

Analysis of the compositional variations of biotite in pelitic hornfelses from northeastern Minnesota

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Abstract

Biotite from pelitic hornfelses, northeastern Minnesota, shows a wide compositional range, from $\text{Mg}/(\text{Mg} + \text{Fe}) = 0.35$ to 0.95 . Strong correlations among Mg, Fe, Ti, $^{\text{VI}}\text{Al}$, and $^{\text{IV}}\text{Al}$ are observed, and the technique of principal components analyses is used to extract independent biotite components. The dependence of composition on assemblage is exemplified by biotite from the assemblage quartz + muscovite + biotite + cordierite + K-feldspar + ilmenite with compositions that contain more dioctahedral component and less Ti than biotite from a similar, but muscovite-free assemblage. Principal components analysis shows that 98% of the total variance in compositions of biotite from the muscovite-bearing assemblage can be ascribed to two substitutions with *phlogopite*: the substitution $^{\text{IV}}\text{Al}_{0.45} + \text{Fe}_{2.29} + ^{\text{VI}}\text{Al}_{0.21} + \text{Ti}_{0.31} + ^{\text{IV}}\square_{0.19} \rightleftharpoons \text{Si}_{0.45} + \text{Mg}_{3.0}$, and the substitution $\text{Ti}_{1.5} + ^{\text{IV}}\square_{0.5} \rightleftharpoons ^{\text{VI}}\text{Al}_2$. The analysis indicates that although biotite is rigorously a six- or more-component mineral, three components are sufficient to describe the bulk of its compositional range. These three components are used to calculate the possible range in biotite compositions for the muscovite-bearing assemblage using ideal-mixing activity models. The calculated range is very similar to the observed range; however, the absolute value of $K_D(\text{Mg}/\text{Fe}, \text{Cord}/\text{bio})$ is underestimated. In addition, the amounts of octahedral Al, Ti, and vacancies are poorly estimated, especially for Mg-rich biotite. These faults are probably the result of treating biotite as a three-component rather than a six-component phase. The observed cation correlations are believed to result from crystal chemical constraints on the volume of the biotite unit cell. It is proposed that biotite compositions from a particular assemblage might be sensitive indicators of the thermal gradient.

Introduction

Biotite occurs in a great variety of rock types and has a structure that can accommodate most of the abundant elements. The large range in composition of natural biotite makes it a valuable source of information regarding equilibrium conditions. The composition of biotite depends principally on the bulk composition and the extents of the various continuous reactions among the minerals in the rock. The latter dependence can be used to deduce the prevailing conditions during equilibration of the mineral assemblage. For example, the partitioning of Fe and Mg between biotite and garnet can be used to determine temperature (Goldman and Albee, 1977, Ferry and Spear, 1978), and the $\text{Fe}/(\text{Fe} + \text{Mg})$ value of biotite coexisting with magnetite and sanadine can be used to determine the value of $f\text{H}_2\text{O}/f\text{O}_2$ (Wones and Eugster, 1965). The composition of biotite in these examples is governed by the progress of the continuous reactions that involve biotite end-members like *phlogopite* and *annite*. In order to obtain the values of the desired intensive parameters, the activities of the end-member components

must be determined. Previous workers have expressed the activity of the end-member component using the ionic model of Kerrick and Darken (1975). For example, Ghent *et al.* (1979) expressed the activity of *phlogopite* as $(X_K)(X_{\text{Mg}})^3(X_{\text{OH}})^2$ in which X refers to the mol fraction of the cation or anion in the appropriate crystallographic site. Thompson (1976) used the activity model $(X_K)(X_{\text{Fe}})^3$ for *annite* in his calculations of continuous and discontinuous mineral equilibria during progressive metamorphism of pelitic schists. In this type of model cations and anions are presumed to substitute on their respective sites independently.

Holdaway (1980) addressed the problem of picking end-member biotite compositions to use in thermodynamic calculations involving natural or experimental systems. Holdaway determined an iron end-member composition for biotite from pelitic schists by linear regression of the various cations or groups of similar cations like $^{\text{VI}}(\text{Al} + \text{Cr})$ against Ti. The end-member biotite is given by Holdaway as the composition at $\text{Ti} = 0$, determined by the regression coefficients.

In a study of the argillaceous rocks from the contact-

metamorphosed aureole of the Duluth Complex, north-eastern Minnesota, Labotka *et al.* (1981) found that the amount of iron in biotite covaried with the amount of tetrahedral aluminum in biotite. This apparent dependence of Fe-content on ^{IV}Al-content was reflected in the partitioning of Fe and Mg between coexisting cordierite and biotite which indicated non-ideal exchange of Fe and Mg, particularly for Mg-rich compositions. A similar relationship was described by Guidotti *et al.* (1977) for Mg-rich biotite from pelitic schists from Maine.

The correlations between major substitutions like Fe $\rightleftharpoons$ Mg and substitutions of minor elements like Ti and ^{VI}Al, described by Holdaway (1980), Guidotti *et al.* (1977), and Labotka *et al.* (1981), suggest that biotite might be described by end-member components that comprise minor as well as major elements. These types of components are chemically more complex than the simple end-member components like *annite* and are perhaps specific to one mineral assemblage. However, the complex components might eliminate the need to consider the non-ideal solution of simple components like *annite* and *phlogopite* in a thermodynamic description of the variance of a mineral assemblage.

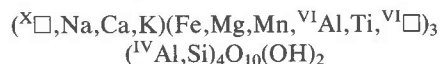
The object of this study is to examine cation-correlations in detail for biotite that crystallized in a low-pressure, contact-metamorphic environment. These correlations result both from differences in bulk composition and from continuous reactions among coexisting minerals. Each of these effects on the composition of biotite is examined. The observed cation correlations are used to construct biotite components that are effective in describing the composition of biotite from a constant assemblage over a range in metamorphic grade. Biotite compositions are calculated for the assemblage quartz + muscovite + biotite + cordierite + K-feldspar + ilmenite and are compared to compositions of biotite from the Rove Formation. The discrepancies in using complex biotite components to describe natural biotite compositions and possible reasons for the observed correlations are then discussed. This study concludes by suggesting that observed cation correlations for compositions of biotite from a constant assemblage might be indicators of pressure during metamorphism.

Samples and methods

The samples used in this study were collected from the Rove Formation within the contact aureole of the Duluth Complex in northeastern Minnesota. The Rove Formation consists of a sequence of argillite and greywacke which was deposited $\sim 2 \times 10^9$ years ago and contact metamorphosed $\sim 1 \times 10^9$ years ago by the intrusive Duluth Complex. At distances of more than 100 m from the gabbroic complex, argillites and metagreywackes contain the assemblage quartz + muscovite + biotite + chlorite + plagioclase. Within 100 m of the contact the rocks had recrystallized to the assemblage quartz + muscovite + biotite + cordierite + K-feldspar. Locally,

the hornfels lack muscovite, and at the contact with the gabbro, hypersthene occurs in the assemblage. Ilmenite occurs in most assemblages except some of the highest-grade ones in which rutile occurs. Labotka *et al.* (1981) estimated temperatures of 500 to 600°C based on the partitioning of K and Na between coexisting muscovite and K-feldspar and pressures of about 1500 bars based on the amount of overburden near the contact. The samples, their assemblages, and metamorphic grade are given in Appendix I.

The compositions of biotites were determined by electron microprobe analysis using an automated ARL EMX, at SUNY Stony Brook. Biotite grains were analyzed for the elements Si, Ti, Al, Cr, Fe, Mg, Mn, Ca, Na, and K. Data were reduced on-line using the method of Bence and Albee (1968). Precision is monitored by analysis of standard minerals and by replicate analyses of biotite grains and is found to be 2–3% for elements more abundant than 10 wt.% and about 10% for minor elements. Normalization of the microprobe analysis to a chemical formula is difficult because biotite contains ferric iron and crystallographic-site vacancies which cannot be measured. However, none of the rocks contains a ferric-iron phase, microprobe analysis of ilmenite indicates no appreciable ferric iron, and Labotka *et al.* (1981) calculated that one sample formed under *f*O₂ conditions of the FMQ buffer. Thus, the ferric-iron content of biotite is probably small and is assumed to be zero. Likewise, the substitution of O²⁻ for (OH)⁻ is assumed not to occur. F and Cl were not analyzed, but wavelength scans indicate no appreciable amounts of these anions. Cation proportions are normalized to a total positive charge of 22, and cations are assigned to crystallographic sites for the stoichiometry



in which the vacancies are determined by difference. Cr, Ca, Na and Mn occur in amounts that are generally less than the detection limit of the microprobe. Biotite analyses used in this study are given in Appendix II.¹

The composition of biotite depends not only on metamorphic grade, but also on mineral assemblage; the effects of the two dependences must be separated if the components of biotite are to be used as indicators of grade or facies series. All biotites from the Rove Formation coexist with quartz, cordierite or chlorite, and ilmenite or rutile. The samples are divided into two groups, the first contains samples with muscovite + microcline + ilmenite-bearing assemblages, and the second contains samples that lack muscovite and contain either ilmenite or rutile in the assemblages. By "tagging" the biotite

¹ To receive a copy of Appendix II, order Document AM-83-234 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit \$1.00 in advance for the microfiche.

analyses so that the assemblage can be identified, compositional variations resulting from differences in assemblage can be separated from variations resulting from differences in metamorphic grade.

