

Estimation of elemental microvariation within minerals analyzed by the microprobe: Use of model population estimates

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ABSTRACT

This paper presents a method of model population estimates that serves to distinguish elemental heterogeneity from error of analysis within a set of approximately 40 replicate microprobe analyses of a single mineral and within a single thin section. A set of muscovite analyses from a granite gneiss metamorphosed to the amphibolite facies is used as an example.

The method of model population estimates is a search for plausible parent populations to which the analyzed sample could belong at a 95% confidence level. Underlying assumptions governing construction of the models are (1) careful analysis of the real sample sufficed to minimize systematic errors; (2) nonsystematic analytical error is in part removed by charge-sum normalization of each analysis and is in part random; and (3) compositional heterogeneity, if present, follows a single equation of charge-coupled substitution.

The models are compared to the real sample at the 95% confidence level by an *F* test for standard deviations and a *t* test for correlations. Both a central model, which best fits the real analyzed sample, and a range of models that pass the tests for standard deviations and correlations may be ascertained. The result is an estimate of the allowed extent of compositional heterogeneity and analytical error.

Assumption of a single equation of charge-coupled substitution to cover all elemental heterogeneity of a given mineral is the simplest assumption beyond that of no heterogeneity at all. Should this assumption fail to produce a satisfactory model for a set of well-made mineral analyses, the presence of independent and competing substitutions should be suspected. Conversely, success of this modeling assumption suggests that any independent substitutions are obscured by analytical error but does not necessarily suggest their absence.

The method of model population estimates represents a logical advance in the use of microprobe analyses and may become useful to many types of analytical studies. For example, a large covariation in the extent of tschermakitic and alkali substitution is ascertained within the muscovite analyzed for this study. Application of this covariation to muscovite-plagioclase geothermometry yields a range of 57 °C in the apparent temperature of metamorphism for the sample. In contrast, use of a mean muscovite analysis for the studied sample yields a somewhat lower apparent range of only 10 °C.

INTRODUCTION

Within a set of replicate microprobe analyses, both real elemental heterogeneity of the sample and error of analysis contribute to variation in analyzed abundance of the elements. Such analytical error tends to obscure information resulting from real elemental variation and sub-

stitution in the sample. This paper presents methods, based on computer simulation and statistical analysis, to estimate the nature and extent of sample heterogeneity as well as the extent of indeterminate or random error of analysis within microprobe data. These methods were devised to ascertain the microvariation in composition of metamorphic minerals whose zoning cannot be deter-

mined directly, for reasons of complex zoning patterns or small crystal size. Such methods may also find a use in many other problems of petrology and materials science.

Apparently, no work similar to this study has been previously attempted. Chayes (1971) has written on the problems inherent in similar treatment of whole-rock geochemical data. The compositional heterogeneity of biotite within single thin sections of metamorphic rocks, chiefly within rocks of the granulite facies, has been discussed (Tracy and Dietsch, 1982; Indares and Martignole, 1985). However, this sort of study is generally limited to discussion of the variability of specific atomic ratios, such as the ratio of Mg to total Fe. Typically two sets of averaged analyses, for apparently prograde and obviously retrograde biotite, or map plots of the Mg/Fe ratio within single biotite crystals are presented.

Several papers have presented studies of compositional variation for muscovite (Hollocher, 1987; Mohr et al., 1986) and biotite (Dymek, 1983), based on virtually complete cationic microprobe analyses of mica. Linear-regression analysis was employed to attempt elucidation of trends in covariation of elements and partial elemental sums. However, no attempt was made to distinguish genuine trends from those induced by autocorrelation. In fact, these authors frequently make use of partial elemental sums, such as [6] Al and total octahedral site occupancy, which are highly derived from the total cationic sums. This type of sum is radically affected by normalization, and any correlations affecting these sums should be treated with caution. Also, the emphasis of both Dymek (1983) and Hollocher (1987) was upon regional variation in mica composition. For example, Hollocher (1987), sought to determine the variation of muscovite composition with regional extent of metamorphic retrogression, and many of his arguments were based on averages of microprobe analyses. In contrast, the method advanced in this paper seeks to elucidate the compositional microvariation within apparently unzoned minerals of a single thin section.

A set of 39 replicate analyses of a metamorphic muscovite from a single thin section will be used for illustration. Model population estimates are generated and compared to the real data set in a search for plausible model populations to which the analyzed sample might belong. Each of these models incorporates a single linear equation of charge-coupled substitution (representing the chemical heterogeneity of the sample), as well as random variation in the abundance of each element (representing uncertainty of analysis). Statistical tests are used to determine, at a 95% confidence level, whether a given model constitutes a plausible population estimate for the analyzed sample.

Incorporation of all elemental microvariation within one, all-inclusive equation of substitution may represent an ideal state not often attained during metamorphism. However, use of a single equation greatly facilitates construction of the models, and statistical tests will determine to what extent such a simplistic approach is ade-

quate to describe the microvariation within a given sample. These points will be addressed again later.

Once it is shown that a plausible population exists for a given analyzed sample, one may explore the range of plausible population estimates to determine the limits of geochemical information that may be retrieved from the analyzed sample. Subsequent sections of this paper outline methods of gathering and treatment of the replicate muscovite analyses, underlying assumptions and construction of the model population estimates, and statistical methods for comparison of the models to the real data set.

