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Error propagation in calculations of structural formulas

MARIO J. GIARAMITA, HOWARD W. DAY
Department of Geology, University of California, Davis, California 95616, U.S.A.

ABSTRACT

We have derived the algorithms for propagating analytical uncertainty through calculations of structural formulas including relative formula proportions of Fe^{2+} and Fe^{3+}, the distribution of cations among structural sites, and relevant cation sums. We analyzed approximately 50 spots each on a standard augite, bytownite, and hornblende and propagated the uncertainties in the measured oxide concentrations through the calculation of structural formulas of each mineral.

The analytical uncertainty of the oxide weight percent of an element severely underestimates the true uncertainty in the formula proportions of multivalent cations and cations that are assigned to more than one structural site. If the contributions of covariance to the total uncertainty are neglected, however, the uncertainty in the formula proportions of Si and of multivalent or multisite cations may be overestimated by as much as 25%. Covariance makes a relatively small contribution to the observed standard deviations of other cations except for data sets in which a few "bad" analyses are present. Whether uncertainties in formula proportions are magnified or reduced, compared to the uncertainties in the corresponding oxide weight percent, depends not only on the composition of the mineral, the structural formula to which the cations are assigned, and the type of normalization used in the calculation, but also on the relative sizes of the uncertainties in the oxide weight percent and the magnitude of the covariance terms.

For the bytownite, augite, and hornblende we studied, the propagated uncertainties of formula proportions of cations of major elements generally are less than 1–3%. However, they range as high as 36% for calculated Fe^{3+} and 25% for cations that lie in more than one structural site.

INTRODUCTION

The electron microprobe yields chemical data in the form of weight percents of the oxides from which structural formulas of minerals are calculated. Analytical uncertainties in the oxide concentrations can be determined by standard statistical methods, but determining the precision associated with cation proportions is not as simple.

Understanding the effect of analytical uncertainty on calculations of structural formulas is especially important for two reasons. First, we commonly want to know whether a microprobe analysis conforms to stoichiometric constraints. Unless uncertainties in calculated numbers of cations can be determined, it is not clear whether cation sums are significantly different than those required by stoichiometry. The smallest uncertainties that can be expected are derived by propagating counting errors through the calculation of the structural formula.

Second, there are certain petrologically important parameters derived from a calculated structural formula for which a corresponding oxide cannot be analyzed directly. Examples of these include the distribution of cations among sites in a mineral structure and the relative abundances of multivalent cations such as Fe. The uncertainties associated with these parameters cannot be estimated directly by using the uncertainty of a measured oxide concentration; they must be determined by propagating the errors in all the oxide concentrations through the calculation.

In this paper, we evaluate several methods of determining the uncertainties in structural formulas and the principal controls on error magnification. Our results demonstrate that complete error propagation including covariance terms is advisable for precise work. For many routine applications, however, there is little difference between measured uncertainties of oxide concentrations and the propagated uncertainties of the corresponding calculated cation proportions, except for multivalent cations and cations assigned to more than one structural site.

The basic equation

If some calculated value Y is a function of several measured variables, $Y = f(x_1, x_2, \cdots x_n)$, then the uncertainty of Y is given by the basic equation for error propagation (Bevington, 1969):

$$\sigma_Y^2 = \sigma_{x_1}^2(\partial Y/\partial x_1)^2 + \sigma_{x_2}^2(\partial Y/\partial x_2)^2 + 2\sigma_{x_1x_2}(\partial Y/\partial x_1)(\partial Y/\partial x_2) + \cdots$$

or (Hahn and Shapiro, 1967)

$$\sigma_Y^2 = \sum_{i=1}^{n}\sum_{j=1}^{n} \sigma_{x_ix_j}(\partial Y/\partial x_i)(\partial Y/\partial x_j) \qquad (1)$$

Table 1 contains the definition of all variables. Two assumptions underlie the derivation of these expressions: (1) The measured variables and calculated parameters are derived from approximately normally distributed populations, and (2) the error-propagation equation is an approximation based on a Taylor series expansion about the point where each of the variables takes on its mean value. The contribution of terms of higher order than the first partial derivatives is assumed to be negligible (Roddick, 1987).

Both of these assumptions are satisfied by calculations of structural formulas based on microprobe analyses. Measured oxide concentrations are likely to be normally distributed because, if a series of replicate measurements are subject only to random errors, the frequency distribution of those values will be Gaussian or normal (Bertin, 1980). In addition, instrumental error often is normally distributed (Hahn and Shapiro, 1967), and a major source of uncertainty in microprobe measurements is the counting error, which also has a normal distribution (Bertin, 1980). Finally, the mean of a parameter dependent on four or more variables from different populations tends to be normally distributed even for small values of n (Roddick, 1987, who credited Eisenhart, 1963, and Hahn and Shapiro, 1967).

Roddick (1987) also pointed out that the omission of the higher-order terms of the Taylor expansion produces exact errors for linear functions and is usually valid for other functions. It is necessary to verify that the functions employed in calculations of structural formulas are linear within the limits of analytical uncertainty of the measured variables. We examined this problem by calculating the contribution of the next-higher-order term in the error-propagation equation to the uncertainties associated with the calculated structural formulas of the three examples below. The worst case we found was a higher-order contribution equal to 0.53% of the value calculated by the basic equation. Therefore, we concluded that the functions for calculating structural formulas from oxide data are linear within the regions of interest.

TABLE 1. Definition of variables

b^c	cation basis for structural-formula calculation
b^o	oxygen basis for structural-formula calculation
c_i	number of cations of the ith element in a structural formula
c_i^c	number of cations of the ith element in cation-basis structural formula
c_i^o	number of cations of the ith element in oxygen-basis structural formula
c_i^{ox}	number of cations in the oxide of the ith element
E_c	counting error $= (n_c)^{1/2}$
f_i	formula weight of the oxide of the ith element
Fe*	total Fe
k_i^c	$= c_i^{ox}/f_i$
k_i^o	$= c_i^{ox}/f_i$
l_i	number of cations of the last element (i) to fill a structural site
n	number of measurements
n_c	number of counts
o_c	$= \dfrac{\sum_{i=1}^{n} w_i k_i^o b^c}{\sum_{i=1}^{n} w_i k_i^c}$: total number of oxygens on a cation basis
o_i^{ox}	number of oxygen anions in the oxide of the ith element
r_i	number of cations of element i remaining after element i is last to fill a site
s	number of cations that can be accommodated in a structural site
s^c	$= \sum_{i=1}^{n} w_i k_i^c$: sum of mole numbers of cations
s^o	$= \sum_{i=1}^{n} w_i k_i^o$: sum of mole numbers of oxygen anions
w_i	weight percent of the oxide of the ith element
X_i^o	$= w_i k_i^o / s^o$: fraction of total oxygen anions that reside in the ith oxide
X_i^c	$= w_i k_i^c / s^c$: fraction of total cations that reside in the ith oxide
$x_{i,k}$	kth measurement of the ith variable
$x_{i,m}$	$= \sum_{i=1}^{n} x_i/n$: mean value of the ith variable
$\partial x_i/\partial v_j$	partial derivative of x_i with respect to v_j, evaluated at $x_{i,m}$, all $(v_k)_{k \neq j}$ constant
$\rho_{x_i x_j}$	$= \sigma_{x_i x_j}/\sigma_{x_i}\sigma_{x_j}$: coefficient of correlation between x_i and x_j
$\sigma_{x_i x_j}$	$= [1/(n-1)] \sum_{k=1}^{n} (x_{i,k} - x_{i,m})(x_{j,k} - x_{j,m})$: covariance of n measurements of x_i and x_j
$\sigma_{x_i}^2$	$= \sigma_{x_i x_j}$: variance, a special case of covariance
σ_{x_i}	$= (\sigma_{x_i}^2)^{1/2}$: standard deviation of n measurements x_i

Previous work

Several approaches to error propagation appear in the geological literature (Dalrymple and Lanphere, 1971; Anderson, 1976; Ludwig, 1980; Rees, 1984; Hodges and Crowley, 1985; Hodges and McKenna, 1987; see Roddick, 1987, for a complete summary), but, to our knowledge, analysis of uncertainties in calculated structural formulas in minerals has not been reported. The Monte Carlo method (e.g., Anderson, 1976) simulates an error distribution in the calculated value by large numbers of repeated calculations. The input parameters for each cycle are derived from random variations in the measured values within the limits of their measured uncertainties. Roddick (1987) presented a standard numerical method, derived from the basic error-propagation equation, that takes correlation of errors among variables into account and incorporates a test for linearity.

