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Stoichiometry-based estimates of ferric iron in calcic, sodic-calcic and sodic amphiboles: A comparison of various methods

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ABSTRACT

An important drawback of the electron microprobe is its inability to quantify Fe^{3+}/Fe^{2+} ratios in routine work. Although these ratios can be calculated, there is no unique criterion that can be applied to all amphiboles.

Using a large data set of calcic, sodic-calcic, and sodic amphibole analysis from A-type granites and syenites from southern Brazil, we assess the choices made by the method of Schumacher (1997, Canadian Mineralogist, 35: 238-246), which uses the average between selected maximum and minimum estimates. Maximum estimates selected most frequently are: 13 cations excluding Ca, Na, and K (13eCNK – 66%); sum of Si and Al equal to 8 (8SiAl – 17%); 15 cations excluding K (15eK – 8%). These selections are appropriate based on crystallochemical considerations. Minimum estimates are mostly all iron as Fe^{2+} (*all* Fe2 – 71%), and are clearly inadequate. Hence, maximum estimates should better approximate the actual values.

To test this, complete analyses were selected from the literature, and calculated and measured values were compared. 13eCNK and maximum estimates are precise and accurate (concordance correlation coefficient – $r_c \approx 0.85$). As expected, averages yield poor estimates ($r_c = 0.56$).

We recommend, thus, that maximum estimates be used for calcic, sodic-calcic, and sodic amphiboles.

Key words: amphiboles, stoichiometry, ferric iron, EPMA.

INTRODUCTION

The electron microprobe analyzer (EPMA) has become the standard instrument for the chemical analysis of minerals. It allows for very good spatial resolution and reasonable detection limits for the vast majority of the materials of interest to Earth scientists. However, one of the most crucial problems is its inability, at least in routine work, to discriminate between different oxidation states of chemical elements.

Due to the mineralogical and petrologic relevance of such determinations, particularly the importance of the Fe^{3+}/Fe^{2+} ratio as an indicator of intensive and extensive parameters of crystallization, several techniques have been applied in order to estimate them.

Quantitative determinations of Fe^{2+} and total Fe in mineral concentrates have been widely used (e.g. Cosca et al. 1991, Dyar et al. 1993, Enders et al. 2000). However, the technique is excessively

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time-consuming and its applicability may be questioned in most cases due to the presence of inclusions and chemical zoning.

Recently, there has been an effort to develop microanalytical methods sensitive to these variations. Yet, although some techniques have been successful, none of them became widespread until now. Some of them depend on the availability of very specialized equipment (e.g. microXANES – cf. Sutton et al. 1993, Delaney et al. 1996), while other potential methods employing the EPMA (e.g. flank method – cf. Enders et al. 2000, and references therein) require much more care and time than it is usually possible in routine work.

In this sense, estimates based on stoichiometric considerations are still the best choice for ordinary analyses. For several minerals with relatively simple structures and in which only one element is present in two valence states (e.g. pyroxene, garnet), these calculations are sufficiently good, provided the analyses are of high quality (Droop 1987).

Amphiboles, however, have long challenged researchers and, consequently, an extensive literature has developed on the subject (e.g. Papike et al. 1974, Robinson et al. 1982, Hawthorne 1983, Schumacher 1991, 1997).

The presence of vacancies in the A-site and the potential substitution of $(OH)^-$, F^- and Cl^- for O^{2-} prevent the determination of a unique crystallochemical criterion on which to base the calculations. It has been recognized that different criteria may apply to different amphibole groups (cf. Robinson et al. 1982). Accordingly, the IMA has recently proposed a method to choose from among the various criteria (Leake et al. 1997, Schumacher 1997) that is very similar to that of Holland and Blundy (1994). However, some recent studies suggest this method may yield unsatisfactory results (Enders et al. 2000, Martins 2001).

In this paper, we use a large dataset of calcic, sodic-calcic, and sodic amphibole compositions obtained along the study of the mineralogy of the Graciosa A-type Granites, southern Brazil (Gualda 2001), to critically evaluate the choices made by the method of Schumacher (1997). Also, we compare the results obtained from published complete analyses with the calculated Fe^{3+} and Fe^{2+} contents in order to assess the quality of the estimates. Finally, we propose that a variation of the method of Schumacher (1997) be used for calcic, sodic-calcic, and sodic amphiboles.

BACKGROUND

Methods for the calculation of Fe^{2+} and Fe^{3+} contents from total Fe are based on an assumption of electroneutrality (Hawthorne 1983). In fact, the same approach may be applied for any other element, provided it is the only one present in two different oxidation states. The solution consists in distributing total Fe contents in a way that the positive charges equal the negative ones. However, the analytical determination of the number of negative charges is seldom viable. Although the measurement of oxygen concentrations with the EPMA is possible in some cases, it is usually problematic, at least in routine work with silicates.