DESCRIPTION OF SAMPLE AND ANALYSES

The analyzed muscovite sample is from a single thin section of granite gneiss metamorphosed to the middle amphibolite facies. The sample was collected from the Wiley Gneiss of Hatcher (1971), specifically from an outcrop listed as field stop 10 of Hatcher and Butler (1979). The Wiley Gneiss (WG), located within the Southern Blue Ridge, is of Precambrian (Grenville) age but was deformed and metamorphosed to the middle amphibolite facies during the Paleozoic. The mineral assemblage contains quartz + microcline + oligoclase + muscovite + biotite + garnet + ilmenite. The texture is gneissic with a concentration of aligned mica plates within bands several millimeters thick. Individual muscovite crystals are up to several millimeters across and 0.5 mm thick.

Microprobe analyses, of WDS type, were gathered on a JEOL JXA733 microprobe equipped with Tracor-Northern automation and located at the Department of Geology, Southern Methodist University, Dallas, Texas. Operating conditions included an acceleration potential of 15 kV and beam current of 20 nA. Elements analyzed included Na, Mg, Al, Si, K, Ba, Ti, and Fe. The elements Ca and Mn were also analyzed but not detected. Standards used included andalusite for Al and Si, Kakahanui hornblende for Ti, Amelia albite for Na, orthoclase for K, garnet for Mg and Fe, and barite for Ba. ZAF corrections were applied to all analyses as part of the Tracor-Northern automation package.

Several steps were taken to minimize systematic error during analysis. All analyses were gathered during a single working session. The beam spot was adjusted to a diameter of 20 μm ; repeated analyses of the same spot showed no consistent change in mineral analyses for this beam diameter. For each analysis, an automatic peak-search routine was performed for all elemental peaks except Ba. To check spectrometer drift for the elements Al and Si, five replicate analyses of the standard andalusite were performed immediately before and after the replicate muscovite analyses. Relative changes in averaged abundances amounted to +0.009 for Al and -0.004 for Si. An attempt to apply linear corrections to analyzed Al and Si to compensate for the apparent drift resulted in an increase in standard deviation for these elements among the 39 muscovite analyses. Thus it is assumed that

TABLE 1. Normalized mean formula and standard deviations of the analyzed sample

Element	Mean	Standard deviation	Elemental counting error for unnormalized analyses
Si	6.262	0.0675	0.0129
²⁷ Al	1.738		
	8.000		
²⁹ Al	3.453	0.0649	
Ti	0.125	0.0156	0.0021
Fe ³⁺	0.063		
Mg	0.219	0.044	0.0032
Fe ²⁺	0.178		
	4.040	0.0136	
Na	0.095	0.0143	0.0032
K	1.785	0.0274	0.0098
Ba	0.008	0.0012	0.0008
	1.888	0.0242	
Σ	13.931	0.0229	
ΣAl	5.191	0.1285	0.0121
ΣFe	0.242	0.037	0.0055

any spectrometer drift is obscured by indeterminate error of analysis.

The oxidation state of Fe in muscovite was determined on a bulk mineral separate, using the wet-chemical method of Fritz and Popp (1985). The resulting ratio of Fe³⁺ to Fe_{tot}, 0.262, was applied uniformly to all replicate muscovite analyses.

TREATMENT OF MICROPROBE DATA

The initial step in treatment of the 39 replicate analyses of the muscovite sample consisted of charge-sum normalization of each analysis to an assumed cationic charge of 44 (22 O atoms). Fe_{tot} was assigned a functional valence of 2.262, based on the results of wet-chemical analysis. All subsequent treatment and interpretation of data are based on the resulting charge-balanced formulae. Mean abundances and standard deviations in abundance, calculated for the elements as well as for partial elemental sums, are listed in Table 1. Linear-regression correlations (Table 2) were calculated for each of the 28 resulting pairs of elements, as well as for three pairs involving the partial elemental sums FM (Mg + Fe²⁺) and AF (Al + Fe³⁺).

The mean analysis of the WG muscovite sample is rather typical of muscovite analyses from amphibolite-grade rocks (Guidotti, 1984, Fig. 33). A slight excess of octahedral cations and deficiency of interlayer cations is evident (Table 1). An excess of Si and a deficiency of Al relative to ideal muscovite are also unremarkable. The low ratio of Na to K reflects the presence of microcline within the sample rock. The abundance of Ti is high but not unusually so. High values for the standard deviations of some of the elements suggest the presence of elemental heterogeneity.

Although observed correlations of elements (Table 2) suggest substantial variation in elemental abundance, these correlations are obscured by the presence of random or indeterminate error of analysis, and autocorrelation has

