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Accommodation of Fe^{3+} in natural, Fe^{3+}-rich, calcic and subcalcic amphiboles: Evidence from published chemical analyses

Robert K. Popp
Department of Geology, Texas A&M University, College Station, Texas 77843, U.S.A.
Michael W. Phillips, James A. Harrell
Department of Geology, University of Toledo, Toledo, Ohio 43606, U.S.A.

Abstract

In order to evaluate the extent to which the oxy-amphibole and "Al-substitution" mechanisms are involved in accommodating Fe^{3+} in amphiboles, linear bivariate regression and correlation analyses were carried out for those Fe^{3+}-rich amphiboles (>0.7 atoms per formula unit) tabulated by Leake (1968) and Steffe (1979) that met a set of criteria related to quality of chemical analysis and that could be unambiguously classified as metamorphic, intrusive igneous, or extrusive igneous. The statistical analyses were used to relate Fe^{3+} content to octahedral Al content (which is related to the Al-substitution mechanism), as well as to (OH + F + Cl) content, A-site content, and excess positive charge over +46 per formula unit (which are related to the presence of an oxy-amphibole component).

Of the three groups of amphiboles, only those from metamorphic rocks exhibited a significant correlation between Fe^{3+} and octahedrally coordinated Al. The slope of the best-fit straight line for the two variables (-0.72 ± 0.52) agrees well with the theoretical value of -1.00 that results if all Fe^{3+} is accommodated by Al substitution.

Extrusive igneous varieties show significant correlation between Fe^{3+} content and A-site occupancy. Even though a statistically significant correlation was not observed between Fe^{3+} content and excess positive charge, as a group, the extrusive varieties have an excess positive charge significantly higher than zero, suggesting that they are relatively more oxidized. The lack of significant correlation between (OH + F + Cl) is considered to be the result of possible inaccuracies in analysis of water contents, to the uncertainty of the maximum possible OH contents of amphiboles, and to the possible accommodation of Ti by changes in the proportions of oxy- and hydroxy-amphibole.

Significant correlation between Fe^{3+} and any of the variables was not observed in intrusive igneous rocks, suggesting that neither mechanism dominates in that sampled population.

The results obtained here, as well as those of Phillips et al. (1988) suggest that, in general, the presence of substantial oxy-amphibole component imparts a relative instability to the crystal structure such that the Al-substitution mechanism dominates in those samples crystallized over relatively long time periods, as in metamorphic and intrusive igneous environments. Amphiboles in which the oxy-amphibole mechanism dominates are considered to be the result of later-stage oxidation processes at the Earth's surface or in the shallow subsurface.

Introduction

Recently, Clowe et al. (1988) and Phillips et al. (1988) investigated ferric-ferrous equilibrium in clinoamphiboles using four different igneous and metamorphic samples. The amphiboles were subjected to heating in air and hydrothermal treatment in order to define the relationship between oxygen fugacity and ferric-ferrous ratio, as well as to determine changes in crystal structure that accompany the formation of oxy-amphibole component by the reaction

$$Fe^{2+} + OH^- = Fe^{3+} + O^{2-} + \tfrac{1}{2}H_2. \quad (1)$$

Those studies showed that certain of the natural amphiboles initially contained small, but still significant, amounts of oxy-amphibole component, and that the dehydrogenation-hydrogenation reaction described by Equation 1 is readily reversible and occurs relatively rapidly, on the order of hours to days at 650 °C. Crystal-structure refinements of the treated samples (Phillips et al., 1988) identified a number of adjustments of the amphibole crystal structure that occur in response to the dramatic change in bond strength that results when O^{2-} replaces OH^- at the O(3) anion site. Those adjustments include shortening of the M-O(3) bond, preferential or-

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dering of trivalent cations into the M(1) and M(3) sites, and interaction of the A-site cation with the O^{2-} anion at O(3).