If a group of cations is restricted to one or more crystallographic sites, it becomes possible to convert the measured cation proportions into absolute cations per unit formula. This is done by normalizing all cations so that the sum of the selected group equals the expected value (for example, in pyroxenes, the sum of all cations should be normalized to 4). The positive charges can then be balanced to the expected number of negative charges in the same unit cell (in the case of pyroxenes, total Fe is split into Fe^{3+} and Fe^{2+} so that the sum of positive charges equals twelve, equivalent to the 6 oxygen anions). This general formalism was presented by Droop (1987), and is an exact solution to the iterative method of Papike et al. (1974).

In the case of the amphiboles, however, the presence of vacancies in the A site precludes the normalization to 16 total cations. Likewise, the potential presence of Al in both T and C sites, of Fe^{2+}, Mn, and Mg in both C and B sites, and of Na in B and A sites, does not allow the universal use of any of these partial sums to normalize the cationic contents.

Although no single criterion is suitable for all possible amphibole compositions (Hawthorne 1983), it has been argued that each criterion may be applicable to some specific amphibole groups (Robinson et al. 1982), in which case, site occupancy considerations show that corrected analyses tend to be more satisfactory than uncorrected ones (Schumacher 1991). The distribution of elements present among multiple sites is not reliable, though. Consequently, the challenge is to choose, from among the possible criteria, the best suited for a given amphibole analysis. The IMA recently recommended the adoption of a method to make such a decision (Schumacher 1997).

Each of the nine crystallochemical criteria considered by Schumacher (1997) leads to a different estimate of Fe^{3+}. Four of them result in minimum Fe^{3+} estimates:

(a) 8 Si cations (8Si);

(b) 16 total cations (16Cat);

(c) 15 total cations excluding Na and K (15eNK);

(d) all Fe as bivalent (*all* Fe2);

whereas five result in maximum estimates:

(e) 8 (Si+Al) cations (8SiAl);

(f) 15 total cations excluding K (15eK);

(g) 13 total cations excluding Ca, Na and K (13eCNK);

(h) all Fe as trivalent (*all* Fe3);

(i) all tri- and tetravalent cations in the M2 sites (10SFe3).

The actual value of Fe^{3+} should lie between the larger Fe^{3+} value among the minimum estimates and the smaller one among the maximum estimates. Schumacher (1997) proposes that the final Fe^{3+} result be calculated based on the average between these two values. It is pointed out, however, that this last recommendation is a rather arbitrary one, because the actual values may lie anywhere between the two estimates.

ANALYTICAL PROCEDURES

Amphibole analysis (wavelength-dispersive spectrometry, WDS) were obtained at the Instituto de Geociências, Universidade de São Paulo, using standard carbon-coated thin sections on a JEOL-8600S EPMA with five WD spectrometers, a Noran EDS (energy-dispersive spectrometry) detector, and a Voyager (v. 3.6.1) automation and data reduction system.

A total of 20 samples from alkaline and other 19 from aluminous A-type granite associations covering the observed petrographic variation within the Graciosa granites and syenites were selected for this work.

Analytical conditions were 15 kV, 20 nA, and 5μm for accelerating voltage, current, and beam diameter, respectively. Si, Ti, Al, Fe, Mn, Mg, Zn, Ca, Na, K, Cl, and F Ka line intensities were quantified along core to rim traverses and/or over areas with contrasted patterns as revealed in transmitted light or back-scattered electron compositional images. Zr (L_α line) contents were below detection limits (*ca.* 400 ppm) in most analysis. Total counting times were between 20s (major elements) and up to 80s (minor elements, <1wt.%), equally distributed for peak and background measurements.

Analytical standards included both natural and synthetic compounds: wollastonite (Si, Ca), Arenal hornblende (Al), synth rutile (Ti), Mn-olivine (Fe, Mn), diopside (Mg), zircon (Zr), Amelia Albite (Na), Asbestos microcline (K), synth Cl-apatite (Cl), fluorite/F-apatite (F), synth ZnO (Zn). Elemental calibrations were checked against the Arenal and Kakanui hornblende standards in all runs. The PROZA scheme (e.g. Bastin et al. 1984) was used for matrix corrections and data reduction.

THE AMPHIBOLES OF THE GRACIOSA A-TYPE GRANITES

A set of 554 analyses (WDS) of amphiboles from metaluminous, peralkaline and moderately peraluminous granites and syenites has been obtained as part of the detailed characterization of the mineralogical evolution of the Graciosa A-type Granites, which crop out in the Serra do Mar Granitic Province, Southern Brazil (Gualda 2001).

The studied amphiboles show a broad range of compositions, varying from calcic to sodic-calcic to sodic (Figure 1). Calcic amphiboles are present in metaluminous to slightly peraluminous granites that form *aluminous* A-type associations (Vlach et al. 1990, King et al. 1997). Calcic, sodic-calcic, and sodic amphiboles are present in metaluminous to peralkaline varieties that compose *alkaline* A-type associations (Lameyre and Bowden 1982; for details, see Gualda 2001).