APPLICATION TO CALCULATIONS OF STRUCTURAL FORMULAS

The method of propagating errors proposed herein is to derive analytical formulations that make use of the basic error-propagation equation (Eq. 1). The method produces errors that are "exact" provided the assumptions implicit in the use of the basic equation are valid.

Analytical solutions are specific to individual types of calculations because they require partial derivatives of the functions by which desired values are obtained. Such specific solutions may be desirable for routine procedures such as the calculation of mineral formulas from chemical data. Calculations of structural formulas are based on simple functions having simple derivatives. Consequent-

ly, the analytical formulation for propagating uncertainties of cation proportions is widely applicable and easily programmed.

The formula proportion of a cation is a function of the measured concentrations of all the oxides, or $c_i = f(w_1, w_2, \cdots w_n)$. Hence, by Equation 1,

$$\sigma_{c_i}^2 = \sum_{j=1}^{n} \sum_{k=1}^{n} \sigma_{w_j w_k} (\partial c_i / \partial w_j)(\partial c_i / \partial w_k). \quad (2)$$

Equation 2 reveals that determining the uncertainty associated with a calculated formula proportion of cations requires only the covariance matrix for the measured oxide concentrations ($\sigma_{w_j w_k}$, Table 1) and partial derivatives of the functions for the calculated numbers of cations ($\partial c_i / \partial w_j$). If the errors in the oxide concentrations are uncorrelated, the covariance terms can be dropped from the equation, and the resulting expression is

$$\sigma_{c_i}^2 = \sum_{j=1}^{n} \sigma_{w_j}^2 (\partial c_i / \partial w_j)^2. \quad (3)$$

The function for calculating the formula proportion of a particular cation depends upon whether it is normalized on an oxygen basis (superscript O) or on a cation basis (superscript c). For an oxygen-basis calculation,

$$c_i^{\mathrm{O}} = \frac{w_i (c_i^{\mathrm{ox}}/f_i) b^{\mathrm{O}}}{s^{\mathrm{O}}} = \frac{w_i k_i^{\mathrm{c}} b^{\mathrm{O}}}{s^{\mathrm{O}}}. \quad (4)$$

The partial derivative of c_i^{O} with respect to the weight percent of the oxide of the same cation is given by

$$\partial c_i^{\mathrm{O}} / \partial w_i = \frac{s^{\mathrm{O}} k_i^{\mathrm{c}} b^{\mathrm{O}} - w_i k_i^{\mathrm{c}} k_i^{\mathrm{O}} b^{\mathrm{O}}}{(s^{\mathrm{O}})^2},$$

whereas the partial derivative of c_i^{O} with respect to the weight percent of an oxide of a different cation is given by

$$(\partial c_i^{\mathrm{O}} / \partial w_j)_{i \neq j} = -\frac{w_i k_i^{\mathrm{c}} k_j^{\mathrm{O}} b^{\mathrm{O}}}{(s^{\mathrm{O}})^2}.$$

The function for the formula proportion of a particular cation normalized to a cation basis is

$$c_i^{\mathrm{c}} = \frac{w_i (c_i^{\mathrm{ox}}/f_i) b^{\mathrm{c}}}{s^{\mathrm{c}}} = \frac{w_i k_i^{\mathrm{c}} b^{\mathrm{c}}}{s^{\mathrm{c}}}. \quad (5)$$

The two forms of the partial derivatives of this function are

$$\partial c_i^{\mathrm{c}} / \partial w_i = \frac{s^{\mathrm{c}} k_i^{\mathrm{c}} b^{\mathrm{c}} - w_i (k_i^{\mathrm{c}})^2 b^{\mathrm{c}}}{(s^{\mathrm{c}})^2},$$

and

$$(\partial c_i^{\mathrm{c}} / \partial w_j)_{i \neq j} = -\frac{w_i k_i^{\mathrm{c}} k_j^{\mathrm{c}} b^{\mathrm{c}}}{(s^{\mathrm{c}})^2}.$$

In order to propagate the uncertainties in the measured oxides through the calculation of structural formulas, the derivatives and the elements of the covariance matrix must be substituted into Equation 2.

In addition to the formula proportions of cations of each element, the relative abundances of Fe^{2+} and Fe^{3+}, the distribution of cations among sites, and cation sums are routinely included in calculations of structural formulas. Below, we analyze the functions by which these parameters are derived and calculate their partial derivatives. In all cases, the functions are simply linear combinations of the functions for calculating formula proportions, derived above, and, hence, should also behave in a linear fashion within the ranges of their uncertainties.

The valence of Fe

The electron microprobe cannot discriminate between Fe^{2+} and Fe^{3+} and the analyst has the option of reporting all the Fe in a sample as either FeO or Fe_2O_3. If total Fe (Fe*) is reported as FeO, the abundances of Fe^{2+} and Fe^{3+} cations can be calculated from the oxygen deficiency that arises from the attempt to normalize the structural formula to a fixed number of oxygens and fixed number of cations. The oxygen deficiency is the difference between b^{O}, the number of oxygens to which the structural formula is normalized, and o_{c}, the number of oxygens calculated on a cation basis. For each missing oxygen, 2 FeO's are converted to Fe_2O_3, and the extra oxygen "created" balances the deficiency.

The function for calculating the number of Fe^{3+} cations is $c_{Fe^{3+}} = 2(b^{\mathrm{O}} - o_{\mathrm{c}})$ (Table 1). Expanding o_{c}, this expression can be written as

$$c_{Fe^{3+}} = 2\left(b^{\mathrm{O}} - \frac{\sum_{i=1}^{n} w_i k_i^{\mathrm{O}} b^{\mathrm{c}}}{\sum_{i=1}^{n} w_i k_i^{\mathrm{c}}} \right). \quad (6)$$

The partial derivatives of this function with respect to the oxide weight percents have the form

$$\partial c_{Fe^{3+}} / \partial w_i = 2b^{\mathrm{c}} \left(\frac{s^{\mathrm{O}} k_i^{\mathrm{c}} - s^{\mathrm{c}} k_i^{\mathrm{O}}}{(s^{\mathrm{c}})^2} \right).$$

The number of Fe^{2+} cations is calculated by the difference

$$c_{Fe^{2+}} = c_{Fe^*} - c_{Fe^{3+}}, \quad (7)$$

and the partial derivatives by

$$\partial c_{Fe^{2+}} / \partial w_i = \partial c_{Fe^*} / \partial w_i - \partial c_{Fe^{3+}} / \partial w_i.$$

The terms on the right-hand side of the derivatives of Equations 6 and 7 have the form of the derivatives of Equation 5. The uncertainties associated with the formula proportions of Fe^{2+} and Fe^{3+} can be calculated by substituting the partial derivatives of Equations 6 and 7 and the elements of the covariance matrix of oxide concentrations into Equation 2.

Site assignments

The uncertainties associated with formula proportions before assignment of the total Fe to Fe^{2+} and Fe^{3+} cations and cations to structural sites are the same as for the general structural-formula calculations described previously. However, major differences arise as a result of distributing cations of a single element between two structural sites. For example, Al is distributed between tetrahedral and octahedral sites in many minerals.

