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Statistical analysis of Fe^{3+}, Ti, and OH in kaersutite from alkalic igneous rocks and mafic mantle xenoliths

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ABSTRACT

Statistical analyses were carried out on the ion contents of 70 titanium pargasite and kaersutite samples from alkalic igneous rocks and mafic mantle xenoliths, in order to evaluate the extent to which Fe^{3+} and Ti are accommodated by substitution mechanisms involving oxy-component in these amphiboles. Sixty-five of the amphiboles occurred in extrusive rocks, the remaining five in dike rocks. Linear, bivariate regression and correlation analyses were carried out to relate the Fe^{3+} and Ti contents to the relevant ion contents that are required if Fe^{3+} and Ti, respectively, are accommodated by the following substitution mechanisms:

$$Fe^{2+} + OH^- = Fe^{3+} + O^{2-} \quad (1)$$

$$^{[6]}Al^{3+} + OH^- = Ti^{4+} + O^{2-}. \quad (2)$$

Statistically significant correlations (generally at the 99+% level of significance) were observed only between variable pairs that are indicative of the oxy-component. Namely, there is an inverse correlation between the univalent anion content of the O3 site (i.e., OH + F + Cl) and both Fe^{3+} and Ti contents, an inverse correlation between $^{[6]}Al^{3+}$ and Ti, and a positive correlation between the amount of positive charge in excess of 46.0 per formula unit and both Fe^{3+} and Ti. The induced negative correlation that results from the fact that these are variables of a constant sum could lower the statistical significance of the inverse correlations but would increase the significance level of the positive correlations. A statistically significant correlation was not observed among any of the variables related to the accommodation of Fe^{3+} by the Al-substitution mechanism. It is concluded that the Fe^{3+}-, Ti-, and OH contents in this population of amphiboles are controlled mainly by the coupled substitution mechanisms described in Equations 1 and 2.

INTRODUCTION

Fe^{2+} within an amphibole crystal structure can be oxidized to Fe^{3+} by the formation of oxy-amphibole and subsequent release of H. The amounts of Fe^{3+} and Fe^{2+} are controlled by an oxidation-dehydrogenation equilibrium of the type

$$Fe^{2+}_7Si_8O_{22}(OH)_2 = Fe^{2+}_5Fe^{3+}_2Si_8O_{22}(O)_2 + H_2$$

which was first documented by the experiments of Barnes (1930). As a consequence of the oxidation process, Fe^{3+} is accommodated as an oxy-amphibole component because O^{2-} replaces OH^- in the O3 site of the amphibole crystal structure. These substitutions can be represented by the following mechanism:

$$Fe^{2+} + OH^- = Fe^{3+} + O^{2-}. \quad (1)$$

More recent experimental studies carried out on a variety of natural and synthetic amphiboles have documented that Fe^{3+}-Fe^{2+} ratios can be varied continuously and reversed by treatment at the appropriate conditions. In the 1960s considerable interest was directed toward heating experiments on asbestiform varieties (see Hawthorne, 1981, 1983, for a review of relevant studies), but more recent studies have concentrated on nonasbestiform varieties (e.g., Ernst and Wai, 1970; Clowe et al., 1988).

Despite the results of experimental studies, and even though terms such as "basaltic hornblende" have been used in the literature to denote amphiboles with a relatively high oxy-amphibole content, presumed to be the result of oxidation upon extrusion, a statistically significant inverse correlation between OH^- and/or H_2O content and Fe^{3+} has not been documented in large numbers of natural amphiboles. In a series of seven kaersutitic amphiboles from Japan, Aoki (1963) observed higher Fe^{3+}-Fe^{2+} ratios and lower H_2O contents in extrusive samples as compared with intrusive varieties. He attributed the difference to oxidation upon extrusion. Leake

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(1968) compiled analyses of more than 1200 calcic and subcalcic amphiboles from the published literature, but his analyses of the overall data set did not reveal a statistically significant relationship between univalent anion content of the O3 site (i.e., OH + F + Cl) and Fe^{3+}. Despite his observations, he did not reject the hypothesis that Fe^{3+} is negatively correlated to OH + F + Cl by the presence of an oxy-amphibole component. Rather, he concluded that the relatively large number of coupled ionic substitutions available within the amphibole crystal structure and, in particular, the possible inverse relation between Ti and OH, complicate the interpretation. Boettcher and O'Neil (1980) observed an inverse correlation between wt% H_2O and the Fe^{3+}-Fe^{2+} ratio in eight kaersutitic amphiboles from alkali basalts and from xenoliths in alkali basalts. Dyar et al. (1992) reported similar results for hornblende megacrysts from continental rift environments but did not report the sample size. Saxena and Ekstrom (1970) carried out principal-component analysis of 639 of the Leake samples of superior and moderate quality but also failed to observe a significant correlation between OH and Fe^{3+}. They did, however, observe a significant negative correlation between OH and Ti content and proposed the coupled substitution

$$^{[6]}Al^{3+} + OH^{-} = Ti^{4+} + O^{2-} \qquad (2)$$

to control the Ti content of the sampled amphibole population. If this substitution mechanism is operative, Ti is also accommodated within the amphibole crystal structure as an oxy-amphibole component. Hamish and Seck (1974) proposed the same mechanism to account for the Ti contents of synthetic amphiboles on the join pargasite–titanium pargasite.

More recently, Popp et al. (1990) carried out regression and correlation analyses on the Fe^{3+}-rich samples (>0.7 Fe^{3+} per formula unit) in the Leake compilation, as well as on amphiboles in an additional compilation of approximately 350 samples published by Steffe (1979). Using the description of the environment of formation provided in the compilations, Popp et al. (1990) separated the amphiboles into metamorphic, intrusive igneous, and extrusive igneous varieties. On the basis of constraints of cation substitution mechanisms necessary to accommodate Fe^{3+} within the amphibole structure, as well as charge-balance constraints, they concluded that oxy-amphibole was the dominant substitution mechanism only in extrusive varieties and presumed that the oxy-component most likely formed as the result of posteruption oxidation. However, a statistically significant correlation between Fe^{3+} and univalent anion content of the O3 site was still not observed. Recent crystallographic studies on experimentally oxidized and reduced natural amphiboles (Phillips et al., 1988, 1989, 1991) concluded that chemically diverse amphiboles such as hornblende and grunerite have differing capacities and mechanisms to accommodate Fe^{3+} formed by postcrystallization oxidation. Therefore, the use of amphiboles with a wide range of chemical compositions in statistical analyses, even if they are from a single environment such as extrusive igneous rocks, still might not produce a significant correlation between Fe^{3+} and OH + F + Cl.