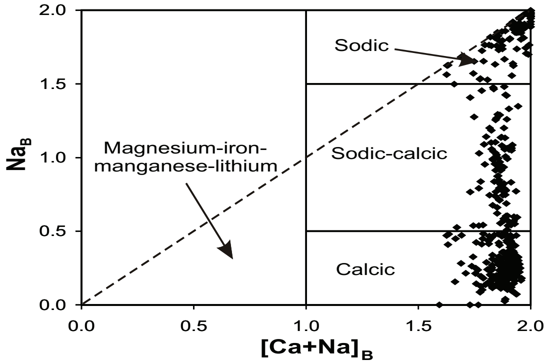

Fig. 1 – Na_B versus $[Ca+Na]_B$ classification plot (after Leake et al. 1997) showing the array variation from calcic to sodic-calcic, and sodic among the amphiboles of the Graciosa A-type Granites, southern Brazil. Calculated on the basis of 23O anions. Fe^{2+} and Fe^{3+} corrected using the method of Schumacher (1997).

Both the presence of widespread chemical zoning patterns and, in many samples, the post-magmatic replacement of sodic-calcic amphibole by sodic varieties prevented the determination of Fe^{3+}/ Fe^{2+} ratios from concentrates. The existence of a whole range of calcic to sodic amphibole compositions in our dataset makes it possible to critically assess the adequacy of the method proposed by Schumacher (1997).

The chosen approach was to consider the crystallochemical criteria selected by the method (i.e. which minimum and maximum estimates were selected, denoted hereafter as minimum and maximum estimates, respectively), which is possible using the program MINCAL developed by us.

Figures 2 and 3 summarize the results. Figure 2 shows the relative frequencies with which each crystallochemical criterion was selected by the method, while Figure 3 details the relative frequencies of selection of each possible combination of minimum and maximum estimates, for the different amphibole groups from the Graciosa granites and syenites.

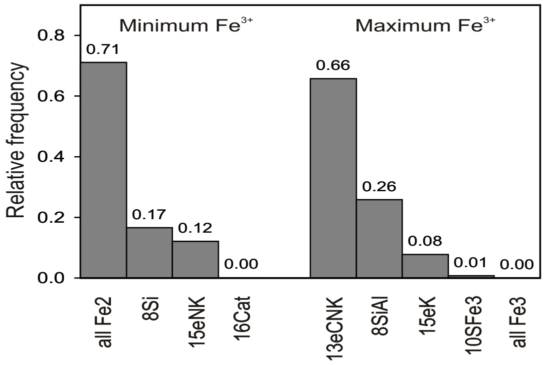

Fig. 2 – Histogram of the relative frequencies with which the crystallochemical criteria were selected by the method of Schumacher (1997), for the amphiboles of the Graciosa A-type Granites.

MINIMUM Fe^{3+} ESTIMATES

Among the minimum Fe^{3+} estimates, 16Cat was selected only once in the whole set, and hence, there is no need to discuss its applicability. Meanwhile, *all* Fe2, 8Si and 15eNK were chosen a significant number of times. The *all* Fe2 estimates, selected on 71% of the times, are too unrealistic, as there is abundant evidence that Fe^{3+} is present in calcic, sodic-calcic, and sodic amphiboles (e.g. Hawthorne 1983, Deer et al. 1997, Enders et al. 2000).

Similarly, Al is present in tetrahedral coordination in almost every amphibole, with the possible exception of compositions very close to Al-free end-members (Robinson et al. 1982), especially Al-poor sodic amphiboles (e.g. glaucophane-riebeckite). The data of Enders et al. (2000) demonstrate, however, that ^{IV}Al is commonly present even in these amphiboles. Hence, 8Si estimates should be adequate only in very specific cases.

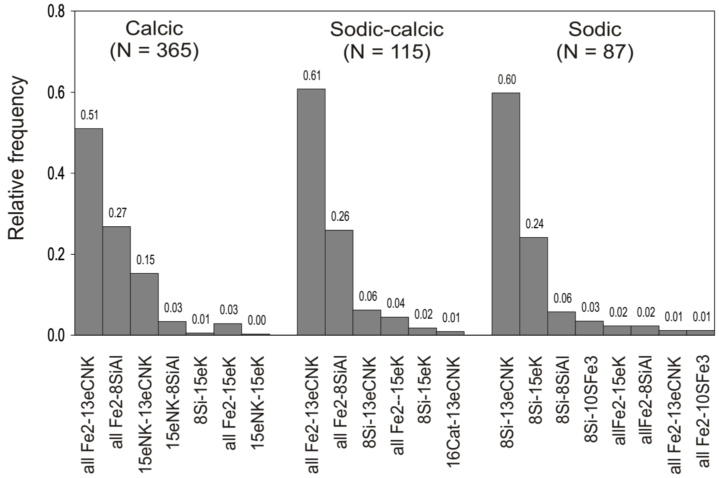

Fig. 3 – Histogram of the relative frequencies with which the combinations of crystallochemical criteria were selected by the method of Schumacher (1997), for the amphiboles of the Graciosa A-type Granites. Calcic, sodic-calcic, and sodic amphibole groups (classification according to Leake et al. 1997) are presented separately. Combinations with frequencies lower than 0.01 were omitted.

As already pointed out by Robinson et al. (1982), 15eNK estimates – which exclude all Na from the B positions – may be appropriate only for Fe-Mg-Mn amphiboles and possibly for those of the tremolite-ferro-actinolite series, but there is no representative of these groups in our dataset. Consequently, there seems to be no justification to the selection of these estimates.