The knowledge gained from the experimental studies posed the question of whether, in general, oxy-amphibole component is important in natural varieties and whether any of the structural-adjustment mechanisms might also have been operative in natural amphiboles that contain a significant Fe^{3+} component. Attempts to elucidate the role of oxy-amphibole component in natural samples are complicated, however, by the fact that octahedrally coordinated Fe^{3+} ($^{[6]}Fe^{3+}$) can also be accommodated in the amphibole crystal structure by the same mechanisms that accommodate $^{[6]}Al^{3+}$. The substitution of $^{[6]}Al$ for a divalent octahedral cation in an amphibole requires one of two types of coupled substitutional solid solution in order to maintain electroneutrality: either a tschermakitic-type substitution or substitution of a univalent cation in the M(4) position. In a tschermakitic-type substitution, replacement of each divalent cation by $^{[6]}Al$ is coupled with substitution of an Al for $^{[4]}Si$. This mechanism is also involved in other amphibole end-member compositions such as magnesio-gedrite [$Mg_5Al_2Si_6Al_2O_{22}(OH)_2$], sodium gedrite [$NaMg_6AlSi_6Al_2O_{22}(OH)_2$], and pargasite [$NaCa_2Mg_4AlSi_6Al_2O_{22}(OH)_2$]. Even though the latter two end-members also contain Na in the A site, the presence of such Na is not involved in restoring the charge imbalance that results from the $^{[6]}Al$. A-site Na, in fact, increases the amount of positive charge relative to an amphibole with the A site vacant and must be balanced by replacement of $^{[4]}Si$ by Al, as in sodium gedrite and pargasite. In amphiboles such as alumino-winchite [$NaCaMg_4AlSi_8O_{22}(OH)_2$] and glaucophane [$Na_2Mg_3Al_2Si_8O_{22}(OH)_2$], substitution of $^{[6]}Al$ for divalent cations is coupled with substitution of Na^+ or Li^+ for Ca^{2+} in the M(4) site. Fe^{3+} analogues exist for most of the Al end-members, but Fe^{3+}-Al substitution, no doubt, occurs to some extent in most natural specimens. In this study, tschermakitic and glaucophanitic types of coupled substitution are termed "Al-substitution," implying that Fe^{3+} can be considered to substitute for $^{[6]}Al$.

The possibility exists that other mechanisms may also be involved in accommodating Fe^{3+} within the amphibole crystal structure. For example, Rebbert and Hewitt (1986) have suggested that the presence of anion vacancies in the biotite structure may be involved in controlling the proportions of Fe^{3+} and Fe^{2+} in that mineral. If such a mechanism were operative in the amphiboles, increasing amounts of Fe^{3+} could possibly be accommodated within the crystal structure by decreasing the numbers of anion vacancies at O(3), which is the only anion site that would possibly be vacated. In the absence of any data relevant to the amphiboles, anion vacancies are not considered further.

In order to investigate the relative importance of each of the two mechanisms (oxy-amphibole vs. Al substitution) for accommodating Fe^{3+} in naturally occurring, Fe^{3+}-rich calcic and subcalcic amphiboles, regression and correlation analyses were carried out on a number of chemical-composition variables that might be indicative of the type of mechanism.

Data sources

Despite the fact that large numbers of electron-microprobe analyses of amphiboles exist in the mineralogic, petrologic, and geochemical literature, Fe^{3+}/Fe^{2+} ratios, as well as H_2O contents must be known in order to quantify the role of oxy-amphibole component. Because those quantities are not obtainable by the electron microprobe, only amphiboles for which complete chemical analyses are available can be used here.

The data used in this study are those of Leake (1968) and Steffe (1979). Leake assembled a catalogue of 1217 chemical analyses of calcic and subcalcic amphiboles published between 1890 and 1968. Included for each sample, if available, is a description of the geologic occurrence and the associated minerals. The compilation of Steffe contains additional chemical analyses and environments of formation for approximately 350 calcic and subcalcic amphiboles published between 1968 and 1979.

