Empirical ferric iron corrections: necessity, assumptions, and effects on selected geothermobarometers

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Abstract

The ferromagnesian silicate minerals, such as garnets, pyroxenes, micas, and amphiboles, appear in a variety of geothermometers and geobarometers. Where complete chemical analyses are available and regardless of bulk composition (metamorphosed pelitic or mafic), the aforementioned minerals commonly contain ferric iron. In mineral analyses using the electron microprobe, ferric and ferrous iron are not distinguished, and all the iron is treated as FeO. In ferric Fe-bearing minerals, this treatment results in (1) low analytical sums and (2) excess cations in the mineral formulae. Assuming ideal stoichiometry (ideal formula cations and oxygens) allows direct ferric estimates in garnets and pyroxenes; amphiboles require additional assumptions concerning site occupancies, and, for micas, no acceptable constraint exists for a ferric estimate. Based on ferric iron determinations for some metamorphic ferromagnesian silicates, the proportion of ferric to total iron increases at higher X_{Mg} values. The influence of ferric estimates on T and P calculations depends on the model used and on the extent the ferric estimate alters the relative proportions of end-members. Several examples suggest that, in general, if ferric estimates (or determinations) are made, they should be made for all the relevant minerals.

KEYWORDS: ferric iron, ferromagnesian minerals, geothermometer, geobarometer.

Introduction

THE advent of the electron microprobe as a common analytical tool in the Earth Sciences is, at least partly, responsible for the proliferation of calibrated geobarometers and geothermometers. This instrument provides quick and high-quality, major-element analyses of cubic-micron-size volumes of minerals in thin sections. As a result, petrologists can simultaneously examine textural variations among minerals in rocks and chemical variations within minerals, and this ability has opened the door for the application of various geobarometers and geothermometers. Although these are positive developments 'every silver lining has a dark cloud', and the electron microprobe's dark cloud is its inability to distinguish ferrous and ferric iron. Because in most common ferromagnesian silicate minerals, ferrous iron dominates over ferric iron, by convention, total iron in the analyses is reported as weight percent or weight fraction FeO at most microprobe facilities.

This discussion is concerned with the ferrous–ferric problem in microprobe analyses and various themes are covered. These topics include the ferric content of common minerals, a detailed example of an empirical ferric estimate, the influence of analytical imprecision on the estimates, the stoichiometric assumptions (basis of the estimates), and the effects of ferric iron estimates on some selected geothermobarometers.

Ferric iron in common rock-forming silicates

The most important ferromagnesian silicate phases that are used for geothermometry and geobarometry in metamorphic rocks are garnet, pyroxene, calcic amphibole, and biotite. A catalogue of amphibole analyses (Leake, 1968) illustrates the common presence of ferric iron in this mineral, and this aspect will not be treated here. However, compilations of complete analyses for the other minerals (Deer et al., 1962, 1978, 1982) are used to portray relationships between Fe^{2+}, Fe^{3+}, and Mg contents in these minerals.
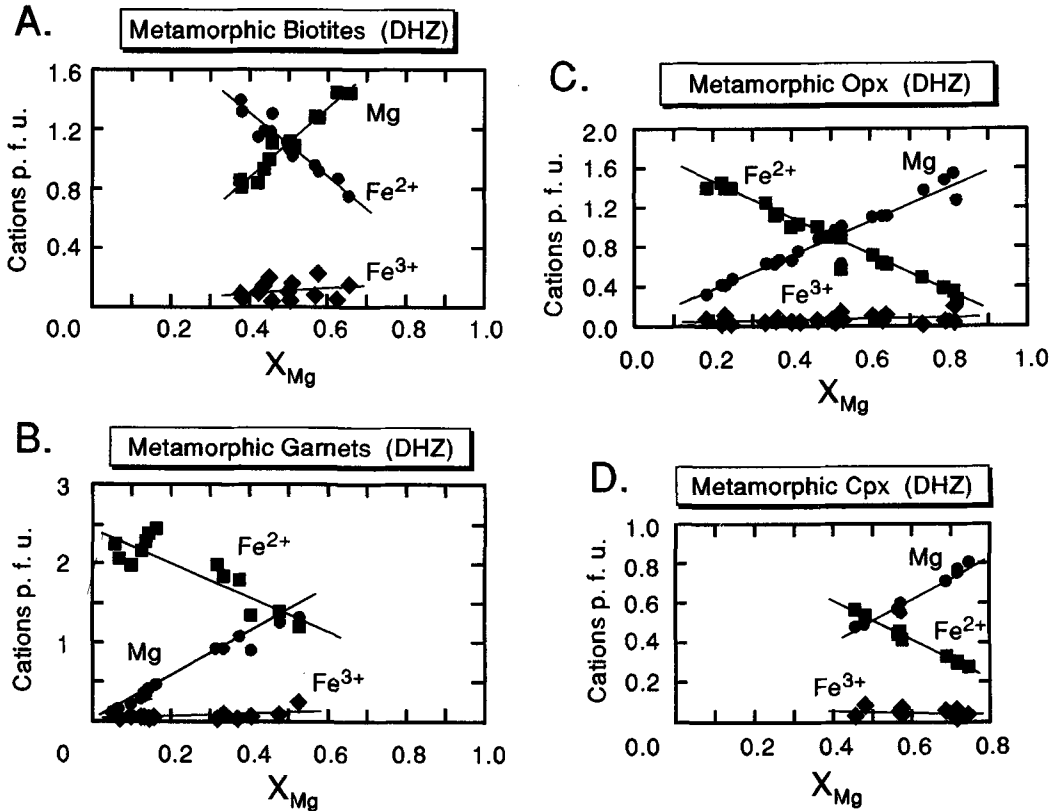
FIG. 1. Plots of cations of Mg, Fe^{2+}, and Fe^{3+} versus X_{Mg} [Mg/(Mg + Fe_{2+})] for metamorphic (A) orthopyroxenes—Deer *et al.* (1978), (B) calcic clinopyroxenes—Deer *et al.* (1978), (C) garnets—Deer *et al.* (1982), and (D) biotites—Deer *et al.* (1962). Lines are linear regressions of the three values versus X_{Mg} for each mineral.

Fig. 1 A–D shows plots of Mg, Fe^{3+}, and Fe^{2+} versus X_{Mg} for metamorphic biotites, garnets, orthopyroxenes, and clinopyroxenes taken from Deer *et al.*, 1962, 1978, 1982). The diagrams for all four minerals have common features. Each mineral contains Fe^{3+}, but Fe^{2+} is the dominant type of iron. Not surprisingly, Mg and Fe^{2+} show linear relationships when plotted against X_{Mg}; however, the Fe^{3+} remains essentially constant over the X_{Mg} range. As a consequence, for these data, the ratio of Fe^{3+} to total Fe increases with increasing X_{Mg} in each mineral group, and, with the exception of clinopyroxene, Fe^{3+} content is also positively correlated with X_{Mg}.

Calculation of mineral formulae and ferric iron estimation

A complete discussion of mineral formula calculation is found in appendix 1 of Deer *et al.* (1966). Nevertheless, to illustrate the principles

of ferric iron estimates a simplified mineral formula calculation is presented in Fig. 2.

Mineral formula calculation is a straightforward task; the only requirement is a complete and accurate mineral analysis. Example 1 (Fig. 2) shows the procedure for calculating a mineral formula from a ferric iron-bearing orthopyroxene analysis. The *weight percent* (wt.%) values are divided by the *molecular weight* (Mol. Wt.) of each oxide, which yields a list of *molecular proportions* (Fig. 2, example 1, column 2). The amounts of single cations and oxygens (atomic proportions) are needed for the mineral formulae, and these are obtained from the molecular proportion and the numbers of cations and oxygens in the oxide. For example (Fig. 2, example 1, columns 3 & 4), the atomic proportions of aluminium and oxygen for Al_2O_3 are: Al Cations = 2 × (Mol. Prop. Al_2O_3) (here, 0.0642) and the corresponding Oxygens = 3 × (Mol. Prop. Al_2O_3) (here, 0.0963).