MAXIMUM Fe^{3+} ESTIMATES

Among the maximum estimates, 10SFe3 was selected only four times, while *all* Fe3 was not selected (Figure 2). Therefore, these criteria need not be considered here. 13eCNK estimates (66% of the selections) are certainly the most recommended ones for calcic, sodic-calcic, and sodic amphiboles (Robinson et al. 1982, Enders et al. 2000). However, they exclude all Mn, Fe, and Mg from the B sites, and there is strong evidence that these elements may be present in this position (Hawthorne 1983).

In some of the studied amphiboles, the 13eCNK estimates led to partially occupied tetrahedral positions, in which cases, the 8SiAl estimates were selected (17%). Although Hawthorne (1983) strongly discourages the use of these estimates, it seems rather improbable that vacancies exist in these positions, and the approximation made by the 8SiAl estimates results, at least apparently, more reasonable (cf. also section ''The oxy-amphibole substitution''). Only in these cases, though, the use of 8SiAl estimates is justified, since octahedral Al is expected to be present in the majority of the cases.

Finally, apart from Fe-Mg-Mn amphiboles, 15eK estimates (8%) are reasonable only for calcic, sodic-calcic, and sodic amphiboles without Na in the A position (e.g. tremolite, hornblende, winchite, barroisite, glaucophane-riebeckite ideal compositions). It should be noted that some of the sodic and sodic-calcic amphiboles on our dataset show compositions very close to these ones, and the selection of this criterion would be justified for them.

AVERAGE ESTIMATES

From the previous discussion, it can be concluded that only 15eNK estimates among the minimum ones, and 13eCNK, 15eK, and possibly 8SiAl estimates among the maximum ones may lead to reasonable estimates for calcic, sodic-calcic, and sodic amphiboles from the Graciosa granites and syenites. In this context, the use of averages between 15eNK and the maximum estimates may be supported. It should be pointed out that the use of the average between 15eNK and 13eCNK has been proposed quite long ago by Stout (1972).

Yet, in only 10% of our cases was this the selected combination (Figure 3), whereas the 15eNK-15eK combination corresponded to only 1% of the cases.

As evident in Figures 2 and 3, approximately 88% of the combinations include *all* Fe2 or 8Si as the minimum estimates. It is clear, thus, that the use of averages in these cases is not recommended as the actual Fe^{3+} values should be much closer to the maximum estimates than to the minimum ones for calcic, sodic-calcic, and sodic amphiboles. The maximum estimates, consequently, should yield more reliable results.

A NOTE ON THE TREMOLITE-FERRO-ACTINOLITE SERIES

The use of the 15eNK-13eCNK average may be relevant for minerals of the tremolite-ferro-actinolite series, since the 15eNK estimates allow Fe, Mg, and Mn and exclude Na in the B-site, whereas the 13eCNK estimates do the reverse. Most probably, natural compositions lie somewhere between these extremes; however, the above discussion should be sufficient to warn about the risks inherent to the use of averages. In this sense, if Deer et al. (1992) are correct in their statement that minerals of the tremolite-ferro-actinolite series show more extensive solid solution with the richterite-ferro-richterite series than with the glaucophane-riebeckite series, natural compositions should also be closer to 13eCNK estimates.

CALCULATED *VERSUS* MEASURED Fe^{3+} VALUES

In order to test the validity of the above conclusion that the maximum estimates should be a better approximation than the averages, three previously published datasets that included complete analyses of calcic, sodic-calcic, and sodic amphiboles were selected from the literature.

The first one (Cosca et al. 1991) consists of 22 metamorphic hornblendes, while the second one (Enders et al. 2000) consists of 11 metamorphic amphiboles of the glaucophane-riebeckite join. Not only were these datasets carefully prepared, but also the results were tested against microprobe determinations of Fe^{3+}/Fe_T (Delaney et al. 1996, Enders et al. 2000). Moreover, as part of the determinations (e.g. Fe^{2+}/Fe_T, H_2O^+) was performed on concentrates, the use of more homogeneous metamorphic minerals is clearly more appropriate than usually zoned igneous ones. As a similar dataset of sodic-calcic amphibole analyses was not found in the literature, superior complete analyses were selected from Deer et al. (1997).

For all these analyses, Fe^{3+} estimates were computed using the nine criteria discussed above, as well as the maximum, minimum, and average of the method of Schumacher (1997). The results are compared on Figure 4.

It is evident that the Fe^{3+} contents are in almost every case much closer to the maximum estimates than to either the average or the minimum ones. Only in very few cases (e.g. Sample 1298), the average estimates may be considered better than the maximum ones (Figure 4).

In general, 13eCNK has been selected as the maximum estimate. That is the case for all calcic amphiboles (22 out of 22), 91% of the sodic (10 out of 11), and 43% of the sodic-calcic ones (3 out of 7) (Figure 4). To test the quality of the calculation procedures, concordance correlation coefficients (Lin 1989) between the estimated (13eCNK, maximum and average) and the measured values were calculated, considering both all the data and each group independently (Table I).