TABLE 1. Average amphibole composition ($n = 70$; ±1 sd)

Ion	Mean	1 sd
Si	5.94	0.17
$^{[4]}$Al	2.07	0.17
$^{[6]}$Al	0.42	0.18
Ti	0.54	0.18
Fe^{3+}	0.66	0.39
Fe^{2+}	0.71	0.39
Fe_{tot}	1.37	0.39
Mg	2.80	0.51
Cr	0.02	0.06
Mn	0.02	0.01
Ca	1.76	0.13
Na	0.74	0.11
K	0.29	0.10
OH + F + Cl	0.97	0.54
A site	0.92	0.14

Note: Ions per formula unit, based on 24 anions pfu.

An oxidation-dehydrogenation reaction analogous to that described in mechanism 1 above has also been proposed to contribute to the accommodation of Fe^{3+} in micas (Wones and Eugster, 1965; Vedder and Wilkins, 1969). However, recent studies on the relationship between OH content and Fe^{3+} in synthetic biotite (Rebbert and Hewitt, 1986) and natural micas in mantle xenoliths (Dyar, 1990) have established no significant correlation between Fe^{3+} and OH content.

Presented here are the results of correlation and regression analyses carried out on the cation and anion contents of a group of 70 kaersutitic amphiboles from both alkaline igneous rocks and mafic mantle xenoliths. These samples represent a better case than previous studies for delimiting the role of OH in accommodating Fe^{3+} and Ti^{4+} because the variation in the chemical compositions of the amphibole population is relatively small, with the exception of the Fe^{3+}-Fe^{2+} ratio and OH content (Table 1).

AMPHIBOLE ANALYSES

The majority of the amphibole analyses used in the regressions and correlations were compiled from the literature during a study of amphiboles in mafic mantle xenoliths in alkaline igneous rocks (Bryndzia et al., 1990). Other analyses performed by L.T.B. and Andrew M. Davis are reported here for the first time. The sources of analyses are cited in the Appendix 1.[1] The complete chemical analysis of each amphibole, its normalized ionic content per formula unit, and a description of the analytical methods are contained in Table 2.[1] All but five of the amphiboles occurred in extrusive igneous rocks. Those five occurred in alkaline dike rocks.

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[1] A copy of Appendix 1 and Table 2 may be ordered as Document AM-92-510 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036. Please remit $5.00 in advance for the microfiche.

The weight percents of the oxides for each amphibole were converted to the numbers of cations and anions per formula unit (pfu) by normalizing to 24 anions pfu by the procedure described in the appendix of Deer et al. (1966). The cation populations of the tetrahedral sites, the M1, M2, M3, M4, and A sites were assigned by the standard method, as described by Robinson et al. (1982). The resulting ionic site populations of each amphibole were compared to the eight criteria defined by Leake (1968) to evaluate the quality of amphibole analyses. Of the 70 samples, 53 were classified as superior analyses based on seven of the eight criteria. The other criterion, namely that the OH + F + Cl content pfu not be less than 1.0, is clearly not valid for evaluating the quality of oxy-amphibole analyses, since an amphibole with 100% oxy-component, by definition, contains no OH + F + Cl. The 17 remaining samples probably fall into Leake's "moderate quality," but the exact criteria used to define that group were not described in detail by Leake (1968). The elimination of the 17 moderate-quality analyses from the sampled population did not change the statistical significance of the correlations, and therefore, the entire data base was used in the statistical tests reported below.

The mean and standard deviation of cation contents for all 70 samples are given in Table 2. It can be seen from the table that the average composition corresponds to kaersutite (Leake, 1978) but that titanium pargasite is included in the population. The ion contents on a per formula basis fall within a relatively narrow range, with the exception of OH + F + Cl and the Fe^{3+} and Fe^{2+} contents.

REGRESSION AND CORRELATION PARAMETERS

As discussed by Popp et al. (1990), the presence of octahedrally coordinated trivalent Fe within an amphibole crystal structure requires one of three types of coupled substitution in order to maintain charge balance: (1) the formation of oxy-amphibole component as defined by mechanism 1; (2) a ferritschermakitic substitution

$$^{[6]}(Mg,Fe^{2+}) + {}^{[4]}Si = {}^{[6]}Fe^{3+} + {}^{[4]}Al^{3+} \quad (3)$$

as in $Ca_2Mg_3Fe_2^{3+}Si_6Al_2O_{22}(OH)_2$, in which the presence of each Fe^{3+} is coupled with replacement of one Si^{4+} by Al^{3+} in tetrahedral coordination; and (3) a substitution in which $^{[6]}Fe^{3+}$ is coupled with the replacement of Ca^{2+} by Na^+ in the M4 position:

$$Ca^{2+} + (Mg,Fe^{2+}) = Na^+ + {}^{[6]}Fe^{3+} \quad (4)$$

as, for example, in magnesio-riebeckite [$Na_2Mg_3Fe_2^{3+}Si_8O_{22}(OH)_2$]. Mechanisms 3 and 4 are analogous to those by which $^{[6]}Al$ is accommodated in amphiboles and were collectively termed "Al substitution" by Popp et al. (1990).

It is well documented that the relatively large number of coupled substitutions possible in chemically complex minerals such as amphiboles and micas may make it impossible to define the exact substitution mechanisms that control the presence of any individual cation (e.g., Leake, 1968; Saxena and Ekstrom, 1970; Hewitt and Abrecht, 1986). Nevertheless, regression and correlation analyses on the cation contents of the amphibole population sampled here can provide insight into the accommodation of both Fe^{3+} and Ti.

