A general equation for estimating Fe^{3+} concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria

G. T. R. DROOP

Department of Geology, University of Manchester, Oxford Road, Manchester M13 9PL

Abstract

A simple general equation is presented for estimating the Fe^{3+} concentrations in ferromagnesian oxide and silicate minerals from microprobe analyses. The equation has been derived using stoichiometric criteria assuming that iron is the only element present with variable valency and that oxygen is the only anion. In general, the number of Fe^{3+} ions per X oxygens in the mineral formula, F, is given by;

$$F = 2X(1 - T/S)$$

where T is the ideal number of cations per formula unit, and S is the observed cation total per X oxygens calculated assuming all iron to be Fe^{2+}. Minerals for which this equation is appropriate include pyralspite and ugrandite garnet, aluminate spinel, magnetite, pyroxene, sapphirine and ilmenite. The equation cannot be used for minerals with cation vacancies (e.g. micas, maghemite) unless, as in the case of amphiboles, the number of ions of a subset of elements in the formula can be fixed. Variants of the above equation are presented for some of the numerous published schemes for the recalculation of amphibole formulae. The equation is also inappropriate for minerals showing $Si^{4+} = 4H^{+}$ substitution (e.g. staurolite, hydrogarnet), minerals containing an unknown proportion of an unanalysed element other than oxygen (e.g. boron-bearing kornerupine) and minerals containing two or more elements with variable valency.

KEYWORDS: Fe^{2+}/Fe^{3+} estimation, microprobe analyses, iron-bearing minerals.

Introduction

IT has long been known from wet chemical analysis, and more recently from Mössbauer spectroscopy, that many iron-bearing oxide and silicate minerals contain appreciable quantities of both Fe^{2+} and Fe^{3+}. Unfortunately, the most commonly used technique nowadays for analysing minerals, electron-probe microanalysis, cannot detect the two oxidation states of iron separately. Consequently Fe^{2+}/Fe^{3+} ratios in minerals analysed in this way have to be estimated by indirect means, i.e. by computation after the analysis has been performed.

The problem of estimating Fe^{2+}/Fe^{3+} ratios in minerals from microprobe analyses has received much attention, particularly with respect to pyroxenes (e.g. Cawthorn and Collerson, 1974; Brown and Bradshaw, 1979; Carpenter, 1979). However, most published Fe^{3+}-recalculation schemes are mineral-specific and usually applicable only to certain ranges of composition (e.g. metamorphic sodic pyroxenes: Carpenter, 1979). For petrologists, who commonly need to analyse several coexisting ferromagnesian phases in each rock, the implementation of such diverse schemes can be cumbersome, and a generally applicable method would be more convenient.

In this paper, I derive a simple general equation for estimating the Fe^{3+} content of oxides and silicates from microprobe analyses. Although variations of this method have been published for individual minerals (e.g. pyroxenes: Robinson, 1980; amphiboles: Stout, 1972; Robinson et al., 1982), there seems to be no general statement on the topic anywhere in the literature.

Rationale

If it can be assumed that iron is the only element present with variable oxidation state in a mineral, the number of Fe^{3+} ions per formula unit can, in principle, be determined uniquely from a microprobe analysis by specifying any two of the following three criteria in the calculation of the formula:

(i) The total cation charge. In order to maintain an electrostatically neutral mineral, this number (usually an integer in conventionally defined mineral formulae) is constrained to be exactly twice the number of oxygens in the formula unit if oxygen is the only anion present.

(ii) The total number of cations. Again, this is usually an integer as the formula generally represents the atomic content of a whole unit cell or a simple fraction thereof.

(iii) Any equation based on crystal chemical arguments linking the Fe^{3+} content to the concentrations of other elements. (For example, one such equation that could be specified in the recalculation of Ti-free garnets might be: $Al^{3+} + Cr^{3+} + V^{3+} + Fe^{3+} = 2.000$.)

In the method described below, the Fe^{3+} content of a mineral is estimated by fixing criteria (i) and (ii). One assumption inherent in the choice of this combination is that there are no vacant cation sites in the mineral. For some minerals (e.g. micas, maghemite, högbomite) this assumption is clearly unjustified and the method is inappropriate unless some other criterion is brought to bear (see below in the discussion on amphiboles). On the other hand, many common rock-forming minerals do not seem to contain significant concentrations of vacancies (e.g. aluminosilicate garnets, pyroxenes, sapphirine, aluminate spinels) and for these the method may be used with greater confidence. The method is also inappropriate for minerals which display variable numbers of oxygen atoms per anhydrous formula unit on account of $Si^{4+} = 4H^+$ substitution, such as hydrogarnets (Meagher, 1982) and staurolites (Richardson, 1968), and for minerals with uncertain cation totals due to the presence of an unknown proportion of an unanalysed element other than oxygen (e.g. boron-bearing kornerupine).

