

H deficiency in kaersutitic amphiboles: Experimental verification

ROBERT K. POPP

Department of Geology and Geophysics, Texas A&M University, College Station, Texas 77843, U.S.A.;
and Center for High Pressure Research, Geophysical Laboratory, Washington, DC 20015, U.S.A.

DAVID VIRGO

Center for High Pressure Research, Geophysical Laboratory, Washington, DC 20015, U.S.A.

MICHAEL W. PHILLIPS

Department of Geology, University of Toledo, Toledo, Ohio 43606, U.S.A.

ABSTRACT

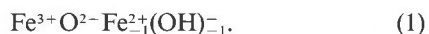
Experiments conducted on a natural kaersutitic amphibole, combined with statistical analysis of high-quality chemical analyses reported in the literature, document that both Fe^{3+} and Ti in this group of Ti-rich hornblendes are accommodated by the oxy substitutions $\text{Fe}^{3+}\text{O}^{2-}\text{Fe}^{2+}_1(\text{OH})_{-1}$ and $\text{Ti}^{4+}\text{O}^{2-}\text{R}^{2+}_1(\text{OH})_{-1}$. The valence of the cation R^{2+}_1 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., $\text{OH}^- + \text{F}^- + \text{Cl}^- + \text{O}^{2-}$) 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

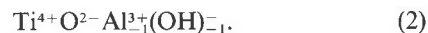
Kaersutitic amphiboles (Ti-rich varieties of hornblende) occur mainly in mantle-derived xenoliths associated with alkalic lavas. Chemical and textural studies of natural samples, combined with experimental studies of the stability of Ti-rich amphibole, have led to the consensus that poikilitic, vein, 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 ($\text{OH} + \text{F} + \text{Cl}$) 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,



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



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, $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, and bulk chemical compositions of the experimentally treated amphiboles have not been systematically determined.

In the present study, quantitative measurements of $\text{Fe}^{3+}/\text{Fe}^{2+}$ 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

TABLE 1. Experimental results

T (°C)	t	Buffer	R*	H**	Fe ³⁺ **	Fe ²⁺ **
Natural starting material						
			0.317	1.26	0.301	0.650
Air-heating experiments						
700	2 d		1.00	0.54	0.952	0.000
700	1 d		0.931	0.62	0.886	0.066
700	4 h		0.609	0.88	0.580	0.372
700	2 h		0.535	1.00	0.509	0.443
700	1 h		0.439	1.12	0.418	0.533
700	0.5 h		0.390	1.12	0.371	0.581
1 kbar hydrothermal experiments						
800	3 d	HM	0.453	1.22	0.429	0.519
800	2 d	NNO	0.198	1.40	0.188	0.762
800	2 d	GM	0.099	1.36	0.094	0.859
800	2 d	GM	0.104	1.41	0.098	0.854
800	11 h	IQF	0.065	1.51	0.063	0.887
700	7 d	HM	0.396	1.24	0.376	0.573
700	7 d	HM	0.387	1.11	0.368	0.584
700	14 d	GM	0.124	1.41	0.118	0.833
700	6 d	GM	0.102	1.41	0.097	0.854
700	11 h	IQF	0.073	1.51	0.070	0.888
600	11 d	HM	0.325	1.24	0.309	0.642
600	11 d	NNO	0.192	1.35	0.182	0.769
600	10 d	GM	0.146	1.39	0.143	0.808
600	13 h	IQF	0.119	1.48	0.113	0.837
500	11 d	HM	0.337	1.22	0.349	0.601
500	10 d	HM	0.298	1.31	0.283	0.667
500	10 d	GM	0.232	1.33	0.220	0.730
500	10 d	NNO	0.234	1.31	0.223	0.728

Note: Buffer abbreviations: HM = hematite + magnetite; NNO = nickel + nickel oxide; GM = graphite + methane; IQF = iron + quartz + fayalite.

* R = Fe³⁺/(Fe³⁺ + Fe²⁺) obtained from Mössbauer spectra as described in text. Error of measurement is ±3% relative. R for starting materials is observed R; for all others it is final R.

** Ions pfu normalized to 24 apfu on the basis of the bulk amphibole composition reported by Popp et al. (1995).

by P. Dunn). The sample was exposed to conditions from 500 to 800 °C, 1 atm–1 kbar, and f_{H_2} ranging from that of the IQF solid-state buffer to that of air. The details of the experimental methods were previously reported by Popp et al. (1995). The relevant experimental results are given in Table 1, which lists the experimental conditions, the amphibole Fe³⁺/(Fe³⁺ + Fe²⁺) determined from Mössbauer spectra, and the ionic contents of H, Fe³⁺, and Fe²⁺ on the basis of 24 anions pfu.