Cations are assigned to sites in three possible ways. If all of the cations of a particular element are assigned to a single site, for example, $c_{Si} = c_{[4]Si}$, then the derivatives required are simply those of Equations 4 or 5.

If a cation is the last to fill a site, but the site is filled without using all the cations of that element, the function for calculating the number of cations of the last species assigned to the site is

$$l_i = s - \sum_{j \neq i} c_j^c \tag{8}$$

where l_i is the number of cations of the last species to fill the site, s is the total number of cations the site can accommodate, the c_j^c values are numbers of cations calculated on a cation basis, and j includes only species in the site besides l_i. The partial derivatives of this function are given by

$$\partial l_i / \partial w_k = -\sum_{j \neq i} \partial c_j^c / \partial w_k,$$

where the j again refers only to cations in the site other than l_i. Note that similar functions would also apply to structural formulas normalized to an oxygen basis, in which case c_i^o would be the appropriate term in the previous two equations. These derivatives commonly imply that $\sigma_{[4]Al} = \sigma_{Si}$ for minerals in which all Si is tetrahedrally coordinated and that $\sigma_{M4Na} = \sigma_{M4Ca}$ in those normalization schemes that exclude transition-metal cations from the M4 site of amphiboles.

The cations of an element remaining after previous assignment to another site are usually allocated to only one other site. For example, the Al cations remaining after assignment to the tetrahedral site are usually allocated to a single, octahedral site. The function for calculating the number of cations assigned to a second site in this manner is

$$r_i = c_i^c - l_i, \tag{9}$$

where r_i is the remaining number of cations of element i. The partial derivatives necessary for error propagation are then

$$\partial r_i / \partial w_k = \partial c_i^c / \partial w_k - \partial l_i / \partial w_k.$$

The terms on the right-hand side of the derivatives of Equations 8 and 9 have the form of one of the derivatives of Equations 4–9. Substitution of the appropriate derivatives and the covariance matrix of the oxide analyses into Equation 2 permits the calculation of uncertainties in l_i or r_i.

Cation sums

Cation sums commonly are used to judge the quality of a microprobe analysis and to examine petrological behavior in discriminant diagrams (e.g., Laird and Albee, 1981). In order to calculate the uncertainty associated with a cation sum, it is necessary to calculate the partial derivatives of the function by which the sum is calculated. The partial derivative of the sum is given by $\partial c_{sum} / \partial w_i = \partial c_x / \partial w_i + \partial c_y / \partial w_i + \partial c_z / \partial w_i \cdots$. The terms on the right are the derivatives of one or more of the Equations 4–9, and the uncertainty of the cation sum is calculated by inserting this expression into Equation 1.

Methods

In order to test the efficiency and applicability of these uncertainty calculations, we analyzed three natural minerals using the automated WDS Cameca SX50 electron microprobe at the University of California, Davis. Analyses of 30 s for between 50 and 60 spots were performed on each of three standard natural minerals using other analyzed natural minerals as standards. The operating conditions were 15 keV accelerating potential, a spot size of approximately 3 μm, and a beam current of 20 nA for both hornblende and augite analyses and 10 nA for bytownite. Matrix corrections were done using a ZAF scheme.

Three standards were analyzed as unknowns: Kakanui hornblende and augite (Jarosewich and others, 1980) and a bytownite collected from a gabbro sill in Crystal Bay, Minnesota. Structural formulas for bytownite were normalized to eight oxygens assuming all Fe to be Fe^{3+}. Augite structural formulas were normalized to four total cations and six oxygen anions. Hornblende formulas were calculated on a 23-oxygen basis and by three cation normalization schemes as discussed below. Analyses in which any of the oxides differed by three or more standard deviations from the mean were discarded as "bad" analyses. Average analyses are presented in Table 2.

Results

Comparison of propagated and measured uncertainties

Tables 3, 4, and 5 contain the structural formulas of bytownite, augite, and hornblende calculated from the mean oxide analyses in Table 2 and the uncertainties in the cation proportions calculated in four ways. Column 1 in each table contains the standard deviations of the cation proportions calculated by a complete error propagation (Eq. 2) of the uncertainties in the weight percent oxide analyses (Table 2). We tested the validity of the complete error propagation by calculating structural formulas for each individual spot analysis and determining the standard deviations of the ~50 such cation proportions. These estimates (column 4, Tables 3, 4, and 5) are virtually identical to uncertainties obtained by complete propagation of the uncertainties in the weight percent ox-

TABLE 2. Average microprobe analyses of bytownite, augite, and hornblende

	Bytownite* $n = 59$				Augite** $n = 52$				Hornblende** $n = 54$			
	w_i	σ	σ%	E_c (%)	w_i	σ	σ%	E_c (%)	w_i	σ	σ%	E_c (%)
SiO_2	48.94	0.26	0.53	0.16	50.16	0.23	0.45	0.08	40.20	0.30	0.76	0.15
TiO_2	n.d.	—	—	—	0.84	0.05	5.92	0.87	4.93	0.15	3.07	0.59
Al_2O_3	32.13	0.22	0.68	0.18	8.04	0.08	0.98	0.18	15.02	0.18	1.21	0.25
Fe_2O_3	0.43	0.09	20.14	0.35	—	—	—	—	—	—	—	—
Cr_2O_3	n.d.	—	—	—	0.15	0.05	36.28	2.98	n.d.	—	—	—
FeO	n.d.	—	—	—	6.18	0.16	2.57	0.54	10.54	0.45	4.28	0.42
MnO	n.d.	—	—	—	0.15	0.04	27.49	2.40	0.10	0.11	102.92	3.50
MgO	n.d.	—	—	—	16.59	0.14	0.83	0.14	12.96	0.32	2.49	0.17
CaO	15.22	0.23	1.49	0.40	15.97	0.15	0.96	0.19	9.74	0.25	2.54	0.23
Na_2O	2.76	0.09	3.11	0.83	1.20	0.04	2.96	0.59	2.40	0.09	3.83	0.60
K_2O	0.07	0.02	32.83	4.56	n.d.	—	—	—	2.03	0.07	3.47	0.38
	99.29				99.12				97.92			

Note: E_c (%) = percent counting error = $100(\sqrt{n_c})/n_c$, where n_c = counts; n = number of analyses; n.d. = not determined; w_i = weight percent of the oxide; σ = standard deviation; σ% = percent standard deviation.
* Total Fe as Fe_2O_3.
** Total Fe as FeO.

ides (column 1, Tables 3, 4, and 5). We conclude that our analytical formulations of the error propagation yield a correct estimate of the true dispersion of the structural formulas due to analytical uncertainty.

It might be proposed that the uncertainty in the oxide weight percent (Table 2) is an adequate measure of the uncertainty in a cation proportion. Our results show that this can be a dangerous assumption in cases for which the proportion of multivalent cations must be estimated or cations must be distributed among structural sites, but otherwise the estimate is very good. The relative uncertainties in many cations (column 1, Tables 3, 4, and 5) are very similar to the relative uncertainties in the corresponding oxides (Table 2; column 3, Tables 3, 4, and 5). However, the relative uncertainties of the oxide concentrations of Al_2O_3, FeO, and Na_2O (Table 2) severely underestimate the relative uncertainties of $^{[4]}Al$,, $^{[6]}Al$, Fe^{2+}, and Fe^{3+} in augite and hornblende and ^{M4}Na and ^{A}Na in hornblende. Thus, our calculations show that uncertainty in multisite and multivalent cations cannot be estimated directly from the uncertainty in the corresponding oxide concentrations.

Correlation effects

Complete error propagation (Eq. 2) is time consuming, and it would be useful to know if comparable results could be obtained by partial error propagation (Eq. 3). Complete error propagation (column 1, Tables 3, 4, and 5) requires a covariance matrix and takes correlation of analytical errors into account, whereas partial error propagation (column 2; Tables 3, 4, and 5) requires only standard deviations of the measured variables and is valid only if the analytical errors are uncorrelated.