The equation

Consider an ideal microprobe analysis of a stoichiometric pyroxene of composition 50% diopside, 50% aegirine. If the microprobe software treats all analysed Fe as Fe^{2+}, the formula calculated on the basis of 4.000 cations will be as listed in Table 1(a). The same analysis recalculated on the basis of 6.000 oxygens (i.e. total cation charge of 12.000+)

TABLE 1. An example of an ideal microprobe analysis of a stoichiometric pyroxene of composition 50% diopside 50% aegirine, (a) calculated to 4.000 cations, assuming all iron to be Fe^{2+}, and (b) calculated to 6.000 oxygens, assuming all iron to be Fe^{2+}.

(a)		Cations	Charge	Nominal Oxygens
	Si	2.0000	+ 8.0000	4.0000
	Fe	0.5000	+ 1.0000	0.5000
	Mg	0.5000	+ 1.0000	0.5000
	Ca	0.5000	+ 1.0000	0.5000
	Na	0.5000	+ 0.5000	0.2500
	Tot	4.0000 (= T)	+11.5000	5.7500 (= N)
(b)	Si	2.0870	+ 8.3480	4.1740
	Fe	0.5217	+ 1.0434	0.5217
	Mg	0.5217	+ 1.0434	0.5217
	Ca	0.5217	+ 1.0434	0.5217
	Na	0.5217	+ 0.5217	0.2609
	Tot	4.1738 (= S)	+11.9999	6.0000 (= X)

will yield the formula shown in Table 1(b). The discrepancy between the tabulated oxygen total (N) and the correct number (6.000 in this case; X in the general case) in Table 1(a) is due to the fact that one oxygen atom has been assigned to each iron atom, not 1.5 oxygens which would have been more appropriate in this case. Likewise, in the analysis in Table 1(b) (the normal mode of delivery of most microprobe analyses), the discrepancy between the observed cation total (S) and the correct number (4.000 in this case; T in the general case) is also due to the incorrect assumption that all the iron is present as Fe^{2+}.

The magnitudes of these discrepancies ($X - N$ and $S - T$) are a measure of the amount of Fe^{3+} present. In Table 1(a), for every Fe^{3+} ion present there is a deficiency in the nominal oxygen total of 0.5. Thus one can write:

$$N = X - \tfrac{1}{2}F \qquad (1)$$

where F is the number of Fe^{3+} ions present per X oxygens. The relationship between the cation and oxygen totals of the two formulae in Table 1 is:

$$S/T = X/N. \qquad (2)$$

Substituting equation (1) into (2) and rearranging yields:

$$F = 2X(1 - T/S). \qquad (3)$$

This is a completely general equation and can be used to estimate the Fe^{3+} content of any ferromagnesian oxide or silicate mineral from 'raw'

microprobe analyses in which the formulae are calculated on the basis of a specified number of oxygens with all iron initially as Fe^{2+} [i.e. as in Table 1(b)], provided that the numbers of cations and oxygen atoms per anhydrous formula unit are known. The equation yields a direct solution, and there is no need to iterate. A major advantage of this formulation over mineral-specific schemes is that it can be incorporated as a subroutine in any mineral recalculation program and called repeatedly to deal with analyses of different minerals. All that need be changed with a new mineral species are the values of X and T (see Table 2). The value of S changes with each analysis.

Table 2. Values of oxygen total (X) and cation total (T) of various minerals for use with equation (3):

Mineral	X	T
Pyroxene	6	4
Garnet (i)	12	8
Garnet (ii)	24	16
Spinel (i)	4	3
Spinel (ii)	32	24
Chloritoid	12	8
Sapphirine	20	14
Ilmenite	3	2

A modification of equation (3) can be used for minerals with vacancies, provided that one can assume that the total number of cations of a subset of elements in the formula has a fixed value. Amphiboles are a good example. Robinson et al. (1982) list several schemes for the recalculation of amphibole formulae, three of which are discussed here.

(i) Formula calculated on the basis of 16.00 cations per 23 oxygens anhydrous (suitable only for amphiboles with full A-sites).

For this method, in which it is assumed that there are no A-site vacancies, equation (3) can be used directly:

$$F = 46(1 - 16/S). \qquad (4)$$

(ii) Formula calculated on the basis of 23 oxygens anhydrous, assuming a total of 15.000 cations exclusive of Na and K (suitable for Fe–Mg-amphiboles and coexisting calcic amphiboles).

