The role of H$_2$O in Martian magmatic systems

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ABSTRACT

We have estimated the water content of Mars’ interior by using analyzed water contents of kaersutite inclusions from shergottites nakhlites chassignites (SNC) meteorites in conjunction with an experimentally-derived crystal-chemical model of kaersutite amphibole. This model predicts quantitatively the relationships between iron oxidation and hydrogen deficiency in the kaersutite. The H$_2$O content of the magma from which the kaersutites in SNC meteorites could have crystallized is in the 100–1000 ppm range. That H$_2$O content leads to an estimated water content of 1–35 ppm for a Martian mantle that could have been the source rock for such magmas.

INTRODUCTION

Information on the H$_2$O abundance in the Martian interior is required to characterize the accretional and degassing history of the planet (McSween and Harvey 1993; Carr and Wänke 1992; Dreibus and Wänke 1985, 1987). The H$_2$O abundance also affects the composition of partial melts (Kushiro 1972; Stolper 1980; Treiman 1985; Longhi and Pan 1989; Johnson et al. 1991) and the physical properties of the magma [density, compressibility, and viscosity (Lange 1994; Schulze et al. 1996; Kushiro 1976)]. Those properties, in turn, govern the dynamics of magma ascent and the style of eruption.

Previous estimates of H$_2$O contents of the Martian interior vary widely, ranging from several tens of ppm (Dreibus and Wänke 1985) to perhaps 2000–3000 ppm (Reid and Bunch 1975; McSween and Harvey 1993; Harvey and McSween 1992). The lower estimates are based on solar element abundances and abundance ratios in shergottites nakhlites chassignites (SNC) meteorites and in carbonaceous chondrites. The SNC meteorites most likely are of Martian origin (Bogard and Johnson 1983; Becker and Pepin 1984; McSween 1985). The high estimates derive from the existence of hydrous minerals, such as kaersutitic amphibole, coexisting with glass in inclusions in olivine and pyroxene in SNC meteorites (Harvey and McSween 1992; Treiman 1985; Johnson et al. 1991) coupled with the assumption of H$_2$O saturation of the kaersutite [2(OH) pfu]. Kaersutite is a Ti-rich amphibole with the formula, Ca$_2$ (Na,K) (Mg,Fe$_{0.1}$,Fe$_{0.8}$)$_{5-6}$ (Ti,Al)(Si$_{6}$ Al$_{2}$ O$_{22}$ (O,OH,F)$_{2}$ (Deer et al. 1963). In its structure there are two tetrahedral sites (T1 and T2) containing Si and Al, and five octahedral sites (two M1, two M2, and one M3 site) containing Fe$^{2+}$, Fe$^{3+}$, and Mg in the M1 and M3 sites and Ti and Al in the M2 site. There are three O sites (O1, O2, and O3) with 2(OH,O,F) in the O3 site associated with the M3 octahedral site (Pechar et al. 1989).

Amphiboles that are water-saturated [that is 2(OH) pfu ~2 wt% H$_2$O in these kaersutites] most likely would crystallize from a magma that contains several weight percent H$_2$O. A Martian mantle source of such magma would probably contain several thousand ppm H$_2$O (Harvey and McSween 1992) or several times the concentration estimated for the interior of the Earth (Jambon and Zimmermann 1990).

The H$_2$O contents of kaersutite in Chassigny and Zagami SNC meteorites are, however, 0.1–0.2 wt% (Watson et al. 1994), or only 5–10% of the H$_2$O content of kaersutite with 2(OH) pfu (Table 1). These analyzed H$_2$O contents can be used to derive realistic H$_2$O contents of the magma with which the kaersutites were in equilibrium by using experimentally established quantitative relationships between H$_2$O content, redox ratio of Fe, and Ti content of kaersutite as a function of $T$, $P$, and $f_{O_2}$.