The uncertainties estimated by partial error propagation are, generally, somewhat higher than those estimated by including covariance terms (Tables 3, 4, and 5), but a few values are actually slightly lower. If covariance is neglected, the standard deviation of Si is overestimated by 10–15% (relative), the standard deviations of the Fe^{3+} and Fe^{2+} contents of augite and hornblende are overes-

TABLE 3. Average structural formula* and various measures of analytical uncertainty for bytownite

	cations (c_i^o)	1		2		3		4	
		σ	σ%	σ	σ%	σ	σ%	σ	σ%
Si	2.2476	0.0069	0.31	0.0080	0.36	0.0119	0.53	0.0069	0.31
Al	1.7392	0.0091	0.52	0.0099	0.57	0.0118	0.68	0.0091	0.52
Fe^{3+}**	0.0147	0.0030	20.41	0.0030	20.41	0.0030	20.14	0.0030	20.41
	4.0015	0.0064	0.17	0.0067	0.17			0.0060	0.15
Na	0.2458	0.0073	2.97	0.0076	3.09	0.0076	3.11	0.0073	2.79
K	0.0040	0.0013	32.50	0.0013	32.50	0.0013	32.83	0.0013	32.50
Ca	0.7490	0.0098	1.31	0.0105	1.40	0.0112	1.49	0.0098	1.31
	0.9988	0.0124	1.24	0.0128	1.28			0.023	1.23
Σc_i^o	5.0003	0.0070	0.14	0.0075	0.15			0.0070	0.14

Note: (1) complete error propagation (Eq. 2); (2) partial error propagation (Eq. 3); (3) product of fractional standard deviation of oxide and c_i; (4) standard deviations of cation proportions calculated from individual spot analyses.
* Cations normalized to 8 oxygens.
** Fe reported as Fe_2O_3.

TABLE 4. Average structural formula* and various measures of analytical uncertainty for augite

	cations (c_i^s)	1		2		3		4	
		σ	σ%	σ	σ%	σ	σ%	σ	σ%
Si	1.8264	0.0061	0.33	0.0070	0.38	0.0083	0.45	0.0061	0.33
$^{[4]}$Al	0.1736	0.0061	3.50	0.0070	4.04	0.0017	0.98	0.0061	3.50
	2.0000								
$^{[6]}$Al	0.1716	0.0070	4.07	0.0074	4.29	0.0017	0.98	0.0070	4.07
Ti	0.0231	0.0014	6.01	0.0014	5.90	0.0014	5.92	0.0014	6.02
Fe^{3+}**	0.0363	0.0130	35.90	0.0145	40.11	0.0009	2.57	0.0130	35.94
Cr	0.0043	0.0015	36.23	0.0015	36.25	0.0015	36.28	0.0010	36.29
Mn	0.0048	0.0013	27.53	0.0013	27.46	0.0013	27.49	0.0013	27.52
Mg	0.9002	0.0061	0.67	0.0064	0.71	0.0075	0.83	0.0061	0.67
Fe^{2+}	0.1520	0.0117	7.69	0.0139	9.12	0.0039	2.57	0.0117	7.69
Ca	0.6230	0.0052	0.84	0.0054	0.87	0.0060	0.96	0.0052	0.84
Na	0.0848	0.0024	2.84	0.0025	2.92	0.0025	2.96	0.0024	2.84
	2.0001								

Note: (1) complete error propagation (Eq. 2); (2) partial error propagation (Eq. 3); (3) product of fractional standard deviation of oxide and c_i; (4) standard deviations of cation proportions calculated from individual spot analyses.

* Cations normalized to 4 total cations.

** Fe^{3+} calculated as described in text.

timated by 12–25%, and the uncertainty in ^{A}Na of hornblende is overestimated by 17%. With the exception of Si, cations assigned only to one site and having only one valence state show little difference between the complete and partial error propagations.

If covariance terms are neglected, a small number of "bad" or "outlying" data may lead to either overestimates or underestimates of the uncertainty. The bytownite data in Table 3 are based on 59 analyses. We repeated the error analysis including a single "bad" analysis that originally was excluded because it had a low oxide total and because the concentrations of many of the oxides were greater than three standard deviations from the mean. The resulting differences between the complete and partial propagation of errors are larger when the bad analysis is included than when it is not (Table 3). The single bad analysis imparts a greater correlation among errors in the oxides that results in the covariance terms having a greater contribution to the uncertainty.

The differences between complete and partial error propagation are not large, but the relative differences may be as high as 25%. Partial error propagation (Eq. 3) is a better estimate of the complete uncertainty than the percent uncertainty in the oxide concentration for all cations except Si in hornblende (Table 5). Clearly, it is advisable to include the covariance terms (Eq. 2) where high precision is necessary.

Evaluating the quality of microprobe analyses

Bytownite. A problem facing any microprobe user is determining what constitutes a good analysis. Obviously, oxide totals for an anhydrous mineral should be near 100%. In addition, stoichiometric constraints on some minerals are well understood. For example, a feldspar analysis calculated with 8 oxygens should have 5 cations. Moreover, the sum of the trivalent and tetravalent cations in the tetrahedral sites should be 4, the sum of the divalent and univalent cations should be 1, and the number of trivalent cations in the tetrahedral site should be equal to one more than the total number of divalent cations.

It is possible to decide whether the cation sums are consistent with stoichiometric constraints by propagating the errors in the oxide concentrations through the calculation of the structural formula. These uncertainties are shown in Table 3. Within analytical uncertainty, by any of the methods of propagating it, the sum of the tetrahedrally coordinated cations is 4, the sum of univalent and divalent cations is 1, and the total number of cations is 5. Furthermore, the difference between total trivalent cations and 1 plus the number of Ca is only 0.0049, well within the uncertainties of both the sum and the difference either by partial or complete error propagation. Therefore, the plagioclase analysis is consistent with stoichiometric constraints within analytical precision.

Commonly, it is necessary to evaluate the quality of published microprobe analyses for which standard deviations of cation proportions are given, but covariances are not. Partial error propagation (Eq. 2) does not require the covariance among the oxide concentrations and for cation sums in bytownite yields very good approximations of the uncertainty. For example, Equation 2 yields an uncertainty of 0.0064 for the sum of Al + Si + Fe^{3+} cations, and Equation 3, 0.0067 (Table 3). Partial error propagation also provides good approximations of the uncertainty for the sums Na + K + Ca and the total number of cations in bytownite (Table 3). Consequently, in the absence of covariance information, we recommend using partial error propagation to obtain the uncertainties associated with cation sums in plagioclase.

In order for an analysis to be considered acceptable, each critical cation sum must lie within uncertainty of the value required by stoichiometry. If there are strong correlations between two cation sums being used to judge

TABLE 5. Average structural formula* and various measures of analytical uncertainty for hornblende

	cations (c_i^*)	1		2		3		4	
		σ	σ%	σ	σ%	σ	σ%	σ	σ%
Si	5.8185	0.0451	0.78	0.0494	0.85	0.0440	0.76	0.0452	0.78
$^{[4]}$Al	2.1815	0.0451	2.07	0.0494	2.26	0.0264	1.21	0.0452	2.07
Σ tet	8								
$^{[6]}$Al	0.3800	0.0606	15.95	0.0617	16.24	0.0046	1.21	0.0608	16.00
Fe^{3+}**	0.6591	0.1281	19.45	0.1588	24.09	0.0279	4.28	0.1281	19.44
Ti	0.5366	0.0161	3.00	0.0164	3.06	0.0165	3.07	0.0161	3.00
Mg	2.7952	0.0602	2.15	0.0573	2.05	0.0697	2.49	0.0605	2.16
Fe^{2+}	0.6162	0.1202	19.51	0.1452	23.56	0.0264	4.28	0.1204	19.54
Mn	0.0128	0.0132	103.13	0.0132	103.13	0.0132	102.92	0.0132	103.13
Σ M1,2,3	5								
Ca	1.5101	0.0373	2.47	0.0402	2.66	0.0384	2.54	0.0374	2.48
Na	0.4899	0.0373	7.61	0.0402	8.21	0.0188	3.83	0.0374	7.63
Σ M4	2								
Na	0.1834	0.0422	23.01	0.0495	26.99	0.0070	3.83	0.0421	22.96
K	0.3757	0.0136	3.62	0.0134	3.56	0.0130	3.47	0.0137	3.65
Σ A	0.5591	0.0453	8.10	0.0523	9.35			0.0452	8.08

Note: (1) complete error propagation (Eq. 2); (2) partial error propagation (Eq. 3); (3) product of fractional standard deviation of oxide and c_i; (4) standard deviations of cation proportions calculated from individual spot analyses.