The sums of either the cations or oxygens are

	1 Analysis	2 Mol. Prop.	3 Cations	4 Oxygens	5 Formula	
SiO_2	48.80	0.8122	0.8122	1.6244	Si	1.900
Al_2O_3	3.27	0.0321	0.0642	0.0963	Al^{IV}	0.100
Fe_2O_3	1.71	0.0107	0.0214	0.0321	Al^{VI}	0.050
FeO	30.71	0.4274	0.4274	0.4274	Fe^{3+}	0.050
MgO	15.51	0.3848	0.3848	0.3848	Mg	0.900
Sum	100.00		1.7100	2.5650	Fe^{2+}	1.000
					Sum	4.000

Example 1

(Complete analysis)

$ONF = 6 / 2.5650 = 2.3392$
$CNF = 4 / 1.7100 = 2.3392$

	1 Analysis	2 Mol. Prop.	3 Cations	4 Oxygens	5 Formula	
SiO_2	48.80	0.8122	0.8122	1.6244	Si	1.908
Al_2O_3	3.27	0.0321	0.0642	0.0963	Al^{IV}	0.092
FeO	32.25	0.4489	0.4489	0.4489	Al^{VI}	0.058
MgO	15.51	0.3848	0.3848	0.3848	Mg	0.904
Sum	99.83		1.7101	2.5544	Fe^{2+}	1.054
					Sum	4.016

Example 2

(Microprobe analysis — all ferrous)

$ONF = 6 / 2.5544 = 2.3489$
$CNF = 4 / 1.7101 = 2.3390$

Calculations

1 Analysis (in Wt. %)
2 Mol. Prop. = Wt % / Mol. Wt
3 Cations = OXD. CAT. × Mol. Prop.
4 Oxygens = OXD. OX. × Mol. Prop.
5 Formula = Cations × ONF (oxygen basis)

Explanation

CNF – Cation Normalization Factor (ideal cations / sum of cations)
Mol. Prop. – Molecular Proportion
Mol. Wt. – Molecular weight
ONF – Oxygen Normalization Factor (ideal oxygens / sum of oxygens)
OXD. CAT. & OXD. OX. – number of cations & oxygens in the analyzed oxide (e. g., 2 & 3 in Al_2O_3).

FIG. 2. Two examples that show the procedural steps of mineral formula calculation for a hypothetical, ferric-iron-bearing orthopyroxene composition. Example 1 is a 'complete' analysis, and example 2 is the same except that all the iron is treated as ferrous, as would be the case for an electron microprobe analysis.

used to calculate mineral formulae on either a cation or an oxygen basis. An oxygen basis is normally used. The mineral formulas are normalized values of the cations (Fig. 2, example 1, column 3). The *normalization factor (ONF)* for an oxygen-based mineral formula is *ideal stoichiometric oxygen/oxygen sum*. For this orthopyroxene, the amount of ideal stoichiometric oxygen is 6.000, the *oxygen sum* is 2.5650 (Fig. 2, example 1, sum of column 4), and the *ONF* is 6.0/2.5650 = 2.3392; multiplying each cation value (column 3) by the *ONF* gives the orthopyroxene mineral formula (Fig. 2, example 1, column 5) that is based on 6 oxygens.

A cation-based mineral formula is calculated analogously, but, instead of normalizing the cations to yield a specific number of oxygens, it gives a specified number of cations. For orthopyroxene, the ideal cations are 4.000, and the cation normalization factor (*CNF*) is *ideal cations/cation sum* (2.3392 in Fig. 2, example 1). For perfect and complete analyses, the cation- and oxygen-based formulae will be identical. In example 1 (Fig. 2), both the *ONF* and *CNF* are the same and would give identical mineral formulae.

For example 1, the amounts (wt.%) of FeO and Fe_2O_3 were known. As stated earlier, valence state of iron cannot be determined by electron microbe, and example 2 (Fig. 2, column 1) shows the all-ferrous (microprobe) analysis of example 1 pyroxene. The steps in calculating a mineral formula are the same; however, since total iron is considered to be ferrous, the *oxygen sum* is less (2.5544 in Fig. 2, example 2, column 4), and, as a result, the *ONF* is larger (2.3489). Consequently, the all-ferrous mineral formula that is based on 6.000 oxygens (Fig. 2, example 2, column 5) shows excess cations—4.016 instead of the stoichiometric maximum of 4.000. This cation excess is characteristic of the all-ferrous formulae of ferric-bearing minerals. The significance and subsequent recognition of this effect depends on the amount of ferric iron present and the type mineral.

Estimating ferric iron for minerals of known stoichiometry can be accomplished through two variants of the same basic method. In the first variation, the ferric content is estimated from the all-ferrous, oxygen-based formula—a detailed discussion of this method and a generalized

	5	6	7	8
	Formula (Cat./ 6 Ox.)	Norm Cat.	Norm Ox.	Ferric Formula
Si	1.908	1.900	3.8000	1.900
Al^{IV}	0.092	0.100	0.1500	0.100
Al^{VI}	0.058	0.049	0.0735	0.049
Fe^{3+}	– –	– –	– –	0.053
Mg	0.904	0.900	0.9000	0.900
Fe^{2+}	1.054	1.050	1.0500	0.997
Sum	4.016	3.999	5.9735	3.999

$$FNF = 4 / 4.016 \quad = 0.9960$$
$$Fe^{3+} = 2 \times (6 - 5.9735) = 0.053$$
$$Fe^{2+} = 1.050 - 0.053 = 0.997$$

	5A	6A	7A
	Formula (Cat./ 4 Cat.)	Form. Ox.	Ferric Formula
Si	1.900	3.8000	1.900
Al^{IV}	0.100	0.1500	0.100
Al^{VI}	0.050	0.0750	0.050
Fe^{3+}	– –	– –	0.050
Mg	0.900	0.9000	0.900
Fe^{2+}	1.050	1.0500	1.000
Sum	4.000	5.9750	4.000

$$Fe^{3+} = 2 \times (6 - 5.9750) = 0.050$$
$$Fe^{2+} = 1.050 - 0.0500 = 1.000$$

Ferric formula calculated from:

Oxygen based formula

5 Formula (Oxygen basis)
   = Cations × ONF
6 Norm. Cat. = FNF × Formula
7 Norm. Ox. = Ox. per Norm. Cat.
   (eg, 1.5 Ox. per 1.0 Al)
8 Ferric Formula

Cation based formula

5A Formula (cation basis)
    = Cations × CNF
6A Form. Ox. = Ox. per cation in the
    formula
7A Ferric Formula

Explanation

Cat. & Ox. – Cations & Oxygens
CNF – Cation Normalization Factor
Form. – Formula
FNF – Ferric Normalization Factor (ideal cations / formula sum)
Norm. Cat. & Norm. Ox. – Normalized cation & oxygen values

FIG. 3. The procedural steps for two variations of empirical ferric estimation for example 2 (Fig. 2). In steps 5 to 8, the ferric content is derived from an oxygen-based mineral formula, and in steps 5A to 7A, it is derived from a cation-based mineral formula.

formula for estimating ferric iron is given by Droop (1987). Note well, these formulae must have excess, i.e. greater than ideal cations, which is the feature that justifies the ferric estimation procedure. In the second variation of the ferric estimation procedure, the calculation of an all-ferrous, oxygen-based formula is by-passed. Instead an all-ferrous formula that is based on *ideal cations* is used.

The all-ferrous, oxygen-based formula orthopyroxene formula from example 2 (Fig. 2) is used to illustrate the variation-1 ferric correction procedure. The cations are normalized such that they sum to their ideal value. This normalization factor (*FNF*—ferric normalization factor) is: *ideal cations/formula sum*, and here is: 0.9960 = 4.000/4.016 (Fig. 3, column-5 sum). Each cation is multiplied by the *FNF* which gives the normalized cations (*Norm. Cat.* in Fig. 3, column 6). The normalized formula then has the proper cation values, but the sum of the oxygens (*Norm. Ox.* sum) that are assigned to each cation are less than ideal (here, 5.9735). This *oxygen deficiency* is

made up by converting ferrous iron to ferric iron. In this example (Fig. 3), the $Fe^{3+} = 2 \times (6.000 - 5.9735)^*$ and Fe^{2+} (from column 8) = Fe^{2+} (from column 6) $-Fe^{3+}$, or more generally stated, $Fe^{3+} = 2 \times$ (*ideal oxygen−normalized oxygen sum*), Fe^{2+} (ferric formula) = Fe^{2+} (normalized) $-Fe^{3+}$. The end result is a mineral formula nearly identical to the example-1 formula in Fig. 2 (discrepancies arise due to rounding errors).