In Table I, r_c is the concordance correlation coefficient, which measures the overall precision and accuracy of the calculated values; it ranges from –1 (perfect negative correlation) to 1 (perfect positive

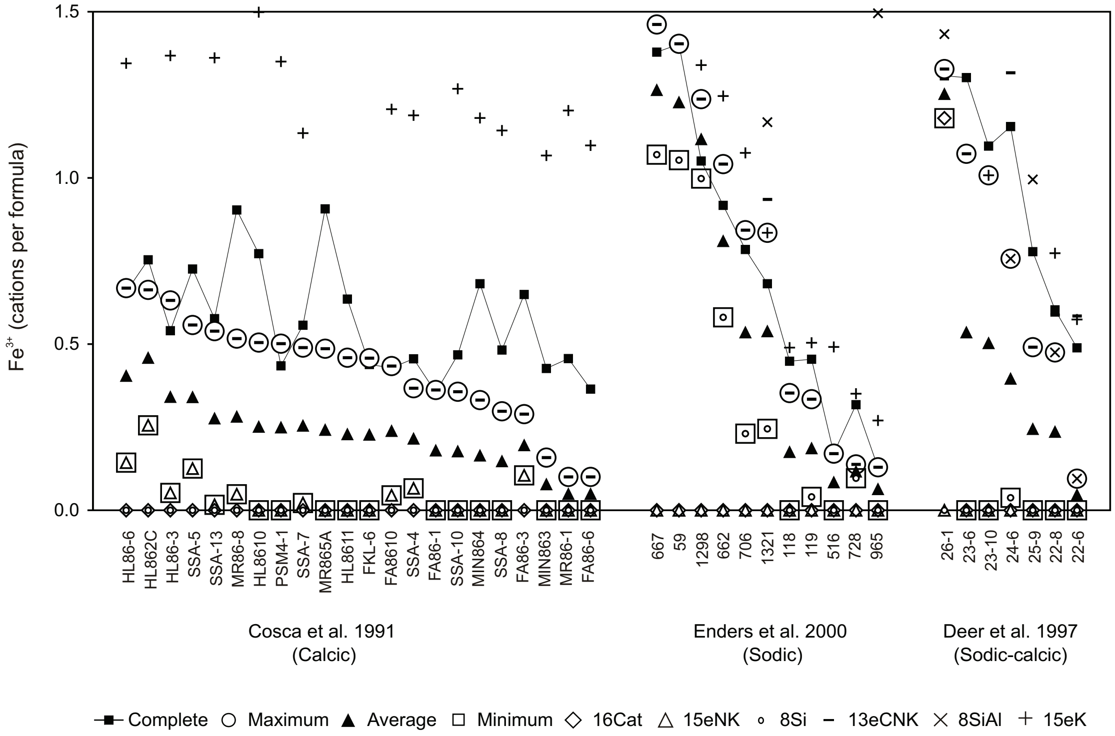

Fig. 4 – Diagram comparing the Fe^{3+} values calculated according to the various stoichiometry-based methods and the measured values for selected amphiboles from the literature (Cosca et al. 1991, Enders et al. 2000, Deer et al. 1997). Complete analysis calculated on the basis of 24 [O, OH, F, Cl]. Most 8SiAl and some 15eK results with cations per formula greater than 1.5 were omitted.

correlation); also shown is the Pearson correlation coefficient (r). This latter assesses only the precision, while coefficients u and v measure the accuracy of the estimates, namely the location and scale shifts (u=0: no location shift; v=1: no scale shift), respectively (cf. Lin 1989).

Both 13eCNK and maximum estimates are in good agreement ($r_c > 0.8$) with the measured Fe^{3+} values, which attest the validity of these calculation procedures. Moreover, the confidence intervals of r_c calculated for the 13eCNK and the maximum estimates are found to be statistically equal (P=0.84), the same being true when each group is considered separately. In other words, it is not possible to statistically distinguish 13eCNK and maximum estimates.

For the sodic amphiboles, the correlation is extremely good, in terms of both precision and accuracy; indeed, parameters are slightly better for the maximum estimates (Table I).

Estimates for the sodic-calcic amphiboles show reasonably good correlation as well, but the maximum estimates are somewhat more precise but less accurate (i.e. greater location shift) than 13eCNK ones. This leads to similar concordance correlation coefficients (Table I).

A much poorer correlation is observed in the calcic amphiboles. In general, the estimates are smaller than the measured values, yielding relatively large location shifts (Table I). It is clear, however, that 13eCNK estimates are certainly the best ones also for these amphiboles (Figure 4).

It should be also noted that all deviations in the hornblendes of Cosca et al. (1991) are towards higher Fe^{3+} values (Figure 4), suggesting that Fe-rich inclusions might be present in the analyzed

TABLE I

Relevant statistical parameters to evaluate the correlation between the measured Fe^{3+} values and those calculated by selected stoichiometry-based methods for selected amphiboles from the literature (Cosca et al. 1991, Enders et al. 2000, Deer et al. 1997). Complete analysis calculated on the basis of 24 [O, OH, F, Cl]. See text for discussion.