The amphibole analyses used in the statistical analyses were limited to those considered to be relatively Fe^{3+}-rich. The rationale for this decision was to avoid complications related to minor variations in the precision and/or accuracy of the analyses. That is, if the predicted correlations are present, they are most likely to be observed in those amphiboles with the highest amounts of Fe^{3+}. In amphiboles containing smaller amounts of Fe^{3+}, correlation is more likely to be obscured by the analytical uncertainties of the data. A value of 0.7 Fe^{3+} per formula unit (pfu) was selected as the minimum Fe^{3+} content. This value was arbitrarily selected because it represents 10% occupancy of Fe^{3+} in the seven nontetrahedral, non-A cation sites per formula unit. Fe^{3+} contents of the amphiboles in the Leake and Steffe databases range from 0.0 to 1.6 Fe^{3+} per formula unit, and thus approximately the upper one-half of the total range is included in the populations used here. For comparison, the IMA nomenclature for amphiboles (Leake, 1978) approves the prefix "ferri" for calcic and subcalcic amphiboles containing ≥ 1.0 Fe^{3+} per formula unit and "ferrian" for those containing 0.75–0.99 Fe^{3+} per formula unit. Analysis of the data for compositions less Fe^{3+} rich has not been attempted.

For purposes of the statistical analyses, the amphiboles were divided into those from metamorphic rocks, intrusive igneous rocks, and extrusive igneous rocks. For the Leake data, the selection was based on the name of the rock type given in the compilation. A significant number of analyses were rejected because no information of the occurrence was provided with the analysis or because the description was not definitive. The distinction of extrusive igneous rocks was generally straightforward, whereas in many cases, that between intrusive igneous and metamorphic rocks was not. All rock types with a "meta-" prefix were considered to be metamorphic, as were skarns.

Rocks with typical igneous mineral assemblages (granites and feldspathoid-bearing rocks), but with gneissic texture, were also considered to be nondefinitive and were eliminated from the data set. The compilation of Steffe contained the classification as to the environment of formation, and that classification was used directly.

Leake (1968) grouped the analyses into three classes, superior, moderate, and inferior, on the basis of the extent to which an analysis fulfilled the following eight criteria. The rationale for each criterion is discussed in detail by Leake (1968). (1) The analysis results in a total weight percent between 99.44 and 100.60. (2) The Si per formula unit does not exceed 8.08. (3) The Si + Al per formula unit is not less than 7.92. (4) The sum of Ca + Na + K per formula unit lies between 1.75 and 3.05. (5) The sum of $^{[6]}Al + Fe^{3+} + Fe^{2+} + Mn + Mg + Cr + Ni$ per formula unit lies between 4.75 and 5.25. (6) The sum of OH + F + Cl lies between 1.00 and 2.99. (7) $^{[6]}Al$ does not exceed the maximum amount possible for the (Si + $^{[4]}Al$) per formula unit. (8) The analysis is corrected for the presence of any impurities. Amphiboles classified as superior were those that met all eight criteria, but the specific procedure used to distinguish between those of moderate and inferior quality was not described (Leake, 1968).

Ideally, use of only "superior" type analyses should provide the best correlation, but limiting the data to only those such amphiboles resulted in significantly smaller sample population sizes. The inclusion of amphiboles from Leake's "moderate" quality group that contain >1.0 Fe^{3+} per formula unit essentially doubled each population size. The rationale for their inclusion is that the additional samples provide a larger database, but as above, the analytical uncertainties are less likely to be significant for amphiboles that contain higher amounts of Fe^{3+}. The correlation and regression analyses discussed below were carried out separately for both groups of amphiboles, the "superior" group and the "superior + moderate" group. The somewhat higher correlation coefficients (r) obtained in several cases for the "superior" group were not better than those for the "superior + moderate" group because the smaller sample size decreased the statistical significance of the correlations. As a result, the larger database was used. The resulting population sizes obtained from the Leake data were metamorphic varieties, 16 samples; extrusive igneous varieties, 15 samples; intrusive igneous varieties, 20 samples.