Here, it is assumed that Na and K are confined to the A-site, which may be partially vacant. In this case:

$$F = 46(1 - 15/\psi) \qquad (5)$$

where $\psi = \Sigma$ (Si, Ti, Al, Cr, Fe, Mn, Mg, Ca) in the uncorrected formula.

(iii) Formula calculated on the basis of 23 oxygens anhydrous, assuming a total of 13.000 cations exlusive of Ca, Na and K (suitable for many calcic amphiboles).

In this case it is assumed that Ca is confined to the M_4-site, K to the A-site, and Na to the A- and M_4-sites. The appropriate formula is:

$$F = 46(1 - 13/\Phi) \qquad (6)$$

where $\Phi = \Sigma$ (Si, Ti, Al, Cr, Fe, Mn, Mg) in the uncorrected formula.

Implementation of the equation

The sequence of operations recommended for the calculation of an Fe^{3+}-corrected analysis is as follows:

(i) Read the oxide wt.% list and formula (calculated to X oxygens) from the microprobe printout.

(ii) Read the cation total (S). If $S > T$ proceed. If not, abandon calculation and leave all iron as Fe^{2+}, otherwise a negative Fe^{3+} will appear!

(iii) Calculate the number of Fe^{3+} ions per X oxygens (F) from equations (3), (5) or (6).

(iv) Normalise the formula to T cations (i.e. multiply each number by T/S).

(v) Check that the calculated number of Fe^{3+} ions (F) is less than the new value of total iron available. If not, abandon the calculation and set all iron as Fe^{3+}, otherwise a negative Fe^{2+} will appear!

(vi) Write the corrected formula as obtained from (iv) but with iron separated into Fe^{3+} [from (iii)] and Fe^{2+} [the remainder].

(vii) Amend the oxide wt.% list. Make the new wt.% FeO = old wt.% FeO $\times$ $Fe^{2+}/(Fe^{2+} + Fe^{3+})$. Make the new wt.% $Fe_2O_3 = 1.1113 \times$ old wt.% FeO $\times$ $Fe^{3+}/(Fe^{2+} + Fe^{3+})$.

The formula may be recast into end-member molecules at this point, but mineral-specific routines are still required for this purpose. The calculation of end-member proportions is beyond the scope of this paper, but there are numerous discussions of the topic in the literature (e.g. Rickwood (1968) for garnets; Yoder and Tilley (1962), White (1964), Essene and Fyfe (1967) and Cawthorn and Collerson (1974) for pyroxenes).

Some examples of Fe^{3+}-corrected microprobe analyses of various minerals are listed in Table 3 alongside the 'raw' uncorrected data, for comparison. Analyses where iron is a major component and the Fe^{2+}/Fe^{3+} division is significant (e.g. the garnet in Table 3) are substantially altered by this type of calculation, especially in regard to 'improving' the

TABLE 3. A comparison of corrected and uncorrected microprobe analyses of selected ferromagnesian minerals. In each case, analysis A (the original probe output) has been calculated to an integer number of oxygens assuming all iron to be Fe^{2+}; B is the same analysis with the Fe^{3+} content calculated by whichever of equations (3) (5) or (6) is most appropriate. Cation proportions were reduced to 3 decimal places after all the calculations were completed. The original analyses were performed by energy dispersive spectrometry on the Cameca Camebax electron-probe at Manchester.

OXIDES	GARNET A	B (Eq. 3)	PYROXENE A	B (Eq. 3)	SPINEL A	B (Eq. 3)	SAPPHIRINE A	B (Eq. 3)	AMPHIBOLE 1 A	B (Eq. 6)	AMPHIBOLE 2 A	B (Eq.5)
SiO_2	35.94	35.94	56.21	56.21	–	–	12.93	12.93	42.89	42.89	43.43	43.43
TiO_2	0.12	0.12	0.00	0.00	0.00	0.00	0.03	0.03	1.80	1.80	0.20	0.20
Al_2O_3	0.28	0.28	10.56	10.56	61.99	61.99	60.99	60.99	11.55	11.55	18.26	18.26
Cr_2O_3	18.11	18.11	–	–	0.00	0.00	0.00	0.00	–	–	–	–
Fe_2O_3	–	12.43	–	3.39	–	4.09	–	4.02	–	2.74	–	0.80
FeO	11.37	0.18	6.10	3.05	24.68	21.00	8.75	5.13	14.96	12.50	12.85	12.13
MnO	0.03	0.03	0.01	0.01	0.11	0.11	0.04	0.04	0.00	0.00	0.21	0.21
MgO	0.00	0.00	7.33	7.33	13.70	13.70	17.05	17.05	11.12	11.12	19.67	19.67
CaO	33.33	33.33	12.13	12.13	–	–	0.00	0.00	11.49	11.49	0.64	0.64
ZnO	0.19	0.19	–	–	0.00	0.00	0.04	0.04	–	–	–	–
Na_2O	–	–	7.64	7.64	–	–	–	–	1.87	1.87	1.97	1.97
K_2O	–	–	0.04	0.04	–	–	–	–	1.06	1.06	0.00	0.00
Tot.	99.37	100.61	100.02	100.36	100.48	100.89	99.83	100.23	96.74	97.02	97.23	97.31