Biotite and its components

The composition of a chemically complex mineral like biotite can be expressed in many ways. A first method is to consider the composition as a point in n -dimensional space in which the coordinate axes are the number of cations per 12 (O,OH). A second simple method is described by Thompson *et al.* (1982) in which a mineral composition is represented by an end-member and several appropriate element exchanges. A biotite composition can be expressed as *phlogopite*, $\text{KMg}_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$, and substitutions like $\text{Fe}^{2+} \rightleftharpoons \text{Mg}^{2+}$, $\text{Na}^+ \rightleftharpoons \text{K}^+$, and ${}^{\text{VI}}\text{Al}^{3+} + {}^{\text{IV}}\text{Al}^{3+} \rightleftharpoons \text{Mg}^{2+} + \text{Si}^{4+}$. The end-member is called an additive component, and the substitutions are called exchange components. The choice of additive and exchange components is arbitrary as long as the chosen components are linearly independent. Using *phlogopite* as the additive component, the compositions of biotite other than compositions produced by the substitution of Fe^{2+} or Mn^{2+} for Mg^{2+} , of Na^+ for K^+ , or of F^- or Cl^- for $(\text{OH})^-$ are constrained to satisfy the relation

$${}^{\text{X}}\text{Ca} + 2{}^{\text{VI}}\text{Ti} + {}^{\text{VI}}\text{Al} + {}^{\text{VI}}\text{Fe}^{3+} + {}^{\text{VI}}\text{Cr} = {}^{\text{X}}\square + 2{}^{\text{VI}}\square + ({}^{\text{IV}}\text{Al} - 1) + ({}^{\text{OH}}\text{O})^{-2}$$

which equates the charge excess to the charge deficiency. In this expression X refers to the interlayer site, VI and IV are the octahedral and tetrahedral sites, respectively, and $\square$ refers to vacancy. Biotite from the Rove Formation contains very small amounts (generally less than the detection limit of the microprobe) of Na, Ca, and Cr, and the Fe^{3+} and $({}^{\text{OH}}\text{O})^{-2}$ contents are assumed to be zero. The site-charge-balance equation thus reduces to ${}^{\text{VI}}\text{Al} + 2\text{Ti} = ({}^{\text{IV}}\text{Al} - 1) + 2{}^{\text{VI}}\square + {}^{\text{X}}\square$. Figure 1 shows that this equation is satisfied for the biotite analyses considered here.

Despite the simple elegance of this method of representing biotite compositions, continuous reactions that are written with both additive and exchange components are unfamiliar and can be difficult to understand (for examples, see Thompson *et al.*, 1982). A third, more traditional, but cumbersome method is using only additive, end-member components to describe the compositions of biotite. Continuous reactions written with only additive components can be more easily related to reactions that occur among phases with end-member compositions.

The number of independent components necessary to describe a biotite composition equals the number of variables minus the number of constraints. Using the method of describing biotite as a point in n -dimensional space in which each of the n coordinates is the amount of a cation in a particular crystallographic site, the number of variables considered for biotite from the Rove Forma-

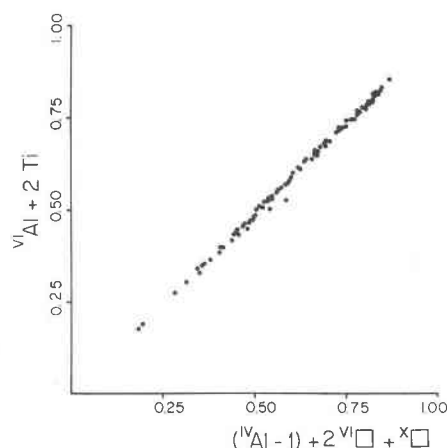


Fig. 1. Plot of ${}^{\text{VI}}\text{Al} + 2\text{Ti}$ versus $({}^{\text{IV}}\text{Al} - 1) + 2{}^{\text{VI}}\square + {}^{\text{X}}\square$ for 82 biotite analyses used for principal components analysis illustrating satisfaction of site-charge balance.

tion is nine: the amounts of ${}^{\text{X}}\square$, K, Fe, Mg, ${}^{\text{VI}}\text{Al}$, Ti, ${}^{\text{VI}}\square$, ${}^{\text{IV}}\text{Al}$, and Si per 12(O,OH). The number of constraints is four, three from stoichiometry: $\text{K} + {}^{\text{X}}\square = 1$, $\text{Fe} + \text{Mg} + {}^{\text{VI}}\text{Al} + \text{Ti} + {}^{\text{VI}}\square = 3$, ${}^{\text{IV}}\text{Al} + \text{Si} = 4$, and one from the site-charge-balance relation. Thus, five independent components may be chosen and the remaining four are determined by the constraints. If, for example, the amounts of Mg, Fe, ${}^{\text{VI}}\text{Al}$, Ti, and ${}^{\text{IV}}\text{Al}$ are arbitrarily chosen, the amount of ${}^{\text{VI}}\square = 3 - (\text{Mg} + \text{Fe} + {}^{\text{VI}}\text{Al} + \text{Ti})$, of $\text{Si} = 4 - {}^{\text{IV}}\text{Al}$, of ${}^{\text{X}}\square = 1 + {}^{\text{VI}}\text{Al} + 2\text{Ti} - {}^{\text{IV}}\text{Al} - 2{}^{\text{VI}}\square$, and of $\text{K} = 1 - {}^{\text{X}}\square = {}^{\text{IV}}\text{Al} + 2{}^{\text{VI}}\square - {}^{\text{VI}}\text{Al} - 2\text{Ti}$.

If exchange components are used, then the three stoichiometric constraints are automatically satisfied by the one additive component. If *phlogopite* is chosen as the additive component, the remaining variables are six: ${}^{\text{X}}\square$, Fe, ${}^{\text{VI}}\text{Al}$, Ti, ${}^{\text{VI}}\square$, and ${}^{\text{IV}}\text{Al}$. However, the exchange components must satisfy the site-charge-balance constraint which reduces the number of possible, independent exchange components to five. A possible set of exchange components contains $\text{Fe} \rightleftharpoons \text{Mg}$, ${}^{\text{VI}}\text{Al} + {}^{\text{IV}}\text{Al} \rightleftharpoons \text{Mg} + \text{Si}$, $2{}^{\text{VI}}\text{Al} + {}^{\text{VI}}\square \rightleftharpoons 3\text{Mg}$, ${}^{\text{X}}\square + \text{Si} \rightleftharpoons \text{K} + {}^{\text{IV}}\text{Al}$, and $1.5\text{Ti} + 0.5{}^{\text{VI}}\square \rightleftharpoons 2{}^{\text{VI}}\text{Al}$. Other sets of exchange components can be created by linear combination of these.

If biotite compositions are expressed by mole fractions of additive components only, the stoichiometric and site-charge-balance constraints are all automatically satisfied. The number of components is then just the number of elements that can be varied; these are six: K, Si, Al, Mg, Fe, and Ti. The number of independent components is five because closure requires that the sum of the mole fractions of the components equals one. The reduction of a biotite formula to a set of components represents a transformation of coordinates from the cation basis $\hat{e}$ to the biotite-components basis $\hat{e}'$. The relation between the bases is $\hat{e}'_j = \sum_i \Gamma_{ij} \hat{e}_i$; $\hat{e}'_j$ is the j^{th} biotite-component vector, $\hat{e}_i$ is the i^{th} cation vector and Γ_{ij} is the transformation

matrix relating to the composition of the new components to the old (Matthews and Walker, 1970). If $\mathbf{x}$ is a biotite composition in the cation basis, then $\mathbf{x} = \mathbf{\Gamma}\mathbf{x}'$ where $\mathbf{x}'$ is the same composition in the component basis. In general, if n is the number of cations, then $\mathbf{\Gamma}$ is a matrix of full rank n . For the system described here, $n = 6$; Si, Al, Fe, Mg, Ti, and K are the cation components, and any biotite composition can be represented exactly by six additive components or by one additive and five exchange components. If the matrix $\mathbf{\Gamma}$ is chosen so that the n column vectors are linearly independent, then any desired biotite component can be derived by an appropriate linear combination of the n vectors.

The composition of biotite depends on the mineral assemblage and on the extents of reactions among the minerals in the assemblage. The only way that biotite can change composition during metamorphism is by reaction with the other coexisting phases. The components of biotite can be divided into those that are related to the other components in the rock by reactions among the other phases in the system and those that reflect the bulk chemical composition of the rock only. These types of reactions generally result in changes in the modal abundance of biotite, and the components related by reaction are those that are usually used to calculate values of intensive thermodynamic parameters.

