magmatic minerals [Watson et al., 1994], the apatite crystallized with initially variable water content and uniform D/H = 2000‰. The possibility that the

Results and Discussion

Eleven apatite D/H measurements range from -1680 to +3570‰ with a typical uncertainty of ± 140‰ (2σ) (Table 1). The isotopic data show a striking correlation with OH 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 D/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 D/H 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 D-enrichments [Minitti and Rutherford, 1998].

Either mixing (with atmosphere-derived, D-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 +900 ± 250‰ for the HI isotopic composition of 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 H isotopic variability in martian magmatic minerals [Watson et al., 1994], the apatite crystallized with initially variable water content and uniform δD of -2000‰. The possibility that the

### Table 1. D/H and water contents of QUE94201 apatite

<table>
<thead>
<tr>
<th>Analysis spot *</th>
<th>δD (‰) ± 2σ</th>
<th>Water content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QUE,5, grain 1, spot 1</td>
<td>1683 ± 134</td>
<td>0.53</td>
</tr>
<tr>
<td>QUE,5, grain 1, spot 2</td>
<td>1778 ± 136</td>
<td>0.64</td>
</tr>
<tr>
<td>QUE,5, grain 1, spot 3</td>
<td>2058 ± 114</td>
<td>0.55</td>
</tr>
<tr>
<td>QUE,5, grain 1, spot 4</td>
<td>2138 ± 124</td>
<td>0.42</td>
</tr>
<tr>
<td>QUE,5, grain 2, spot 1</td>
<td>1818 ± 146</td>
<td>nd</td>
</tr>
<tr>
<td>QUE,5, grain 2, spot 2</td>
<td>2336 ± 166</td>
<td>0.42</td>
</tr>
<tr>
<td>QUE,5, grain 3, spot 1</td>
<td>2778 ± 190</td>
<td>0.38</td>
</tr>
<tr>
<td>QUE,5, grain 4, spot 1</td>
<td>2701 ± 188</td>
<td>0.27</td>
</tr>
<tr>
<td>QUE,5 grain 5, spot 1</td>
<td>3565 ± 228</td>
<td>0.22</td>
</tr>
<tr>
<td>QUE,38 grain 1, spot 1</td>
<td>2288 ± 130</td>
<td>nd</td>
</tr>
<tr>
<td>QUE,38 grain 1, spot 1</td>
<td>2157 ± 136</td>
<td>nd</td>
</tr>
</tbody>
</table>

*Analyses were performed in two different polished thin sections: QUE94201,5 and .38. Where multiple analysis 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.

\( \text{nd} \) = not determined
by variable F and C1 abundances in the same minerals. The water content of the grains was initially variable is supported that the magma assimilated crustal material containing D-enriched water during crystallization [Jakosky and Jones, 1983; Kerridge, 1983]. 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; Bockelée-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 accretional and early 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. 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, 1995], 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 ~2× terrestrial, then the percentage of hydrogen lost from the reservoir would be reduced, resulting in a currently remaining water reservoir...
\[ \text{References} \]

Balsiger, H., K. Altwegg, and J. Geiss, \( D/H \) and \( ^{18}O/^{16}O \) ratio in the hydronium ion and in neutral water from in situ ion measurements in comet Halley, \textit{J. Geophys. Res.}, 100, 5827-5834, 1995.


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