* Calculated on a basis of 23 oxygens with cations normalized to 13 excluding Na, K, and Ca.

** Fe^{3+} calculated as described in text.

the analysis, the two criteria are not independent and the former statement may be a necessary, but not sufficient, criterion for acceptability at a given level of confidence. For example, a strong negative correlation between the sum of Na + K + Ca and the sum of Al + Si + Fe in bytownite must exist because the two sums contain all cations and the total cations are approximately constant. For the bytownite we studied,

$$\rho_{c_{Al+Si+Fe}c_{Na+K+Ca}} = -0.91,$$

where ρ is the correlation coefficient. Because of the strong correlation, calculation of the probability that both cation-sum criteria are satisfied simultaneously requires not only the variance of the two sums, but the covariance as well. The derivation of the such probability functions is beyond the scope of this paper, but the necessary covariance terms for the minerals we studied can be calculated by using the covariance matrices of the oxide concentrations given in Appendix 1, the derivatives of Equation 4–9, and Equation 8 of Roddick (1987).

Augite. The stoichiometry of the augite (Table 4) cannot be judged in the same way as that of the bytownite because we have chosen to normalize both the oxygen and the cations in the formula unit and all sites are filled with a specified number of cations. Because the formula unit was normalized to 4 cations, after allocating enough Si and Al to fill 2 tetrahedral sites, the remaining 2 octahedral sites must necessarily contain 2 cations.

The calculated number of Fe^{3+} cations (Table 4) is the only available stoichiometric test of the quality of the augite analysis. Notice that the calculated number of Fe^{3+} cations is significantly different from zero, despite being very small. The calculated value is about 20% higher than the value obtained by wet-chemical analysis (Jarosewich and others, 1980; P. Schiffman, 1986, personal communication), but the uncertainty associated with the calculation is about 36%. The uncertainty is large, in part, because the amount of Fe^{3+} is small, but the method of estimating Fe^{3+} content is accurate within the limits of analytical precision.

Charge-balance criteria that might be used to test the quality of the augite analysis are not independent of the Fe^{3+} calculation. For example, the criterion

$$^{M}[2Ti^{4+} + Al^{3+} + Fe^{3+} + Cr^{3+}] - [^{M}Na + {}^{[4]}Al] = 0$$

requires that the charge excess created by the substitution of trivalent and tetravalent cations in the M sites must be balanced by substitutions of univalent cations in the M sites and trivalent cations in the tetrahedral sites. This criterion is satisfied exactly for the mean augite composition because either positive or negative Fe^{3+} was calculated from each spot analysis in order to achieve charge balance. Unless the amount of Fe in an analysis is very small, it generally will be possible to balance the charge exactly for all spots, and both the mean and standard deviation of the charge-balance criterion will be zero. Consequently, the criterion is not a very stringent test of the quality of the analysis because such charge balance is required by the calculation of the structural formula.

For many Fe-rich minerals, failure to meet such charge-balance criteria may imply that negative Fe^{3+} was not permitted by the calculation procedure. Failure to allow negative Fe^{3+} contents in structural formulas may produce a systematically biased mean and standard deviation of the apparent Fe^{3+}. Consider, for example, an augite that contains *no* Fe^{3+}. Analytical error in the weight

percent of each oxide should lead to a dispersion of the calculated Fe^{3+} to values slightly above *and below* zero. Failure to include negative values will bias the mean value of calculated Fe^{3+} to a small positive value and will bias the standard deviation to lower values in such a way that the small positive mean may appear to be significantly different than zero. If the mean of several analyses leads to a negative Fe^{3+} content that is significantly different from zero, there is serious, systematic error either in the analyses or the assumptions on which the calculation is based. Consequently, it is important to permit negative Fe^{3+} in the calculations in order to evaluate properly the significance of the Fe^{3+} calculation.

Hornblende. The hornblende analyses also cannot be treated in the same way as the bytownite analysis because all sites except the A site are filled with a specified number of cations. Many normalization schemes have been devised to calculate structural formulas in amphiboles (see Robinson et al., 1982, for a detailed review), but we examined only three schemes. In the 13*eNKC* scheme, the sum of all cations excluding Na, K, and Ca are normalized to 13. This scheme excludes Fe and Mg from and maximizes Na in the M4 site (Stout, 1972). In the 15*eNK* scheme, the sum of all cations excluding Na and K is normalized to 15. Of the three schemes considered, this one provides the minimum number of Fe^{3+} cations and forces all the Na into the A site (Stout, 1972).

For each normalization scheme, the cations were assigned to structural sites in the order Si, Al, Fe^{3+}, Ti^{4+}, Mg, Fe^{2+}, Mn, Ca, and Na (Robinson et al., 1982). When a site was filled, the remaining cations were placed in the next available site. The eight tetrahedral sites were filled first with Si, Al, Fe^{3+}, and Ti^{4+} if necessary. The remaining cations were placed first into the five M1, M2, and M3 sites and then into the two M4 sites. All the remaining cations were assigned to the A site.

A poor analysis or poor choice of calculation scheme is indicated by more than eight Si cations, fewer than eight tetrahedral cations or two M4 cations, or by more than one cation in the A site. A negative number of Fe^{3+} cations is unacceptable, and Robinson et al. (1982) suggested that a normalization resulting in Ca in the M1, M2, and M3 sites is also unacceptable.

The 13*eNKC* normalization was the only scheme that yielded an acceptable structural formula for the hornblende analysis. Notice that the calculated Fe^{3+} (Table 5) is significantly different than zero and that other stoichiometric constraints mentioned above are met. Moreover, the calculated proportion of Fe^{3+} exceeds the reported value (Jarosewich and others, 1980) by less than one standard deviation of the calculated value. The 15*eNK* scheme yielded -0.88 ± 0.16 Fe^{3+} cations, demonstrating that the negative value for Fe^{3+} was not entirely the result of analytical uncertainty. Likewise, the 15*eK* normalization scheme required 0.16 ± 0.04 Ca cations in the M1, M2, and M3 sites, and the propagated uncertainty demonstrates that the Ca in these sites is not merely an artifact of analytical error.

The site charge-balance criterion (Papike et al., 1974),

$$[^{A}(Na + K) + {}^{[6]}(Al + Fe^{3+} + 2Ti + Cr) - ({}^{[6]}Al + {}^{M4}Na)] = 0,$$

also is not independent of our treatment of the calculated Fe^{3+}. The mean value of the site charge-balance criterion and its uncertainty are zero because all spots analyzed achieved charge balance by means of calculated Fe^{3+}. Consequently, the site charge-balance criterion provides no information that is independent of the Fe^{3+} calculation.

Application to discriminant diagrams

The structural formulas of minerals are commonly used as discriminators of petrologic behavior. For example, the covariation of ${}^{M4}Na$ and ${}^{[6]}Al + Fe^{3+} + Ti + Cr$ in amphibole was used to discriminate among metamorphic grades in mafic schist from Vermont (Laird and Albee, 1981). Although the data upon which such plots are based seldom contain rigorous estimates of the errors associated with the cation sums, the information is critical for evaluating their significance.