The ⁵⁷Fe Mössbauer spectra of the experimentally treated amphiboles were recorded with an Austin Science drive operated in the constant acceleration mode with a symmetric wave form. The velocity ramp to the drive was approximately ±4 mm/s, and mirror-image spectra were collected over 512 channels with a PC. The velocity was calibrated with an iron foil and values of $g_0 = 3.9156$ and $g_1 = 2.2363$ (Stevens and Stevens, 1972). The half widths (FWHM) were ~0.24 and 0.26 mm/s for the inner and outer lines of the iron foil, respectively. The source was ~40mC ⁵⁷Co in palladium. The amphibole was ground under alcohol, mixed with transoptic powder, and pressed at ~120 °C into pellets. The absorber densities were in the range 2–3 mg/cm². 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 Elek-

TABLE 2. Comparison of wet-chemical and ⁵⁷Fe Mössbauer techniques

Sample	Description*	Fe ³⁺ /(Fe ³⁺ + Fe ²⁺)	
		Wet chem	Mössbauer
Tchermakitic	natural	0.210	0.247
hornblende	AOE 10T	0.300	0.300
Riebeckite	natural	0.330	0.346
	AOE 32	0.560	0.550
	AOE 34	0.280	0.320
	AOE 31	0.260	0.290
Grunerite	natural	0.000	0.000
	AOE 3a/3b	0.160	0.180
	AOE 12A	0.270	0.242

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

* From Clowe et al. (1988), Table 3.

tronik). The Fe³⁺/(Fe³⁺ + Fe²⁺) was calculated from the cumulative area of the absorption doublets assigned to Fe³⁺ relative to the total area of the resonant absorption (cf. Dyar et al., 1993).

The accuracy of Fe³⁺/(Fe³⁺ + Fe²⁺) 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 ⁵⁷Fe 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 Fe³⁺/(Fe³⁺ + Fe²⁺) 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 Fe³⁺/(Fe³⁺ + Fe²⁺) 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 H₂. The pressure in the calibrated volume was measured by a Baratron capacitance manometer. Duplicate measurements on a talc standard supplied by D. Hewitt gave a mean value of 4.74 wt% H₂O (±0.03), which agrees well with the value of 4.76 (±0.03) reported by Rebbert et al. (1995) and with the theoretical value of 4.75 for Mg end-member talc. Duplicate measurements on the amphiboles gave a mean relative error of ±1% of the amount present when expressed as H₂O.

DISCUSSION

The variations of Fe³⁺ 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-

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

The solid circles in Figure 1 show the variation in univalent anion content if the $\text{OH}^- + \text{F}^- + \text{Cl}^-$ is adjusted for the presence of Ti-oxo 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 ± 0.02 for the experimental samples and 2.04 ± 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 ± 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 $\text{OH}^- + \text{F}^- + \text{Cl}^-$, 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 ± 0.04 , 2.10 ± 0.22 , and 2.17 ± 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 $\text{Fe}^{3+}\text{O}^{2-}\text{Fe}^{2+}(\text{OH})_{-1}$, 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.

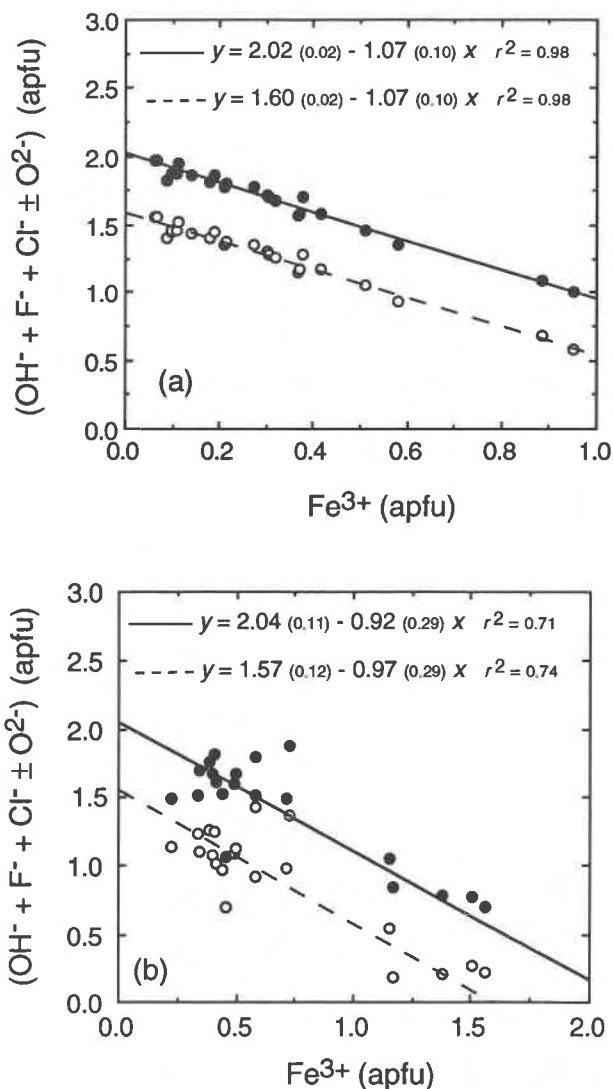


Fig. 1. Plot of Fe^{3+} apfu vs. $\text{OH}^- + \text{F}^- + \text{Cl}^- \pm \text{O}^{2-}$ calculated on the basis of 24 anions pfu for (a) experimentally treated Vulcan's Throne amphibole and (b) amphibole compositions reported by Dyar et al. (1993). Open circles = $\text{OH}^- + \text{F}^- + \text{Cl}^-$, solid circles = $\text{OH}^- + \text{F}^- + \text{Cl}^- + \text{O}^{2-}$, where $\text{O}^{2-} = \text{Ti}$ apfu; dashed and solid lines = reduced major-axis best-fit lines (Davis, 1973; Till, 1974). Equations are the least-squares fit to each data set; numbers in parentheses are 95% confidence limits for the slope and intercept.