The reaction-related components of biotite have compositions given by $\mathbf{R} = \mathbf{\Phi}\mathbf{X}$, in which $\mathbf{\Phi}$ is the $n \times m$ matrix that contains the compositions of the m components in a system, other than the biotite components, and $\mathbf{X}$ is the $m \times \ell$ matrix of stoichiometric coefficients for the ℓ reactions that can alter the composition of biotite. If the rank r of $\mathbf{\Phi}$ is m , then there are no reactions in the system that involve only non-biotite components. If the rank r of $\mathbf{\Phi}$ is less than m , then there are $m - r$ independent reactions among the non-biotite components in the system. If $n = m = r$, then $\mathbf{R} = \mathbf{\Gamma}$. To find $\mathbf{R}$, one must find those vectors γ_i of $\mathbf{\Gamma}$ that satisfy $\mathbf{\Phi}'\mathbf{X}_i = \gamma_i$ in which $\mathbf{\Phi}'$ is the matrix $\mathbf{\Phi}$ with $m - r$ columns removed so that $\mathbf{\Phi}'$ is full rank. A simple test to determine $\mathbf{R}$ is to augment $\mathbf{\Phi}$ by adding a vector γ_i . If the rank of the augmented matrix $[\mathbf{\Phi}\gamma_i]$ is the same as $\mathbf{\Phi}$, then γ_i is a column vector of $\mathbf{R}$.

Biotite from the assemblage quartz + muscovite + biotite + cordierite + K-feldspar + ilmenite is used as an example. The cation-basis in this system is K, Si, Al, Mg, Fe, Ti, and H. The additive-component basis arbitrarily chosen to represent the Rove biotite is *phlogopite*, *tal*c, *muscovite*, *siderophyllite*, *annite*, and *Ti-mica*. The matrix $\mathbf{\Gamma}$, in which the rows are the amounts of cations, and the columns are the biotite-components, is given in Table 1. The matrix is of full rank six and any other component can be constructed by a linear combination of the appropriate columns. The matrix $\mathbf{\Phi}$, also given in Table 1, has rows that are cation compositions of the components *K-feldspar*, *quartz*, *muscovite*, *Mg-cordierite*, *Fe-cordierite*, *ilmenite*, and *H₂O*, which occur in phases other than biotite. $\mathbf{\Phi}$ has the full rank of seven, and if $\mathbf{\Phi}$ is augment-

ed by any of the columns of $\mathbf{\Gamma}$, the rank remains seven. Thus, the matrix of the reaction-related components, $\mathbf{R}$, is identical to $\mathbf{\Gamma}$. The matrix $\mathbf{X}$ has columns that are the stoichiometric amounts of the components *K-feldspar*, *quartz*, *muscovite*, *Mg-cordierite*, *Fe-cordierite*, *ilmenite*, and *H₂O*, representing the biotite components *phlogopite*, *tal*c, *muscovite*, *siderophyllite*, *annite*, and *Ti-mica* (Table 1).

The matrix $\mathbf{\Phi}'$ for the Rove assemblage lacking muscovite does not contain the column *mus*c (Table 1). The rank of this matrix is six, and augmenting the matrix with any one column of $\mathbf{\Gamma}$ results in a matrix of rank 7. If the matrix $\mathbf{\Phi}'$ is augmented with two columns of $\mathbf{\Gamma}$, the rank remains 7. Thus biotite compositions in this assemblage can change only by reactions that involve two biotite end-members; these reactions are exchange reactions and generally do not alter the model abundance of biotite.

One object of this study is to reduce the dimensions of the $\mathbf{\Gamma}$ and $\mathbf{X}$ matrices by using a reduced number of additive components that account for the compositional variations of biotite from the Rove Formation. If this can be satisfactorily accomplished, then the system of differential equations that governs the equilibrium compositions of biotite can be reduced to a manageable size for solution.

Principal components analysis

The variances and covariances of the proportions of cations and vacancies in the biotite formula were analyzed using the technique of principal components analysis (Morrison, 1976). In this analysis, the cations and vacancies are considered to be coordinate axes in n -dimensional space and a biotite composition is considered to be a point in this n -space. The sample variances and covariances,

$$S_{ij} = 1/(m-1) \sum_k^m (x_{ik} - \bar{x}_i)(x_{jk} - \bar{x}_j)$$

in which x_{ik} and x_{jk} refer to amounts of the cations i and j in biotite k , $\bar{x}_i$ is the average amount, and m is the number of biotite analyses, form a real, symmetric matrix with dimensions $n \times n$. The total variance is defined as the trace, $\sum_i S_{ii}$, of the covariance matrix $\mathbf{S}$. Principal components analysis represents a transformation to a new set of coordinates that are linear combinations of the original cation coordinates. The new set of coordinates is chosen so that the new matrix $\mathbf{S}'$, formed from the covariances of biotite compositions expressed in terms of the new coordinates, is diagonal. This means that the new biotite components, which are linear combinations of the original cations, are independent of one another. The new diagonal elements of $\mathbf{S}'$ are the eigenvalues of the original covariance matrix $\mathbf{S}$; the new coordinate axes are the eigenvectors of $\mathbf{S}$ and are called principal components. Because the transformation is orthogonal, the trace of $\mathbf{S}$ is

Table 1. Relation satisfied by reaction-related components

	phl	talc	musc	sid	ann	Ti-mica		ksp	qtz	musc	Mgcd	Fecd	ilm	H ₂ O		phl	talc	musc	sid	ann	Ti-mica	
K	1.0	0.0	1.0	1.0	1.0	1.0	=	1	0	1	0	0	0	0	X	4	3	0	2	4	0	ksp
Si	3.0	4.0	3.0	2.0	3.0	3.0		3	1	3	5	5	0	0		-7.5	-3.5	0	-6	-7.4	3.75	qtz
Al	1.0	0.0	3.0	3.0	1.0	1.0		1	0	3	4	4	0	0		-3	-3	1	-1	-3	1	musc
Mg	3.0	3.0	0.0	0.0	0.0	0.0		0	0	0	2	0	0	0		1.5	1.5	0	0	0	0	Mgcd
Fe	0.0	0.0	0.0	2.0	3.0	0.0		0	0	0	0	2	1	0		0	0	0	1	1.5	-0.75	Fecd
Ti	0.0	0.0	0.0	0.0	0.0	1.5		0	0	0	0	0	1	0		0	0	0	0	0	1.5	ilm
H	2.0	2.0	2.0	2.0	2.0	2.0		0	0	2	0	0	0	2		4	4	0	2	4	0	H ₂ O
$R (= \Gamma)$							=	Φ								X						

invariant. That is, the sum of the eigenvalues is identical to the total variance, and the relative contribution of each eigenvector to the total variance of the data set is given by the associated eigenvalue. The first principal component has the largest associated eigenvalue, the second principal component has the second largest eigenvalue, and so on. A lucid exposition of the mathematics and application of principal components analysis is given by Morrison (1976). The computer programs used in this study are those of Dixon (1975) and Wahlstedt and Davis (1968).

Because the amounts of all cations and vacancies in biotite sum to eight, biotite compositions form a closed set. Closure induces cation correlations that result from stoichiometry and not from other physical-chemical processes, and Chayes and Trochimczyk (1978) have discussed this effect on principal components. The problems associated with closure are circumvented by using the principal components analysis on biotite compositions that are expressed as an additive component plus exchange components; the exchange components form an essentially open set.

Biotite from the Rove Formation

The compositions of 46 biotites from the assemblage quartz + biotite + muscovite + (cordierite or chlorite) + K-feldspar + ilmenite and 36 biotites from the assemblage

quartz + biotite + cordierite + K-feldspar + (ilmenite or rutile) were used in this study. The means, standard deviations s , and correlation coefficients $R_{ij} = S_{ij}/\sqrt{s_i^2 s_j^2}$ for the cations K, Fe, Mg, ^{VI}Al, Ti, and ^{IV}Al and for the vacancy ^{VI}□ are shown in Table 2, and bivariate plots of these variables are shown in Figure 2. To construct the set of variables to be used in the principal components analysis, an additive component must be chosen. Although the choice is arbitrary, examination of Table 2 and Figure 2a shows that the choice of *phlogopite*, $KMg_3AlSi_3O_{10}(OH)_2$, is propitious. Mg is negatively correlated with all other variables, and the value of ^{IV}Al is 1.0 in the limit $Mg \rightarrow 3.0$. By considering *phlogopite* as the additive component, the remaining variables that form exchange components are Fe, ^{VI}Al, Ti, ^{VI}□, and (^{IV}Al-1). These are the variables that are subjected to principal components analysis. The variable ^{VI}□ has been neglected because it shows little, or no correlation with any other variable (Fig. 2), it has a large relative standard deviation (see Table 1 for K), and the error in this variable may be the result of analytical error in the amount of K₂O.