All amphiboles in the Steffe (1979) compilation that met the first seven criteria above were included in the data set. Because Leake's procedure for defining "moderate" quality analyses is not described, the following selection procedure was used for the Steffe data. Analyses that failed to meet two or more of the seven criteria were rejected. Because the Al content of each amphibole is used directly as a variable in the statistical analyses, any sample that did not meet Leake's criterion 7 was also rejected. Analyses that failed to meet only one criterion other than 7 were included in the data set if they fell within Leake's acceptable range expanded by a factor of two. The resulting population sizes obtained from the Steffe data were metamorphic varieties, 10 samples; extrusive igneous varieties, 1 sample; intrusive igneous varieties, 14 samples.

Clearly, the total data set (metamorphic varieties, 26 samples; extrusive igneous varieties, 16 samples; intrusive igneous varieties, 33 samples) is relatively small in size. It should be emphasized, however, that the sampled populations contain all of the analyses of Fe^{3+}-rich, calcic and subcalcic amphiboles existing in the literature up to 1979 that can be considered to be of reliable quality and can be classified as to environment of formation. Despite the small sample size, the study is based on the best, and only existing, set of data.

Regression and correlation parameters

The elemental contents of a population of amphiboles may reflect the relative importance of the two different mechanisms for Fe^{3+} accommodation: oxy-amphibole versus "Al substitution." For example, if Fe^{3+} is present only as oxy-amphibole component, three different variables should exhibit a high degree of correlation with Fe^{3+} per formula unit. (1) An inverse correlation between the univalent anion content in the O(3) site (i.e., $OH^- + F^- + Cl^-$) and Fe^{3+}, as required by Equation 1 should be observed. (2) The presence of oxy-amphibole component increases the total amount of positive charge per formula unit. In the standard amphibole chemical formula, which contains only divalent cations in addition to Si, the sum of the positive charges is +46 and is exactly balanced by the negative charge from the 22 oxygens and 2 (OH + F + Cl). The formation of oxy-amphibole component increases the amount of positive charge by +1 for each atom of Fe^{3+} per formula unit, but this increase is balanced by the replacement of OH^-, F^-, or Cl^- by O^{2-}. Thus, in an ideal oxy-amphibole, there should be a positive 1:1 correlation between Fe^{3+} and "excess positive charge" (the amount of positive charge in excess of +46 pfu). (3) Because the presence of A-site cations should contribute to he stabilization of oxy-amphibole component (Phillips et al., 1988), a positive correlation between Fe^{3+} and A-site occupancy is expected. The presence of an A-site cation does not in itself suggest the presence of oxy-amphibole component; rather, oxy-amphibole component is more readily accommodated if A-site cations are present.

Alternately, if Fe^{3+} is present within an amphibole population as the result of only Al substitution, a negative correlation between Fe^{3+} and Al should be observed, provided that the sum of Fe^{3+} and $^{[6]}Al$ is constant within the population.

Accordingly, linear bivariate correlation and regression analyses were carried out to relate each of the variables described above to Fe^{3+} content in each of the three different amphibole populations.

In the regression and correlation analyses, $^{[6]}Al$ contents calculated on an atom-per-formula-unit basis were

taken directly from Leake (1968) and Steffe (1979), as were values of (OH + F + Cl).

A-site occupancy was calculated as follows. The amounts of octahedral cations presumed to reside in the M(1), M(2), and M(3) sites (i.e., $^{[6]}Al$, Fe^{3+}, Fe^{2+}, Ti^{4+}, Mg, and Mn) were summed and subtracted from 5.0, the theoretical maximum cation content of those sites. Any excess of those cations over 5.0, which presumably would be Fe^{2+} or Mn, is assumed to reside in the M(4) site. All Ca, as well as an amount of Na necessary to fill the 2.0 sites per formula unit, was assigned to M(4). The remaining Na and all of the K per formula unit were then assigned to the A site. In the rare case where M(4) occupancy exceeded 2.0 atoms per formula unit, A-site occupancy was taken to be the sum of total Na plus K. If there was insufficient (Ca + Na) to fill M(4), the A site was considered to be occupied by K only. This scheme for cation ordering assumes that Ca is contained only in the M(4) site, K is contained only in the A site, and Na is contained in both. Whether this distribution of cations is truly that of each amphibole cannot be determined without crystal-structure analyses.