In variation 2 of the ferric estimation procedure, the all-ferrous, *cation based* formula is used (e.g. Fig. 3, column 5A). This formula and the normalized all-ferrous, oxygen-based formula from variation 1 (Fig. 3, column 6) are equivalent, but using the cation-based formula eliminates a normalization step and the rounding errors that accompany it. As before (variation 1), the *oxygen deficiency* is determined and then compensated by

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* The amount of Fe^{2+} that must be converted to Fe^{3+} will be equal to twice the amount of the deficiency, since each ferric Fe has one-half more oxygen ($FeO_{1.5}$) than each ferrous Fe (FeO).

converting ferrous iron to ferric iron. This ferric corrected mineral formula is identical to the example-1 formula in Fig. 2.

In general, variation 2 will give better formulae than variation 1 because of the reduction of the number of steps that require rounding. However, when using variation 2, the sum of the formula oxygen must always be checked; it *must* sum to a total less than the ideal stoichiometric oxygen (e.g. in Fig. 3 the sum of column 6A, 5.9750, is less than 6.000). If the sum of the formula oxygen is equal to or greater than the ideal stoichiometric oxygen, then the analysis *cannot* be corrected for ferric iron.

Ferric estimates for less-than-perfect analyses

Any analytical error that causes a change in the molecular proportions among the oxides will appear in the mineral formula. However, not all types of analytical error produce the change. Systematic errors that cause the same magnitude of relative change in each analysed element will not affect the mineral formula (for example, if each oxide wt.% value is 1.0 relative % too high); the problem will only appear in the analytical total. The mineral formula is only affected when the relative errors in the oxides are different. The significance of the analytical error is influenced by: (1) the amount of the element and (2) the valence of the element (errors in high valence elements have a greater effect on the oxygen total). This is why precise SiO_2 measurement is so important to good silicate mineral analyses.

The orthopyroxene example (Fig. 2, example 2, column 1) is presented below as an example of how analytical error in the two most abundant elements could affect the all-ferrous and ferric corrected formulae. The mineral formulae were recalculated assuming $\pm1.0\%$ relative error in SiO_2 wt.% (Fig. 4A) and $\pm1.0\%$ relative error in FeO wt.% (Fig. 4B) in the all-ferrous analysis (microprobe analysis). To assess the relative quality of this new set of all-ferrous and the ferric corrected formulae, they have been normalized to the ideal values—perfect cation values or X_{Mg} would plot at 1.0 in Fig. 4, deviation to higher or lower values indicates increasing error. For a 1.0% relative error in SiO_2, little difference exists between the Si, Mg, and Al values obtained from the all-ferrous and the ferric corrected formulae; however, the lack of a ferric correction results in worse values for Fe^{2+} and X_{Mg} (Fig. 4A). Analogously, the all-ferrous and the ferric-corrected formulae from an analysis with a 1.0% error in FeO produce comparable Si, Mg, and Al values and dissimilar Fe^{2+} and X_{Mg} values (Fig.

4B). In both cases the ferric corrected cations are closer to their ideal values.

For elements that can occupy more than one distinctive site [for example, tetrahedral (Al^4) and octahedral (Al^6)], the occupancy of each position is much more sensitive to analytical error than absolute amounts of cations or parameters derived from these values (for example, X_{Mg}). A comparison of Fig. 4A and B shows that the severity of the site-occupancy errors depends not only on the amount and sign of the error, but also on the identity of the element that is in error. For this example, neither the all-ferrous nor the ferric-corrected formulae can be said to give generally better values for tetrahedral Al or octahedral Al in the orthopyroxene.

Although the overall accuracy continued to worsen, the ferric-corrected formula will continue to give the best results for even higher values of relative error in the oxides. Again, using the orthopyroxene data from Fig. 2, Fig. 4C shows how increasing the relative error in the SiO_2 affects the amount of Fe^{2+} cations obtained from the all-ferrous and the ferric-corrected formulae. At relative SiO_2 slightly above $\pm2.6\%$, the cation total drops below 4.000 (ideal for pyroxene) and ferric correction is no longer possible. Nevertheless, until this point is reached, the ferric-corrected formula is the better of the two. These examples suggest that ferric estimations will usually give better cation values; site occupancy values may or may not be better.

Ferric estimates for important rock-forming minerals

Knowledge of mineral stoichiometry is critical to the ferric estimation process. Assumptions about mineral stoichiometry can be placed in three rather broad categories: (1) minerals with fixed or only extremely slight variations in amounts of cations and anions, (2) minerals with one partially filled site, and (3) minerals with more than one partially occupied site (the hopeless ones). Table 2 lists some ferric iron-bearing phases that either are or could be important for geothermobarometry of metamorphic rocks and the ideal cation and oxygen contents of the category 1 minerals.

Category 1 minerals

For geothermobarometry, garnets and pyroxenes are the most important metamorphic ferromagnesian minerals in category 1. Ideally, garnets have 8 cations and 12 oxygens, and pyroxenes have 4 cations and 6 oxygens; common whole-

number multiples or factors of these values are also used (e.g. 2.0 cations, 3.0 oxygens for orthopyroxene). See Droop (1987) for other minerals in this category.

Category 2 minerals

The various amphiboles are the only important rock-forming minerals occupying category 2.* The procedure for ferric estimations of amphibole formulae is similar to the orthopyroxene example in Fig. 2; however, generally for amphiboles, subtotals of cations rather than cation totals are normalized to stoichiometric values. A further difference is that the stoichiometric value of any one of these subtotals is merely an upper or lower limit (i.e. a range of acceptable values exists); whereas, for the orthopyroxene example there was a single correct cation value. As a result, each amphibole analysis will have a range of acceptable ferric iron values that can be estimated empirically, and the analyst/petrologist decides whether the minimum, maximum, or some intermediate value of ferric iron is most representative of his or her analyses.

Stoichiometric assumptions. Two kinds of criteria place upper and lower limits on empirical estimates of ferric iron in amphiboles. These are chemical limits (total Fe as FeO or Fe_2O_3) and various stoichiometric criteria, and they have been discussed in detail by Robinson *et al.* (1982). Nevertheless, some underlying assumptions are mentioned. Since, at present, highly accurate, routine analysis of H in amphiboles is impossible and commonly about two OH groups are present, the simplest assumption is that the OH is present in ideal proportions and sums to two (see also Leake, 1968, 1978; Leake and Hey, 1979) in an amphibole mineral formula that is based on 46 negative charges (22 oxygens + 2 OH groups). The ferric estimates for amphiboles can then be calculated for an anhydrous amphibole formula that is based on 23 oxygens (the ideal formula minus one H_2O). Note that, although F and Cl can substitute for OH, failure to analyse for these elements will not affect the ferric estimate. The critical assumption is that OH + F + Cl provide two of the 46 negative charges in the formula; the identity of the balancing monovalent anion or radical is not important.

Structure refinements indicate that specific

cations are largely restricted to certain amphibole sites.† In the generalized amphibole formula, $A_{0-1}B_2C_5T_8O_{22}(OH)_2$ (Leake, 1978), only the A-site occupancy can vary. Only K and Na are present at the A-positions, but K is restricted to these sites. The most abundant cations that are found at the B-sites are Na, Ca, Mn, Fe^{2+}, and Mg, and, for all practical purposes, Ca is restricted to this site (see Hawthorne, 1983). The C-sites are principally the locations of Mn, Fe^{2+}, Zn, Mg, Fe^{3+}, Cr, Ti, and Al (Hawthorne, 1983). The T-sites are the positions of Si, lesser amounts of Al (Hawthorne, 1983). Si is restricted to the T positions. Fig. 5 shows this general site assignment scheme for amphiboles, and the order (top to bottom) of the cations is roughly one of increasing ionic radius. The important stoichiometric limits are: (1) $16 \geqslant$ total cations $\geqslant 15$; (2) Cation subtotal (Si through Ca) $\leqslant 15$; (3) Cation subtotal (Si through Na) $\geqslant 15$; (4) Cation subtotal (Si through Mn) $\geqslant 13$; (5) (Si + Al) > 8, and (6) Si $\leqslant 8$ (Fig. 5). As shown earlier, all-ferrous formulae of ferric-bearing minerals contain excess cations. Consequently, depending upon the actual composition of a ferric amphibole, any of these stoichiometric limits could be overstepped, but, even if ferric iron is actually present, the all-ferrous formula will not necessarily violate any of the stoichiometric assumptions listed above.