Because all variables are of the same type, number/formula unit, and because variables having larger magnitudes are better known than those with smaller magnitudes, e.g., Fe vs. Ti, the structure of the covariance matrix S rather than the correlation matrix R is examined

Table 2. Univariate statistics and multiple correlation coefficients

	Mean	Standard Deviation	Smallest Value	Largest Value	Correlation Coefficients						
					K	Mg	Fe	^{VI} Al	Ti	^{VI} □	^{IV} Al
K	0.882	0.050	0.701	0.993	1.000						
Mg	1.372	0.523	0.719	2.682	-0.246	1.000					
Fe	1.025	0.391	0.066	1.659	0.092	-0.936	1.000				
^{VI} Al	0.291	0.143	0.034	0.590	0.247	-0.523	0.275	1.000			
Ti	0.154	0.069	0.004	0.300	0.194	-0.511	0.489	-0.247	1.000		
^{VI} □	0.145	0.073	0.002	0.320	0.582	-0.608	0.328	0.529	0.536	1.000	
^{IV} Al	1.218	0.084	0.989	1.350	0.200	-0.873	0.840	0.457	0.465	0.400	1.000

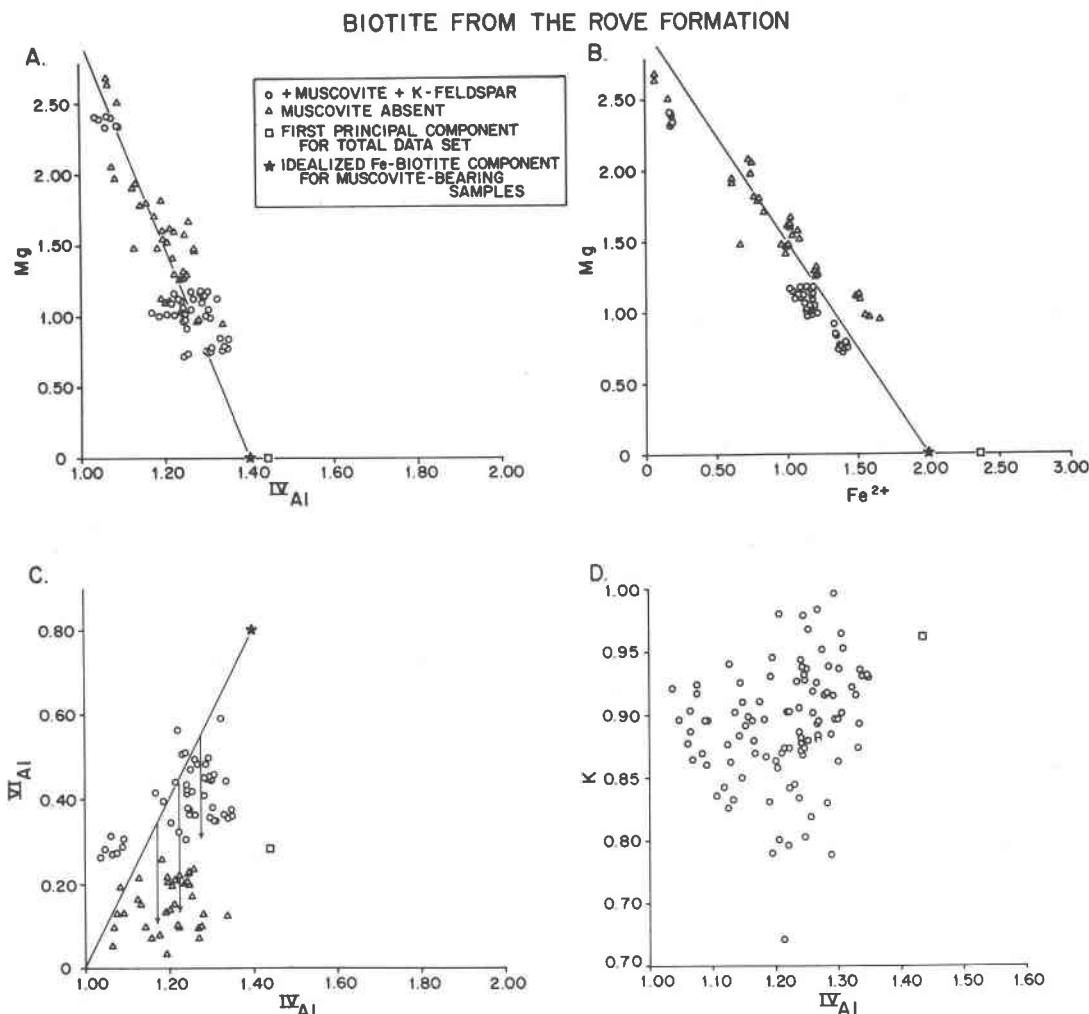
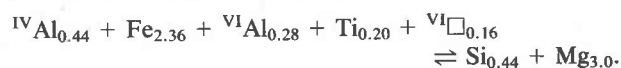


Fig. 2. Bivariate plots of cations and vacancies in biotite illustrating the correlation of Mg, Fe, and ^{IV}Al for all analyses, and separation of biotite compositions in muscovite-bearing assemblages from compositions from muscovite-absent assemblages. Square is the position of the first principal component, and the star is the position of the idealized *Fe-biotite* component. Trend-lines show the effect of the substitution $1.5\text{Ti} + 0.5\text{VI}\square \rightleftharpoons 2\text{VIAl}$ on biotite composition. See following page for continuation of figure.

by principal components analysis. The covariance matrix, its eigenvalues, and its eigenvectors are given in Table 3. The compositions of the eigenvectors are normalized so that the sum of the squares of the amounts of the original variables for each vector is 1.0. These amounts are then direction cosines of the vector in *n*-space and represent the ratios of the original variables along the vector. The first two principal components account for about 95% of the total variance, and thus it appears that only two exchange components are necessary to describe biotite composition from these rocks. A plot of the biotite compositions in terms of these principal components, is shown in Figure 3. In this plot biotite compositions from muscovite-bearing assemblages are separate from compositions from muscovite-free assemblages. Both groups show the same range in the first

component, but the muscovite-bearing group has compositions with more of the second component than any of the muscovite-free compositions.

The types of the exchange components can be determined from the direction cosines of the principal components. Normalizing the direction cosines for the first principal component so that $\text{Fe} + \text{VIAl} + \text{Ti} + \text{VI}\square = 3.0$ gives the exchange component



85% of the total variation in biotite compositions are explained by this exchange. An additional 10% of the variance represents the difference between muscovite-bearing and muscovite-free assemblages, given by the second principal component. This component contains

BIOTITE FROM THE ROVE FORMATION

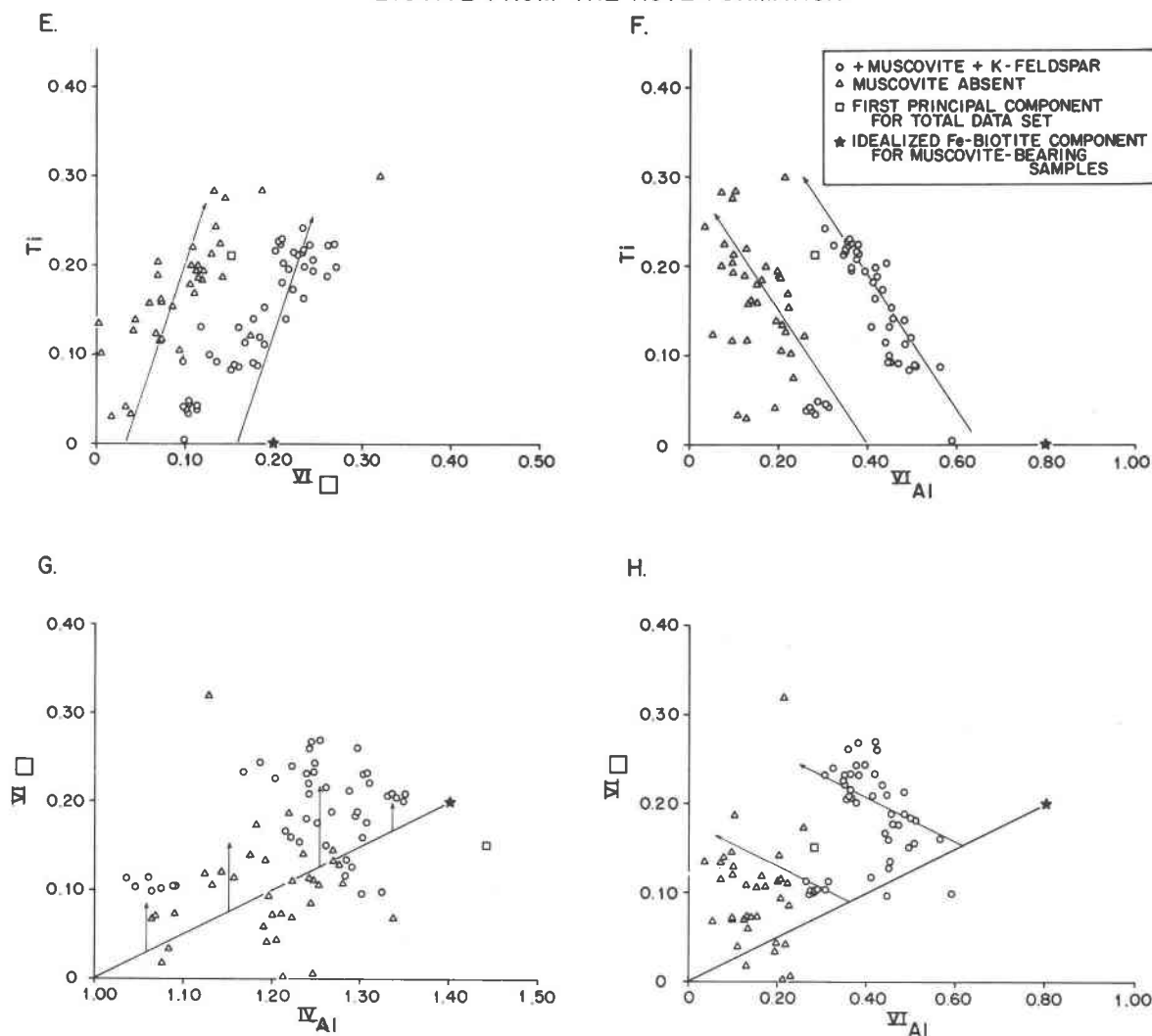
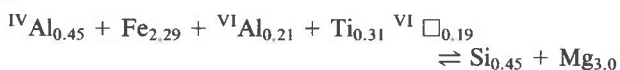