If the Fe^{3+} content of a sampled population is present only as defined by either mechanism 3 or 4 above, a positive 1:1 correlation would be observed between Fe^{3+} and $^{[4]}Al$ pfu and between Fe^{3+} and the Na content of the M4 site, respectively. In addition, because $^{[6]}Al$ may also be accommodated in amphiboles by mechanisms 3 and 4, an inverse 1:1 correlation between Fe^{3+} and $^{[6]}Al$ could result, as was the case of the Fe^{3+}-rich metamorphic varieties described by Popp et al. (1990).

If mechanism 1, the formation of oxy-amphibole component, is solely responsible for accommodating Fe^{3+} within a given amphibole population, an inverse 1:1 correlation between Fe^{3+} and univalent anion content of the O3 position (i.e., OH + F + Cl) would be observed. In addition, the presence of A-site cations has been shown to facilitate the formation of oxy-amphibole component by increasing the bond strength at the O3 anion, and thereby helping to compensate for the charge imbalance that results when O^{2-} replaces OH^- in the O3 position (Ungaretti, 1980; Phillips et al., 1988). Popp et al. (1990) observed a statistically significant correlation between A-site occupancy and Fe^{3+} content only for extrusive igneous amphiboles that contained significant oxy-amphibole content. Furthermore, the standard hydroxy-amphibole chemical formula contains anions whose valence sums to −46 and cations (exclusive of H) whose valence sums to +46. The presence of oxy-amphibole component increases the amount of negative charge by 1 negative unit for every O^{2-} that replaces OH^-, which, in turn, is balanced by the replacement of Fe^{2+} by Fe^{3+}. Therefore, if oxy-amphibole is the only mechanism by which Fe^{3+} enters a population, there should be a positive 1:1 correlation between Fe^{3+} pfu and the amount of positive charge in excess of +46 pfu. The amount of positive charge in excess of +46 (termed excess positive charge by Popp et al., 1990) for any amphibole can be calculated in two ways. In the first method, the cation contents, neglecting H, are simply multiplied by their valences and the total charge summed. The second method uses the cation site populations. That is, substitution of $^{[4]}Al$ for Si, in the tetrahedral sites, and substitution of Na^+ for divalent cations in the M4 site decreases the amount of positive charge relative to +46. Alternately, positive charge is increased relative to +46 by substitution of Al^{3+}, Fe^{3+}, and Ti^{4+} for divalent cations in M sites, as well as by occupancy of the A site. Thus, excess positive charge = $^{[6]}Fe^{3+} + {}^{[6]}Al^{3+} + 2Ti^{4+}$ + A-site occupancy − $^{[4]}Al^{3+}$ − Na^+[M4]. For the analyses reported here, there was no statistical difference at the 95% confidence level between the results obtained using the amounts of excess positive charge calculated by the two different methods.

If Ti is accommodated within an amphibole population only by mechanism 2, the Ti content of the population should be negatively correlated in 1:1 proportions

Table 3. Results of regression (of the form $y = a + bx$) and correlation analyses for selected compositional variables

y	x	a*	b**	r†
Al-substitution mechanisms				
$^{[6]}Al$	Fe^{3+}	0.73(±0.09)	−0.47(±0.11)	−0.14(74)
$^{[4]}Al$	Fe^{3+}	1.78(±0.08)	0.43(±0.10)	0.04(24)
$^{[M4]}Na$	Fe^{3+}	−0.11(±0.06)	0.33(±0.08)	0.19(87)
$^{[4]}Al + ^{[M4]}Na$	Fe^{3+}	1.81(±0.10)	0.54(±0.13)	0.14(75)
Ferric oxy-amphibole mechanisms				
OH + F + Cl	Fe^{3+}	1.89(±0.20)	−1.39(±0.26)	−0.65(99+)
EPC‡	Fe^{3+}	0.26(±0.18)	0.97(±0.24)	0.70(99+)
A site occ.	Fe^{3+}	1.17(±0.07)	−0.37(±0.09)	−0.21(92)
Ti-accommodation mechanisms				
OH + F + Cl	Ti	2.56(±0.39)	−2.96(±0.69)	−0.26(97)
$^{[6]}Al$	Ti	0.95(±0.12)	−1.00(±0.22)	−0.40(99)
EPC‡	Ti	0.11(±0.35)	1.49(±0.61)	0.51(99+)
Combined ferric oxy-amphibole and Ti mechanisms				
OH + F + Cl + Ti	Fe^{3+}	2.40(±0.20)	−1.34(±0.26)	−0.60(99+)
EPC‡	Fe^{3+} + Ti	−0.20(±0.22)	0.92(±0.17)	0.79(99+)
Ti	Fe^{3+}	0.23(±0.09)	0.47(±0.11)	0.20(91)

* The y intercept of the best-fit reduced major axis line (Davis, 1973, p. 200–204; Till, 1974, p. 99–102). The values in parentheses are the 95% confidence intervals for the y intercept (Davis, 1973, p. 204; Till, 1974, p. 102–103).

** Slope of the best-fit reduced major axis line (Davis, 1973, p. 200–204; Till, 1974, p. 99–102). The values in parentheses are the 95% confidence limits for the slope of the best-fit line (Davis, 1973, p. 204; Till, 1974, p. 102–103).

† Sample correlation coefficient (Crow et al., 1960, p. 157–158). The values in parentheses represent the level of statistical significance [$(1 - \alpha) \times 100$] for the correlation coefficient (Crow et al., 1960, p. 159; Dorrer, 1968). See text for discussion.

‡ EPC = Excess positive charge: amount of positive charge in excess of 46 pfu. See text for discussion.