Stoichiometric limits are found in Fig. 5; the ones that give minima are indicated by '$\geqslant$' signs and the ones that give maxima are indicated by '$\leqslant$' signs. Since ferric corrections are based on the stoichiometric limits, the corrected formulae will be either minimum or maximum ferric estimates. If a stoichiometric limit is a maximum, then the corresponding ferric estimate is a 'minimum' estimate. If a stoichiometric limit is a minimum, then the corresponding ferric estimate is a 'maximum' estimate. For each amphibole analysis it should be possible to determine a 'maximum' and 'minimum' (this may be the all-ferrous formula — no ferric iron) ferric content. Caution should be exercised when doing ferric estimates of amphiboles; check to see that the corrected formula does not violate any of the other stoichiometric or chemical limits. If it does, either the wrong limit was used or the analysis is poor quality. Note in particular that in poor-quality analyses of Mg-rich amphiboles, exceeding the chemical limits poses a real problem.

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* The critical constraint is that occupancy of only one site is variable. However, an example with both octahedral A-site vacancies has been provisionally identified (F. C. Hawthorne, pers. comm., 1989). Such amphiboles would be category 3 minerals. Nevertheless, the overwhelming majority of amphiboles would appear to have only partially filled site.

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† Only amphiboles that contain elements (K, Na, Ca, Mn, Fe, Zn, Mg, Cr, Al, Ti, Si) that are routinely measured with the electron microprobe are considered here.
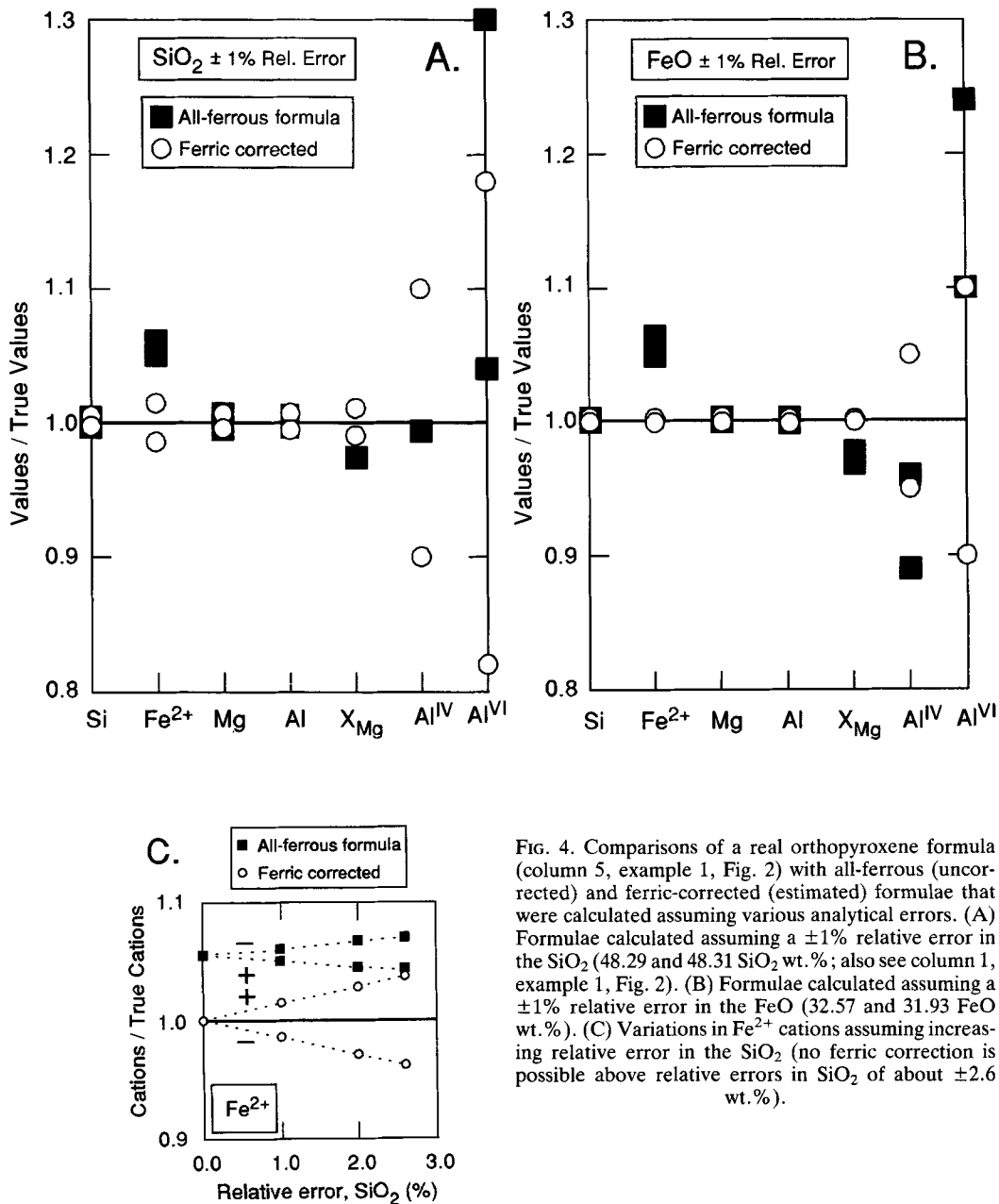
FIG. 4. Comparisons of a real orthopyroxene formula (column 5, example 1, Fig. 2) with all-ferrous (uncorrected) and ferric-corrected (estimated) formulae that were calculated assuming various analytical errors. (A) Formulae calculated assuming a $\pm 1\%$ relative error in the SiO_2 (48.29 and 48.31 SiO_2 wt.%; also see column 1, example 1, Fig. 2). (B) Formulae calculated assuming a $\pm 1\%$ relative error in the FeO (32.57 and 31.93 FeO wt.%). (C) Variations in Fe^{2+} cations assuming increasing relative error in the SiO_2 (no ferric correction is possible above relative errors in SiO_2 of about ± 2.6 wt.%).

Common hornblende. Based on the stoichiometric assumptions, the minimum ferric content in calcic amphiboles (common hornblendes) is usually either (*i*) no Fe^{3+} (no stoichiometric limits are violated in the all-FeO formula) or (*ii*) the Fe^{3+} that is determined from the 15eNK correction (the ferric value that was obtained from normalization of the cation subtotal of Si through Ca to 15). The maximum ferric content is commonly the 13eCNK correction (the ferric value that was obtained from normalization of the cation subtotal of Si through Mn to 13).

Providing the analyses are correct and the assumptions are valid, the true ferric content should lie between the minimum and the maximum. A common approach is to use an amphi-

Site	Element	Limit	Correction Min	Max
T-site	Si	— Si ≤ 8	(8Si)	
	Al	— ΣAl ≥ 8		(8SiAl)
	Ti			
	Cr			
C-site	Fe^{3+}			
	Mg			
	Zn			
	Fe^{2+}			
B-site	Mn	— ΣMn ≥ 13		(13eCNK)
	Ca	— ΣCa ≤ 15	(15eNK)	
	Na	— ΣNa ≥ 15		(15eK)
A-site	K	— ΣK ≤ 16	(16CAT)	
	□			

FIG. 5. Cation site assignments in amphiboles, stoichiometric limits that follow from these assignments, and some ferric normalization factors that are based on the stoichiometric limits. Site names are after Leake (1978), and site assignments are after Hawthorne (1983). *Summation symbols followed by elements* represent the sums of the cations Si (top of list) through the indicated elements (lower in list), e.g. $\Sigma Mn = \Sigma(Si + Al + \ldots + Fe^{2+} + Mn)$. Abbreviations of ferric normalization factors (FNF): *8Si* = 8 ÷ Si (all-ferrous formula); *8SiAl* = 8 ÷ (Si + Al) (all-ferrous formula); *13eCNK* (13 cations *exclusive of* Ca, Na, K) = 13 ÷ ΣMn (all-ferrous formula); *15eNK* = 15 ÷ ΣCa (all-ferrous formula); *15eK* = 15 ÷ ΣNa (all-ferrous formula); *16CAT* = 16 ÷ ΣK (i.e. cation sum of the all-ferrous formula).

bole formula that gives the mean of the ferric values that were acquired from the minimum and maximum values (Spear and Kimball, 1984). Other approaches may also be derived; for example, Schumacher (1986 and in preparation) has used a correlation between Ca and Na assigned to the *B* site in calcic amphiboles that coexist with one or more Ca-richer phases (e.g. epidote, clinopyroxene, or calcic plagioclase) to derive a correction procedure. This ferric content, which also necessarily lies between the minimum and maximum values, is an assemblage-specific alternative to simply using the mean values.