Fig. 2. (continued)

both negative and positive direction cosines. Fe and Ti are negative and ^{VI}Al , $^{VI}\square$, and $(^{IV}Al-1)$ are positive. The second principal component seems to represent the substitution of a muscovite-like component, $K^{VI}\square Al_2 (AlSi_3)O_{10}(OH)_2$, for a titanium component, $K^{VI}\square TiFe (AlSi_3)O_{10}(OH)_2$, although the cosines are not quite in the right proportions for this interpretation. The observation that biotite from muscovite-bearing assemblages contains a greater amount of the second principal component is, however, consistent with the interpretation.

Now that differences in biotite compositions resulting from differences in coexisting minerals have been established, compositional variations within each assemblage-group are examined. By separating the two groups, the principal components for the muscovite-bearing assemblage ought to reflect compositional variations resulting from variations in the intensive thermodynamic variables,

whereas the components for the muscovite-free assemblage ought to reflect the greater degree of freedom resulting from the absence of muscovite. The principal components for each of these groups are given in Table 4. Nearly all of the variance (98%) in biotite compositions from muscovite-bearing assemblages is explained by two components. The first is similar to the first principal component for the combined data set and can be expressed as



The second component is again like a substitution. The direction cosines indicate that as the amount of ^{VI}Al and to a smaller degree ^{IV}Al increase, the amounts of Ti and $^{VI}\square$ decrease, but Fe is unaffected. Biotite from muscovite-absent assemblages also contains two components,

Table 3. Principal components analysis of 82 biotite compositions.

	Covariance Matrix					Principal Component		
	Fe	^{VI} Al	Ti	VI	(^{IV} Al-I)	1	2	3
Fe	0.153					0.972	-0.130	-0.119
^{VI} Al	0.015	0.020				0.114	0.932	-0.074
Ti	0.013	-0.002	0.005			0.085	-0.191	0.674
VI□	0.009	0.005	0.003	0.005		0.066	0.235	0.723
^{IV} Al-I	0.028	0.006	0.003	0.002	0.007	0.180	0.115	0.108
Total Variance =	Diagonal Elements					0.190		
Variance Associated with Principal Component						0.161	0.021	0.006
% of Total Variance						84.7	11.1	3.2

the first appears to be a substitution of Fe for Mg and the second seems to be a substitution of ^{VI}Al for Ti + ^{VI}□, and is similar to the second component for the muscovite-bearing group. The inverse correlation between ^{VI}Al and Ti + ^{VI}□ indicates that the charge-balanced substitution corresponding to the second principal component is $1.5\text{Ti} + 0.5\text{VI}\square \rightleftharpoons 2\text{VIAl}$. Trend lines are shown in Figure 2 to illustrate the effect of the Ti substitution on the first principal components. Each point on the plots of Figure 2 represents the vector sum of the first and second principal components.

Principal components analysis has identified two exchange components that account for greater than 90% of the total variance in biotite compositions. For biotite from muscovite-bearing assemblages, the focus of the next section, 98% of the total variance is explained by the first two principal components. Thus, the variation in biotite composition resulting from changes in *T*, *P*, or $\mu\text{H}_2\text{O}$ might be adequately described by the additive and two principal (exchange) components. If so, the number of differential equations describing the equilibrium compositions of minerals in the assemblage is substantially

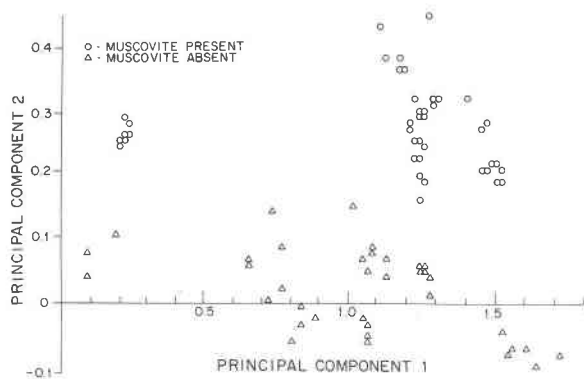


Fig. 3. Compositions of biotite recast as amounts of principal components. Biotite from muscovite-bearing assemblages contains more of the second principal component than biotite from muscovite-absent assemblages.

Table 4. Principal components of biotite compositions from each assemblage group

	Muscovite-Bearing Assemblage			Muscovite-Absent Assemblage		
	1	2	3	1	2	3
Fe	0.964	-0.004	0.044	0.987	0.048	-0.098
^{VI} Al	0.095	0.766	0.394	0.038	0.313	0.845
Ti	0.126	-0.522	0.162	0.040	-0.697	0.188
VI□	0.091	-0.338	0.532	-0.004	-0.610	0.264
^{IV} Al-I	0.192	0.162	-0.731	0.149	-0.204	0.413
% Variance Contributed	93.8	4.2	0.9	90.8	5.1	1.9

reduced from the six that rigorously describe biotite compositions, to three.

The next section describes the composition of biotite in terms of three additive components. Additive components are constructed from the exchange components by linear combination of the two principal components. Because the second principal component is a substitution of Ti for ^{VI}Al, one of the biotite components contains no Ti and another contains no ^{VI}Al. Both of these components must contain the same amount of Fe and ^{IV}Al because the second principal component does not affect these variables. The resulting simplified additive components are $\text{KMg}_3(\text{VIAlSi}_3)\text{O}_{10}(\text{OH})_2$, *phlogopite*, $\text{KFe}_{2.0}\text{VIAl}_{0.8}\text{VI}\square_{0.2}(\text{IVAl}_{1.4}\text{Si}_{2.6})\text{O}_{10}(\text{OH})_2$, *Fe-biotite*, and $\text{KFe}_{2.0}\text{Ti}_{0.06}\text{VI}\square_{0.4}(\text{IVAl}_{1.4}\text{Si}_{2.6})\text{O}_{10}(\text{OH})_2$, *Ti-biotite*.

The mole-fraction of these three model components for each of the original biotite composition is calculated from the relation $\mathbf{x} = \mathbf{I}\mathbf{x}'$ in which $\mathbf{x}$ is the composition in the cation basis, $\mathbf{x}'$ is the same composition in the new-component basis, and $\mathbf{I}$ is the matrix containing the composition of the new components. The least-squares solution for $\mathbf{x}'$ is $(\mathbf{I}^+ \mathbf{I})^{-1} \mathbf{I}^+ \mathbf{x}$ in which $\mathbf{I}^+$ is the transpose of $\mathbf{I}$ and $()^{-1}$ is the inverse of the expression in parentheses. The results are shown in Figure 4, and a summary of the statistics for the transformation of coordinates and of the test of the goodness-of-fit is given in Table 4. For a perfect fit the correlation between the calculated and measured values ought to be identical to the correlation coefficients in Table 2. The three-component model predicts the amounts of Mg, Fe, and ^{VI}Al accurately and the amounts of Ti and ^{VI}□ very well, but the model predicts the amount of ^{VI}□ poorly. The lack of agreement between calculated and measured values of ^{VI}□ is best shown in Figure 4 by those calculated compositions rich in *phlogopite* content that have negative values of *Ti-biotite* or *Fe-biotite*. The reasons for these discrepancies are discussed below.