	13eCNK	Maximum	Average	Maximum (Ti-corrected)
	All			
r_c	0.845	0.832	0.560	0.831
CI (95%)	(0.736, 0.911)	(0.707, 0.906)	(0.403, 0.685)	(0.701, 0.907)
r	0.884	0.887	0.825	0.855
u	0.196	0.341	0.974	0.221
v	0.793	0.875	0.974	0.911
	Calcic			
r_c	0.361	0.361	0.114	0.123
CI (95%)	(0.056, 0.604)	(0.056, 0.604)	(0.023, 0.203)	(–0.242, 0.458)
r	0.522	0.522	0.533	0.146
u	0.945	0.945	2.665	0.574
v	1.006	1.006	1.601	1.240
	Sodic-calcic			
r_c	0.773	0.790	0.394	0.797
CI (95%)	(0.226, 0.950)	(0.385, 0.940)	(0.004, 0.680)	(0.349, 0.948)
r	0.806	0.939	0.777	0.925
u	–0.091	0.570	1.387	0.492
v	0.760	0.792	0.863	0.755
	Sodic			
r_c	0.962	0.970	0.930	0.970
CI (95%)	(0.888, 0.987)	(0.917, 0.990)	(0.804, 0.976)	(0.917, 0.990)
r	0.975	0.982	0.978	0.982
u	–0.058	–0.039	0.316	–0.039
v	0.859	0.864	0.940	0.864

r_c: concordance correlation coefficient; CI (95%): 95% confidence interval of r_c; r: Pearson correlation coefficient; u: location shift coefficient and v: scale shift coefficient.

samples. In this sense, it is worth noting that Fe-oxide inclusions were identified by Delaney et al. (1996) in sample MIN864, and that this sample shows one of the largest differences between calculated and measured values.

The preceding discussion leads to the conclusion that both the maximum estimates and 13eCNK ones are good approximations to the measured values. Furthermore, it highlights the difficulties inherent to the use of measurements made on concentrates, even in relatively homogeneous amphiboles.

The correlation between the average estimates and the measured values, on the other hand, is much poorer (r_c=0.56; cf. Table I). More specifically, the location shift is significant (u=0.94), revealing a relatively large systematic error in the estimates.

THE OXY-AMPHIBOLE SUBSTITUTION

Hawthorne et al. (1998) have recently shown that a substitution of the type $Ti^{4+} + 2\,O^{2-} \leftrightarrow (Mg, Fe^{2+}) + 2\,(OH)^-$ may explain the entrance of Ti in the amphibole structure. In their amphiboles, this substitution mechanism operated when Ti was in excess of 0.13 cpfu, in which case, Ti entered the M1 (instead of the M2) site.

The operation of such a mechanism has important implications for the estimation of Fe^{3+} from EPMA data, as it raises the total number of negative charges in the unit cell.

Using the method of Papike et al. (1974), Hawthorne et al. (1998) concluded that analyses of Ti-rich amphiboles mistakenly revealed low sums for the T and C sites, and underestimated Fe^{3+} values.

The same four analyses presented by Hawthorne et al. (1998) were recalculated using the average between 15eNK and 13eCNK, 13eCNK and 8SiAl methods. The results, as well as the measured values, are summarized in Table II.

The comparison reveals that the cation distributions resulting from both 13eCNK and 8SiAl methods are good approximations of the measured values, while 15eNK-13eCNK averages are poor ones. These results nicely show that the choice of the recalculation method is not only important for the determination of Fe^{2+} and Fe^{3+} contents, but also for the appropriate normalization of the other ions (see also Schumacher 1991).

Either 13eCNK or 8SiAl were selected as the maximum estimates by the method of Schumacher (1997), as indicated on Table II. In the case of sample 745, the choice seems inappropriate, but this is a consequence of the relatively high Li content on the analysis, not considered in a first calculation. When Li is considered, the selected method changes to 8SiAl, a much closer match to the measured values (Table II).

Although the overall cation distributions are calculated correctly, the Fe^{3+} estimates are clearly underestimated (Table II). This results from the fact that the actual negative charges sum to more than 46, as considered in the computations.

A correction based on the results of Hawthorne et al. (1998) was devised. The actual number of negative charges is $46 + 2 * (Ti - 0.13)$; hence, the number of equivalent O is half of this value. Fe^{3+} may then be more adequately estimated using the equation of Droop (1987). A modification of the method of Schumacher (1997) is also possible. There is no essential alteration in the calculation process, except that, when selecting the minimum and maximum estimates, it is necessary to compare the estimated Fe^{3+} values instead of the correction factors, since the Fe^{3+} estimates are no longer a function of the correction factors alone.

The corrected values for the data of Hawthorne et al. (1998) are depicted on Table II. While one of the values is a good approximation (sample 745), the other (sample 741) is overestimated. It should be noted however, that the Fe^{3+} contents of this latter sample is rather low, what leads to larger errors.

Ti-corrected results are also shown on Table II, as computed for the selected complete analytical data of the preceding section. It is clearly seen that the corrected results, at least in general, are not better than the uncorrected ones. Specifically in the case of the calcic amphiboles, the corrections worsened the correlation.