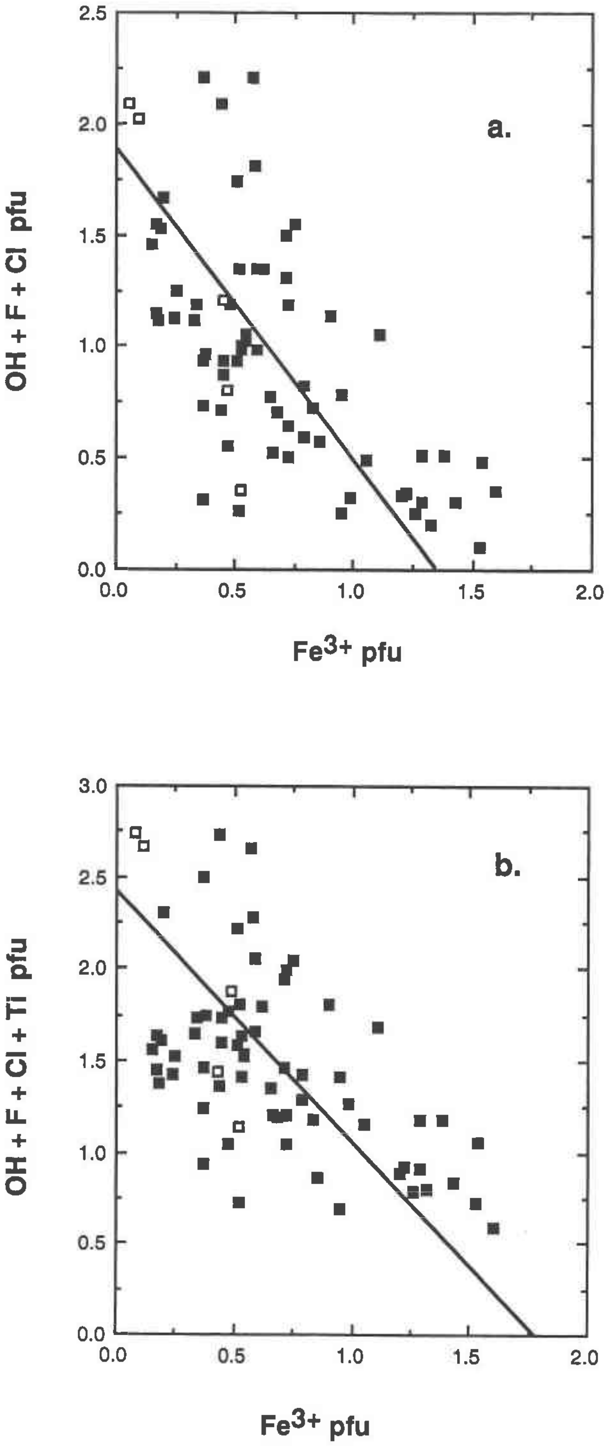
with both $^{[6]}Al^{3+}$ and OH + F + Cl. Also, according to substitution mechanism 2, the presence of each Ti also increases the amount of excess positive charge by 1 charge unit. Thus, a positive 1:1 correlation between Ti content and excess positive charge should be observed for the amphibole population.

RESULTS

Regression and correlation analyses between both Fe^{3+} content and Ti content and the relevant compositional variables discussed in the preceding section were carried out on the sampled amphibole population. The reader is referred to Harrell (1987) for a more complete discussion of the underlying assumptions of the statistical analysis as applied here. In the case of the data used here, where the variable pairs may be related by crystallographic substitution mechanisms, there is no clearly defined predictor (independent) and predicted (dependent) variable nor can the requirement be met that one of the variables is without error. Interchanging the dependent and independent variables in a linear regression analysis can result in differences in the slope and intercept values for the best-fit line, but the correlation coefficient and its level of significance are not changed. Therefore, a reduced major axis line (Davis, 1973; Till, 1974) was used to obtain the best-fit slope and intercept. The results are shown in Table 3. Given in the table are the intercept (a), slope (b), and the sample correlation coefficient (r) of the best-fit straight line ($y = a + bx$). The values in parentheses for the slope and intercept are the 95% confidence limits (Davis, 1973; Till, 1974). The values in parentheses for the correlation coefficient represent the level of statistical significance [$(1 - \alpha) \cdot 100$] (Crow et al., 1960, p. 159; Dorrer, 1968), assuming there is no induced negative correlation (see below). Those values come from the statistical test of the null hypothesis that the given pair of variables has zero correlation in the sampled population. A 90% significance level means that there is a 10% chance of obtaining a correlation larger than the observed correlation when the null hypothesis is true, that is, when there is zero correlation in the sampled population. By convention, a significance level of 95% or higher is considered to be statistically significant.

Of importance to the results presented here is the fact that the regression and correlation analyses have been carried out on variables of a constant sum (Chayes, 1960), for which there may be an induced negative correlation between the variable pairs. The consequence of the induced negative correlation is that variable pairs with a real negative correlation will have an observed correlation that is more negative than it should be. Thus, an observed negative correlation that is large and apparently significant may not be truly significant, depending on the magnitude of the induced part. Alternately, an observed positive correlation that is statistically significant is truly significant because if the induced part is removed, the remaining correlation would be even more positive. Unfortunately, it is not possible to obtain values for the magnitude of the induced correlation between any pair of variables, but the effects of possible induced negative correlation are discussed below.

The results shown in Table 3 suggest that Fe^{3+} is accommodated in the sampled amphibole population mainly by the presence of oxy-amphibole component. There is a statistically significant correlation between Fe^{3+} and the univalent anion content of the O3 site at the 99+% level, if the possible induced negative correlation is ignored (Table 3, Fig. 1a). The observed slope and intercept of the best-fit straight line (−1.39 ± 0.26 and 1.89 ± 0.20, respectively) agree reasonably well with the theoretical values of −1.0 and 2.0 that are required if Fe^{3+} is accommodated solely by oxy-amphibole component. Because the correlation between the two variables is negative, the level of significance could possibly fall below the statistically significant 95% level if the induced part were removed. However, there is also a positive correlation between Fe^{3+} and excess positive charge at the 99+% level (Table 3, Fig. 2a), which could only increase in its level of significance if the induced correlation were removed. Within the errors, the slope (0.97 ± 0.24) and intercept (0.26 + 0.18) are in good agreement with the theoretical values (1.0 and 0.0, respectively) for oxy-amphibole substitution. The lack of significant positive correlation between A-site occupancy and Fe^{3+} is surprising, given the fact that such dependence has been observed in both heat-treated (Phillips et al., 1988, 1989) and natural Fe^{3+}-rich (Popp et al., 1990) varieties. This apparent discrepancy may result from the fact that the A sites of the sampled kaersutitic amphiboles are nearly full (0.92 pfu ± 0.14, Table 3), such that the most Fe^{3+}-poor samples have more than sufficient A-site occupancy to accommodate the amounts of Fe^{3+} that they contain. Thus, the lack of correlation between Fe^{3+} and A-site occupancy is not considered to affect seriously the conclusion that oxy-amphibole is the major mechanism in accommodating the Fe^{3+} content of this amphibole population.