Fe–Mg amphiboles. For anthophyllite–gedrite (orthorhombic) and cummingtonite–grunerite (monoclinic), the minimum ferric content is generally used. For these amphiboles the minimum ferric content is usually either (*i*) no Fe^{3+} (the all-FeO formula) or (*ii*) the Fe^{3+} from the 15eNK correction (i.e. the ferric value that was obtained from normalization of the cation subtotal of Si through Ca to 15).

Soda–calcic and sodic amphiboles. The soda-calcic and sodic amphiboles may contain significant amounts of elements which may be found at multiple sites (i.e. Na at the *A* or *B* site; Al at the *C* or *T* sites). For glaucophane-type amphiboles, useful normalization factors (stoichiometric limits) are likely to be 15eK (normalization of the cation subtotal of Si through Ca to 15), 13eCNK, and Si8 [Si > 8.0; normalization factor = 8.0/Si (all-ferrous formula)]. Soda–calcic amphiboles are likely to give a wide range of permissible formulas, but the 13eCNK will probably be the most useful (maximum ferric estimate).

Excess or deficient oxygen. A potential problem that could seriously impair the reliability of ferric estimates in amphiboles is the dilemma of the 'hydroxy'- and 'oxy'-type substitutions (e.g. in kaersutites or 'basaltic hornblendes', see Deer *et al.*, 1966). These types of substitutions are possible amphibole compositional variations that could occur through the exchange of oxygen + a higher valance cation for OH + a lower valance cation. If this type of substitution were extensive in a particular amphibole, it would negate the assumption of a 23 oxygen anhydrous formula; the amount of oxygen in the actual anhydrous formula would be indeterminate. For example, a 'hydroxy' amphibole in which the OH content approached three could have as few as 22.5 oxygens (anhydrous), while a completely 'oxy'-substituted amphibole with no OH groups would have 24 oxygens (anhydrous). This type of substitution appears to be more common for magmatic amphiboles than for metamorphic ones.

Category 3 minerals

Biotite is particularly problematic because vacancies are possible both at the 12-fold coordinated interlayer sites and the octahedral sites via various substitution mechanism (see end members in Guidotti, 1984). In addition, biotite and phyllosilicates may host minor interlayers (defects) of other sheet silicates. This feature could also cause discrepancies in the subtotals of particular sites. In analyses of natural examples, the interlayer and octahedral sites are rarely filled, and, as a result, the excess cations that are generated by treating total Fe as FeO seldom exceed stoichiometric limits. If, for reasonably pure (single-phase) biotites, a measurable compositional parameter can be correlated with vacancies at either the interlayer or octahedral sites, then empirical ferric estimates may be possible.

Compositional variations due to ferric iron estimation

Ferric estimations only fundamentally alter the following quantities in mineral formulae: the ferric to ferrous ratio (obviously) and the absolute amounts of the cations. Effectively, the major contrast between a mineral's all-ferrous formula and its ferric equivalent is that the proportions of Fe^{3+} and Fe^{2+} to all other cations change; the proportions of the remaining cations to each other are the same in both formulae. As a result, the ferric-iron correction procedure can affect end member or site-occupancy parameters, which would be used in the application of geothermometers and geobarometers, both directly and indirectly. Any ratio that is calculated using total ferrous or ferric iron is directly altered as a result of the correction procedure; examples are X_{Fe} $[Fe^{2+}/(Fe^{2+} + Mg)]$ and X_{Mg} $(Mg/(Fe^{2+} + Mg))$. Any parameters (site occupancies or amounts of end members) that do not involve ferric or ferrous iron can be indirectly influenced by the estimation procedure. In the indirect case, depending upon the parameter, the effects could be large or small. The most drastic changes occur in site occupancies of elements that can be assigned to multiple sites; examples of parameters that are highly dependent upon ferric corrections are the amounts of Na at the A-site in hornblendes or tetrahedral and octahedral Al in pyroxenes.

Fe–Mg variations between ferric and all-ferrous mineral formulae

The data from the DHZ examples (Fig. 1) indicate that the ferric content of some important metamorphic ferromagnesian silicates is essentially independent of the X_{Mg}; obviously, the Fe^{2+} and Mg contents are not. Fig. 6 shows the deviation between 'Ferric' X_{Mg} (ferric formulae) and the 'Apparent' X_{Mg} (all-ferrous formulae). For biotite, garnet, orthopyroxene, and clinopyroxene, the data show the greatest divergence in actual X_{Mg} ('Ferric') and 'apparent' X_{Mg} at compositions richest in Mg, because the ferric proportion of total iron is large. The metamorphic biotites cover a wide range of X_{Mg} values, but show considerable deviation between true and apparent X_{Mg} over most of the range of X_{Mg} (Fig. 6A). Metamorphic garnets show the least divergence because they tend to be richer in Fe (Fig. 6B). Metamorphic orthopyroxenes show a wide range of compositions, and significant divergence in X_{Mg} is only seen in the composition richest in Mg (Fig. 6C). Metamorphic clinopyroxene tends to be Mg-rich, and, as result differences between 'Ferric' and 'Apparent' X_{Mg} can be

meaningful (Fig. 6D). Consequently, if X_{Mg} or X_{Fe} greatly influence a particular geothermometer or geobarometer and the mineral sets cover a range of compositions, then knowledge of the ferric content could be a key factor in resolving inconsistencies in the $P–T$ determinations.

Ferric estimations: effects on specific geothermobarometers

The effects of either estimating or ignoring ferric iron in mineral analyses that are used for geothermometry and geobarometry will vary according to the method that is applied, and a complete survey is not attempted here. Instead, three examples were chosen that involve (i) only a category 1 mineral, (ii) category 1 and 2 minerals, and (iii) category 1 and 3 minerals. Detailed discussion of the first and third examples uses idealized mineral compositions (Table 1) whose formulae or compositions are based on the DHZ data set used in Figs. 1 and 6. The second example uses natural data (Schumacher, unpublished data from southwestern New Hampshire, U.S.A.). These detailed examples are further compared with data from the literature.

A category 1 mineral example: the garnet–Al-silicate–plagioclase–quartz geombarometer