The calculation of H$_2$O content of the parental magma relies on the assumption that the amphiboles did not suffer H$_2$O-loss subsequent to crystallization. Despite suggestions that post-crystallization processes may affect the crystal chemistry of amphibole in terrestrial magmatic systems, the only study that incorporated data on hydrogen diffusion in minerals (Dyar et al. 1993) concluded that the OH content of kaersutite does not change significantly during transport from the Earth’s mantle to the surface. In the Martian environment, the amphiboles may also have been shocked during the impact that led to their transport from Mars to Earth. Amphiboles shocked experimentally to ~30 GPa (Minitti and Rutherford 1998) yield ambiguous results as to whether such exposure may have affected their H content.

METHOD

The initial step in the procedure is to compute, from the experimental calibration data, the fugacity of H$_2$, $f_{H_2}$,


Table 1. Composition of Vulcan’s Throne kaersutite compared with kaersutite from SNC meteorites

<table>
<thead>
<tr>
<th></th>
<th>VT*</th>
<th>C†</th>
<th>Z‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>40.32</td>
<td>39.49</td>
<td>35.15</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.84</td>
<td>7.00</td>
<td>8.94</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.36</td>
<td>14.22</td>
<td>15.13</td>
</tr>
<tr>
<td>FeO‡</td>
<td>7.70</td>
<td>10.47</td>
<td>16.18</td>
</tr>
<tr>
<td>MgO</td>
<td>14.53</td>
<td>11.53</td>
<td>6.40</td>
</tr>
<tr>
<td>CaO</td>
<td>10.46</td>
<td>11.80</td>
<td>11.48</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.74</td>
<td>2.99</td>
<td>2.38</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.60</td>
<td>0.33</td>
<td>0.20</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.27</td>
<td>0.1–0.2</td>
<td>0.1–0.2</td>
</tr>
</tbody>
</table>

* VT = Vulcan’s Throne, Arizona. Fe²⁺/(Fe³⁺ + Fe²⁺) = 0.317 (from Popp et al. 1995a and 1995b).† C = Chassigny (from Johnson et al. 1991).‡ Z = Zagami (from Treiman 1985).§ Total iron as FeO.|| H₂O concentration range from Watson et al. (1994).

Table 2. Log fH₂O values calculated with 0.1 and 0.2 wt% H₂O in Chassigny and Zagami kaersutite

<table>
<thead>
<tr>
<th>Pressure bar</th>
<th>0.1 wt% H₂O</th>
<th>0.2 wt% H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800 °C</td>
<td>900 °C</td>
</tr>
<tr>
<td>Chassigny</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zagami</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-3.422</td>
<td>-3.075</td>
</tr>
<tr>
<td>1000</td>
<td>-3.312</td>
<td>-2.965</td>
</tr>
<tr>
<td>2500</td>
<td>-3.147</td>
<td>-2.800</td>
</tr>
<tr>
<td>4000</td>
<td>-2.982</td>
<td>-2.635</td>
</tr>
<tr>
<td>5000</td>
<td>-2.872</td>
<td>-2.525</td>
</tr>
<tr>
<td>6000</td>
<td>-2.762</td>
<td>-2.415</td>
</tr>
</tbody>
</table>
The experimental relationship between $f_{\text{H}_2\text{O}}$ and $T$ for the QFM buffer is from Chou (1987). Using $f_{\text{H}_2\text{O}}$ higher than that of the QFM buffer results in higher $f_{\text{H}_2\text{O}}$, whereas lower $f_{\text{H}_2\text{O}}$ results in lower $f_{\text{H}_2\text{O}}$ [from the $\text{H}_2\text{O}$ dissociation, the $f_{\text{H}_2\text{O}}$ is proportional to $(f_{\text{H}_2\text{O}})^{-2}$].