TABLE 2. Linear regressions of the analyzed sample

Elements (y/x)		Slope of correlation (b)	Correlation coefficient (r)
y	x		
Mg	Al	-0.332	-0.969
Mg	Si	+0.598	+0.916
Ti	Mg	-0.219	-0.618
Fe	Mg	+0.728	+0.866
Si	Al	-0.511	-0.972
Ti	Al	+0.068	+0.557
Fe	Al	-0.240	-0.832
Ti	Si	-0.143	-0.619
Fe	Si	+0.401	+0.732
Ti	Fe	-0.259	-0.615
Na	K	-0.235	-0.450
Ba	Na	-0.016	-0.190
Ba	K	-0.007	-0.151
K	Mg	+0.309	+0.497
K	Al	-0.094	-0.440
K	Si	+0.132	+0.325
Ti	K	-0.197	-0.346
K	Fe	+0.344	+0.465
Na	Mg	-0.240	-0.740
Na	Al	+0.079	+0.715
Na	Si	-0.131	-0.621
Na	Ti	+0.371	+0.404
Na	Fe	-0.319	-0.827
Ba	Mg	+0.008	+0.279
Ba	Al	-0.003	-0.311
Ba	Si	+0.006	+0.323
Ba	Ti	-0.002	-0.024
Ba	Fe	+0.006	+0.167
Si	AF	-0.547	-0.977
FM	AF	-0.535	-0.933
FM	Si	+0.894	+0.874

resulted from charge-sum normalization (Chayes, 1971). For muscovite analyses, the elements Si and Al account for approximately 55% and 40% of the total cationic charge, respectively, and autocorrelation involving these elements is high. In fact, the contribution of autocorrelation to any observed correlation of Si to Al (or to the partial elemental sum AF) is sufficiently large (Fig. 1) that the observed correlation cannot be interpreted directly. This is unfortunate, since phengitic or tschermakitic substitution has long been recognized as a fundamental control on variability of muscovite composition (Guidotti, 1984).

On the other hand, the effect of random error on correlations among the less abundant elements is simply a lessening of the degree of observed correlation. Since indeterminate error of analysis is random in nature, it cannot be filtered out of the set of analyses. Thus, the observed correlations (Table 2) are not readily interpreted. The method of model population estimates attempts to overcome this difficulty by comparison of the real data set to computer models within which the limits of elemental heterogeneity and indeterminate error of analysis have been assigned.

FORMATION OF THE MODEL POPULATION ESTIMATES

Computer modeling requires that fundamental assumptions or boundary conditions be made regarding the nature of both real chemical heterogeneity and error of

analysis. Three assumptions govern the manufacture of model population estimates:

1. It is assumed that systematic error of analysis is unimportant within the analyzed sample. Possible causes of systematic error include poor standardization, spectrometer drift, and errors within the applied ZAF corrections. Analytical procedures described above are believed sufficient to prevent development of significant systematic error. Thus, all variations in analyzed abundance of the element that are not due to chemical heterogeneity of the sample are ascribed to random analytical error.

2. It is assumed that random analytical error takes two forms. The first is a change in the absolute intensities of all characteristic X-ray peaks from one analysis to the next, without any change in the ratios of peak heights among the elements. Such error could be caused by the uneven character of the sample polish. Without correction, such error would result in a trend toward false positive correlations among the analyzed elements. Charge-sum normalization is used to filter out this type of error.

The second form of random analytical error is strictly random in nature, both among the various elements within a given analysis and among the various analyses for a given element. For sufficiently large samples, distribution of the magnitudes of such error follows a normal, or Gaussian, pattern. The magnitude of the standard deviation of this error is characteristic of each analyzed element. This form of analytical error includes but is not limited to fundamental counting error.

3. Chemical heterogeneity of the analyzed sample is assumed to be governed by variation along a single equation of charge-coupled substitution among the analyzed elements. Thus, real variation in all elemental abundances may be expressed in terms of two end-members. For sufficiently large samples, distribution of the real abundances for each element is assumed to be linear (rather than normal) with definite limits and symmetrical about the mean. Chemical heterogeneity is assumed to be present only if null models, which incorporate only random error of analysis, fail to reproduce the correlations observed in the real analyses of the mineral sample.

Models are constructed using the assumptions outlined above. Each model contains 1000 simulated analyses. Elemental heterogeneity is modeled by incremental change along a single equation of charge-coupled substitution, which is specific to each model. Random error of analysis is modeled by a Monte Carlo method.

Details of the construction of the simulated analyses for the elements Al and Si are shown graphically in Figure 2 and discussed below. A sample of the computer program for the elements Al and Si is given in Basic language:

```

100 RANDOMIZE
110 GOSUB 2000
120 FOR J = 1 TO 1000
130 AL(J) = 5.401 - 0.42*J/1000 + 0.0424*Z(J)
140 NEXT J