The composition of biotite as a function of *T*, *P*, and $\mu\text{H}_2\text{O}$

As a result of the principal components analysis, six-dimensional biotite analyses have been reduced to three

components. These compositions are used to calculate the composition of biotite over a range in T and f_{H_2O} at $P = 1500$ bars using ideal-mixing behavior to test whether problems of non-ideality of Fe–Mg exchange can be circumvented by using the more complicated components. The hornfels assemblage for which the biotite compositions are calculated is quartz + muscovite + biotite + cordierite + K-feldspar + ilmenite. The method was described by Rumble (1976) and applied to pelitic schists by Rumble (1978) and to calcic schists by Ferry (1979). The thermodynamic variance of the assemblage quartz + muscovite + biotite + cordierite + K-feldspar + ilmenite equals the number of variables minus the number of constraints. The variables are the amounts of each of the components and T and P . For this idealized assemblage, muscovite, K-feldspar, and ilmenite are considered to be pure phases with components $KAl_2(AlSi_3)O_{10}(OH)_2$ (abbreviated *musc*), $KAlSi_3O_8$ (*ksp*), and $FeTiO_3$ (*ilm*) respectively. Quartz is pure SiO_2 (*qtz*). Cordierite is composed of $Mg_2Al_4Si_5O_{18}$ (*Mgcd*) and $Fe_2Al_4Si_5O_{18}$ (*Fecd*). Biotite consists of three components: $KMg_3(AlSi_3)O_{10}(OH)_2$ (*phl*), $KFe_2Al_{0.8}□_{0.2}(Al_{1.4}Si_{2.6})O_{10}(OH)_2$ (*Febi*), and $KFe_2Ti_{0.6}□_{0.4}(Al_{1.4}Si_{2.6})O_{10}(OH)_2$ (*Tibi*). One other component of this assemblage is H_2O . The constraints are the Gibbs–Duhem equation for each of the phases i of the form

$$S_i dT - V_i dP + \sum_j n_{ij} d\mu_j = 0$$

where n_{ij} is the number of moles of component j in phase i , and the stoichiometric relations among the components, i.e., the “end member reactions.” Three independent relations among the components can be written:

- I. $2phl + 6musc + 15qtz = 8ksp + 3Mgcd + 8H_2O$
- II. $5Febi + 7musc + 27qtz = 12ksp + 5Fecd + 12H_2O$
- III. $10Tibi + 12musc + 39qtz = 22ksp + 7Fecd + 6ilm + 22H_2O$

The variance is thus 3, and the variables are considered to be T , P and μ_{H_2O} . The H_2O -content of cordierite has been neglected in this analysis. If the water content changes little between the assemblages under consideration this will lead to a small error in the final results.

At constant T and P , the Gibbs–Duhem relations for the phases quartz, muscovite, microcline, and ilmenite take the form $d\mu_j = 0$, and the relations for cordierite and biotite are

$$\begin{aligned} n_{Fecd} d\mu_{Fecd} + n_{Mgcd} d\mu_{Mgcd} &= 0 \\ n_{phl} d\mu_{phl} + n_{Febi} d\mu_{Febi} + n_{Tibi} d\mu_{Tibi} &= 0. \end{aligned}$$

If the *Fecd* in cordierite and the *Tibi* in biotite are considered dependent components and the compositions of these phases are written in terms of mole fraction, the Gibbs–Duhem equations become

$$\begin{aligned} d\mu_{Fecd} &= -X_{Mgcd} d(\mu_{Mgcd} - \mu_{Fecd}) \\ d\mu_{Tibi} &= -X_{phl} d(\mu_{phl} - \mu_{Tibi}) - X_{Febi} d(\mu_{Febi} - \mu_{Tibi}) \end{aligned}$$

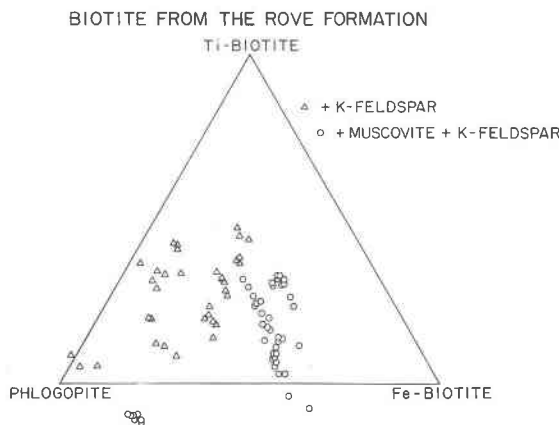


Fig. 4. Compositions of biotite from the Rove Formation represented by the idealized components *phlogopite*, *Fe-biotite*, and *Ti-biotite*.

in which X is the mole fraction. The stoichiometric relations are given by

- I. $8d\mu_{H_2O} = 2d\mu_{phl} - 3d\mu_{Mgcd}$
- II. $12d\mu_{H_2O} = 5d\mu_{Febi} - 5d\mu_{Fecd}$
- III. $22d\mu_{H_2O} = 10d\mu_{Tibi} - 7d\mu_{Fecd}$.

Relations II and III are combined to obtain

$$26d\mu_{H_2O} = 15d\mu_{Tibi} - 35d(\mu_{Febi} - \mu_{Tibi}).$$

As explained by Rumble (1976),

$$\begin{aligned} d(\mu_{Mgcd} - \mu_{Fecd}) &= \frac{\partial^2 g_{cd}}{\partial X_{Mgcd}^2} dX_{Mgcd} \\ d(\mu_{phl} - \mu_{Tibi}) &= \frac{\partial^2 g_{bi}}{\partial X_{phl}^2} dX_{phl} + \frac{\partial^2 g_{bi}}{\partial X_{phl} \partial X_{Febi}} dX_{Febi} \\ d(\mu_{Febi} - \mu_{Tibi}) &= \frac{\partial^2 g_{bi}}{\partial X_{phl} \partial X_{Febi}} dX_{phl} + \frac{\partial^2 g_{bi}}{\partial X_{Febi}^2} dX_{Febi} \end{aligned}$$

in which g_i is the molar Gibbs Free Energy of phase i . If the activities of the various components in cordierite and biotite are given by $a_i = X_i^\alpha$ where α is the number of octahedral sites, then

$$\begin{aligned} \frac{\partial^2 g_{cd}}{\partial X_{Mgcd}^2} &= \frac{2RT}{X_{Mgcd}(1 - X_{Mgcd})}, \\ \frac{\partial^2 g_{bi}}{\partial X_{phl}^2} &= \frac{3RT}{X_{phl}} + \frac{3RT}{X_{Tibi}}, \\ \frac{\partial^2 g_{bi}}{\partial X_{Febi}^2} &= \frac{3RT}{X_{Febi}} + \frac{3RT}{X_{Tibi}}, \text{ and} \\ \frac{\partial^2 g_{bi}}{\partial X_{phl} \partial X_{Febi}} &= \frac{3RT}{X_{Tibi}} \end{aligned}$$

(See Prigogine and Defay, 1954, p. 261).

Combining these relations, the conditions for equilibrium at constant T and P are

$$\text{I.} \quad 8d\mu_{\text{H}_2\text{O}} = 6RT \left(\frac{dX_{\text{phl}}}{X_{\text{phl}}} - \frac{dX_{\text{Mgcd}}}{X_{\text{Mgcd}}} \right)$$

$$\text{II.} \quad 12d\mu_{\text{H}_2\text{O}} = 5RT \left(\frac{3dX_{\text{Febi}}}{X_{\text{Febi}}} + \frac{2dX_{\text{Mgcd}}}{1 - X_{\text{Mgcd}}} \right)$$

$$\text{III.} \quad 26d\mu_{\text{H}_2\text{O}} = -15RT$$

$$\times \left[\frac{10dX_{\text{phl}}}{X_{\text{Tibi}}} + \left(\frac{7}{X_{\text{Febi}}} + \frac{10}{X_{\text{Tibi}}} \right) dX_{\text{Febi}} \right]$$

At constant $\mu_{\text{H}_2\text{O}}$ and $X_{\text{Tibi}} = 1 - X_{\text{phl}} - X_{\text{Febi}}$,

$$\text{I.} \quad \frac{dX_{\text{phl}}}{dX_{\text{Mgcd}}} = \frac{X_{\text{phl}}}{X_{\text{Mgcd}}}$$

$$\text{II.} \quad \frac{dX_{\text{Febi}}}{dX_{\text{Mgcd}}} = -\frac{2}{3} \left(\frac{X_{\text{Febi}}}{1 - X_{\text{Mgcd}}} \right)$$

$$\text{III.} \quad \frac{dX_{\text{phl}}}{dX_{\text{Febi}}} = -\left(\frac{3}{10} - \frac{7}{10} \frac{(1 - X_{\text{phl}})}{X_{\text{Febi}}} \right)$$

There are three equations in three unknowns which can be solved for unique values of X_{phl} , X_{Febi} , and X_{Mgcd} . Equation I is readily integrated to give $X_{\text{phl}} = \kappa X_{\text{Mgcd}}$ where κ is a function of T , P , and $f_{\text{H}_2\text{O}}$. Equations II and III are combined to give

$$\frac{dX_{\text{phl}}}{dX_{\text{Mgcd}}} = \frac{X_{\text{Febi}}}{5(1 - X_{\text{Mgcd}})} + \frac{7}{15} \frac{(1 - X_{\text{phl}})}{(1 - X_{\text{Mgcd}})}$$