In contrast to the Ti-oxo 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 $\text{Ti}^{4+}\text{O}^{2-}\text{R}^{n+}(\text{OH})_{-1}$, where the valence of the cation R^{n+} 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-oxo

substitutions. The extent of Fe-oxy substitution is controlled by T , P , and f_{H_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_{H_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_{H_2} and $a_{\text{H}_2\text{O}}$ 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_{tot} 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, $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ can be calculated from the measured H, Ti, and Fe_{tot} 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_{tot} contents of kaersutite in Zagami, 1.06 and 2.14 apfu, respectively (Treiman, 1985), require $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ of 0.32–0.37 for the observed H contents. Even though values of $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ 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_{tot} 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_{H_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

- Chayes, F., and Trochimczyk, J. (1978) An effect of closure on the structure of principal components. *Mathematical Geology*, 10, 323–333.
- Clowe, C.A., Popp, R.K., and Fritz, S.J. (1988) Experimental investigation of the effect of oxygen fugacity on ferric-ferrous ratios and unit cell parameters of four natural clin amphiboles. *American Mineralogist*, 73, 487–499.
- Davis, J.C. (1973) *Statistics and data analysis in geology*, 550 p. Wiley, New York.
- Dyar, M.D., Mackwell, S.J., McGuire, A.V., Cross, L.R., and Robertson, J.D. (1993) Crystal chemistry of Fe^{3+} and H^+ in mantle kaersutite: Implications for mantle metasomatism. *American Mineralogist*, 78, 968–979.
- Epstein, S., and Taylor, H.P., Jr. (1970) The concentration and isotopic composition of hydrogen, carbon and silicon in Apollo 11 lunar rocks and minerals. *Geochimica et Cosmochimica Acta (Supplement 1)*, 2, 1085–1096.
- Friedman, I., and Hardcastle, K. (1970) A new technique for pumping hydrogen gas. *Geochimica et Cosmochimica Acta*, 34, 125–126.
- Hawthorne, F.C. (1981) Crystal chemistry of the amphiboles. In *Mineralogical Society of America Reviews in Mineralogy*, 9A, 1–102.
- Johnson, M.C., Rutherford, M.J., and Hess, P.C. (1991) Chassigny petrogenesis: Melt compositions, intensive parameters, and water contents of Martian (?) magmas. *Geochimica et Cosmochimica Acta*, 55, 349–366.
- McSween, H.Y., and Harvey, R.P. (1993) Outgassed water on Mars: Constraints from melt inclusions in SNC meteorites. *Science*, 259, 1890–1892.
- Popp, R.K., and Bryndzia, L.T. (1992) Statistical analysis of Fe^{3+} , Ti, and OH in kaersutite from alkalic igneous rocks and mafic mantle xenoliths. *American Mineralogist*, 77, 1250–1257.
- Popp, R.K., Virgo, D., Yoder, H.S., Jr., Hoering, T.C., and Phillips, M.W. (1995) An experimental study of phase equilibria and Fe oxy-component in kaersutitic amphibole: Implications for f_{H_2} and $a_{\text{H}_2\text{O}}$ in the upper mantle. *American Mineralogist*, 80, 534–548.
- Rebbert, C.R., Partin, E., and Hewitt, D.A. (1995) Synthetic biotite oxidation under hydrothermal conditions. *American Mineralogist*, 80, 345–354.
- Stevens, I.G., and Stevens, V.E. (1972) Mössbauer effect data index, covering the 1970 literature, IFI/Plenum Data Corporation, 369 p. New York.
- Stolper, E.M., and McSween, H.Y. (1979) The petrology and origin of the Shergotty meteorite. *Geochimica et Cosmochimica Acta*, 43, 1475–1498.
- Till, R. (1974) *Statistical methods for the earth scientist: An introduction*, 54 p. Wiley, New York.
- Treiman, A.H. (1985) Amphibole and hercynite spinel in Shergotty and Zagami: Magmatic water, depth of crystallization, and metasomatism. *Meteoritics*, 20, 229–243.
- Virgo, D., and Hafner, S.S. (1969) Fe^{2+} , Mg order-disorder in heated orthopyroxenes. *Mineralogical Society of America Special Papers*, 2, 67–87.
- Watson, L.L., Hutcheon, I.D., Epstein, S., and Stolper, E.M. (1994) Water on Mars: Clues from deuterium/hydrogen and water contents of hydrous phases in SNC meteorites. *Science*, 265, 86–90.