The garnet–Al-silicate–plagioclase–quartz geothermobarometer has been applied in numerous metamorphic terranes. In this example, the only potentially Fe^{2+}-bearing ferromagnesian silicate phase is garnet, which is a category 1 mineral (fixed stoichiometry). For sillimanite, garnet, and plagioclase (Table 1), three different sets of results can be obtained from the calibration of Newton and Haselton (1981) by using (i) the all-ferrous garnet formula, (ii) the ferri-corrected garnet formula, or (iii) the ferri-corrected garnet formula plus an adjustment to the mole fraction grossular (Fig. 7A). At a given temperature, the pressure that is obtained using the ferric garnet formula (ferric only, Fig. 7A) is slightly higher (about 100 bars) than the one from the all-ferrous formula (ferrous, Fig. 7A). This is due chiefly to the reduction in almandine component and the corresponding increase in pyrope component. Assigning part of the Ca in the garnet formula to an andradite component reduces the mole fraction of the grossular component in the garnet, and if this reduction is taken into account (adjusted, Fig. 7A), the result is indistinguishable from the all-ferrous results for this example — this is probably not universally true. Results from all three
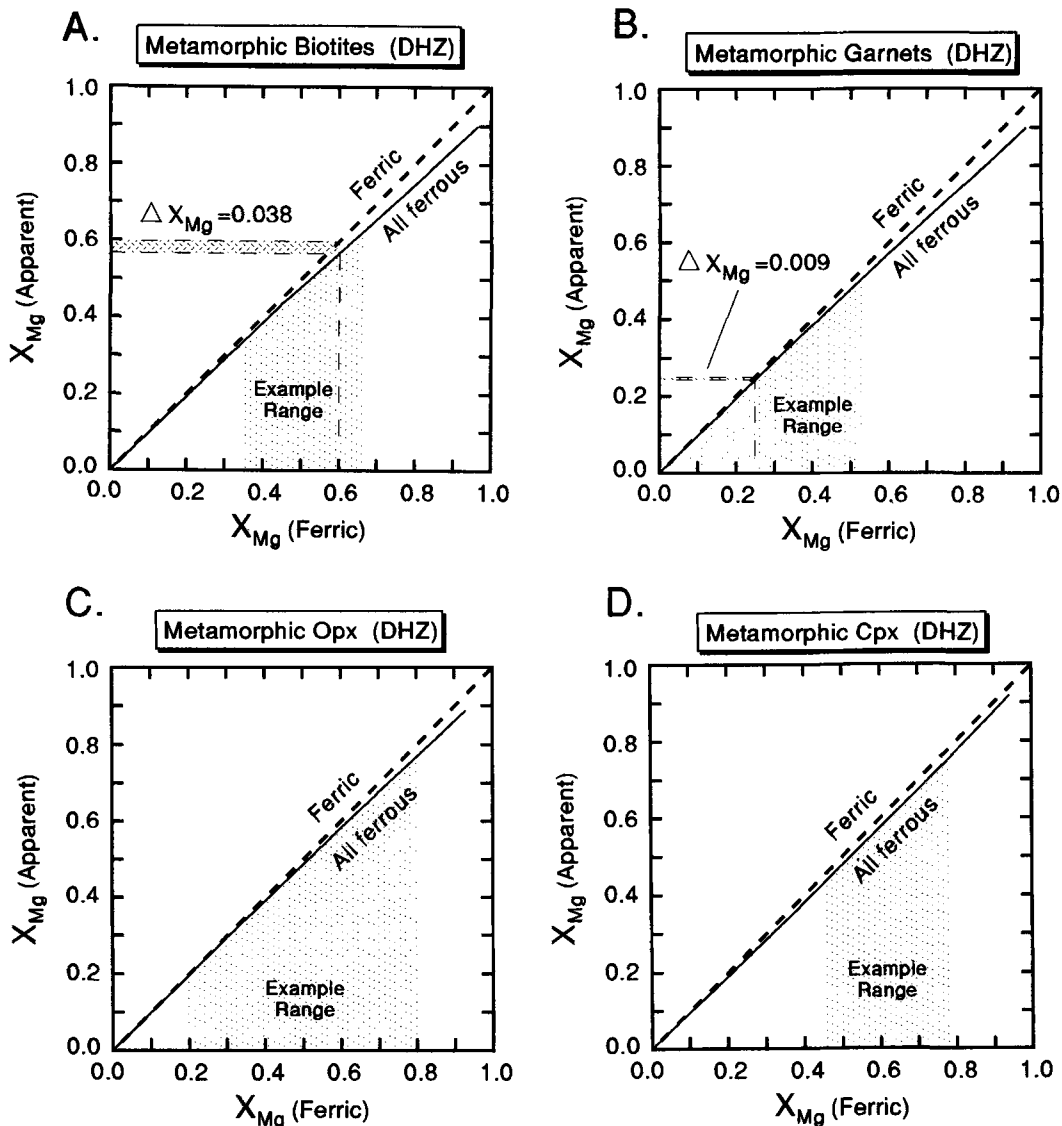
FIG. 6. A comparison of X_{Mg} [Mg/(Mg + Fe^{2+})] values for fully determined mineral analyses (ferric) and the same analyses with total iron assumed to be ferrous (Apparent). Part 1: Metamorphic biotites from Deer *et al.* (1962); Part B: Metamorphic garnets from Deer *et al.* (1982); Part C: Metamorphic orthopyroxenes from Deer *et al.* (1978); Part D: Metamorphic clinopyroxenes from Deer *et al.* (1978). *Example range* (stippled area) gives the extent of the Deer, Howie, and Zussman (DHZ) data set. The delta X_{Mg} (Apparent) values in parts A and B were used to determine the mineral compositions used in Fig. 9.

calculations are nearly identical. Several examples from the literature (Fig. 7B) show the same relatively minor variations in pressure at given temperature. Failure to account for ferric iron in 'normal' garnets in the application of the garnet–Al-silicate–plagioclase–quartz geothermobarometer will probably have very little effect upon the pressure estimates that are obtained.

An example with category 2 and 1 minerals: the hornblende–garnet–plagioclase–quartz geobarometer

The hornblende (Hbl)–garnet (Gar)–plagioclase–quartz geobarometer (Kohn and Spear, 1989) involves two ferromagnesian silicate minerals which may contain ferric iron. The garnet ferric correction is simple, but remember that

Table 1. Garnet, and plagioclase compositions that were used in parts of figures 7A and parts of 7B. Key: FE2 is the all-ferrous garnet formula; FE3 is the ferric corrected garnet formula; X_{An} and X_{Ab} are the mole fractions Ca and Na divided by (Ca + Na).

	Garnet		Plagioclase	
	Cations / 12 Oxygens			
	FE2	FE3		
Si	3.008	3.000	X_{An}	0.500
Al			X_{Ab}	0.500
Al	1.954	1.950		
Fe^{3+}		0.050		
Mg	1.003	1.000		
Fe^{2+}	1.753	1.700		
Ca	0.300	0.300		

normally a range of stoichiometrically valid ferric formulae exist for hornblende analyses. A 'reasonable' hornblende formula choice is the responsibility of the user. For a detailed example, data (unpublished data from southewestern New Hampshire, U.S.A.) that is petrographically familar to the author was used; the formulae are found in Table 2.

The hornblende (Table 2) that is used in the example (Fig. 8A) contains some visible cummingtonite exsolution lamellas and coexists with cummingtonite. Consequently, it is reasonable to assume that it also contains a cummingtonite component. Since the maximum ferric estimate (13eCNK) eliminates the cummingtonite component, it would certainly overcorrect for ferric iron in this case. The correction factor for Ca-saturated hornblende (Schumacher, 1986) indicates about 0.2 Na at B would be appropriate. A cummingtonite-saturated hornblende should contain even less Na at B, and the ferric correction was made assuming 0.1 Na at B (i.e. the $FNF = 14.900/\Sigma Ca$).

Having arrived at a ferric corrected hornblende formula (Table 1, Part B, INT), the ferric and ferrous formulae for hornblende and garnet can be combined four ways to give four sets of

pressure–temperature estimates. Fig. 8A indicates that the ferric iron estimate for the amphibole (category 2 mineral) has a greater effect than estimating ferric iron for the garnet. The difference in the results from the all-ferrous and the ferric formulae for the hornblende is 600 to 700 bars depending upon temperature; whereas, for the garnet the differences are only about 150 bars (Fig. 8A).

In Fig. 8B, data from the above example and from Ghent and Stout (1986) further illustrate the effect of correcting the hornblende for ferric iron upon the derived pressure; these authors gave only the garnet mole fractions, so only the effects of the hornblende are shown in example (B) to (D). The zero point on the diagram (Fig. 8B) is the pressure at 600 °C for the all-ferrous hornblende and garnet formulae. The minimum (MIN) corrections can be quite small but the maximum corrections (MAX) give pressures that are 1.5–3.0 kbar less than the all-ferrous formulae and also significantly less than the minimum corrections.

The dominant effect of hornblende is due principally to the reduction of A-site cations (reassigning Na at A to B) which is a secondary effect of the ferric iron correction. These changes to the A-site lower the Kd by decreasing the value of pargasite activity (numerator) and increasing the value of the tremolite activity (denominator) (see Kohn and Spear, 1989). Consequently, failure to account for ferric iron in the amphiboles will significantly raise the pressure obtained from this geobarometer. Neglecting ferric iron in the garnet results in somewhat lower pressures.

