H deficiency in kaersutitic amphiboles: Experimental verification

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ABSTRACT

Experiments conducted on a natural kaersutitic amphibole, combined with statistical analysis of high-quality chemical analyses reported in the literature, document that both Fe\(^{3+}\) and Ti in this group of Ti-rich hornblendes are accommodated by the oxy substitutions Fe\(^{3+}\)O\(^2-\)Fe\(^{2+}\)(OH)\(^-\) and Ti\(^{4+}\)O\(^2-\)R\(^{n+}\)(OH)\(^-\). The valence of the cation R\(^{n+}\) can be variable, provided that the sum of all substitutions maintains charge balance within the amphibole crystal structure. If the OH lost as a result of the two oxy substitutions is accounted for, the mean amphibole O3 site occupancies (i.e., OH\(^-\) + F\(^-\) + Cl\(^-\) + O\(^2-\)) of both the experimentally treated and naturally occurring sample populations sum to the theoretical value of 2.00, within the statistical uncertainty.

The unusually low H contents reported for kaersutite from Martian meteorites are concluded to result from their unusually high Ti and total Fe contents relative to terrestrial kaersutite.

INTRODUCTION

Kaersutitic amphiboles (Ti-rich varieties of hornblende) occur mainly in mantle-derived xenoliths associated with alkalic lavas. Chemical and textural studies of natural samples, combined with experimental studies of the stability of Ti-rich amphibole, have led to the consensus that poikilitic, vein, and megacrystic kaersutites most likely are near-liquidus phases that crystallized over a range of high pressures, presumably under mantle conditions. On the other hand, interstitial kaersutite is possibly the product of hydration reactions of the general type spinel + diopside + fluid = amphibole. A recent review of the literature pertinent to natural samples and experimental studies is given in Popp et al. (1995).

The major crystal-chemical variations observed in kaersutite involve differences in Fe-oxidation states and H contents. Analyses of natural samples have verified a negative 1:1 correlation between Fe\(^{3+}\) and univalent anion (OH + F + Cl) contents (e.g., Popp and Bryndzia, 1992; Dyar et al., 1993). This relationship has been taken to imply that the Fe\(^{3+}\) content of amphibole is controlled by the Fe-oxy substitution,

Fe\(^{3+}\)O\(^2-\)Fe\(^{2+}\)(OH)\(^-\).

However, the H deficiency relative to the theoretical 2.00 per formula unit (pfu, on the basis of 24 anions) for amphiboles is not fully explained by this Fe-oxy substitution. Popp and Bryndzia (1992) suggested, on the basis of bivariate regression and correlation analysis of simple ionic substitutions, that the total H deficiency in megacryst samples could be explained by the additional charge-balanced oxy substitution

Ti\(^{4+}\)O\(^2-\)Al\(^{3+}\)(OH)\(^-\).

However, the effect of closure, which can arise from constant sums on crystallographic sites (Chayes and Trochimczyk, 1978), may lead to overestimation of the negative correlation in bivariate analysis between both Fe\(^{3+}\) and Ti\(^{4+}\) and the H content.

There have also been several studies of the subsolidus phase equilibria of amphiboles that are pertinent to the iron-oxy substitution (e.g., see Hawthorne, 1981). Overall, the experimental studies have not yielded data of sufficient quality to provide more than a qualitative test of possible substitution mechanisms in amphiboles because H contents, Fe\(^{3+}\)/Fe\(^{2+}\) ratio, and bulk chemical compositions of the experimentally treated amphiboles have not been systematically determined.

In the present study, quantitative measurements of Fe\(^{3+}\)/Fe\(^{2+}\) ratio and H were obtained for experimentally treated kaersutitic amphibole. The results, combined with data on the chemical compositions of natural samples, provide a quantitative evaluation of the H deficiency in kaersutitic amphiboles.