Experimental studies of the relationships between water activity in silicate melts, $a_{\text{H}_2\text{O}}$, and the mole fraction, $X_{\text{H}_2\text{O}}$, at $\text{H}_2\text{O}$ concentrations less than several tens of mole percent is consistent with the relationship (e.g., Burnham and Davis 1974; Burnham 1975; Hamilton et al. 1964; Holtz et al. 1995):

$$a_{\text{H}_2\text{O}} = k(X_{\text{H}_2\text{O}})^2.$$  \hspace{1cm} (6)

Values of $k$ as a function of $T$ and $P$ for feldspar composition melts have been determined by Burnham (1975, 1994). Normative albite+orthoclase (albite$>$orthoclase) dominate the norm of the glass inclusions [We used the melt composition for Chassigny estimated by Johnson et al. (1991), so using Equation 6 with the calibration of the $k$ values by Burnham (1975, 1994) is appropriate.] The activity of $\text{H}_2\text{O}$ in the magma, $a_{\text{H}_2\text{O}}$, is simply the fugacity ratio, $f_{\text{H}_2\text{O}}/f_{\text{H}_2\text{O}}^0$. In order to use the experimentally calibrated $k$ values (Eq. 6), the standard state used for $f_{\text{H}_2\text{O}}^0$ was that of Burnham (1975). The water content in ppm (wt) was calculated by using the compositions of glass inclusions coexisting with Chassigny kaersutite (Johnson et al. 1991).

**RESULTS AND DISCUSSION**

Values of $f_{\text{H}_2\text{O}}$ were calculated from the reported $\text{H}_2\text{O}$ contents of the kaersutite inclusions (Watson et al. 1994) in the range $T = 800°$–$1000 °C$ and $P = 1$–$6000$ bar (Table 2). Values of $f_{\text{H}_2\text{O}}$ and $a_{\text{H}_2\text{O}}$ were then computed from Equation 5 and the dissociation constant of $\text{H}_2\text{O}$ at an $f_{\text{H}_2\text{O}}$ equivalent to the QFM univariant equilibrium. The $\text{H}_2\text{O}$ concentration is derived with Equation 6.

The $\text{H}_2\text{O}$ content of the magma in equilibrium with the Chassigny and Zagami kaersutites with 0.1 and 0.2 wt% $\text{H}_2\text{O}$ is shown in Figure 1. The calculated water concentration in these melts varies with the $\text{H}_2\text{O}$ content of the kaersutite so that an increase from 0.1 to 0.2 wt% regardless of $T$ or $P$, results in a 250–300% increase in the water content of the melt (Fig. 1). A positive pressure dependence on $\text{H}_2\text{O}$ concentration (~8% increase/kbar) is evident. This pressure effect reflects predominantly the influence of $P$ on the $k$ values in Equation 6. The temperature-dependence (15–20% increase/100 °C) reflects primarily the influence of $T$ on the $f_{\text{H}_2\text{O}}$ (Table 2), as the $k$ values in Equation 6 are relatively insensitive to $T$ (Burnham 1975, 1994).

Although precise $T$ and $P$ estimates for crystallization of kaersutite in SNC inclusions are not available, crystallization temperatures near 1000 °C and pressure estimates in the 1–2 kbar range are often suggested (Stolper 1980; Treiman 1985; Johnson et al. 1991; Harvey and McSween 1992). The $\text{H}_2\text{O}$ content of the melt inclusions at the time of kaersutite crystallization, therefore, was between 100 and 300 ppm for Chassigny and between 300 and 1000 ppm $\text{H}_2\text{O}$ for Zagami (Fig. 1). This water concentration range is similar to $\text{H}_2\text{O}$ concentrations in heat-treated bulk SNC meteorites (Yang and Epstein 1985; Kerridge 1988; Karlsson et al. 1992). A kaersutite crystallization temperature lower than 1000 °C results in a lower $\text{H}_2\text{O}$ content of the coexisting melt (Fig. 1) and, therefore, in the source region of the parental magma. Although the pressure assumed for the kaersutite crystallization is not critical to the estimate of water content, the $\text{H}_2\text{O}$ contents for the most likely pressure range, 1–2 kbar, is highlighted in Figure 2.