FORMULA	12(O)		6(O)		32(O)		20(O)		23(O)		23(O)	
Si	3.093	2.993	2.013	1.998	–	–	1.553	1.539	6.456	6.413	6.155	6.144
Ti	0.008	0.008	0.000	0.000	0.000	0.000	0.003	0.003	0.204	0.202	0.021	0.021
Al	0.028	0.027	0.446	0.442	15.509	15.353	8.633	8.555	2.049	2.036	3.050	3.045
Cr	1.233	1.192	–	–	0.000	0.000	0.000	0.000	–	–	–	–
Fe^{3+}	–	0.779	–	0.091	–	0.647	–	0.362	–	0.308	–	0.085
Fe^{2+}	0.818	0.013	0.183	0.091	4.381	3.689	0.879	0.509	1.883	1.563	1.523	1.435
Mn	0.002	0.002	0.000	0.000	0.020	0.020	0.004	0.004	0.000	0.000	0.025	0.025
Mg	0.000	0.000	0.391	0.388	4.335	4.291	3.052	3.024	2.495	2.478	4.156	4.148
Ca	3.074	2.974	0.465	0.462	–	–	0.000	0.000	1.853	1.841	0.098	0.097
Zn	0.012	0.012	–	–	0.000	0.000	0.004	0.004	–	–	–	–
Na	–	–	0.531	0.526	–	–	–	–	0.546	0.542	0.541	0.540
K	–	–	0.002	0.002	–	–	–	–	0.204	0.202	0.000	0.000
Tot.	8.268	8.000	4.031	4.000	24.245	24.000	14.128	14.000	15.690	15.585	15.569	15.540

$\Phi =$ 13.087 $\Psi =$ 15.028

Specimen details :

Garnet : Ferrian uvarovite from chromitite, Edessa, N. Greece. (Analysis courtesy of K. Michailidis).

Pyroxene : Omphacite from metagabbro, Rocciavré, W. Alps. (Analysis courtesy of G. Wayte.)

Amphibole 1 : Hornblende from mafic granulite, Diti Dip, nr. Beitbridge, Limpopo Belt.

Spinel : Pleonaste from sapphirine-bearing granulite, Europe Claim, nr. Beitbridge, Limpopo Belt.

Sapphirine : From the same sample as the spinel.

Amphibole 2 : Gedrite from the same sample as the spinel.

formula. For iron oxide phases such as magnetite, the oxide wt.% totals are also considerably 'improved' from low values (typcially *ca.* 96% for magnetites) to nearer 100%.

In many instances, the method described above yields formulae identical to those generated by published mineral-specific routines. For instance, clinopyroxene formulae calculated in this way are indistinguishable from those obtained using the relationship $Al^{VI} + Fe^{3+} + Cr + 2Ti = Al^{VI} + Na$ (Papike *et al.*, 1974; Lindsley, 1983). With sapphirines the equivalent relationship is $Al^{VI} + Fe^{3+} + Cr + 2Ti = Al^{VI} = 6 - Si$ (which, in Ti-free sapphirines, reduces to the expression $Al^{VI} + Fe^{3+} + Cr = Al^{VI}$ proposed by Higgins *et al.*, 1979).

For minerals such as spinel and ilmenite which have a simple two-site formula unit, the method described above yields the same Fe^{3+} concentrations as methods based on a combination of criteria (i) and (iii) stated earlier. For example, with aluminate spinels, the method gives the same answer as the expression $Fe^{3+} = 16.000 - Al - Cr - V - 2Ti$ per 32 oxygens (see Carmichael, 1967, for a version of this for Fe-Ti-spinels). With ilmenites the analogous equation is $Fe^{3+} = Fe_{tot} + Mg + Mn - Ti - Si$, which, interestingly, is also equivalent to the scheme of Anderson (1968) in which Fe^{3+} contents are calculated by allotting elements to predetermined molecules. However, for minerals with more than two types of cation site per formula unit (e.g. garnet, pyroxenes) equation (3) will not give the same answer as a method based on criteria (i) and (iii), except in the case of a perfect analysis. For such minerals, the analyst must decide which method to use, or else compare the answers from both methods.