The microprobe data and uncertainties reported in Appendix I of Laird and Albee (1981) are an unusual example of data that permit a detailed analysis. We propagated the errors (Eq. 3) in the oxide concentrations through the calculation of the number of ${}^{M4}Na$ cations and the sum of ${}^{[6]}Al + Fe^{3+} + Ti + Cr$ cations for one sample each from the biotite zone, the garnet zone, and the kyanite-staurolite zone of Laird and Albee (1981). Although the uncertainties generally are larger than the symbols published in Figure 2 of Laird and Albee (1981), our analysis demonstrates that analytical error is not a significant source of scatter on this graph (Fig. 1) and supports the conclusion that the observed variations of amphibole chemistry reflect real variations in metamorphic conditions.

Laird and Albee (1981) reported no information about correlation among the oxides analyzed. Using the data from the hornblende analyzed in this study, we attempted to evaluate the validity of error propagation in the absence of this information by examining uncertainty in the sum. The estimated uncertainty of the sum Al + Fe + Ti + Cr is 0.1120 by Equation 3, without covariance terms, and 0.0899 by Equation 2, with all covariance terms. Considering the purposes for which these diagrams are commonly used, the differences in the uncertainties calculated by the two methods are very small.

For some applications, such as regression analysis (e.g., Ludwig, 1980; Roddick, 1987), it is advisable to evaluate correlation between calculated parameters. We used the covariance matrix for our hornblende analyses (App. 1) to examine correlation between the number of ${}^{M4}Na$ cations and the cation sum ${}^{[6]}Al + Fe^{3+} + Ti + Cr$ (Eq. 8 in Roddick, 1987). The strong positive correlation between the calculated parameters in this single sample ($\rho = 0.69$) might pose a problem for curve fitting or discrimination between very similar samples. However, the analytical

TABLE 6. Structural formula, counting errors, and error magnifications for bytownite

	Uncertainties based on counting errors					Magnifications*	
	1 c_i^o (cations)	2 E_c (meas.)	3 E_c (%) (meas.)	4 E_c (hyp.)	5 E_c (%) (hyp.)	6 σ% (meas.)	7 E_c (%) (hyp.)
Si	2.2476	0.0022	0.10	0.0040	0.18	0.58	0.56
Al	1.7392	0.0027	0.16	0.0049	0.28	0.76	0.87
Fe^{3+}	0.0147	0.0001	0.37	0.0001	0.39	1.0	1.2
	4.0015	0.0018	0.04	0.0018	0.04		
Na	0.2458	0.0020	0.81	0.0009	0.37	0.95	1.2
K	0.0040	0.0002	4.88	0.0000	0.35	0.99	1.1
Ca	0.4790	0.0028	0.37	0.0027	0.36	0.88	1.1
	0.9988	0.0034	0.34	0.0030	0.30		
Total	5.0003	0.0020	0.04	0.0021	0.04		

Note: (1) 8-oxygen basis structural formula; (2) absolute uncertainty obtained by propagating measured counting error (Table 2; Eq. 3); (3) column 2 as percent of column 1; (4) absolute uncertainty obtained by propagating a hypothetical counting error of 0.32% (Eq. 3); (5) column 4 as percent of column 1; (6) σ% from column 1, Table 3, based on complete error propagation (Eq. 2), oxide uncertainty from Table 2; (7) E_c (%) from column 5, E_c (%) in oxide = 0.32.

* Error magnifications calculated as (uncertainty% cation)/(uncertainty% oxide).

uncertainties attached to a single sample are clearly much smaller than the size of the fields in which they are enclosed (Fig. 1), and the differences between fields must be real. Assuming our correlation data (App. 1) apply in general, they might be used to estimate correlation among parameters derived from microprobe analyses of other plagioclase, augite, or hornblende samples.

Error magnification

The uncertainties obtained by propagating counting error through the calculations of structural formulas might be considered a measure of the unattainable "best" structural formula for a perfectly homogeneous mineral grain analyzed under perfectly stable analytical conditions. Even if the only source of uncertainty in an oxide analysis is counting statistics, however, uncertainties in the structural formula are commonly magnified by factors of up to 10 or 15. For example, counting errors of about 0.5% of the concentration of iron oxide (Table 2) are magnified to 2.25% and 7.26% of calculated Fe^{3+} in hornblende and augite, respectively (column 3, Tables 7 and 8).

The way in which uncertainties are magnified depends primarily on the composition of the mineral and the normalization scheme by which the structural formula is calculated. In order to isolate the effects of mineral composition from other contributions to error magnification, we considered counting errors for a hypothetical analysis in which each element was analyzed for 10^5 counts. This value is intermediate between the number of counts commonly accumulated for major and minor elements and yields a counting error of 0.32%. The hypothetical counting errors in the oxide analyses were propagated using

TABLE 7. Structural formula, counting errors, and error magnifications for augite

	Uncertainties based on counting errors					Magnifications*	
	1 c_i^o (cations)	2 E_c (meas.)	3 E_c (%) (meas.)	4 E_c (hyp.)	5 E_c (%) (hyp.)	6 σ% (meas.)	7 E_c (%) (hyp.)
Si	1.8264	0.0012	0.07	0.0036	0.19	0.73	0.59
$^{[4]}Al$	0.1736	0.0012	0.72	0.0036	2.05	3.6	6.4
	2.0000						
$^{[6]}Al$	0.1716	0.0013	0.77	0.0033	1.92	4.2	6.0
Ti	0.0231	0.0002	0.86	0.0001	0.36	1.0	1.1
Fe^{3+}	0.0363	0.0026	7.26	0.0068	18.76	14	58
Cr	0.0043	0.0001	2.97	0.0000	0.38	1.0	1.2
Mn	0.0048	0.0001	2.40	0.0000	0.37	1.0	1.2
Mg	0.9002	0.0011	0.12	0.0026	0.29	0.81	0.91
Fe^{2+}	0.1520	0.0025	1.62	0.0066	4.37	3.0	14
Ca	0.6230	0.0011	0.17	0.0019	0.31	0.88	0.97
Na	0.0848	0.0005	0.58	0.0003	0.35	0.96	1.1
	2.0001						

Note: (1) 4-cation basis structural formula; (2) absolute uncertainty obtained by propagating measured counting error (Table 2; Eq. 3); (3) column 2 as percent of column 1; (4) absolute uncertainty obtained by propagating a hypothetical counting error of 0.32% (Eq. 3); (5) column 4 as percent of column 1; (6) σ% from column 1, Table 4, based on complete error propagation (Eq. 2), oxide uncertainty from Table 2; (7) E_c (%) from column 5, E_c (%) in oxide = 0.32.

* Error magnifications calculated as (uncertainty% cation)/(uncertainty% oxide).

TABLE 8. Structural formula, counting errors, and error magnifications for hornblende

	Uncertainties based on counting errors					Magnifications*	
	1 c_i^c (cations)	2 E_c (meas.)	3 E_c (%) (meas.)	4 E_c (hyp.)	5 E_c (%) (hyp.)	6 σ% (meas.)	7 E_c (%) (hyp.)
Si	5.8185	0.0065	0.11	0.0117	0.20	1.0	0.62
$^{[4]}$Al	2.1815	0.0065	0.30	0.0117	0.53	1.7	1.7
Σ tet	8						
$^{[6]}$Al	0.3800	0.0063	1.64	0.0096	2.48	13	7.8
Fe^{3+}	0.6591	0.0145	2.25	0.0203	3.12	4.5	9.8
Ti	0.5366	0.0031	0.58	0.0019	0.35	0.98	1.1
Mg	2.7952	0.0045	0.16	0.0082	0.29	0.86	0.91
Fe^{2+}	0.6162	0.0126	2.00	0.0195	3.06	4.6	9.6
Mn	0.0128	0.0005	3.49	0.0000	0.32	1.0	1.0
Σ M1,2,3	4.9999						
Ca	1.5101	0.0038	0.25	0.0054	0.36	0.97	1.1
Na	0.4899	0.0038	0.77	0.0054	1.12	2.0	3.5
Σ M4	2.0000						
Na	0.1834	0.0057	3.09	0.0064	3.47	6.0	11
K	0.3757	0.0015	0.40	0.0014	0.36	1.0	1.1
Σ A	0.5591	0.0057	1.08	0.0069	1.23		

Note: (1) 13*eNKC*-basis structural formula; (2) absolute uncertainty obtained by propagating measured counting error (Table 2; Eq. 3); (3) column 2 as percent of column 1; (4) absolute uncertainty obtained by propagating a hypothetical counting error of 0.32% (Eq. 3); (5) column 4 as percent of column 1; (6) σ% from column 1, Table 5, based on complete error propagation (Eq. 2), oxide uncertainty from Table 2; (7) E_c (%) from column 5, E_c (%) in oxide = 0.32.