From the $\text{H}_2\text{O}$ contents in Figure 1, the $\text{H}_2\text{O}$ of the Martian mantle that was melted to form the SNC parent magma can be estimated. Derivation of the $\text{H}_2\text{O}$ content in this manner requires assessment of at least three unknowns: (1) How much crystallization occurred in the melt inclusion before kaersutite crystallized? (2) How much partial melting of the Martian interior occurred to produce the parental magma of the SNC meteorites? (3) The SNC meteorites show cumulate textures (McSween 1985). Therefore, did the melt inclusions get trapped in the cumulate olivine and pyroxene as the cumulate layers grew, or were these inclusions formed during early crystallization in the magma chamber?
From mass-balance calculations and considerations of element partitioning and other phase-equilibrium data, the kaersutites equilibrated with a liquid residue representing 30±40% of the original melt volume (Longhi and Pan 1989; Harvey and McSween 1992). We will use 35% here, which yields H2O contents in the SNC parent magma at 1000 °C and 1–2 kbar in the range 35–350 ppm prior to any crystallization (35–105 ppm for Chassigny and 105–350 ppm for Zagami).

Whether or not the inclusions were trapped prior to or during accumulation of crystals cannot be ascertained. It will be assumed, in accord with others (Harvey and McSween 1992), that inclusions were trapped prior to crystal accumulation. This implies that the parent magma of the SNC meteorites contained 35±350 ppm H2O. If this assumption is incorrect, the H2O content of the SNC parental magma would be lower than this estimate. In any event, even the highest calculated H2O content is only about 50% of the lowest H2O contents reported for primitive terrestrial mid-ocean ridge basalt (MORB) (Jambon and Zimmermann 1990) and could be as low as 5% of those values. These results clearly suggest that the source rock of the magma that gave rise to SNC meteorites #1.3 Ga (e.g., Shih et al. 1982; Jones 1989) could be considerably drier than the terrestrial mantle that melts to yield primitive MORB on Earth today.

The bulk-chemical composition suggested for the parental magma of the SNC meteorites is Al-poor tholeiitic basalt (McSween and Harvey 1993; Treiman 1985; Johnson et al. 1991). Results of melting experiments suggest that such magmas probably were derived from source regions previously depleted in an aluminous phase (Longhi and Pan 1989; Longhi 1991a). The approximate degree of melting of those source regions is subject to debate, with estimates ranging from <1 to 30–40% (Longhi and Pan 1989; Longhi 1991a, 1991b). The source regions undoubtedly had a complex history so those estimates are uncertain. Nevertheless, we have used 10% melting in our calculations. By assuming that H2O behaves incompatibly so that all the H2O in the Martian upper mantle entered the partial melt, the H2O content of the magma source region is proportional to the degree of melting. The H2O contents shown in Figure 2 result from 10% melting. For 1% melting, the source regions would contain 10% of the amounts indicated in Figure 2, and for 40% melting, the H2O abundance in the source region would be four times that indicated in Figure 2. Longhi (1991b) suggested that the range in degree of melting suggested for the SNC parent magmas might reflect different petrogenetic histories. Chassigny might reflect ~1% melting, which would correspond to ~1 ppm H2O in its mantle source. Zagami, on the other hand, might have been contaminated by a crustal component thus increasing its H2O content (Longhi 1991b), which could explain the higher H2O content suggested for the source region of its parental magma.

This H2O content is equal to or less than that suggested on the basis of cosmochemical considerations (Dreibus and Wänke 1987) and is ≤5% of that suggested under the assumption that the amphiboles in the SNC inclusions contained stoichiometric proportions of H2O. In the latter case, 2(OH) pfu, there would be about four wt% H2O in the coexisting magma and 2600 ppm H2O in a source mantle of such magma. These numbers were obtained by using the same melt fractions as those used to derive Figure 2.

Even though the results of these calculations depend on the exact H2O content of the kaersutite, it is evident that a Martian upper mantle with 1–35 ppm at the time of SNC parent magma generation is consistent with the existence of kaersutitic amphibole in the inclusions in SNC meteorites. For the first time there is agreement between estimates of H2O of the Martian interior from cosmochemical considerations and from consideration of hydrous minerals in inclusions in SNC meteorites.

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