There is apparently no significant statistical correlation between Fe^{3+} content and any of the cation contents involved in the Al-substitution mechanisms, but this conclusion cannot be made with statistical certainty. The relatively small values for the sample correlation coefficients (Table 3) suggest that a relatively large induced negative correlation would be required to raise the values to statistically significant levels.

On the basis of the results in Table 3, it is concluded that Ti is accommodated within the sampled population by mechanism 2. There are high inverse correlations (99+%) between OH + F + Cl and Ti and between $^{[6]}Al$ and Ti, which may or may not still be significant if the induced correlation is removed. Furthermore, there is a statistically significant positive correlation between excess positive charge and Ti (Table 3). The ideal slope and intercept (1.0 and 0.0, respectively) required by mechanism 2 compare reasonably well with observed values of 1.49 (± 0.61) and 0.02 (± 0.35), respectively. Discrepancies between the ideal and observed slopes and intercepts for the variable pairs containing Ti may result because the relatively larger amounts of Fe^{3+} accommodated as oxy-amphibole also exert control.

Because each of the coupled substitution mechanisms described in Equations 1 and 2 affect both the OH content of the O3 site and the amount of excess positive

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Fig. 1. (**a**) Plot of OH + F + Cl pfu vs. Fe^{3+} pfu for the sampled amphibole population. Open symbols represent samples from dikes. Shown is the best-fit straight line for the data. See Table 3 for the equation of the best-fit line and its statistical significance. (**b**) Plot of OH + F + Cl + Ti pfu vs. Fe^{3+} pfu for the sampled amphibole population. Adding the amount of Ti pfu to the anion content of the O3 site accounts for the deficiency of univalent ions in O3 that results if all Ti is accommodated by mechanism 2 in the text. Solid line is the best-fit straight line for the data; see Table 3 for the coefficients and statistical significance.

charge, regression and correlation analysis of combined variables provides additional confirmation of the substitution mechanisms operating in the sampled amphibole population. With the assumption that all Ti is accommodated by mechanism 2, each amphibole would contain 1.0 fewer OH pfu for every Ti pfu. Thus, an amphibole could contain no ferric oxy-amphibole component but still have less than 2.0 (OH + F + Cl) pfu. Therefore, the extent of ferric oxy-amphibole substitution can be more correctly evaluated if the OH lost due to the presence of Ti is accounted for by adding the Ti pfu to OH + F + Cl pfu. The results of the statistical analyses carried out using OH + F + Cl + Ti and Fe^{3+} as the variables are shown in Table 3 and Figure 1b. Within the 95% confidence limits, the slope (1.34 ± 0.26) is the same as that obtained using OH + F + Cl and Fe^{3+} as the variable pairs. The intercept (2.40 ± 0.20), however, is somewhat larger than the theoretical value of 2.0. The sums of OH + F + Cl + Ti greater than 2.0 for samples shown in Figure 1b suggest that those samples would be capable of accommodating more than 2.0 (OH + F + Cl) pfu if no OH was lost through accommodating Ti and Fe^{3+}. Such discrepancies may indicate that not all the Ti present in the samples population is accommodated by mechanism 2. Recently, Della Ventura et al. (1991) have reviewed several alternative mechanisms by which Ti may be accommodated in amphiboles. The possibility of OH in excess of 2.0 pfu in amphiboles is still not resolved. Many analyses reported in the literature have measured OH + F + Cl contents in excess of 2.0 pfu, and in fact Leake (1968) included analyses with up to 2.99 OH pfu in his superior quality data set. Excess OH in an amphibole analysis may simply result from inaccuracies in analysis technique for H_2O, from the presence of H_2O-rich fluid inclusions, or from the presence of multiple-chain silicate intergrowths within the amphibole. Excess OH has also been observed in synthetically crystallized amphiboles (Witte et al., 1969; Maresch and Langer, 1976).

The results of the statistical analysis carried out using Fe^{3+} + Ti pfu and excess positive charge as the variables are given in Table 3, and shown graphically in Figure 2b. The slope (0.92 ± 0.17) and intercept (−0.20 ± 0.22) are in excellent agreement with the theoretical values (1.0 and 0.0, respectively). The correlation coefficient (0.79) is the highest obtained for any of the correlations described here. Thus, as was the case for the correlations using only Fe^{3+} and Ti, there is a high observed correlation (>95%) between the variables that are indicative of oxy-amphibole substitutions. In each case, there are both positive and negative correlations. The induced negative correlation may lower the true significance level of negative correlations, but it will only increase the true significance of the variable pairs with the positive correlation.