```

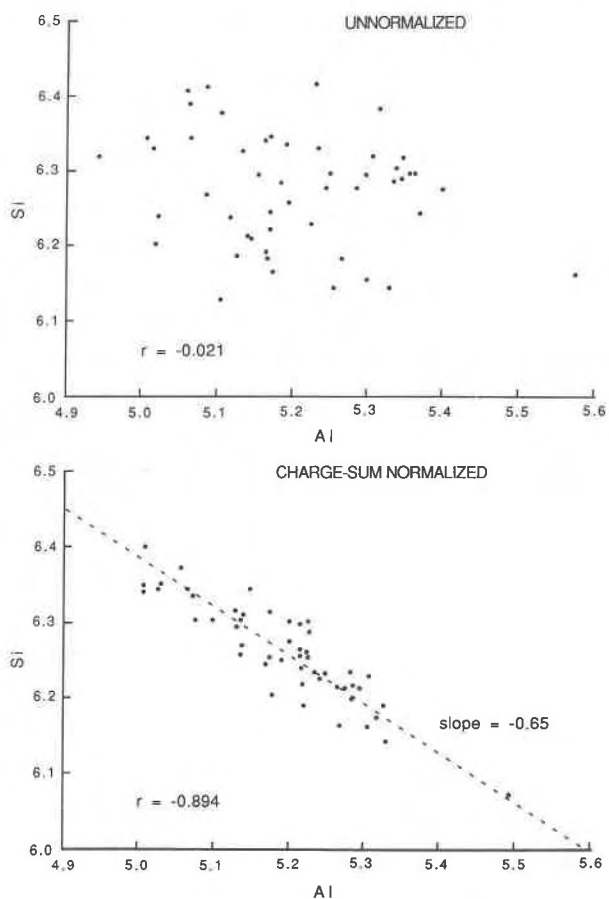


Fig. 1. Charge-sum normalization of muscovite analyses induces false correlations, especially for the elements Si and Al. The graphs show linear-regression correlations Si vs. Al for a model set of muscovite analyses constructed according to methods stated in the paper. The model set of analyses consists of 1000 members; every 20th member is shown for clarity. The elemental mean and standard deviations are those of sample WG, but elemental variations are not correlated at all. The slope of -0.65 that results from charge-sum normalization reflects, in part, the $3/4$ ratio of the cationic charges for Al and Si.

```

150 RANDOMIZE
160 GOSUB 2000
170 FOR J = 1 TO 1000
180 SI(J) = 6.157 + 0.21*J/1000 + 0.0452*Z(J)
190 NEXT J

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The simulated 1000 analyses for Al and Si are calculated by lines 130 and 180, respectively. For each element, the first two terms model elemental heterogeneity, whereas the third term models random error of analysis. The underlined coefficient of the second term represents the elemental coefficient within the equation of charge-coupled substitution that is assumed for this particular model. The constant value of the first term is equal to the mean analysis for the WG sample minus one-half the value of the underlined coefficient of the second term. The third term calculates the extent of random error. The $Z(J)$ vari-

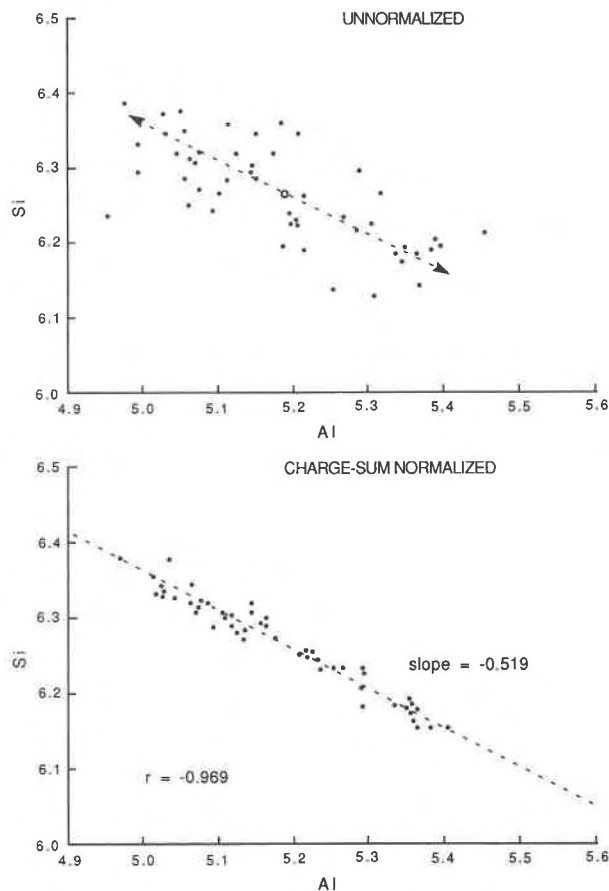


Fig. 2. Graphs demonstrating construction of a model set of analyses incorporating both a single equation of charge-coupled elemental substitution and uncertainty of analysis (see text). The model set of analyses consists of 1000 members; every 20th member is shown for clarity. The equation of charge-coupled substitution and the limits of random error are those of the central model (see text). **Top:** Model analyses for the elements Si and Al before normalization. The line connecting the arrows represents the array of calculated elemental abundances before the terms representing uncertainty of analysis are added; the central circle represents the mean of sample WG. Distortion caused by charge-sum normalization is shown below (**bottom**).

able is constructed within the internal loop entered by the GOSUB command. This loop converts a linear array of 1000 random numbers, generated initially by the RANDOMIZE command, to a normally distributed array with a standard deviation of 1. The underlined coefficient of the third term scales the standard deviation to whatever value of indeterminate error is assumed for the element within a particular model. The purpose of the RANDOMIZE command is to assure that the arrays represented by the Z(J) variable are not correlated from one element to the next.

Variation of the underlined coefficients for either term allows construction of a variety of model population estimates with differing equations of charge-coupled substitution and differing limits of assumed random error.

For all models, each simulated analysis is subsequently charge-sum normalized. Means, standard deviations, and linear-regression correlations are calculated in the same fashion as for the real analyzed sample. The result is a model analysis within which the limits of both elemental heterogeneity and error of analysis are known, despite the subsequent distortion of both elemental standard deviations and correlations caused by charge-sum normalization. Thus, the real analyzed sample may be compared to each model directly.

COMPARISON OF MODEL POPULATION ESTIMATES TO THE ANALYZED SAMPLE

Comparison of model population estimates to the analyzed sample is performed by an *F* test for the standard deviations listed in Table 1 and by a *t* test for the 31 correlations of Table 2. A particular model is considered to represent a plausible population estimate for the real analyzed sample if all calculated values of *F* and *t* match those of the real sample within the interval of 95% confidence. A model is considered to have failed if any one value of *F* or *t* exceeds the critical value for 95% confidence.

The *F* test for comparison of standard deviations is based on the formula (Dixon and Massey, 1969):

$$F = s^2(\text{sample a})/s^2(\text{sample b}),$$

where the larger variance is always in the numerator. This test furnishes an estimate of the probability that the two standard deviations could arise from samples of the same population and is valid as long as the means of the two samples are the same.