EXPERIMENTAL AND ANALYTICAL METHODS

Experiments were conducted on a kaersutitic amphibole megacryst from Vulcan's Throne, Arizona (supplied...
were in the range 2-3 mg/cm<sup>2</sup>. All spectra were taken at 77 K (Virgo and Hafner, 1969). The least-squares fitting of the spectra was conducted with lines of Lorentzian shape and the computer program PC-MOS (CMTE Elektronik). The Fe<sup>3+</sup>/(Fe<sup>3+</sup> + Fe<sup>2+</sup>) was calculated from the cumulative area of the absorption doublets assigned to Fe<sup>3+</sup> relative to the total area of the resonant absorption (cf. Dyar et al., 1993).

The accuracy of Fe<sup>3+</sup>/(Fe<sup>3+</sup> + Fe<sup>2+</sup>) determinations was evaluated by comparison with the results from a suite of natural and heat-treated samples of amphibole (Clowe et al., 1988) that were analyzed by a wet-chemical technique. The <sup>57</sup>Fe Mössbauer spectra of the samples of Clowe et al. (1988) were collected and fitted as described above. As shown in Table 2, a 1:1 correlation exists between Fe<sup>3+</sup>/(Fe<sup>3+</sup> + Fe<sup>2+</sup>) determined by the two analytical techniques. Therefore, conversion factors necessary to reconcile Mössbauer spectra measured at 298 K with wet chemical analyses (e.g., Dyar et al., 1993) are not required in this study. The precision of Fe<sup>3+</sup>/(Fe<sup>3+</sup> + Fe<sup>2+</sup>) is in the range 2-3%, depending on the number of doublets fitted to the spectral data.

The H content of selected products was determined by vacuum fusion with RF induction heating in a system similar to that described by Epstein and Taylor (1970). The hydrogen was pumped by the method of Friedman and Hardcastle (1970) into a volume that had been calibrated with known amounts of pure H<sub>2</sub>. The pressure in the calibrated volume was measured by a Baratron capacitance manometer. Duplicate measurements on the amphiboles gave a mean relative error of ±1% of the amount present when expressed as H<sub>2</sub>O.

**DISCUSSION**

The variations of Fe<sup>3+</sup> vs. OH + F + Cl apfu for the experimentally treated samples and 20 natural megacryst kaersutite samples (Dyar et al., 1993) are shown by open circles in Figure 1. For both data sets, the slopes of the least-squares fits (−1.07 ± 0.10 and −0.97 ± 0.29, re-

### Table 1. Experimental results

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>t</th>
<th>Buffer</th>
<th>R*</th>
<th>H**</th>
<th>Fe&lt;sup&gt;3+&lt;/sup&gt;</th>
<th>Fe&lt;sup&gt;2+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>2</td>
<td>d</td>
<td>1.00</td>
<td>0.54</td>
<td>0.952</td>
<td>0.000</td>
</tr>
<tr>
<td>700</td>
<td>1</td>
<td>3</td>
<td>0.63</td>
<td>0.62</td>
<td>0.886</td>
<td>0.066</td>
</tr>
<tr>
<td>700</td>
<td>2</td>
<td>h</td>
<td>0.55</td>
<td>0.50</td>
<td>0.509</td>
<td>0.443</td>
</tr>
<tr>
<td>700</td>
<td>1</td>
<td>h</td>
<td>0.10</td>
<td>0.12</td>
<td>0.418</td>
<td>0.533</td>
</tr>
<tr>
<td>700</td>
<td>0.5</td>
<td>h</td>
<td>0.39</td>
<td>0.12</td>
<td>0.371</td>
<td>0.581</td>
</tr>
</tbody>
</table>

### Table 2. Comparison of wet-chemical and <sup>57</sup>Fe Mössbauer techniques

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description*</th>
<th>Fe&lt;sup&gt;3+&lt;/sup&gt;/(Fe&lt;sup&gt;3+&lt;/sup&gt; + Fe&lt;sup&gt;2+&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tchermatic hornblende</td>
<td>AOE 10T</td>
<td>0.210</td>
</tr>
<tr>
<td>Riebeckite</td>
<td>AOE 32</td>
<td>0.330</td>
</tr>
<tr>
<td></td>
<td>AOE 34</td>
<td>0.560</td>
</tr>
<tr>
<td></td>
<td>AOE 31</td>
<td>0.300</td>
</tr>
<tr>
<td>Grunerite</td>
<td>AOE 3a/b</td>
<td>0.180</td>
</tr>
<tr>
<td></td>
<td>AOE 12A</td>
<td>0.270</td>
</tr>
</tbody>
</table>