DISCUSSION

On the basis of the statistical analyses carried out here, it is concluded that mechanisms 1 and 2 are the major

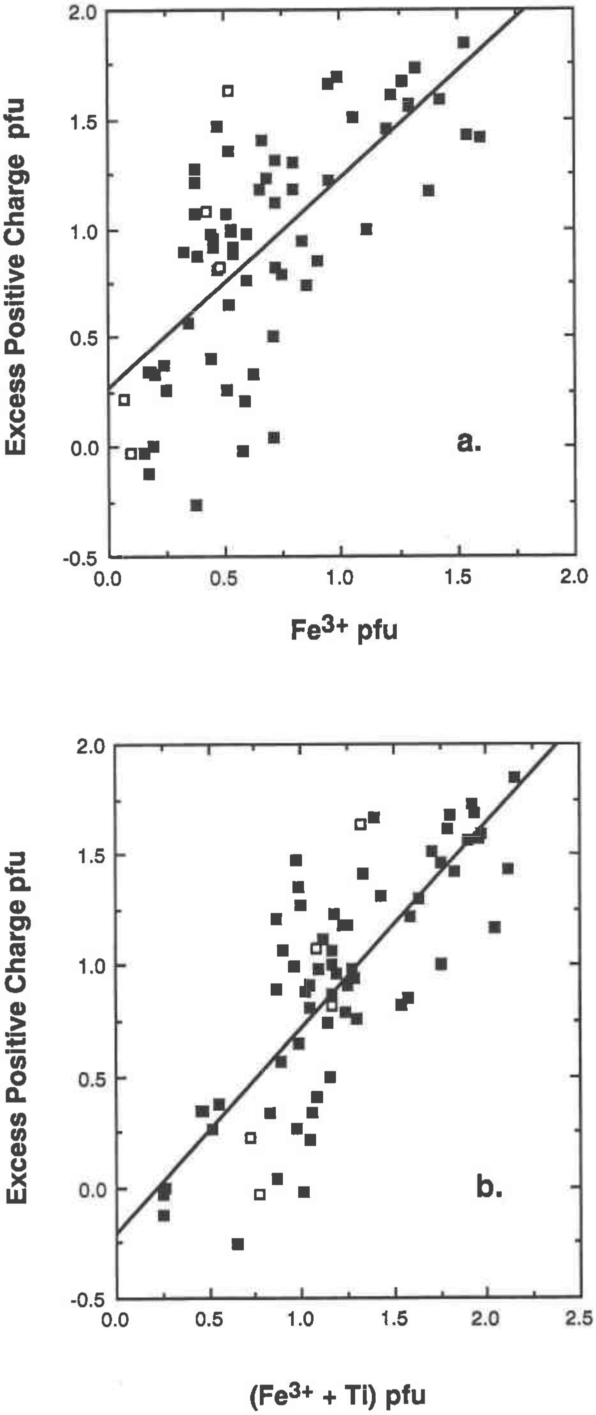

Fig. 2. (**a**) Plot of excess positive charge pfu vs. Fe^{3+} pfu for the sampled amphibole population. Open symbols represent samples from dikes. Shown is the best-fit straight line for the data. See Table 3 for the equation of the best-fit line and its statistical significance. (**b**) Plot of excess positive charge pfu vs. Fe^{3+} + Ti pfu for the sampled amphibole population. Solid line is the best-fit straight line for the data; see Table 3 for the equation of the best-fit line and its statistical significance.

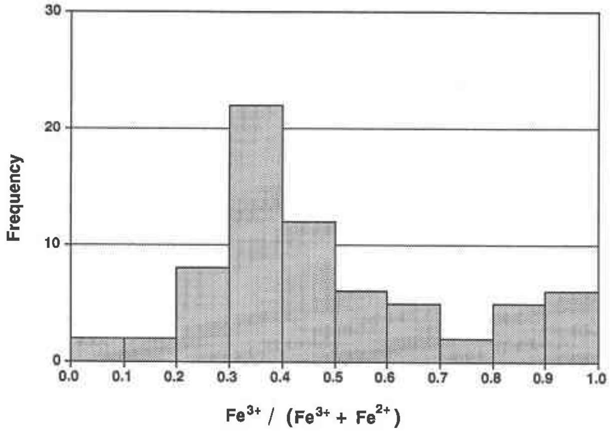

Fig. 3. Histogram of the frequency of occurrence of molar ferric-ferrous ratio [$Fe^{3+}/(Fe^{3+} + Fe^{2+})$] in the sampled kaersutite population.

mechanisms by which Fe^{3+} and Ti, respectively, are accommodated in the sampled population of kaersutitic amphiboles. That some of the Fe^{3+} is accommodated by coupled substitutions involving either $^{[4]}Al$ or Na in the M4 site cannot be ruled out statistically because of the unknown magnitude of the induced negative correlation.

It is likely that the Ti contents of the sampled amphibole population were fixed during crystallization in the mantle and have not changed since eruption. Mechanism 2 is unlikely to produce high Ti contents in response to highly oxidizing conditions at the surface, because it does not, in fact, involve oxidation of any elements. Mechanism 2 is also unlikely to occur in response to dehydrogenation at the Earth's surface because the reaction cannot occur unless the bulk chemical composition of the amphibole changes. That is, Al must be gained and Ti lost by some other phase.

Oxy-amphibole plays the major role in accommodating Fe^{3+} in this population of kaersutitic amphiboles. A histogram of the frequency of molar ferric-ferrous ratios [$Fe^{3+}/(Fe^{3+} + Fe^{2+})$] in the sampled amphibole population is shown in Figure 3. The entire range of ferric-ferrous ratios from 0.0 to 1.0 is represented, but 60% of the samples have values between 0.2 and 0.5. The inference has often been made that the oxy-component in kaersutitic amphiboles reflects posteruption oxidizing conditions (e.g., Aoki, 1963; Irving and Frey, 1984; references summarized by Hawthorne, 1983; Popp et al., 1990). The oxidation-dehydrogenation reaction that controls mechanism 1 (see Introduction) involves only the loss of H to the coexisting fluid phase and the oxidation of existing Fe^{2+} and, therefore, does not require chemical exchange with other mineral phases. The relatively rapid reaction rates for oxy-amphibole formation observed in experiments are clearly adequate for significant amounts of oxy-amphibole to form as the result of posteruption oxidation. Clowe et al. (1988) observed significant dehydrogenation of several Ti-poor varieties in times shorter than 15 min and in some cases complete dehydrogenation in under 1 h at temperatures in the range of 650 °C. However, it is also known from hydrothermal treatment of natural samples (Ernst and Wai, 1970; Clowe et al., 1988) that the oxy-amphibole component of sodic amphiboles and some Ti-poor hornblende samples can be changed significantly by varying f_{O_2} in the range defined by the graphite + methane and hematite + magnetite solid buffer assemblages.