As with all indirect methods, Fe^{3+} contents calculated by equation (3) are extremely sensitive to errors in the concentrations of the most abundant elements present. Even quite small departures from

the true stoichiometry due to statistical fluctuations in count rate, instrumental drift, poor analytical procedure, poor choice of standards or use of incorrect ZAF correction factors will lead to large errors in the estimated Fe^{3+} concentrations. If, for example, the detected wt.% SiO$_2$ in the garnet analysis in Table 3 is 99% of its true value, then the true amount of Fe^{3+} would be 0.747 ions per 12 oxygens, not 0.779 as stated. Thus the method is unlikely to yield accurate estimates unless the analyses are of superior quality. The onus is on the analyst to ensure that this is so. Its vulnerability to such errors renders the method unsuitable for estimating trace quantities of Fe^{3+} in ferrous iron-rich minerals such as olivine and cordierite or trace quantities of Fe^{2+} in ferric iron-rich minerals such as epidote.

In principle, equation (3) can be used directly to calculate Fe^{2+}/Fe^{3+} ratios in sulphides in which iron is the only polyvalent element. An expression similar to equation (3) could also be derived to calculate ionic ratios of any other polyvalent element (e.g. V) so long as that element is the only one with variable valency in the mineral(s) concerned.

Acknowledgements

References

Anderson, A. T. (1968) Oxidation of the La Blache Lake titaniferous magnetite deposit, Quebec. *J. Geol.* **76**, 528–47.

Brown, E. H., and Bradshaw, J. Y. (1979) Phase relations of pyroxene and amphibole in greenstone, blueschist and eclogite of the Franciscan Complex, California. *Contrib. Mineral. Petrol.* **71**, 67–84.

Carmichael, I. S. E. (1967) The iron–titanium oxides of salic volcanic rocks and their associated ferromagnesian silicates. Ibid. **14**, 36–64.

Carpenter, M. A. (1979) Omphacites from Greece, Turkey and Guatemala: composition limits of cation ordering. *Am. Mineral.* **64**, 102–8.

Cawthorn, R. G., and Collerson, K. D. (1974) The recalculation of pyroxene end-member parameters and the estimation of ferrous and ferric iron content from electron microprobe analyses. Ibid. 59, 1203–8.

Essene, E. J., and Fyfe, W. S. (1967) Omphacite in Californian metamorphic rocks. *Contrib. Mineral. Petrol.* **15**, 1–23.

Higgins, J. B., Ribbe, P. H., and Herd, R. K. (1979) Sapphirine. I: Crystal chemical contributions. Ibid. **68**, 349–56.

Lindsley, D. A. (1983) Pyroxene thermometry. *Am. Mineral.* **68**, 477–93.

Meagher, E. P. (1982) Silicate garnets. In *Reviews in Mineralogy*, **5** *Orthosilicates* (P. H. Ribbe, ed.) 25–66. Mineral. Soc. America.

Papike, J. J., Cameron, K. L., and Baldwin, K. (1974) Amphiboles and pyroxenes: characterisation of other than quadrilateral components and estimates of ferric iron from microprobe data. *G.S.A. Abstracts with Programs*, **6**, 1035–5. (abs.)

Richardson, S. W. (1968) Staurolite stability in a part of the system Fe–Al–Si–O–H. *J. Petrol.* **9**, 467–88.

Rickwood, P. C. (1968) On recasting analyses of garnet into end-member molecules. *Contrib. Mineral. Petrol.* **18**, 175–98.

Robinson, P. (1980) The composition space of terrestrial pyroxenes—internal and external limits. In *Reviews in Mineralogy*, **7** *Pyroxenes* (C. T. Prewitt, ed.) 419–94. Mineral. Soc. America.

—— 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. Ibid. **9B** *Amphiboles: Petrology and experimental phase relations* (D. R. Veblen and P. H. Ribbe, eds.) 1–227.

Stout, J. H. (1972) Phase petrology and mineral chemistry of coexisting amphiboles from Telemark, Norway. *J. Petrol.* **13**, 99–145.

White, A. J. R. (1964) Clinopyroxenes from eclogites and basic granulites. *Am. Mineral.* **49**, 883–8.

Yoder, H. S. and Tilley, C. E. (1962) Origin of basalt magmas: an experimental study of natural and synthetic rock systems. *J. Petrol.* **3**, 342–532.