Naturally, it is yet to be proven whether the correlation between Ti^{4+} and O^{2-} deducted for the Coyote Peak amphiboles (Hawthorne et al. 1998) is of general applicability. Consequently, this correction should be used with caution, only when there is additional, independent evidence of the presence of oxy-amphibole components. In these cases, it is suggested that factor (i) (10SFe3) of the method of Schumacher (1997) be calculated with a maximum of 0.13 Ti cpfu.

It is important to point out that the oxy-Fe substitution ($Fe^{2+} + O^{2-} \leftrightarrow Fe^{3+} + OH^-$) may also be

TABLE II

Comparison of cationic distributions calculated (basis of 24 [O, OH, F, Cl]) from selected complete analysis of Hawthorne et al. (1998) and those obtained after calculation of Fe^{3+} by selected stoichiometry-based methods (basis of 23 O).

	Measured	Average of 13eCNK and 15eNK	13eCNK *§	8SiAl	Maximum (Ti-corrected)
	7 4 1				
Si	7.978	7.902	7.966	7.955	7.966
Al	0.022	0.044	0.034	0.045	0.034
ΣT	**8.000**	**7.946**	**8.000**	**8.000**	**8.000**
Al	0.023	0.000	0.011	0.000	0.011
Ti	0.361	0.358	0.361	0.360	0.361
Fe^{3+}	0.020	0.000	0.000	0.000	0.087
Fe^{2+}	1.361	1.368	1.379	1.377	1.292
Mn	0.017	0.017	0.017	0.017	0.017
Mg	3.237	3.206	3.232	3.227	3.232
ΣC	**5.019**	**4.949**	**5.000**	**4.982**	**5.000**
Ca	0.727	0.720	0.726	0.725	0.726
Na	1.273	1.280	1.274	1.275	1.274
ΣB	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**
Na	0.653	0.628	0.649	0.645	0.649
K	0.301	0.298	0.301	0.300	0.301
ΣA	**0.954**	**0.926**	**0.950**	**0.946**	**0.950**
	7 4 5				
Si	7.993	7.900	8.026	7.984	8.026
Al	0.007	0.016	0.000	0.016	0.000
ΣT	**8.000**	**7.916**	**8.026**	**8.000**	**8.026**
Al	0.009	0.000	0.016	0.000	0.016
Ti	0.746	0.737	0.749	0.745	0.749
Fe^{3+}	0.520	0.000	0.000	0.000	0.502
Fe^{2+}	2.348	2.835	2.881	2.866	2.379
Mn	0.019	0.019	0.019	0.019	0.019
Mg	1.303	1.288	1.309	1.302	1.309
ΣC	**4.945**	**4.880**	**4.974**	**4.932**	**4.974**
Ca	0.147	0.145	0.147	0.147	0.147
Na	1.853	1.855	1.853	1.853	1.853
ΣB	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**
Na	0.716	0.685	0.728	0.713	0.728
K	0.293	0.290	0.295	0.293	0.295
ΣA	**1.009**	**0.975**	**1.022**	**1.006**	**1.022**

TABLE II (continuation)

	Measured	Average of 13eCNK and 15eNK	13eCNK *§	8SiAl	Maximum (Ti-corrected)
	749				
Si	7.905	7.814	7.907	7.934	7.934
Al	0.066	0.065	0.066	0.066	0.066
ΣT	**7.971**	**7.879**	**7.972**	**8.000**	**8.000**
Al	0.000	0.000	0.000	0.000	0.000
Ti	0.438	0.433	0.438	0.439	0.439
Fe^{3+}	0.000	0.000	0.000	0.000	0.000
Fe^{2+}	1.557	1.539	1.557	1.563	1.563
Mn	0.032	0.032	0.032	0.032	0.032
Mg	3.000	2.965	3.000	3.011	3.011
ΣC	**5.027**	**4.969**	**5.028**	**5.045**	**5.045**
Ca	0.854	0.845	0.855	0.857	0.857
Na	1.146	1.155	1.145	1.143	1.143
ΣB	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**
Na	0.659	0.628	0.660	0.669	0.669
K	0.277	0.274	0.277	0.278	0.278
ΣA	**0.936**	**0.902**	**0.936**	**0.947**	**0.947**
	750				
Si	7.947	7.785	7.942	7.959	7.959
Al	0.041	0.040	0.041	0.041	0.041
ΣT	**7.988**	**7.825**	**7.982**	**8.000**	**8.000**
Al	0.000	0.000	0.000	0.000	0.000
Ti	0.643	0.630	0.643	0.644	0.644
Fe^{3+}	0.000	0.000	0.000	0.000	–0.000
Fe^{2+}	2.144	2.101	2.143	2.148	2.148
Mn	0.042	0.041	0.042	0.042	0.042
Mg	2.191	2.147	2.190	2.194	2.194
ΣC	**5.020**	**4.919**	**5.018**	**5.029**	**5.029**
Ca	0.767	0.751	0.766	0.768	0.768
Na	1.233	1.249	1.234	1.232	1.232
ΣB	**2.000**	**2.000**	**2.000**	**2.000**	**2.000**
Na	0.664	0.610	0.662	0.668	0.668
K	0.288	0.282	0.287	0.288	0.288
ΣA	**0.952**	**0.891**	**0.950**	**0.956**	**0.956**

(*) maximum estimate of the method of Schumacher (1997); (§) maximum estimate of the method of Schumacher (1997) when Li is included.

significant, especially for igneous amphiboles. If this substitution is important, the preceding analysis suggests that Fe^{3+} will be underestimated, but the overall cation distributions can be well approximated by proper choice of calculation procedure.