Note: The best-fit-reduced, major-axis line (Davis, 1973; Till, 1974) obtained using the wet-chemical and Mössbauer techniques as the independent and dependent variable, respectively, is y = −0.02 ± 0.03 + 1.02 ± 0.10 x. The numbers in parentheses are the 95% confidence levels.

* From Clowe et al. (1988), Table 3.
respectively, as shown by dashed lines in Fig. 1) agree well with the theoretical value of -1.0 required for the Fe-oxy substitution. However, the y intercept, which represents the univalent ion content for an amphibole with no Fe-oxy component, is significantly lower than the 2.0 value that should result if the oxy content is controlled entirely by Fe-oxy substitution.

The solid circles in Figure 1 show the variation in univalent anion content if the OH + F + Cl is adjusted for the presence of Ti-oxy component by adding $O'^{2-}$ in 1:1 proportions for the number of Ti apfu. Although the least squares slope is statistically unchanged, the y intercept for the solid curves ($2.02 \pm 0.02$ for the experimental samples and $2.04 \pm 0.12$ for the samples of Dyar et al. (1993)) is in excellent agreement with the theoretical value of 2.00. A similar analysis based on the chemical compositions of 70 samples compiled from the literature yielded an intercept of $2.40 \pm 0.20$ (Popp and Bryndzia, 1992), but the quality of some of those analyses is suspect.

In very simple terms, the total O3 site occupancy can be calculated by adding the OH + F + Cl, Fe$^{3+}$, and Ti apfu, where Fe$^{3+}$ and Ti represent the $O'^{2-}$ apfu in the O3 site. The means and 95% confidence limits of the O3 occupancies calculated in this manner for the Vulcan's Throne samples, the Dyar et al. (1993) population of 20 samples, and the Popp and Bryndzia (1992) population of 70 samples are $2.00 \pm 0.04$, $2.10 \pm 0.22$, and $2.17 \pm 0.42$, respectively. The relatively larger uncertainty and poorer agreement in the Popp and Bryndzia data set probably reflects the poor quality of some of the earlier literature analyses, particularly the H contents and Fe-oxidation state.

Although it is clear that the total H deficiency in kaersutitic amphiboles can be fully explained by the presence of the two oxy reactions, the bivariate plots in Figure 1 may still include the effect of closure induced by constant sums. To evaluate that possibility, principal-components analysis was conducted on the chemical compositions of the 24 experimentally treated amphiboles and the 20 analyses, of megacryst samples reported by Dyar et al. (1993). Prior to the statistical analyses each amphibole composition was recast from the standard 24 anions pfu into a single additive component and a set of linearly independent exchange components. This transformation of variables eliminates closure effects (Chayes and Trochimczyk, 1978). The details of the statistical approach are the topic of further discussion (D. Virgo, E. D. Young, and R. K. Popp, in preparation). The main conclusion from the statistical analysis, however, shows that the first principal component is consistent with a substitution of the type $Fe^{3+}O^{2-}Fe^{2+}_{\text{apfu}}(OH)_{-1}$, and accounts for 99.6% of the total variance in the experimentally treated Vulcan's Throne amphiboles and for 96% in the population of Dyar et al. (1993). This result supports the earlier conclusions (Popp and Bryndzia, 1992; Dyar et al., 1993) and the conclusions based on bivariate analysis made in this paper.

In contrast to the Ti-oxy mechanism proposed in Reaction 2 by Popp and Bryndzia (1992), the results of the principal-components analysis suggest that the substitution of Ti$^{4+}$ in these amphiboles occurs by a multivariate substitution of the simplified form $Ti^{4+}O^{2-}R^{2+}_{\text{apfu}}(OH)_{-1}$, where the valence of the cation $R^{2+}$ can be variable, provided that the sum of all such substitutions maintains charge balance within the amphibole crystal structure.