Oxygen fugacities estimated from mantle assemblages are commonly within ±1.5 log units of that of the fayalite + magnetite + quartz buffer (e.g., Wood and Virgo, 1989; Bryndzia et al., 1990; Canil et al., 1990), but values up to approximately 2 log units higher have been reported (Mattioli and Wood, 1986; Wood et al., 1990). Bryndzia et al. (1990) concluded that ferric-ferrous ratios of 0.32–0.39 (and corresponding OH contents of 1.0–1.5 per 23 O atoms) observed in mantle kaersutitic amphiboles from three distinct tectonic environments reflect primary upper mantle f_{O_2} unmodified by later oxidation. Experimental calibration of the oxy-amphibole contents of such amphiboles over the range of temperature-pressure-f_{O_2} conditions relevant to the mantle has not been carried out, however. Experiments reported by Popp et al. (1992) show that ferric-ferrous ratios in a titanium pargasite sample from an alkali basalt megacryst vary between 0.18 and 0.41 for f_{O_2} in the range defined by the fayalite + magnetite + quartz and hematite + magnetite buffer assemblages at 700 °C and 1 kbar. These results are consistent with O thermobarometric estimates of mantle redox states for amphibole-bearing spinel peridotites (Bryndzia et al., 1990).

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REFERENCES CITED

Aoki, K. (1963) The kaersutites and oxykaersutites from alkalic rocks of Japan and surrounding areas. Journal of Petrology, 4, 198–210.

Aoki, K., and Kushiro, I. (1968) Some clinopyroxenites from ultramafic inclusions in Dreiser Weiher, Eifel. Contributions to Mineralogy and Petrology, 18, 327–337.

Barnes, V.E. (1930) Changes in hornblende at about 800 °C. American Mineralogist, 15, 393–417.

Best, M.G. (1970) Kaersutite-peridotite inclusions and kindred megacrysts in Basanitic lavas, Grand Canyon, Arizona. Contributions to Mineralogy and Petrology, 27, 25–44.

Binns, R.A. (1969) High-pressure megacrysts in basanitic lavas near Armidale, New South Wales. American Journal of Science, 267A, 33–49.

Boettcher, A.L., and O'Neil, J.R. (1980) Stable isotope, chemical, and petrographic studies of high-pressure amphiboles and micas: Evidence for metasomatism in the mantle source regions of alkali basalts and kimberlites. American Journal of Science, 280A, 594–621.

Bryndzia, L.T., Davis, A.M., and Wood, B.J. (1990) The isotopic composition (δD) of water in amphiboles and the redox state of amphibole-bearing upper-mantle spinel peridotites. Geological Society of America Abstracts with Program, 22, A254.

Canil, D.D., Virgo, D., and Scarfe, C.M. (1990) Oxidation state of mantle xenoliths from British Columbia, Canada. Contributions to Mineralogy and Petrology, 104, 453–462.

Chayes, F. (1960) On correlations between variables of a constant sum. Journal of Geophysical Research, 65, 4185–4193.

Clowe, C.A., Popp. R.K., and Fritz, S.J. (1988) An experimental investigation of the relation between oxygen fugacity, ferric-ferrous ratio, and unit-cell parameters in four natural clinoamphiboles. American Mineralogist, 73, 487–499.

Crow, E.L., Davis, F.A., and Maxfield, M.W. (1960) Statistics manual, 288 p. Dover Inc., New York.

Davis, J.C. (1973) Statistics and data analysis in geology, 550 p. Wiley, New York.

Deer, W.A., Howie, R.A., and Zussman, J. (1963) Rock-forming minerals, vol. 2: Chain silicates, 379 p. Longman, London.

——— (1966) An introduction to the rock-forming minerals, 528 p. Wiley, New York.

Della Ventura, G., Robert, J.-L., and Bény, J.-M. (1991) Tetrahedrally coordinated Ti^{4+} in synthetic Ti-rich potassic richterite: Evidence from XRD, FTIR, and Raman studies. American Mineralogist, 76, 1134–1140.

Dickey, J.S. (1968) Eclogitic and other inclusions in the Mineral Breccia Member of the Deborah Volcanic Formation at Kakanui, New Zealand. American Mineralogist, 53, 1304–1319.

Dorrerr, E. (1968) Algorithm 322—F distribution. Association of Computing Machinery Communications, 11, 116–117.

Dyar, M.D. (1990) H, O, and Fe^{3+} in biotite and muscovite. Geological Society of America Abstracts with Program, 22, A215.

Dyar, M.D., McGuire, A.V., and Mackwell, S.J. (1992) Fe^{3+}/H$^+$ and D/H in kaersutites—Misleading indicators of mantle source fugacities. Eos, 73, 141.

Ernst, W.G., and Wai, C.M. (1970) Infrared and optical study of cation ordering and dehydrogenation in natural and heat treated sodic amphiboles. American Mineralogist, 55, 1226–1258.

Hamish, M., and Seck, H.A. (1974) Synthese und Phasenbeziehungen Tihaltiger Pargasite (abs.). Fortschritte der Mineralogie, 51, 18–19.

Harrell, J.A. (1987) The analysis of bivariate association. In W.B. Size, Ed., Use and abuse of statistical methods in the earth sciences, p. 142–165. Oxford University Press, New York.

Hawthorne, F.C. (1981) The crystal chemistry of the amphiboles. In Mineralogical Society of America Reviews in Mineralogy, 9A, 1–95.

——— (1983) The crystal chemistry of amphiboles. Canadian Mineralogist, 21, 173–480.

Hewitt, D.A., and Abrecht, J. (1986) Limitations on the interpretation of biotite substitutions from chemical analyses of natural samples. American Mineralogist, 71, 1126–1128.

Irving, A.J., and Frey, F.A. (1984) Trace element abundances in megacrysts and their host basalts: Constraints on partition coefficients and megacryst genesis. Geochimica et Cosmochimica Acta, 48, 1207–1221.