* Error magnifications calculated as (uncertainty% cation)/(uncertainty% oxide).

Equation 3, which does not include covariance terms and assumes that errors are uncorrelated.

Columns 4 and 5 (Tables 6, 7, and 8) contain the absolute and relative uncertainties obtained by partial error propagation (Eq. 3) of the "hypothetical" 0.32% counting errors in the oxide concentrations. Column 7 lists the corresponding error magnification, measured by the ratio of the percent standard deviations in the cation and the corresponding oxide (cation/oxide). The uncertainties in most single-site or single-valence cations (e.g., column 5, Table 6) are comparable to the assumed counting error of 0.32%, and the errors in cation sums are much less than in the individual cations. On the other hand, the uncertainty in cations of major elements such as Si commonly is smaller than 0.32%, and the uncertainties of multivalent and multisite cations are much larger (column 5, Tables 6, 7, and 8).

For the hypothetical analyses in columns 4 and 5 (Tables 6, 7, and 8), the magnification of uncertainty in a single-site, single-valence cation compared to the corresponding oxide (column 9, Tables 6, 7, and 8) is entirely the effect of the mineral composition and normalization scheme. Although covariation and variable uncertainties in the oxide concentrations affect such magnifications in a real analysis, the uncertainties reported in columns 4 and 5 and the magnifications in column 7 were calculated using Equation 3, which contains no covariance terms, and the same relative uncertainty for all oxides. Consequently, columns 5 and 7 illustrate only the effects of the relative abundances of the oxides on the error propagation for the chosen normalization scheme.

Equation 3 can be rewritten to show the dependence of error magnification on composition for hypothetical analyses in which the relative uncertainties are the same in all oxides (See App. 2 for the derivation). For the special case in which $\sigma_{w_i}/w_i = \sigma_{w_j}/w_j$ for all i and j,

$$\frac{\sigma_{c_i}/c_i}{\sigma_{w_i}/w_i} = \left[(1 - X_i^O)^2 + \sum_{j \neq i}^{n} (X_j^O)^2\right]^{1/2}. \qquad (10)$$

The first term on the right side of Equation 10 is the main control on the error magnification. That term is the proportion of total oxygen that resides in all the oxides j not equal to i. The effect of this term is best understood

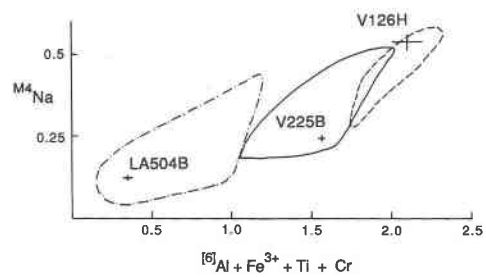

Fig. 1. Propagated uncertainties in graph of ^{M4}Na versus $^{[6]}$Al + Fe^{3+} + Ti + Cr in amphiboles from mafic schist in Vermont. The dot-dash line encloses samples from the biotite zone; the solid line, samples from the garnet zone; and the dashed line, samples from the staurolite-kyanite zone. One-sigma uncertainties obtained by partial error propagation (Eq. 3) of reported uncertainties in oxide concentrations are shown for a representative sample from each zone. Modified after Fig. 2b in Laird and Albee (1981).

by considering an example. The bytownite (Table 2) contains about 49 wt% SiO_2, which contains about 56% of the total oxygen anions in the analysis. If Si is considered to be the *i*th cation, the first term in Equation 10 is about $(0.44)^2 = 0.19$. The summation term in Equation 10 is always a small positive number less than one because the average value of the five terms (X_j^o) is about 0.09, which must be squared, and the sum is about 0.04. Consequently, the error magnification is commonly less than one for Si and other cations of major elements.

The uncertainty and error magnification in the formula proportion of Si are significantly larger for a fixed-cation normalization than for a fixed-oxygen normalization. For formula proportions normalized to a fixed number of cations,

$$\frac{\sigma_{c_i}/c_i}{\sigma_{w_i}/w_i} = \left[(1 - X_i^c)^2 + \sum_{j \neq i}^{n} (X_j^c)^2\right]^{1/2}, \qquad (11)$$

where the X_i^c terms are the fraction of all cations that are contributed by the oxide *i* (Table 1). The derivation of this equation follows from Equations 3 and 5 is parallel to that presented in Appendix 2.

The larger error magnification for Si arises primarily because SiO_2 contains more anions than cations. For example, the augite (Table 2) contains about 50 wt% SiO_2, accounting for about 61% of the anions and 46% of the cations. If Si is the *i*th cation, the first terms on the right side of Equations 10 and 11 are, respectively, $(0.39)^2 = 0.15$ and $(0.54)^2 = 0.29$. Because the second terms on the right tend to be small in both cases, the error magnification is larger for the fixed-cation normalization than for the fixed-oxygen scheme. The formula proportion of Si in the augite for the fixed-cation normalization scheme is 1.8264 ± 0.0061 (Table 4, column 1) whereas for a six-oxygen basis, we calculated 1.8320 ± 0.0044, or a difference in the standard deviations of 30–50%. For cations other than Si, the differences in the standard deviations and error magnifications obtained from fixed-cation and fixed-anion normalizations are less pronounced and, for the most part, insignificant.

The error magnification is normally greater than one for minor elements in the hypothetical analyses (columns 5 and 7, Tables 6, 7, and 8). If the *i*th oxide is only 1 wt% of the total sample, the proportion of oxygen that resides in other oxides is commonly more than 99% so that the first term on the right side of Equation 11 is about $(0.99)^2 = 0.98$. The summation term is small but larger than the case for which Si is the *i*th cation because the average value of X_j^o now must include contributions from SiO_2 that are larger than those from other oxides. Consequently, the right-hand side of Equation 10 is commonly larger than one for minor elements, and the uncertainty in the oxide is magnified in the formula proportion of cations.

The error magnification for minor amounts of calculated Fe^{3+} is very large. FeO is a major oxide in both augite and hornblende, yet the propagated uncertainties of Fe^{3+} (columns 5 and 7, Tables 7 and 8) are about 58 and 10 times larger, respectively, than the assumed 0.32% error in the weight percent of FeO. The small, calculated amount of Fe^{3+} and the error magnification depend on the analyses of all oxides (Eq. 6). From Equations 3 and 6, we find that the error magnification for Fe^{3+} is given by

$$\frac{\sigma_{c_{Fe^{3+}}}/c_{Fe^{3+}}}{\sigma_{w_{FeO}}/w_{FeO}} = \left[\frac{b^o}{b^c}\Big/\frac{s^o}{s^c} - 1\right]^{-1} \cdot \left[\sum_i (X_i^c - X_i^o)^2\right]^{1/2}. \qquad (12)$$

The first term on the right side of Equation 12 dominates for all silicates poor in Fe^{3+}. From Equation 6, it can be shown that the ratio s^o/s^c approaches b^o/b^c as the amount of calculated Fe^{3+} approaches zero and the first term must become very large. The second term on the right is always a small number because the mole fractions are between 0 and 1 and their differences are squared. For example, the first term for the augite is about 322 and the second term is about 0.18.