On the basis of the above discussion, it is concluded that the H deficiencies observed in kaersutitic amphiboles are totally accounted for by the Fe- and Ti-oxy
substitutions. The extent of Fe-oxy substitution is controlled by $T$, $P$, and $f_{O_2}$ and requires only exchange of $H$ between amphibole and the coexisting fluid (Popp et al., 1995). The actual charge-balanced substitutions required for the Ti-oxy mechanism are unknown but probably depend not only on intensive parameters such as $T$, $P$, and $f_{O_2}$ but also on the bulk composition of silicate melts or rocks from which the amphiboles crystallize. Experimental results bearing on the Ti-oxy substitution have not been reported.

Popp et al. (1995) discussed how the oxy content of kaersutitic amphiboles can be used to infer $f_{O_2}$ and $a_{H_2O}$ of the Earth's upper mantle. The results of this study have bearing on the interpretation of $H$ contents of kaersutite in melt inclusions in SNC meteorites (e.g., Treiman, 1985; Johnson et al., 1991; McSween and Harvey, 1993; Watson et al., 1994). The presence of hydrous phases in these meteorites has been used to infer $H_2O$ contents of Martian magmas, which in turn, bear on the amount of $H_2O$ likely to have been degassed from the planet and its role in surface and atmospheric processes. The $H_2O$ contents of Martian magmas (McSween and Harvey, 1993) have been inferred not from absolute measurements of amphibole $H$ contents but rather from the results of phase-equilibrium studies of amphibole in the presence of $H_2O$-bearing melts (Johnson et al., 1991). Nevertheless, the results of this study lead to the conclusion that meteoritic amphiboles with exceedingly low $H$ contents may result simply from the high Ti contents and $Fe^{3+}$ contents typical of the amphiboles. For example, Watson et al. (1994) measured $H$ contents of $0.1 - 0.2$ wt% in kaersutite samples from both the Chassigny and Zagami meteorites. Even though the bulk chemical compositions and $H$ contents have not been analyzed for the same amphibole samples, Johnson et al. (1991) reported Ti and $Fe^{3+}$ contents of 0.79 and 1.31 apfu, respectively, in a kaersutite from Chassigny. Assuming that both $Fe^{3+}$ and Ti are accommodated as oxy component as indicated by this study, $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ can be calculated from the measured $H$, Ti, and $Fe^{3+}$ contents. For the Chassigny sample, those values range from 0.58 to 0.65 for the reported 0.1 - 0.2% $H$ contents. Similarly, the Ti and $Fe^{3+}$ contents of kaersutite in Zagami, 1.06 and 2.14 apfu, respectively (Treiman, 1985), require $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ of 0.32 - 0.37 for the observed $H$ contents. Even though values of $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ of the meteoritic samples have not been determined, the calculated ranges of both samples fall well within those of terrestrial samples (see Fig. 1, Popp et al., 1995). Therefore, the low $H$ contents are to be expected on the basis of the Ti and $Fe^{3+}$ contents.

It must be emphasized that $H_2O$ activities in the coexisting melts do not directly control the $H$ contents of the coexisting amphiboles. Rather, because the oxy substitutions involve loss of $H$ from the mineral, $f_{O_2}$ is the critical volatile parameter that controls the oxy content of kaersutitic amphiboles (Popp et al., 1995). The fugacities (or activities) of $O_2$ and $H_2O$ are involved only to the extent that the three fugacities are related by the dissociation equilibria for $H_2O$. On the basis of the composition of ilmenite-magnetite solid solutions, Stolper and McSween (1979) estimated that the $f_{O_2}$ of shergottites corresponds to that of the fayalite + magnetite + quartz solid-buffer assemblage and, therefore, is in the general range characteristic of kaersutite-bearing terrestrial rocks.

REFERENCES CITED


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