Jarosewich, E., Nelson, J.A., and Newberg, J.A. (1980) Reference samples for electron microprobe analyses. Geostandards Newsletter, 4, 257.

Kesson, S., and Price, R.C. (1972) The major and trace element chemistry of kaersutite and its bearing on the petrogenesis of alkaline rocks. Contributions to Mineralogy and Petrology, 35, 119–124.

Leake, B.E. (1968) A catalog of analyzed calciferous and subcalciferous amphiboles together with their nomenclature and associated minerals, 210 p. Geological Society of America Special Paper 98.

——— (1978) Nomenclature of amphiboles. American Mineralogist, 63, 1023–1052.

Maresch, M.V., and Langer, K. (1976) Synthesis, lattice constants, and OH-valence vibrations of an orthorhombic amphibole with excess OH in the system Li$_2$O-MgO-SiO$_2$-H$_2$O. Contributions to Mineralogy and Petrology, 56, 27–34.

Mason, B. (1966) Pyrope, augite and hornblende from Kakanui, New Zealand. New Zealand Journal of Geology and Geophysics, 9, 474–480.

——— (1968) Kaersutite from San Carlos, Arizona, with comments on the paragenesis of this mineral. Mineralogical Magazine, 36, 997–1002.

Mattioli, G.S., and Wood, B.J. (1986) Upper mantle oxygen fugacity recorded by spinel lherzolites. Nature, 322, 626–628.

Phillips, M.W., Popp, R.K., and Clowe, C.A. (1988) Structural adjustments accompanying oxidation-dehydrogenation in amphiboles. American Mineralogist, 73, 500–506.

Phillips, M.W., Draheim, J.E., Popp, R.K., Clowe, C.A., and Pinkerton, A.A. (1989) Structural investigation of oxidation-dehydrogenation effects in tschermakitic hornblende. American Mineralogist, 74, 764–773.

Phillips, M.W., Popp, R.K., and Clowe, C.A. (1991) A structural investigation of oxidation effects in air-heated grunerite. American Mineralogist, 76, 1502–1509.

Popp, R.K., Phillips, M.W., Harrell, J.A. (1990) Accommodation of Fe^{3+} in natural, Fe^{3+}-rich, calcic and subcalcic amphiboles: Evidence from published chemical analyses. American Mineralogist, 75, 163–169.

Popp, R.K., Virgo, D., Hoering, T.C., and Phillips, M.W. (1992) Experimental investigation of ferric-ferrous ratios in kaersutitic amphiboles. Eos, 73, 337.

Rebbert, C.R., and Hewitt, D.A. (1986) Biotite oxidation in hydrothermal systems: An experimental study. Fourteenth General Meeting of the International Mineralogical Association, Abstracts with Program, p. 207. Mineralogical Society of America, Washington, DC.

Robinson, P., Spear, F.S., Schumacher, J.C., Laird, J., Klein, C., Evans, B.W., and Doolan, B.L. (1982) Phase relations of metamorphic amphiboles: Natural occurrence and theory. In Mineralogical Society of America Reviews in Mineralogy, 9B, 1–211.

Saxena, S.K., and Ekstrom, T.K. (1970) Statistical chemistry of calcic amphiboles. Contributions to Mineralogy and Petrology, 26, 276–284.

Steffe, D.D. (1979) The chemistry of calcic and subcalcic amphiboles from selected igneous and metamorphic environments, 164 p. M.S. thesis, University of Vermont, Burlington, Vermont.

Till, R. (1974) Statistical methods for the earth scientist, an introduction, 154 p. Wiley, New York.

Ungaretti, L. (1980) Recent developments in X-ray single crystal diffractometry applied to the crystal-chemical study of the amphiboles. Godisnjak Jugoslavenskog centra za kristalografiju, 15, 29–65.

Vedder, W., and Wilkins, R.W.T. (1969) Dehydroxylation and rehydroxylation, oxidation and reduction of micas. American Mineralogist, 54, 482–509.

Vinx, D., and Jung, D. (1977) Pargasitic-kaersutitic amphibole from a basanitic diatreme at the Rosenberg, North of Kassel (North Germany). Contributions to Mineralogy and Petrology, 65, 135–142.

White, A.J.R., Chappell, B.W., and Jakes, P. (1972) Coexisting clionpyroxene, garnet, and amphibole from an "eclogite," Kakanui, New Zealand. Contributions to Mineralogy and Petrology, 34, 185–191.

Wilkinson, J.F.G. (1961) Some aspects of the calciferous amphiboles, oxyhornblende, kaersutite, and barkevikite. American Mineralogist, 46, 340–354.

——— (1962) Mineralogical, geochemical, and petrogenetic aspects of an analcite-basalt from the New England district of New South Wales. Journal of Petrology, 3, 192–214.

Wilshire, H.G., and Trask, N.J. (1971) Structural and textural relationships of amphibole and phlogopite in peridotite inclusions, Dish Hill, California. American Mineralogist, 56, 240–255.

Wilshire, H.G., Calk, L.C., and Schwarzman, C. (1971) Kaersutite—A product of reaction between pargasite and basanite at Dish Hill, California. Earth and Planetary Science Letters, 10, 281–284.

Witte, P., Langer, K., Seifert, F., and Schreyer, W. (1969) Synthetische Amphibole mit OH-überschuß im System Na$_2$O-MgO-SiO$_2$-H$_2$O. Naturwissenschaften, 56, 414–415.

Wones, D.R., and Eugster, H.P. (1965) Stability of biotite: Experiment, theory, and application. American Mineralogist, 50, 1228–1272.

Wood, B.J., and Virgo, D. (1989) Upper mantle oxidation state: Ferric iron contents of lherzolite spinels by iron-57 Mössbauer spectroscopy and resultant oxygen fugacities. Geochimica et Cosmochimica Acta, 53, 1277–1291.

Wood, B.J., Bryndzia, L.T., and Johnson, K.E. (1990) Mantle oxidation state and its relationship to tectonic environment and fluid speciation. Science, 248, 337–345.

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