CATION DISTRIBUTIONS AND IMPLICATIONS FOR THE IMA CLASSIFICATION

It has been conclusively demonstrated (Schumacher 1991) that cation distributions including Fe^{3+} and Fe^{2+} estimates result in much better approximations to the expected values than the uncorrected results. The resulting partitioning of elements occurring in more than one site (e.g. Al in T and C sites), on the other hand, is very sensitive to the calculation procedure.

These two findings are nicely demonstrated by the results on Table II. For example, total Al contents in sample 741 are well predicted by all models. Nevertheless, none of them leads to good approximations of the measured ^{IV}Al-^{VI}Al partitioning. The same is true for partial sums (e.g. C- and A-sum; Table II).

It should be noted that the parameters used in the IMA classification (Leake et al. 1997) are either the contents of an element present in more than one site, or partial sums: ^{IV}Al, Na_B, $[Na+K]_A$, $^{VI}Al/Fe^{3+}$ ratio. In this sense, the classification is strongly model-dependent (see also Schumacher 1997), and it follows that a range of names is possible for any given analysis. Evidently, this difficulty will persist until a method that allows the determination of Fe^{3+} at the micrometer scale and can be used routinely is available.

CONCLUSIONS

Although several authors have strongly criticized the estimation of Fe^{3+} and Fe^{2+} through stoichiometric calculations (e.g. Hawthorne 1983, Czamanske and Dillet 1988), these kinds of calculation are not only desirable, but also necessary, considering the existing volume of available microprobe amphibole analyses and the general employment of the EPMA as the standard microanalytical tool.

It has been shown here that the quality of the results is strongly dependent on the choice of the crystallochemical criterion, and this choice depends primarily on the amphibole group of interest. This is in accordance with the conclusions of previous workers (Robinson et al. 1982, Schumacher 1997).

For calcic, sodic-calcic, and sodic amphiboles, 13eCNK estimates are, in general, satisfactorily precise and accurate. In some instances, however, other crystallochemical criteria, namely 8SiAl and 15eK, lead to more appropriate results. In these cases, the method of Schumacher (1997) correctly identifies the best minimum and maximum estimates. Yet, as the actual values are much closer to the maximum estimates than to the minimum ones, the use of the average between them is not adequate. It is recommended, thus, that for calcic, sodic-calcic, and sodic amphiboles, the maximum estimates of the method of Schumacher (1997) be used instead of the average ones.

Fe^{3+} is underestimated when the oxy-amphibole component is present, even though the overall cationic distribution is correctly calculated. A correction procedure is proposed here, but it should be applied with caution, since it is based on data on a single suite of rocks of very particular origin (Czamanske and Atkin 1985, Hawthorne et al. 1998).

The program MINCAL may be obtained from the authors.

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RESUMO

Uma importante limitação da microssonda eletrônica é a sua incapacidade de medir razões Fe^{3+}/Fe^{2+} em trabalhos de rotina. Apesar destas razões poderem ser calculadas, não existe critério único que possa ser usado para anfibólios.

Um grande número de análises de anfibólios cálcicos, sódico-cálcicos e sódicos de granitos e sienitos Tipo-A aflorantes no Sul do Brasil foi utilizado para avaliar as escolhas feitas pelo método de Schumacher (1997, Canadian Mineralogist, 35: 238-246), que utiliza a média entre estimativas máximas e mínimas selecionadas. As estimativas selecionadas com maior freqüência são: 13 cátions excluindo Ca, Na e K (13eCNK – 66%); soma de Si e Al igual a 8 (8SiAl – 17%); 15 cátions excluindo K (15eK – 8%). Estas estimativas são apropriadas tomando por base critérios cristaloquímicos. Estimativas mínimas são principalmente todo ferro como Fe^{2+} (*all* Fe2 – 71%) e se mostram claramente inadequadas. Portanto, estimativas máximas devem aproximar melhor os valores verdadeiros.

Como teste, análises completas foram selecionadas da literatura, e valores calculados e medidos foram comparados. Estimativas 13eCNK e máximas são precisas e exatas (coeficiente de concordância – $r_c \approx 0.85$). As médias, em contrapartida, aproximam mal os valores medidos ($r_c = 0.56$).

Recomenda-se, portanto, que as estimativas máximas do método de Schumacher sejam utilizadas para anfibólios cálcicos, sódico-cálcicos e sódicos.

Palavras-chave: anfibólios, estequiometria, ferro férrico, EPMA.

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