However, use of both linear and Gaussian elemental distributions for construction of the model population estimates renders the standard *F* tables invalid. Therefore, critical values of *F* for 95% confidence were estimated empirically. Two hundred sets, each of 39 simulated analyses, were constructed using a modified version of the computer program for the model population estimates. Assigned coefficients of charge-coupled substitution and the limits of uncertainty of analysis were constant in all 200 sets. Resulting elemental standard deviations for each of these sets were compared to those of the model population estimate, based on 1000 simulated analyses, whose assigned coefficients for charge-coupled substitution and error of analysis were the same. Comparison of standard deviations was performed by an *F* test. For each element and tested partial elemental sum, the 190th highest value of *F* (within a set of 200 calculated *F* values) was assumed to represent the critical value for 95% confidence. This test was conducted once for a model population estimate that most closely matched the analyzed sample. In general, critical values of *F* are less than those seen in standard statistical tables but approach the standard values, as the assumed indeterminate analytical error constitutes more of the total calculated variation of the element.

The test for correlations is that given by Dixon and

Massey (1969, p. 207–209), without modification. This test allows direct comparison of linear-regression correlations among two samples, provided that standard deviations for each element within the two samples are compatible with a single overall population. For the WG muscovite sample, the test for correlations was more stringent than the test for standard deviations. Although many models that would have passed the *F* test in fact failed the *t* test for correlations, the converse was almost never observed.

The model equation of charge-coupled substitution, normalized to the charge-sum of 44, was varied among the test models by increments of 0.001 formula units for each element. The amount of model indeterminate error was varied by increments of 0.5 of the counting error estimate for each element within the real analyzed sample (Table 1). Tracor-Northern automation on the JEOL microprobe reports sufficient information to estimate counting error for each element in terms of formula abundance. The formulas used are

$$\epsilon_{(ce,i)} = [N_{(p,i)}]^{1/2} / [N_{(p,i)} - N_{(b,i)}],$$

where *i* refers to a specific element, $N_{(p)}$ and $N_{(b)}$ represent the number of photon counts for peak and background positions respectively, and $\epsilon_{(ce)}$ is a dimensionless number that expresses the relative counting error for each element. An estimate of the magnitude of the counting error for each element follows, using the formula

$$\sigma_{(ce,i)} = \epsilon_{(ce,i)} X_i,$$

where X_i is the mean abundance of each element within the average reported analysis (Table 1).

By trial and error, a central model was identified that most closely reflects the standard deviations and correlations of the real analyzed sample. The extent to which models departing from this central model could also constitute plausible population estimates for the real sample was tested by incremental variations in the elemental coefficients. Variations within the equation of charge-coupled substitution were tested in models whose indeterminate error of analysis remained the same as that of the central model. Variation in the elemental indeterminate error of analysis were tested in models whose formula of charge-coupled substitution remained the same as that of the central model.

RESULTS OF COMPUTER MODELING

Null models, or those incorporating only random error of analysis, fail to match the correlations of the real WG muscovite sample. The central model that most closely reflects the observed standard deviations and correlations contains the following charge-coupled substitution equation:

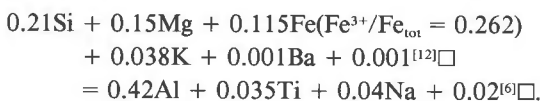


TABLE 3. Comparison of the central model to the real analyzed sample

Standard deviations			
Element	Standard deviation of model	Observed value of <i>F</i> statistic	Critical value of <i>F</i> statistic
Si	0.0660	1.05	1.39
¹⁶ Al	0.0640	1.03	1.35
Ti	0.0164	1.11	1.52
Fe _{tot}	0.0363	1.04	1.44
Mg	0.0443	1.01	1.33
¹⁶ R	0.0148	1.18	1.60
Na	0.0142	1.01	1.48
K	0.0275	1.01	1.61
Ba	0.0012	1.00	1.48
¹² R	0.0268	1.23	1.54
Σ	0.0229	1.00	1.61
ΣAl	0.1255	1.05	1.36

Linear-regression correlations				