Excess positive charge was calculated by two different procedures. In the first, the number of moles of each cation in the chemical formula was multiplied by its valence, the total charge summed, and the standard charge of +46 subtracted from that total. The second procedure relies on the fact that the standard charge of +46 is based on the presence of only divalent cations and Si^{4+}. Thus, only substitution of a cation with a valence of other than +2 will affect the amount of positive charge. That is, substitution of $^{[4]}Al$ for Si and substitution of Na for Ca in M(4) will decrease the charge relative to +46, whereas the presence of A-site cations and the presence of Fe^{3+}, Al, or Ti^{4+} in the octahedral sites will increase the total charge relative to +46. Therefore,

$$\text{"excess positive charge"} = {}^{[6]}Fe^{3+} + {}^{[6]}Al + 2{}^{[6]}Ti^{4+} + \text{A-site occupancy} - {}^{[4]}Al - {}^{M(4)}Na. \quad (2)$$

If the chemical analysis of a given amphibole is accurate, and the cations are distributed within the sites as described in the preceding paragraph, the excess positive charge calculated by the two different methods should be the same.

Results

The results of the regression and correlation analyses are summarized in Tables 1 and 2. Given in the tables are the slopes of the best-fit straight lines and their 95% confidence limits for the variation in $^{[6]}Al$ content, (OH + F + Cl) content, A-site occupancy, and "excess positive charge" as a function of Fe^{3+} ions per formula unit. The meaning of the confidence limits is that there is a 95% chance that the true slope (i.e., that which exists in the sampled population) lies within the ± interval about the slope. Also in the tables are the corresponding correlation coefficients with their significance levels. These significance levels come from a statistical test of the null hypothesis that a given pair of variables has a correlation of zero in the sampled population. This is also equivalent to testing the null hypothesis that the slope of the best-fit straight line is zero. For example, an 83% significance level means that there is a 17% chance of obtaining an entirely spurious correlation larger than the observed correlation when the null hypothesis is true. It is conventional to consider an observed correlation "statistically significant" if its significance level is 95% or higher. It must be kept in mind, however, that the stated statistical significance of the confidence limits and correlation coefficients are strictly valid only when all the underlying assumptions for the statistics are met (Harrell, 1987). In this study, some of these assumptions have been violated as a result of the nonrandom sampling of the amphibole population, the combining of data obtained by different analysts using different analytical techniques, and the requirement that the compositional variables (those in Table 1 plus others) sum to 100 wt%. When correlation analysis is performed on "variables of a constant sum," there is an induced negative correlation between the variable pairs (Chayes, 1960). Depending upon the characteristics of the data set, the induced correlation can, at times, be large. The significance levels stated in this study cannot then be taken literally; they serve merely to suggest relative levels of statistical significance. Nevertheless, for convenience in the discussion that follows, the results in Tables 1 and 2 will be used as though they are statistically valid.

Of the three classes of amphiboles, only those from metamorphic rocks show significant covariation between $^{[6]}Al$ and Fe^{3+} (Table 1). The calculated slope of the best-fit line (−0.72 ± 0.52) agrees well with the theoretical 1:1 inverse correlation that would be observed if the two elements are related by a solid-solution substitutional relationship, *and* the sum of $^{[6]}Al$ and Fe^{3+} is identical in all amphiboles used in the regression. Even if the two elements were related by a substitutional relationship, no correlation between the two variables could result if that sum varied significantly within the population. For the three groups of amphiboles, the mean and one-standard-deviation values for ($^{[6]}Al + Fe^{3+}$) are 1.22 (0.20), 1.14 (0.26), and 1.40 (0.28) for metamorphic, intrusive igneous, and extrusive igneous amphiboles, respectively. The differences in the standard deviations between the three groups are considered not likely to have a deleterious effect on the significance of the observed correlations. Plots of $^{[6]}Al$ vs. Fe^{3+} for the three groups of amphiboles are shown in Figure 1.