An example with category 3 and 1 minerals: the bottle–garnet geothermometer

The garnet–biotite geothermometer of Ferry and Spear (1978) has been extensively used in various metamorphic regions. This geothermometer is based on the experimental calibration of the temperature dependence of Fe–Mg partitioning between garnet, a category 1 mineral that was encountered in the first two examples, and biotite, a category 3 mineral. Since empirical estimation of ferric contents in biotite is not possible, this case was analysed using the X_{Mg} values of the all-ferrous and ferric formulae of the biotite and garnet in Fig. 6A and B (DHZ data set). For biotite the all-ferrous X_{Mg} is 0.562 and the actual X_{Mg} is 0.600 ($\Delta X_{Mg} = 0.038$, Fig. 6A); for garnet the all-ferrous X_{Mg} is 0.241 and the actual X_{Mg} is 0.250 ($\Delta X_{Mg} = 0.009$, Fig. 6B). Using the original calibration of Ferry and Spear (1978) and a pressure of 5.0 kbar, the actual
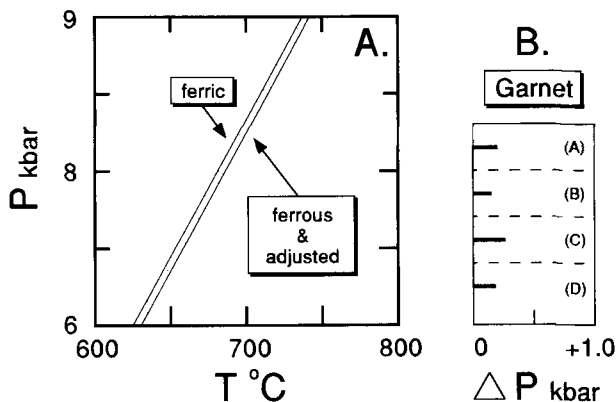
FIG. 7. Part A. A pressure (*P*)–temperature (*T*) diagram showing variations in *P–T* that are dependent upon garnet formula calculation parameters for the garnet–plagioclase–sillimanite–quartz geothermobarometer (Newton and Haselton, 1981). Lines show a range of *P* and *T* obtained using an all ferrous (*ferrous*) and a ferric iron corrected (*ferric*) garnet formula or if the grossular activity in the garnet is corrected for the andradite component (*adjusted*). Part B. Comparison of pressure variations (delta *P* kbar) as a function of garnet ferric estimates. *Solid bars* indicate the difference between the values obtained from the all-ferrous (zero difference points) and ferric corrected formulae. (A)—example based on DHZ values from Fig. 1 and 6; example (B)—assemblage S130 (lowest ferric content) and (C) assemblage S142 (highest ferric content) both from Sevigny and Ghent (1989); and (D) assemblage HHG007 from Humphreys and Van Bever Donker (1990).

garnet and biotite compositions give a temperature of 662 °C.

For the garnet–biotite geothermometer, the nearer the $Kd_{Fe-Mg}^{Bio-Gar}$ is to 1.000, or in other words, the smaller the difference in X_{Mg} between the garnet and the biotite, the higher the temperature. Since garnet is richer in Fe than biotite, neglecting ferric iron in garnet increases the difference between the X_{Mg}'s of the garnet and biotite, thus lowering the temperature estimate. For example, the all-ferrous garnet ($X_{Mg} = 0.241$) and the actual biotite give a temperature of 642 °C, 20° less than the correct temperature (Fig. 9A). Neglecting ferric iron in biotite has the opposite effect; this decreases the temperature estimate. The all-ferrous biotite ($X_{Mg} = 0.562$) and the actual garnet give a temperature of 730 °C, 68° more than the 'correct' temperature (Fig. 9B).

Since ferric estimation in biotite is not possible, this geothermometer can be applied to the above example using two formula options: (*i*) the all-ferrous formulae for both biotite and garnet or (*ii*) the all-ferrous biotite formula and a ferric corrected garnet formula. As seen above, if both the garnet and biotite contain ferric iron, the errors produced by neglecting ferric iron (using all-ferrous formulae for both minerals) tend to cancel one another. In this example, the all-ferrous compositions give 707 °C, 45° too high. Interestingly, the other alternative, a ferric garnet formula and an all-ferrous biotite formula, will

give a worse result (730°, see above) even though the formula of the garnet is improved. This is because the all-ferrous biotite and a ferric-corrected garnet formula give the minimum possible difference in X_{Mg}. So, correcting the garnet compounds the error of the biotite.

Examples taken from the literature give similar results (Fig. 9C) to those of the generalized example (composition based on average DHZ data, above). These examples also indicate that the presence of ferric iron in the biotite will have the greatest effect on the garnet–biotite geothermometer.

For this Fe–Mg exchange geothermometer the best results are obtained by using either ferric corrected (if the biotite can be analyzed) or all-ferrous formulae for both minerals. Using only the ferric-corrected garnet formula produces the largest discrepancies.

Summary

In metamorphic rocks, ferromagnesian silicate minerals that are commonly used for geothermometry and geobarometry ordinarily contain some ferric iron. The consequence of treating total iron as ferrous in ferric-iron-bearing minerals is that each cation value will be proportionally too large. In minerals with fixed numbers of cations and oxygens (e.g. pyroxenes and garnet) the effect of neglecting ferric iron is most easily seen in the

Table 2. Hornblende, garnet, and plagioclase formulas that were used in parts of figure 8. Key: FE2 is the all-ferrous formula; MIN is the 15eNK amphibole correction; INT is intermediate amphibole correction with Na at B set to about 0.100 (0.099); MAX is the 13eCNK amphibole correction; FE3 is the ferric corrected garnet formula; X_{An}, X_{Ab}, and X_{Or} are the mole fractions Ca, Na, and K divided by (Ca + Na + K). Hornblende formula site designations are T, C, B, and A.

	Hornblende					Garnet		Plagioclase	
	Cations / 23 Oxygens					Cations / 12 Oxygens			
	FE2	MIN	INT	MAX		FE2	FE3		
Si	6.447	6.440	6.397	6.308	Si	3.008	2.996	X_{An}	0.376
Al	1.553	1.560	1.603	1.692	Al		0.004	X_{Ab}	0622.
								X_{Or}	0.002
Al	0.795	0.785	0.727	0.605	Al	1.921	1.909		
Ti	0.119	0.119	0.118	0.116	Ti	0.003	0.003		
Fe^{3+}		0.050	0.355	0.993	Cr	0.002	0.002		
Mg	2.253	2.251	2.236	2.205	Fe^{3+}		0.092		
Fe^{2+}	1.833	1.795	1.564	1.067	Mg	0.638	0.635		
Mn				0.014	Fe^{2+}	2.029	1.930		
					Mn	0.091	0.091		
Fe^{2+}	0.272	0.258	0.170		Ca	0.333	0.331		
Mn	0.014	0.014	0.014		Na	0.006	0.006		
Ca	1.714	1.728	1.717	1.693					
Na			0.099	0.307					
Ca	0.016								
Na	0.401	0.401	0.299	0.085					
K	0.086	0.086	0.085	0.084					

cation sum which will be in excess of the ideal value in an oxygen-based mineral formula. In such cases the ferric iron content can be calculated, and, providing the analysis is complete and accurate, and the mineral stoichiometry is known, the calculated value will be absolutely correct.

In amphiboles one site, the A position, may range from empty to full; this effectively removes the constraint of fixed cations which makes the excess cations in the all-ferrous, oxygen-based formula more difficult to recognize. Nonetheless, limits can be placed on possible ferric iron contents through evaluation of amphibole site occupancy. These limits are basically ranges of acceptable values for various cation subtotals and

lead to the calculation of either minimum or maximum ferric contents.

Biotite may contain vacancies both in the octahedral sheets and at the interlayer sites. As a result, site occupancy cannot be used to constrain ferric contents.