Elements (<i>y/x</i>)		Slope of correlation in model (<i>b</i>)	Correlation coefficient in model (<i>r</i>)	<i>t</i> statistic
<i>y</i>	<i>x</i>			
Mg	Al	-0.334	-0.947	-0.125
Mg	Si	+0.593	+0.883	-0.089
Ti	Mg	-0.225	-0.609	-0.127
Fe	Mg	+0.743	+0.908	+0.268
Si	Al	-0.508	-0.966	+0.111
Ti	Al	+0.072	+0.552	+0.256
Fe	Al	-0.258	-0.891	-0.834
Ti	Si	-0.161	-0.647	-0.580
Fe	Si	+0.439	+0.797	+0.692
Ti	Fe	-0.257	-0.571	+0.020
Na	K	-0.160	-0.310	+0.918
Ba	Na	-0.018	-0.207	-0.133
Ba	K	+0.005	+0.107	+1.597
K	Mg	+0.240	+0.387	-0.719
K	Al	-0.087	-0.396	+0.209
K	Si	+0.128	+0.307	-0.058
Ti	K	-0.173	-0.291	+0.253
K	Fe	+0.271	+0.358	-0.633
Na	Mg	-0.260	-0.812	-0.632
Na	Al	+0.089	+0.784	+0.804
Na	Si	-0.161	-0.749	-1.269
Na	Ti	+0.431	+0.498	+0.464
Na	Fe	-0.300	-0.769	+0.454
Ba	Mg	+0.006	+0.225	-0.342
Ba	Al	-0.002	-0.212	+0.597
Ba	Si	+0.004	+0.185	-0.797
Ba	Ti	-0.012	-0.165	-0.838
Ba	Fe	+0.008	+0.233	+0.460
Si	AF	-0.547	-0.971	0
FM	AF	-0.556	-0.936	-0.627
FM	Si	+0.917	+0.870	+0.275

Note: *t* critical = 1.646.

The standard deviations and correlations for this model, as well as the results of statistical comparison to those of the real sample, are given in Table 3. The limits of indeterminate error, in terms of multiples of the counting error for each element, are 1.5 for Ba, 2.5 for Na, Mg, K, and Fe, 3.5 for Al and Si, and 6.0 for Ti. The range of allowed variations in both the coefficients of the equation of charge-coupled substitution and of limits of indeterminate error of analysis are furnished in Table 4.

Compositional heterogeneity is ascribed to variation along a single equation of charge-coupled substitution, whose nature is dominantly phengitic. For the WG mus-

TABLE 4. Allowed ranges for successful models

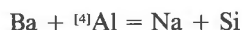
Possible ranges for coefficients of selected elements and site vacancies within the equation of charge-balanced substitution (increments of 0.001):			
Na	0.038–0.041	Ba	0.001 only
Mg	0.14–0.163	Ti	0.023–0.044
K	0.036–0.04	Fe	0.107–0.125
⁽⁶⁾ □	0.013–0.029	⁽¹²⁾ □	0–0.001
			investigated only

Possible ranges for uncertainty of analyses, expressed as both multiples of the extent of Poisson counting error and as numerical values (increments of 0.5 times counting error of the element):

Range in standard deviation of successful models		
Element	As multiple of counting error	Numerical value
Na	2–3.5	0.0064–0.0112
Mg	0–5	0–0.016
Al	2–5.5	0.0242–0.0666
Si	1–5.5	0.0129–0.082
K	2.5 only	0.0245 only
Ba	1.5 only	0.0012 only
Ti	5–7.5	0.0105–0.0158
Fe	1.5–3.5	0.0083–0.0192

Standard deviation of central model		
Element	As multiple of counting error	Numerical value
Na	2.5	0.008
Mg	2.5	0.008
Al	3.5	0.0424
Si	3.5	0.0452
K	2.5	0.0245
Ba	1.5	0.0012
Ti	6	0.0126
Fe	2.5	0.0138

covite sample, an increase in content of K and Ba and a decrease in Ti correlate to the phengitic substitution within all successful models. Assuming charge balance, all successful models suggest that substitution of Ti into the muscovite structure is accommodated by decrease in the total number of octahedral cations. In all cases, the total number of octahedral cations remains above the ideal value of 4 (per 44 cationic units). No change in the number of interlayer cations need be assumed. A partial charge-coupled substitution of the form:



would also produce successful models that require no change in interlayer site occupancy.

Results generally agree with what is known regarding chemical substitution within muscovite (Guidotti, 1984) and with the extent of indeterminate error to be expected from good microprobe analyses. The major exception to this rule is the high degree of model indeterminate error for the element Ti. When this element is excluded, the ratio of indeterminate error to counting error increases with elemental abundance, being lowest for Ba and highest for Si and Al. The limits of indeterminate error in terms of elemental abundance are also controlled by the detection efficiency of the characteristic photons, which is lowest for Fe.

DISCUSSION

It is necessary to point out several inadequacies of the method of model population estimates set forth in this paper. Although some shortcomings are due to relatively simplistic assumptions of the modeling method, others arise from the shortcomings of standard microprobe analyses.

First of all, electron microprobe analyses do not allow investigation of all possible forms of elemental microvariation within muscovite. Analyses cannot be made for microvariation of either the ratio of Fe^{3+} to Fe_{tot} or H content. The simplest assumptions, of constant $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ and absence of microvariation involving elements not analyzed, were used by default.