Significant correlation between (OH + F + Cl) and Fe^{3+} was not observed in any of the three groups (Table 1), but such results do not necessarily imply that oxyamphibole is not a significant component in any of the groups. Of all the analytical techniques for amphibole chemical components, that for H_2O is generally considered to be the most unreliable, which may contribute to the scatter of the data. The presence of excess OH over

TABLE 1. Results of regression and correlation analyses for Fe^{3+} and the compositional variables

Variables*	Slope**	Correlation†
$^{[6]}Al$ vs. Fe^{3+} per formula unit		
Metamorphic	−0.72 (± 0.52)	−0.50 (99)
Intrusive	−0.05 (± 0.37)	−0.07 (28)
Extrusive	−0.17 (± 0.47)	−0.20 (54)
(OH + F + Cl) vs. Fe^{3+} per formula unit		
Metamorphic	−0.71 (± 1.15)	−0.25 (78)
Intrusive	0.01 (± 1.07)	0.005 (2)
Extrusive	−0.73 (± 1.34)	−0.30 (74)
A-site occupancy vs. Fe^{3+} per formula unit		
Metamorphic	0.23 (± 0.74)	0.13 (47)
Intrusive	0.36 (± 0.59)	0.27 (87)
Extrusive	0.35 (± 0.30)	0.56 (98)

Note: All statistical calculations were made using the GLM, MEANS, and CORR procedures of the Statistical Analysis System software for mainframe computers (SAS Institute, Inc., Cary, North Carolina 27511, U.S.A.).

* Linear bivariate regression and correlation analysis were performed with Fe^{3+} as the predictor variable, and $^{[6]}Al$, (OH + F + Cl), and A-site occupancy as the response variables. Sample sizes for the three types of amphiboles: metamorphic, $n = 26$; intrusive igneous, $n = 33$; extrusive igneous, $n = 16$.

** Slope of the best-fit straight line (i.e., b in $y = a + bx$, where x and y are the predictor and predicted response variables, respectively) (Crow et al., 1960, p. 152–156; Draper and Smith, 1981, p. 8–17). The values in parentheses are the 95% confidence limits for the slope (Crow et al., 1960, p. 160–161; Draper and Smith, 1981, p. 24–27).

† Product-moment or sample correlation coefficient, r (Crow et al., 1960, p. 157–158; Draper and Smith, 1981, p. 43–46). The values in parentheses represent the level of statistical significance ($[1 - \alpha] \cdot 100$) for the correlation coefficient and slope (Crow et al., 1960, p. 159; Dorrerr, 1968).

the standard value of two per formula unit has been reported in synthetic amphiboles (Witte et al., 1969; Maresch and Langer, 1976), and approximately ⅓ of the amphiboles used in the regression analyses contain greater than 2 OH per formula unit, ranging up to a maximum of 2.99 pfu. In addition, Ti may be accommodated in amphiboles by a coupled substitution involving oxy- and hydroxy- components (Leake, 1968; Hamich and Seck, 1974). As a result of these complicating factors, it is concluded that even if highly accurate H_2O analyses were available, the relation between ferric-oxy-amphibole component and the number of OH per formula unit may not be highly constrained.

TABLE 2. Results of regression and correlation analyses for Fe^{3+} and excess positive charge

Variables*	Slope**	Correlation**
Metamorphic varieties		
All cations	0.71 (± 1.151)	0.25 (79)
Equation 2	0.72 (± 1.07)	0.27 (82)
Intrusive igneous varieties		
All cations	−0.05 (± 1.11)	−0.02 (8)
Equation 2	0.31 (± 0.84)	0.17 (64)
Extrusive igneous varieties		
All cations	0.57 (± 1.31)	0.24 (64)
Equation 2	0.78 (± 0.96)	0.42 (90)

* Linear bivariate regression and correlation analyses were performed with Fe^{3+} as the predictor variable and excess positive charge (both with all cations and as described in Eq. 2 in text) as the response variable. See Table 1 for sample sizes.