Mineral analyses that are used in the application of geothermometers and geobarometers can be presented in two forms, as all-ferrous or ferric-iron-corrected formulae. The difference this makes to either pressure or temperature determinations will naturally depend on the method, or more specifically, which cation values are used in the method. With the exception of iron, the ratios between all other cations do not
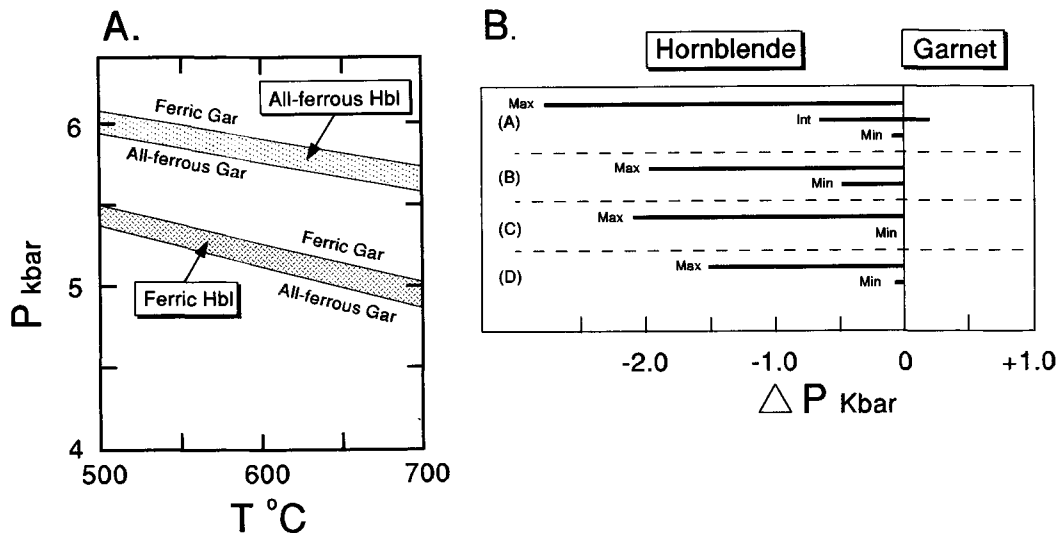
FIG. 8. Part A. A pressure (P)–temperature (T) diagram showing variations in P–T that are dependent upon hornblende and garnet formula calculation parameters for the hornblende–garnet–plagioclase–quartz geobarometer (Kohn and Spear, 1989). Patterned bands show ranges of P and T obtained using an all-ferrous (*All-ferrous Hbl*) and a ferric iron corrected (*Ferric Hbl*) hornblende formulae. The widths of the bands reflect P–T fluctuations that are due to the use of either an all-ferrous (*All-ferrous Gar*) or a ferric iron corrected (*Ferric Gar*) garnet formula. Part B. Comparison of pressure variations (delta P kbar) as a function of amphibole ferric estimate. *Solid bars* indicate the pressure differences between the all-ferrous (zero difference points) and ferric corrected hornblende formulae. *Max* and *Min* identifies the results from the maximum or minimum ferric-corrected hornblende formulae; in all cases the 13eCNK correction gave the maximum and the 15eNK correction gave minimum ferric estimates. *Int* is an intermediate value (see text). Example (A)—example from Table 1; example (B)—assemblage CK-77-117, (C) assemblage GM-73-82, and (D) assemblage GM-73-44 all from Ghent and Stout (1986). Note the effects of ferric estimates in the garnet could not be evaluated in assemblages (B) to (D) because only the mole fractions of Mg, Fe, Mn, and Ca for garnet were given. Pressures used to determine the differences were calculated at 600 °C. Note that the pressure difference for any two hornblende formulae (different ferric estimates) could be calculated using either ferric or all-ferrous garnet formulae (i.e. two delta P values could be calculated for each ferric hornblende formula); however, the effects of the garnet are essentially constant, so both calculations give the same delta P value.

change in ferric and ferrous mineral formulae. The absolute amounts of cations vary only slightly or not all, but X_{Mg} can show moderate differences between the two formulae. However, site occupancy of elements that may be located at more than one distinct structural site (e.g. tetrahedral and octahedral Al) may be very different in the ferric and ferrous mineral formulaa.

The three examples of geothermobarometers showed different sensitivities to ferric iron correction. The garnet–plagioclase–Al-silicate–quartz model was not strongly affected, which indicates small amounts of ferric iron are not particularly important. The hornblende–garnet–plagioclase–quartz geobarometer was moderately affected by ferric iron estimation in hornblende and rather less so by ferric iron estimation in garnet, and ferric estimations are recommended. Ferric iron strongly influences the garnet–biotite geothermometer, but empirical ferric estimates in biotite

are not possible. Interestingly, for this example, correcting the garnet alone for ferric iron will lead to worse results than simply using the all-ferrous formulae for both minerals.

Acknowledgements

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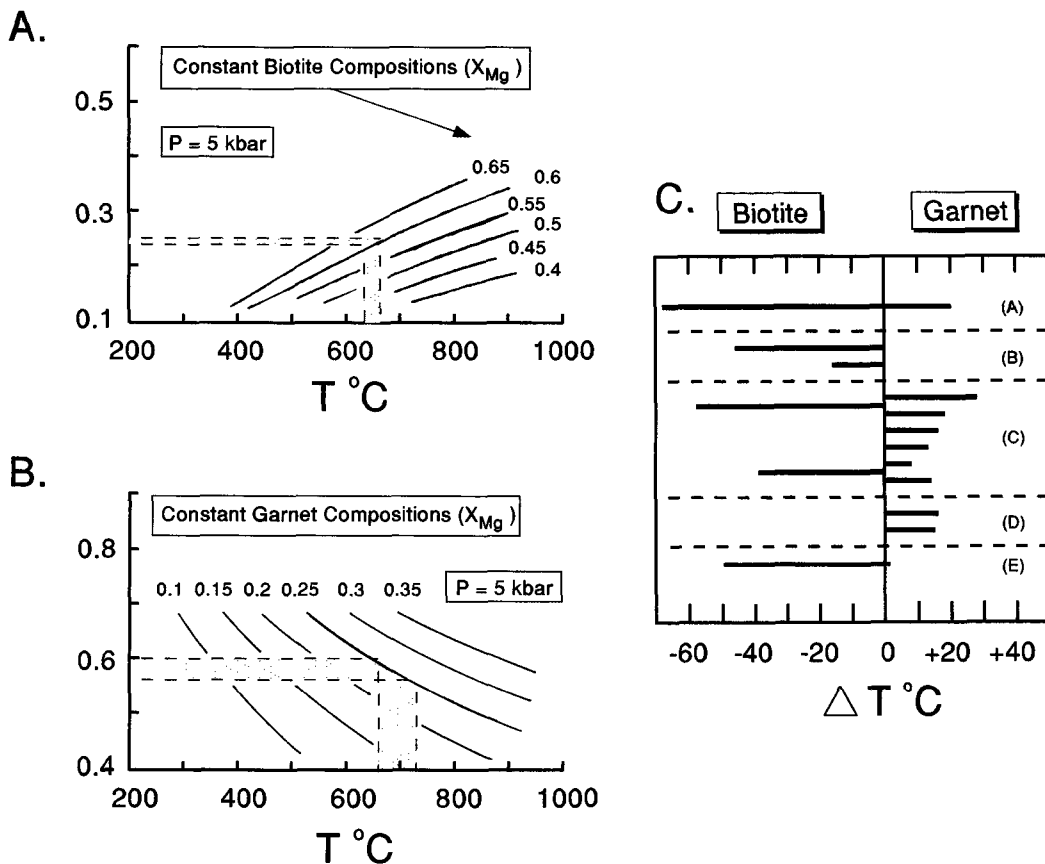
A.

B.

C.

FIG. 9. Parts A and B. Temperature (T) versus X_{Mg} [Mg/(Mg + Fe^{2+})] diagrams that show the extent to which X_{Mg} variation in garnet and biotite effects the T that is obtained from the garnet–biotite geothermometer (Ferry and Spear, 1978). Part A: Lines give T and X_{Mg} of garnet for various constant biotite compositions (X_{Mg}). Part B: Lines give T and X_{Mg} of biotite for various constant garnet compositions (X_{Mg}). Part C: Comparison of temperature variations (delta $T°C$) as a function of ferric estimates in garnet or biotite. *Solid bars* indicate differences between the all-ferrous garnet and biotite temperatures (zero difference points) and those obtained using the ferric corrected formulae. Example (A)—example composition from parts A and B; example (B)—temperature differences for biotite given by Dyar *et al.* (1987); example (C) data and temperature difference for biotite from Sevigny and Ghent (1989); example (D)—data from Humphreys and Van Bever Donker (1990); example (E)—biotite BL2925 and garnet BL2915E (core) from Yardley *et al.* (1980). Note: these analyses are not from the same sample, but come from the same zone.

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