In fact, both variations in the ratio of Fe^{3+} to Fe_{tot} and oxy mica substitution of the type $\text{Al}^{3+} + (\text{OH})^- = \text{Ti}^{4+} + \text{O}^{2-}$ could produce successful models with only minor adjustments. Also, in the absence of microanalyses for H_2O , microvariation in the extent of oxy mica substitution of the type $\text{Fe}^{2+} + (\text{OH})^- = \text{Fe}^{3+} + \text{O}^{2-}$ cannot be tested at all. Hence, this method of computer modeling reflects the well-known weaknesses of standard microprobe analyses.

A second issue is the extent to which genuine heterogeneity within the sample analyzed is reflected within the successful models. The choice of a single equation of charge-coupled substitution to represent chemical heterogeneity of the sample is governed by simplicity. Once null models, incorporating only random analytical error, are shown to fail, models incorporating a single equation constitute the next logical step. Success of a single-equation model precludes development of more complex models, such as those involving several unrelated partial equations of charge-coupled substitution. The same hierarchical order of complexity applies to the individual elements. If the correlations of a particular element with the other elements are adequately reproduced within models that ascribe all variation for this element to analytical error, this element should not be included within the linear equation. With the analyzed WG muscovite sample, successful models were generated only upon inclusion of all elements, including Ba, within a single equation of charge-coupled substitution.

It is recognized that models that include all mineral heterogeneity within a single equation of substitution may fail to reflect the chemical complexity of metamorphic processes. Indeed, actual validity of a single equation of substitution would require strict crystal-chemical control of elemental variation or a metamorphic history analogous to the ideal concept of perfect fractional crystallization within igneous rocks. In fact, neither condition is likely to have been met within the analyzed WG sample. Natural muscovite does not possess rigid stoichiometry, and the parent rock formation has undergone both Grenvillian and Paleozoic orogenies.

Nevertheless, incorporation of a single equation of charge-coupled substitution yields successful results for

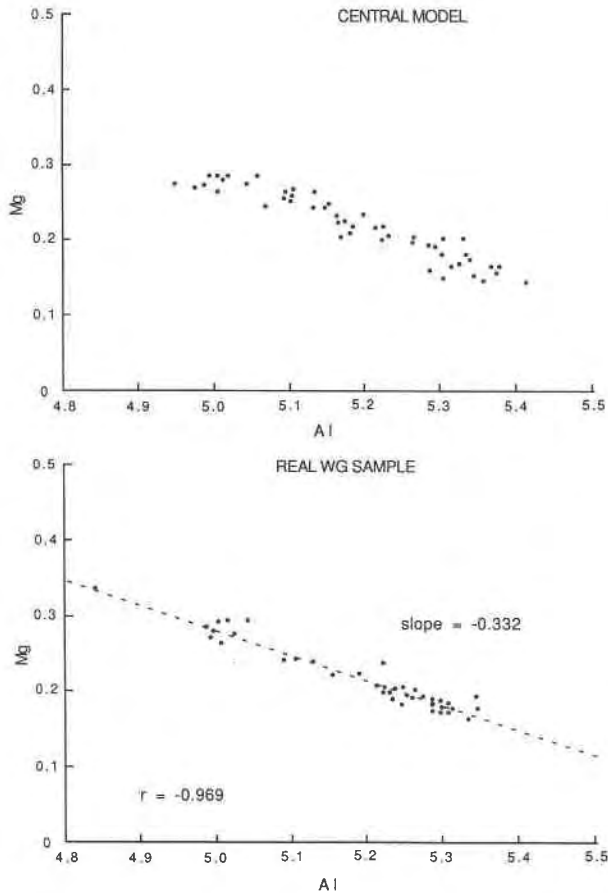


Fig. 3. Comparison of the central model to the real set of WG muscovite analyses is shown for correlation of the elements Mg and Al. The model set of analyses consists of 1000 members; every 20th member is shown for clarity. Covariation of the two elements is well constrained, and little room is left for any conflicting patterns of substitution not incorporated within the single equation.

the WG muscovite sample, and it is reasonably certain that the magnitude of any additional complex patterns of elemental substitution is not large. These points are addressed in Figures 3 and 4. Figure 3 shows that the covariation of Mg with Al is tightly constrained within the analyzed sample and that this constraint is reflected within the central model. In contrast, Figure 4 shows somewhat lower correlation between Ti and Fe_{tot} . The large indeterminate error for Ti in the model, as well as the relatively poor correlations involving this element, is not readily explained in terms of real analytical error for this element within the muscovite sample. Apparently some additional cause of heterogeneity not reflected in the equation of charge-coupled substitution is present. Heterogeneity could be caused by an additional uncorrelated equation of substitution. In any event, the fact that heterogeneity for Ti is well modeled by a large degree of indeterminate error means that information regarding the cause of this element's heterogeneity cannot be retrieved from the data set by the methods presented here.

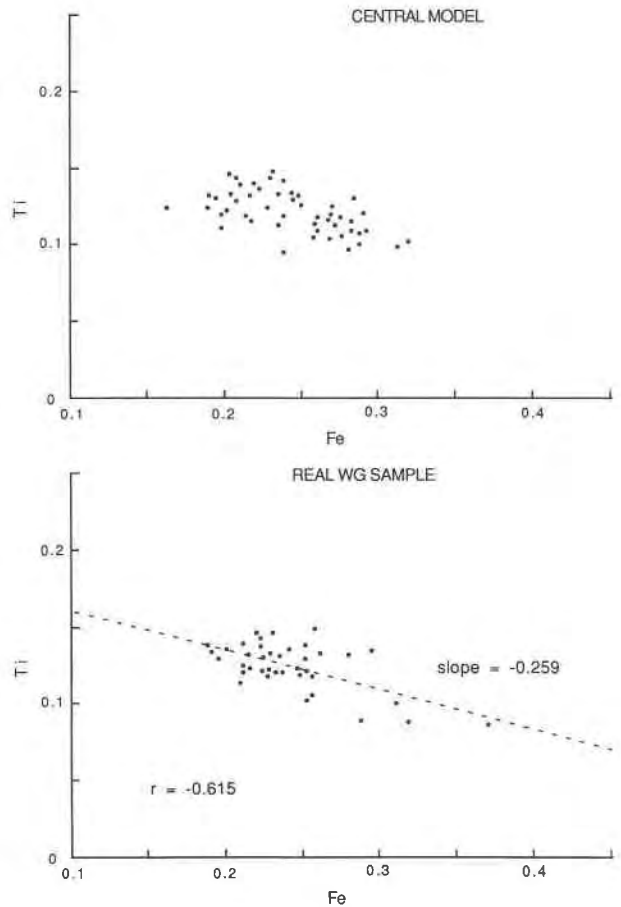


Fig. 4. Comparison of the central model to the real set of WG muscovite analyses is shown for correlation of the elements Ti and Fe_{tot} . The model set of analyses consists of 1000 members; every 20th member is shown for clarity. In contrast to the case displayed in Figure 3, covariation of the elements Ti and Fe_{tot} is only loosely constrained by the single equation of charge-coupled substitution of the central model. Independent and conflicting trends of substitution may be hidden within the diffuse cloud of data points.