** See corresponding footnotes in Table 1.

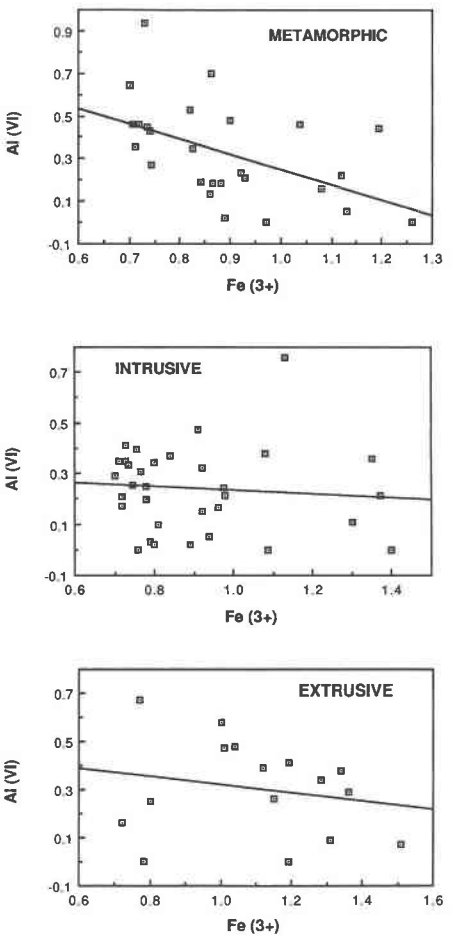

Fig. 1. Plots of $^{[6]}Al$ vs. Fe^{3+} per formula unit for the three amphibole groups. Straight lines were obtained by linear-regression analysis. See Table 1 for results of the statistical analyses. The range and distribution of Fe^{3+} contents of each group are evident in the plots.

Significant correlation between A-site occupancy and Fe^{3+} content was observed only for extrusive igneous varieties. Even though the presence of A-site cations should facilitate the formation of oxy-amphibole component (Phillips et al., 1988), the relation between the two variables has not been quantified. Therefore, there is no theoretical basis for predicting an expected slope, other than the fact that a positive correlation is to be expected.

Comparison of the two different procedures for calculating excess positive charge is shown in Table 2. For metamorphic rocks, no significant difference is observed in the correlation coefficients between the two different calculation procedures, whereas large differences are observed for extrusive and intrusive igneous rocks. For the latter groups, the correlation coefficient for excess charge calculated by the first method is considerably lower than that calculated from Equation 2. One possibility for the difference is that the cation distributions within certain of the amphiboles in these two groups is different than that of the ideal case described in the preceding section.

It should be noted that the selective partitioning of Na and Ca from M(4) into A, with resultant vacancies in M(4), has been observed in highly oxidized amphiboles heated in air (Ungaretti, 1980; Hawthorne, 1983; Phillips et al., 1988). A statistically significant correlation between excess positive charge and Fe^{3+} content was not observed for any of the three groups, but the highest correlation (significant at the 90% level) was observed for extrusive igneous varieties. Interestingly, all extrusive samples have positive values of excess charge, whereas 13 of the 26 metamorphic amphiboles and 11 of the 33 intrusive igneous amphiboles have less than 46 positive charges per formula unit. The mean (and one-standard deviation) values for excess positive charge in the extrusive igneous, intrusive igneous, and metamorphic populations are, respectively, 1.02 (0.44), 0.32 (0.38), and 0.11 (0.42). These observations lend support to the conclusion that extrusive varieties are more highly oxidized.

Discussion

The regression and correlation analyses suggest that there are significant differences in the major Fe^{3+}-accommodation mechanisms among the amphiboles from the three different environments. Despite these differences, it should be noted that amphiboles from none of the groups are inherently richer in Fe^{3+}, i.e., the scatter and maximum Fe^{3+} contents are similar in all three varieties (see Fig. 1).