From I,

$$\frac{dX_{\text{phl}}}{dX_{\text{Mgcd}}} = \kappa \text{ and } X_{\text{phl}} = \kappa X_{\text{Mgcd}};$$

therefore $X_{\text{Febi}} = 5\kappa - 2\frac{2}{3} X_{\text{phl}} - 2\frac{1}{3}$. The final set of equilibrium conditions is

$$\text{I.} \quad X_{\text{phl}} = \kappa X_{\text{Mgcd}}$$

$$\text{II.} \quad X_{\text{Febi}} = \psi(1 - X_{\text{Mgcd}})^{2/3}$$

$$\text{III.} \quad X_{\text{Febi}} = 5\kappa - (2\frac{2}{3}) X_{\text{phl}} - 2\frac{1}{3}$$

in which κ and ψ are integration constants that depend on T , P , and $f_{\text{H}_2\text{O}}$. The value of $K_D(\text{Mg/Fe, cord/bio})$ can be determined without knowledge of the integration constants:

$$K_D = \frac{2}{3} \frac{(1 - X_{\text{phl}})}{X_{\text{phl}}} \frac{X_{\text{Mgcd}}}{(1 - X_{\text{Mgcd}})}$$

Values of K_D and κ for the whole range in biotite composition are shown in Figure 5a. The compositions of biotite and cordierite as functions of T , P , and $f_{\text{H}_2\text{O}}$ can be calculated if κ and the integration constant of II are

known. Labotka *et al.* (1981) give the equilibrium constant for reaction I as

$$\ln K_{\text{eq}} = -\frac{9.004 \times 10^4}{T} + 159.7 - \frac{1.022P}{T}$$

in which $\ln K_{\text{eq}} = 3\ln \alpha_{\text{Mgcd}}^{\text{cd}} + 8\ln f_{\text{H}_2\text{O}} - 2\ln \alpha_{\text{phl}}^{\text{bio}}$. This relation was derived from the data of Schreyer and Seifert (1967). At 1500 bars, $\ln \kappa = \ln X_{\text{phl}} - \ln X_{\text{Mgcd}} = \frac{1}{3} \ln f_{\text{H}_2\text{O}} + 1526/T - 26.2$; values of κ are shown in Figure 5b. There are no experimental data available for reaction II;

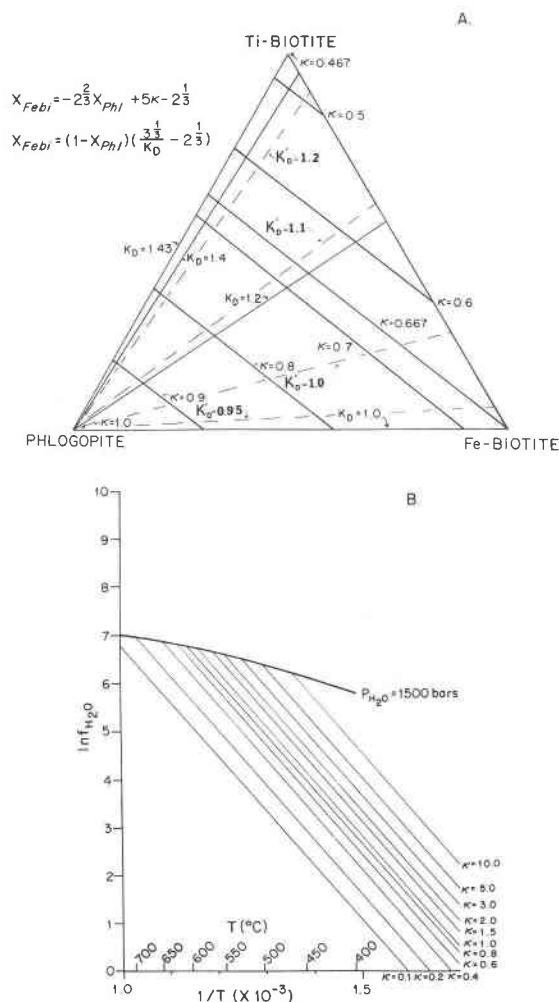


Fig. 5. A. Values of K_D (Mg/Fe, cord/bio) and κ for the range in equilibrium compositions of biotite in the assemblage quartz + muscovite + biotite + cordierite + K-feldspar + ilmenite. For K_D , solid lines represent random mixing on the octahedral sites; dashed lines represent random mixing on both octahedral and tetrahedral sites. κ is the integration constant for relation I: $\frac{dX_{\text{phl}}}{dX_{\text{Mgcd}}} = \frac{X_{\text{phl}}}{X_{\text{Mgcd}}}$ and depends on T , P , and $f_{\text{H}_2\text{O}}$. B. Values of κ at $P = 1500$ bars calculated from the equilibrium constant for the reaction muscovite + phlogopite + quartz = cordierite + K-feldspar + H_2O .

Table 5. Test of fit of biotite compositions to three components

	Mean	Standard Deviation	Smallest Value	Largest Value
phlogopite	0.460	0.175	0.240	0.901
Fe-biotite	0.329	0.154	-0.014	0.695
Ti-biotite	0.197	0.151	-0.111	0.499
Sum	0.986	0.036	0.898	1.087
χ^2	0.136	0.162	0.005	9.42

Multiple Correlation Coefficients						
Calculated Value	Measured Value					
	Mg	Fe	VI _{Al}	Ti	VI _□	IV _{Al}
Mg	0.999	-0.946	-0.504	-0.511	-0.591	-0.866
Fe	-0.976	0.988	0.386	0.507	0.440	0.888
VI _{Al}	-0.680	0.540	0.928	-0.230	0.371	0.619
Ti	-0.495	0.652	-0.424	0.849	0.158	0.449
VI _□	-0.849	0.936	-0.002	0.740	0.350	0.772
IV _{Al}	-0.830	0.965	0.123	0.444	0.108	0.836

the equilibrium constant for this reaction was estimated from the data of Labotka *et al.* (1981), Table 4. At 1500 bars the equilibrium constant is given by

$$\ln K_{eq} = \frac{-130,580}{T} + 233.2 \quad (r^2 = 0.95) \text{ in which}$$

$$\ln K_{eq} = 12 \ln f_{H_2O} + 5 \ln a_{FeCd}^{cd} - 5 \ln a_{FeBi}^{bi}.$$

This gives

$$\begin{aligned} \ln \psi &= \ln X_{FeBi} - \frac{1}{3} \ln (1 - X_{MgCd}) \\ &= 0.8 \ln f_{H_2O} + 8705/T - 15.55. \end{aligned}$$

The error in κ is associated with a ± 15 K error in T derived from locating the reaction from the experimental data (see Labotka *et al.*, 1981, for discussion). The error in ψ is associated with analytical error in determining mineral compositions, error in the temperature calibration of the Na/K partitioning between muscovite and K-feldspar, used to determine temperature, and the error in κ used to determine f_{H_2O} for the samples in Table 5 of Labotka *et al.* (1981). These errors in ψ render calculated values of T and f_{H_2O} for Fe-rich biotite compositions suspect over a range of 50K and 50 bars; the actual errors are unknown. The compositions of biotite and cordierite were calculated as a function of T for the condition $P_{H_2O} = P_{solid} = 1500$ bars and as a function of f_{H_2O} for $T = 550^\circ\text{C}$, $P_{solid} = 1500$ bars; the results are shown in Figure 6.

Discussion

The degree of success of the three-component model to describe adequately the composition of biotite in the assemblage quartz + muscovite + biotite + cordierite + K-feldspar + ilmenite is shown in Figures 6 and 7. The

compositions of biotite calculated from the model, as shown on the triangular diagram *phl-Febi-Tibi*, (Fig. 6) are somewhat similar to the compositions shown on Figure 4, even to the extent of showing negative values of *Tibi* for Mg-rich biotite. This similarity results from the use of the data to calculate the constant ψ . The partition coefficients $K_D(\text{Mg/Fe, cord/bio})$ calculated from the three components is also similar to the actual coefficients, although the calculated range is considerably smaller. Figure 7 compares the observed range with the calculated range in K_D as a function of the IVAl content in biotite; observed K_D 's range from ~ 0.75 to ~ 1.9 , whereas the calculated values range from 1.0 to ~ 1.15 . In general the three-component model seems to represent actual biotite compositions well.

In detail, though, the model fails in two respects. The first is magnitude of K_D . One possible source of this failure is the choice of the activity-composition relations for the components. The activity of biotite components is considered as the result of ideal mixing on three octahedral sites. This type of model was shown by Mueller (1972) to be consistent with the data of Wones and Eugster (1965) for compositions on the join phlogopite-annite and with data for the partitioning of Fe and Mg

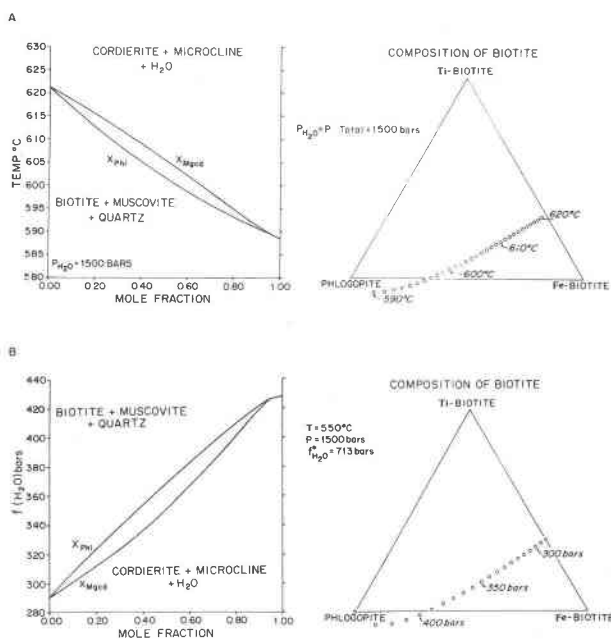


Fig. 6. A. Calculated composition of biotite and cordierite as a function of temperature along the section $P_{H_2O} = P_{total} = 1500$ bars. The left-hand diagram illustrates the partitioning of Fe and Mg between biotite and cordierite along the divariant loop for the continuous reaction. The right-hand diagram shows biotite compositions at various temperatures for the assemblage quartz + muscovite + biotite + cordierite + K-feldspar + ilmenite. B. Calculated compositions of biotite and cordierite as a function of f_{H_2O} along the section $T = 550^\circ\text{C}$, $P = 1500$ bars. Under these conditions $P_{H_2O} = 1500$ bars at $f_{H_2O} = 713$ bars.