Anyone who chooses to use the methods of this paper must remain aware of the rather simplistic assumptions underlying the methods. That complex patterns of elemental substitution are neither revealed nor required within a particular sample by the method of model population estimates does not mean that such patterns are not present.

CONCLUSION

The method of model population estimates allows resolution and quantification of the nature and extent of elemental heterogeneity within a mineral to a scale that is comparable to that of analytical error. Thus, this method is ideally suited to the study of replicate microprobe analyses within single thin sections and other small samples. Such studies represent a logical advance in the use of microprobe analyses.

TABLE 5. Calculations for plagioclase-muscovite thermometry, using the method of Green and Usdansky (1986)

Plagioclase mole fractions			
	Center	Rim	
X_{Ab}	0.749	0.712	
X_{An}	0.248	0.285	
X_{Cr}	0.011	0.010	
Muscovite mole fractions			
	Most phengitic	Least phengitic	Mean
X_{Mu}	0.773	0.799	0.786
X_{Ps}	0.040	0.061	0.050
Calculated temperatures at an assumed pressure at 5 kbar			°C
Most phengitic muscovite/plagioclase centers			525
Least phengitic muscovite/plagioclase rims			582
Mean muscovite/plagioclase centers			551
Mean muscovite/plagioclase rims			561

For example, the method of model population estimates may be applied to studies of metamorphic geothermometry. Application of the muscovite-plagioclase geothermometer of Green and Usdansky (1986) to the central model for the WG muscovite sample is outlined in Table 5. Oligoclase crystals, to several millimeters across, show inverse zoning with rims richer in Ca. Use of the mean composition for WG muscovite, along with center and rim compositions of oligoclase, results in a calculated temperature range of 551–561 °C at an assumed pressure of 5 kbar. Use of the two end-members of the linear equation of charge-coupled substitution results in a somewhat wider temperature range of 525 to 582 °C. Thus, mean mineral compositions, typically used for many geothermometric calculations, may hide important information regarding the metamorphic history of the rock, and any conclusions based on use of such mean compositions must be suspect.

A method that would allow quantification of heterogeneity within complex minerals is clearly needed for a more accurate study of metamorphism. The method of model population estimates may furnish such a method.

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REFERENCES CITED

- Chayes, F. (1971) Ratio correlation. University of Chicago Press, Chicago, Illinois.
- Dixon, W.J., and Massey, F.J., Jr. (1969) Introduction to statistical analysis. McGraw Hill, New York, New York.
- Dymek, R.F. (1983) Titanium, aluminum, and interlayer cation substitutions in biotite from high-grade gneisses, West Greenland. *American Mineralogist*, 68, 880–899.
- Fritz, S.J., and Popp, R.K. (1985) A single dissolution technique for determining FeO and Fe₂O₃ in rock and mineral samples. *American Mineralogist*, 70, 961–969.
- Green, N.L., and Usdansky, S.I. (1986) Toward a practical plagioclase-muscovite thermometer. *American Mineralogist*, 71, 1109.
- Guidotti, C.V. (1984) Micas in metamorphic rocks. In *Mineralogical Society of America Reviews in Mineralogy* 13, 357–467.
- Hatcher, R.D., Jr. (1971) Geology of Rabun and Habersham Counties, Georgia: A reconnaissance study. *Georgia Geological Survey Bulletin*, 83.
- Hatcher, R.D., Jr., and Butler, J.R. (1979) Guidebook for the Southern Appalachian field trip in the Carolinas, Tennessee, and northeastern Georgia. North Carolina Geological Survey, Raleigh, North Carolina.
- Hollocher, K. (1987) Systematic retrograde metamorphism of sillimanite-staurolite schists, New Salem area, Massachusetts. *Geological Society of America Bulletin*, 98, 621–634.
- Indares, A., and Martignole, J. (1985) Biotite-garnet geothermometry and granulite-facies rocks: Evaluation of equilibrium criteria. *Canadian Mineralogist*, 23, 187–193.
- Mohr, D.W., Barnett, R.L., and Michie, J. (1986) Chemical processes and migration of elements during retrogression of a staurolite-zone assemblage in western North Carolina. *Contributions to Mineralogy and Petrology*, 92, 400–411.
- Tracy, R.J., and Dietsch, C.W. (1982) High-temperature retrograde reactions in pelitic gneiss, central Massachusetts. *Canadian Mineralogist*, 20, 425–437.

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