In metamorphic varieties there is an approximate 1:1 inverse correlation between Fe^{3+} and $^{[6]}Al$ contents, but no significant correlation for those variables that are related to the formation of oxy-amphibole component. Based on these results, it is concluded that oxy-amphibole component does not play the major role in controlling the Fe^{3+} content of the metamorphic amphiboles in the sampled population. The experimental results of Clowe et al. (1988) have revealed the presence of both oxy-amphibole and Al-substitution mechanisms in two natural hornblendes, but the amounts of Fe^{3+} present as oxy-amphibole are relatively low (0.20 and 0.12 pfu). The results obtained here clearly do not preclude such amounts of oxy-amphibole component in metamorphic varieties. The precision of the chemical analyses is not sufficient to calculate the absolute contribution of each mechanism to the total Fe^{3+} content.

The results are consistent with the formation of oxy-amphibole component as the major mechanism by which Fe^{3+} occurs in extrusive igneous amphiboles. This conclusion is evidenced by the lack of correlation between Fe^{3+} and $^{[6]}Al$, as well as the significant correlation of A-site occupancy and the relatively high values of excess positive charge.

For intrusive igneous rocks, no significant correlation was observed between Fe^{3+} and any of the parameters. Apparently, neither of the two accommodation mechanisms dominates in all intrusive igneous amphiboles. Whether one mechanism dominates in certain samples or both mechanisms are involved equally in some samples cannot be ascertained with certainty. As discussed below, the former is considered more likely.

The different behavior of amphiboles from the three rock types can be explained to some extent by the environments of formation. In general, it is assumed that higher Fe^{3+} contents are associated with higher oxygen fugacity in the environment of formation, but crystal-chemical and bulk chemical variables are also involved (Clowe et al., 1988; Phillips et al., 1988). The extrusive igneous amphiboles are likely to have been phenocrysts if grains were able to be separated from the matrix for chemical analysis. If so, the extrusive amphiboles represent pre-existing phases that were exposed to the highly oxidizing conditions at the Earth's surface at high temperature. The relatively rapid quench times, as well as the rapid rates at which the formation of oxy-amphibole proceeds (Clowe et al., 1988), would be sufficient for oxy-amphibole to form, but would tend to inhibit decomposition or major redistribution of elements between amphibole and other phases.

For metamorphic amphiboles, on the other hand, the relatively long periods of equilibration and cooling give ample time for redistribution of elements between amphibole and other phases. Even though there are compensation mechanisms that act to relieve local charge imbalances in oxy-amphiboles, Phillips et al. (1988) suggested that such imbalances are not totally compensated, and thus amphiboles high in oxy-amphibole component may be inherently less stable than those with lower oxy-component. As a result, amphiboles may generally accommodate relatively low amounts of Fe^{3+} as oxy-amphibole component upon their initial crystallization or when they re-equilibrate under conditions where significant redistribution of elements between coexisting phases can occur.

The relatively slow crystallization rates of intrusive igneous rocks should more closely resemble metamorphic rather than extrusive processes, which would favor relatively low oxy-component values. However, oxidation of magmas by processes such as assimilation of groundwater at shallow levels in the crust and loss of H_2 by devolatilization has been documented (see Wones and Gilbert, 1982). Such processes could oxidize earlier-formed amphiboles by the formation of an oxy-component, but their likelihood and extent cannot be evaluated for individual amphiboles in the sample population, given the simple descriptions provided in Leake (1968) and Steffe (1979). Thus, of the three different varieties, intrusive igneous rocks are considered the most likely to contain individual amphiboles in which either of the two mechanisms could dominate.

Whether the observed trends also apply to Fe-Mg or sodic amphiboles is unknown. Similar compilations of data with Fe^{3+} analyses are not available for those groups of amphiboles.

The intent of this study was to evaluate the extent to which amphibole compositions might reflect the two different mechanisms of Fe^{3+} accommodation. The results

do, in fact, suggest that differences exist in the data set used in the regression and correlation analyses. However, given the constraints of the chemical analyses, the conclusions obtained here would be strengthened considerably by larger numbers of high-quality amphibole analyses.

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