It is widely appreciated that the uncertainty in calculated Fe^{3+} depends heavily on the silica analysis, but *all* major elements and some minor elements may contribute in a major way depending upon the relative sizes of the derivatives and variances in Equation 3. For example, the observed uncertainty of wt% SiO_2 in the augite studied here (Table 2) contributes

$$[\sigma^2_{w_{SiO_2}} (\partial c_{Fe^{3+}}/\partial w_{SiO_2})^2]$$

—only about 33% of the total variance in Fe^{3+}—whereas MgO, CaO, and FeO contribute 26%, 17%, and 11%, respectively, and Na_2O contributes about 12% despite its low abundance. This large contribution arises, in part, because the partial derivative of Fe^{3+} cations with respect to wt% Na_2O is about four times larger than the derivatives with respect to other oxides.

These calculations show that whether errors are magnified or reduced is primarily a function of the composition of the mineral for a given normalization scheme. With few exceptions, the complete analysis (column 6), including the measured and variable uncertainties of the oxides and covariance terms, produced the same direction of magnification or reduction of errors as column 7, which included no covariance and constant hypothetical uncertainties in the oxides. Error magnification for calculated amounts of multivalent cations may be extreme and may depend in a significant way on oxides other than SiO_2.

Conclusions

The analytical method of propagating uncertainties is a useful method for calculations of structural formulas that correctly reproduces the true dispersion of structural formulas due to analytical uncertainty. For many routine applications, our results show that the uncertainties of measured oxide concentrations can be reasonable estimates of the complete uncertainties for single-valence,

single-site cations. However, partial error propagation (Eq. 3), which omits the covariance terms, is not a difficult calculation and is a better approximation of the complete uncertainty for virtually all cations. It is advisable to include the covariance terms in the calculated uncertainties of Fe^{2+}, Fe^{3+}, multisite cations, or in any case for which high precision is needed.

Uncertainties in structural formulas are commonly magnified or reduced compared to the uncertainties in the corresponding oxide concentrations. The error magnification depends not only on the composition of the mineral, the normalization scheme used, and the structural formula to which the cations are assigned, but also on the relative sizes of uncertainties in the oxides and the contribution of covariance. Error magnifications commonly depend on the analyses of all elements. For example, the uncertainty of Fe^{3+} in the augite studied here contains major contributions not only from SiO_2 but also from the other major oxides and Na_2O. Consequently, an analyst wanting to minimize uncertainties in a particular application may determine the dependence of the error magnification on the various elements in order to find an optimum analytical scheme.

Microprobe analysts commonly use stoichiometric criteria as indicators of the quality of an analysis. The error-propagation technique outlined here permits a rigorous evaluation of how well a structural formula meets such criteria for cases where information concerning correlation is available. The method also establishes a means of evaluating the quality of microprobe analyses in the literature for which laboratory reproducibilities are the only reported uncertainties. Finally, calculated uncertainties of cation sums can also be used to evaluate the effect of analytical error on discriminant diagrams. The chemical variations of calcic amphiboles on the graph of ^{M4}Na versus $^{[6]}Al + Fe^{3+} + Ti + Cr$, illustrated by Laird and Albee (1981), are clearly larger than any effects of analytical uncertainty, supporting their conclusion that the variations represent real differences in metamorphic conditions. Covariance among parameters derived from a single microprobe analysis can be obtained by inserting the derivatives of Equations 4–9 and covariance matrices of oxide concentrations into Equation 8 of Roddick (1987) for applications where such correlation is of interest.

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Appendix 1. Covariance matrices

Appendix Table A1. Correlation matrix for bytownite analysis

	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3
Na_2O	1.00					
Al_2O_3	0.11	1.00				
SiO_2	0.26	0.21	1.00			
K_2O	0.02	−0.28	−0.12	1.00		
CaO	0.14	0.18	0.24	0.00	1.00	
Fe_2O_3	0.00	−0.22	−0.10	0.05	−0.21	1.00

Appendix Table A2. Correlation matrix for augite analysis

	Na_2O	MgO	Al_2O_3	SiO_2	CaO	TiO_2	Cr_2O_3	MnO	FeO
Na_2O	1.00								
MgO	0.01	1.00							
Al_2O_3	−0.07	0.12	1.00						
SiO_2	0.28	0.17	0.29	1.00					
CaO	0.16	0.07	−0.05	0.15	1.00				
TiO_2	0.16	−0.21	0.18	−0.24	−0.04	1.00			
Cr_2O_3	−0.08	0.15	0.18	−0.12	0.60	−0.09	1.00		
MnO	−0.15	−0.36	0.23	−0.05	−0.11	−0.01	0.06	1.00	
FeO	0.13	0.24	−0.07	0.21	0.11	−0.30	−0.04	−0.09	1.00

Appendix Table A3. Correlation matrix for hornblende analysis

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	FeO
Na_2O	1.00								
MgO	−0.47	1.00							
Al_2O_3	0.15	−0.12	1.00						
SiO_2	0.18	−0.01	0.31	1.00					
K_2O	0.16	−0.20	0.02	0.04	1.00				
CaO	−0.24	0.40	−0.12	−0.04	−0.14	1.00			
TiO_2	−0.13	0.02	−0.02	−0.09	−0.21	−0.01	1.00		
MnO	−0.03	−0.05	−0.16	−0.30	0.22	−0.17	−0.04	1.00	
FeO	0.10	−0.18	0.04	−0.03	0.02	0.05	0.12	−0.06	1.00

Appendix 2. Error magnification

The calculated abundance of a cation, c_i, has a variance that is given by Equation 3, in the absence of significant covariance terms:

$$\sigma_{c_i}^2 = \sum_{j=1}^{n} \sigma_{w_j}^2 (\partial c_i/\partial w_j)^2. \tag{3}$$

We are interested to know how the ratio σ_{c_i}/c_i compares to σ_{w_i}/w_i for an oxygen-basis calculation. Dividing Equation 3 by c_i^2, we have

$$\frac{\sigma_{c_i}^2}{c_i^2} = \frac{\sigma_{w_i}^2}{c_i^2}\left(\frac{\partial c_i}{\partial w_i}\right)^2 + \frac{1}{c_i^2}\sum_{j\neq i}^{n} \sigma_{w_j}^2 \left(\frac{\partial c_i}{\partial w_j}\right)^2.$$

Substituting for c_i, $\partial c_i/\partial w_i$, and $\partial c_j/\partial w_j$ from Equations 4 and canceling terms,

$$\frac{\sigma_{c_i}^2}{c_i^2} = \frac{\sigma_{w_i}^2}{w_i^2}\left(\frac{s^O - w_i k_i^O}{s^O}\right)^2 + \sum_{j\neq i}^{n} \sigma_{w_j}^2 \left(\frac{k_j^O}{s^O}\right)^2$$

$$\frac{\sigma_{c_i}^2/c_i^2}{\sigma_{w_i}^2/w_i^2} = \left(\frac{s^O - w_i k_i^O}{s^O}\right)^2 + \frac{w_i^2}{\sigma_{w_i}^2}\sum_{j\neq i}^{n}\left(\frac{\sigma_{w_j}^2}{w_j^2}\right) w_j^2 \left(\frac{k_j^O}{s^O}\right)^2.$$

For the case in which $\sigma_{w_i}/w_i = \sigma_{w_j}/w_j$ for all i and j, and taking the square root,

$$\frac{\sigma_{c_i}/c_i}{\sigma_{w_i}/w_i} = \left[(1 - X_i^O)^2 + \sum_{j\neq i}^{n} (X_j^O)^2\right]^{1/2}. \tag{10}$$

Equation 10 clearly shows that the error magnification of a cation i depends on the proportion of total oxygen that resides in the oxide of that cation.