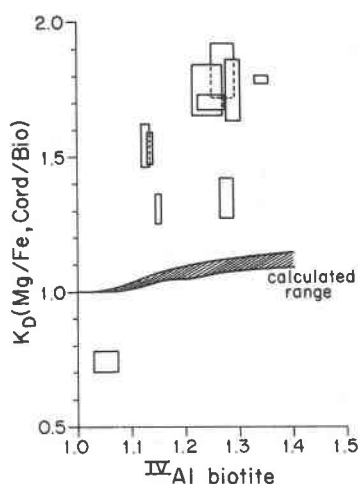


Fig. 7. Comparison of calculated range in K_D versus observed range as a function of ^{IV}Al in biotite. Rectangles represent error in determining K_D for individual samples.

between biotite and amphiboles and pyroxenes. The activities of components on the join *phlogopite-Fe-biotite* on which charge balance must be maintained might not be related to the mole fraction in a simple way. Kerrick and Darken (1975) have discussed the system albite-anorthite, in which the activities of the components depend on the crystal chemistry of the plagioclase solution. The model used above, $\alpha_{\text{Febi}} = X_{\text{Febi}}^3$ is similar to Kerrick and Darken's (1975) model #4 for plagioclase; random mixing of Fe-Mg-Al on octahedral sites but mixing of ordered $\text{AlSi}_3\text{-Al}_2\text{Si}_2$ on tetrahedral sites. This model does not correspond to the structure refinement of Bohlen *et al.* (1980) in which there is no apparent ordering of Al and Si on tetrahedral sites.

An ionic activity model for random mixing on both octahedral and tetrahedral sites gives

$$a_{\text{phl}} = \frac{256}{27} X_{\text{phl}}^3 \left(\frac{1.4 - 0.4 X_{\text{phl}}}{4} \right) \left(\frac{2.6 - 0.4 X_{\text{phl}}}{4} \right)^3$$

and

$$a_{\text{Febi}} = \frac{5548}{64.3} \left(\frac{2}{3} X_{\text{Febi}} \right)^2 \left(\frac{0.8 X_{\text{Febi}}}{3} \right)^{0.8} \left(\frac{1 + 0.4(1 - X_{\text{phl}})}{4} \right)^{1.4} \left(\frac{3 - 0.4(1 - X_{\text{phl}})}{4} \right)^{2.6}$$

(cf. Kerrick and Darken, 1975). Using these activity expressions, the system of differential equations governing equilibrium becomes algebraically complicated, as shown in Table 6. The partition coefficient can be determined from this system of equations and is shown on Figure 5a. The more complicated activity expression gives results similar to those described in the previous section except that the observed reversal in sense of partitioning is accounted. However, the magnitude of K_D is smaller than observed, and the fault probably lies in the simplistic three-component description of biotite.

This second aspect is evident in Figure 4 which shows that the three components are a good representation of biotite composition. Biotite from the Rove Formation is actually a six-component phase, and yet, the principal components analysis suggests that the amounts of the components covary in an essentially linear fashion. For example, if biotite compositions are expressed as fractions of the additive components shown in Table 1, the principal components analysis suggests that the ratio of *annite:siderophyllite* equals 1 and that one end member has the ratio *annite:siderophyllite:muscovite* equal to 4:4:2. Figure 8 shows these ratios for the Rove biotite and illustrates that the ratio *annite:siderophyllite* is not accurately 1, nor is the maximum *muscovite* content accurately represented by the component *Fe-biotite*. These same results are expressed analytically by the multiple correla-

Table 6. System of differential equations using random mixing on octahedral and tetrahedral sites in biotite

$$\begin{bmatrix} 2 \left(\frac{3}{x_{\text{phl}}} - \frac{0.1}{0.35 - 0.1x_{\text{phl}}} + \frac{0.3}{0.65 + 0.1x_{\text{phl}}} \right) \\ 5 \left(\frac{-1.4}{3.5 - x_{\text{phl}}} + \frac{2.6}{6.5 + x_{\text{phl}}} \right) \\ \left(\frac{26}{x_{\text{Tibi}}} + \frac{4.2}{3.5 - x_{\text{phl}}} - \frac{7.8}{6.5 + x_{\text{phl}}} \right) \end{bmatrix} \begin{bmatrix} 0 \\ \frac{14}{x_{\text{Febi}}} \\ \left(\frac{26}{x_{\text{Tibi}}} + \frac{19.6}{x_{\text{Febi}}} \right) \end{bmatrix} \begin{bmatrix} \frac{-6}{x_{\text{Mgad}}} \frac{dx_{\text{phl}}}{dx_{\text{Febi}}} \\ \frac{10}{1 - x_{\text{Mgad}}} \frac{dx_{\text{Febi}}}{dx_{\text{Mgad}}} \\ 0 \frac{dx_{\text{Mgad}}}{dx_{\text{Febi}}} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

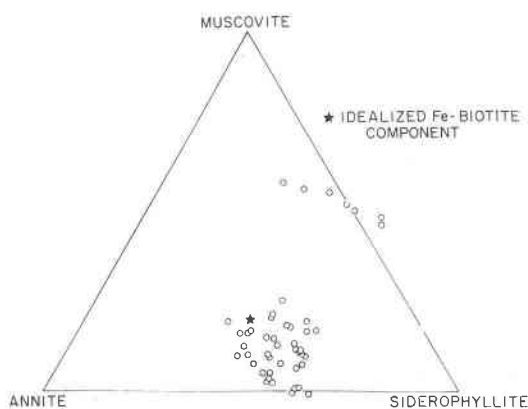


Fig. 8. Proportions of the components *muscovite*, *annite* and *siderophyllite* which make up the idealized *Fe-biotite* component. The range in biotite compositions show a lack of constant proportion of these elementary components and thus, in detail biotite is not a three-component mineral.

tion matrix, Table 5. Phenomenologically, there is no reason why the components shown in Table 1 should be linearly correlated as indicated by the principal components analysis. Each biotite component is related to the other components in the system by the continuous reactions shown in Table 1, and each reaction can be represented by a separate equilibrium constant. There are no *a priori* relations between any of the equilibrium constants for these independent reactions. Thus, the nearly constant ratios of some of the biotite components must indicate that the enthalpy changes of some of the continuous reactions are similar to one another. This similarity would result in nearly identical temperature dependences for some of the equilibrium constants and, therefore, in nearly constant ratios of the biotite components.

Estimates of the enthalpy changes of the reactions in Table 1 were made from enthalpies of formation at 298 K taken from Helgeson *et al.* (1978) and Burnham *et al.* (1969). The enthalpies of *siderophyllite* and *Ti-mica* were estimated by adding the enthalpies of appropriate oxides to those of *annite* and *muscovite*, respectively. The estimated ΔH 's of the reactions are *phlogopite*: 100 kcal, *talc*: 100 kcal, *muscovite*: ~ 0 , *siderophyllite*: 27 kcal, *annite*: -47 kcal, *Ti-mica*: 254 kcal. The three distinct values of ΔH , 100 kcal, -30 to 50 kcal, and 250 kcal are consistent with the apparent existence of only three biotite components. The enthalpy difference of the transfer of the *muscovite* component between muscovite and biotite is unknown, but is probably close to zero. Thus the *muscovite* content in biotite would not change appreciably during an increase in temperature. The existence of a low, nearly constant *muscovite* content would be most noticeable in *phlogopite* rich compositions, which is the region that conforms least to the three-component model.

Principal components analysis identifies multiple correlations among cations in biotite analyses. Why do these particular correlations occur? Why is there a positive correlation between Fe and ^{IV}Al and not between Mg and ^{IV}Al ; that is, why is *phlogopite* a stable biotite com-

position in the Rove assemblage, and $K(Mg_2Al)(Al_2Si_2O(OH)_2)$ not? Similarly, why does $K_D(Mg/Fe, cord/bio)$ correlate with ^{IV}Al in biotite? The answers can be formulated thermodynamically in terms of the Gibbs Free Energy surfaces of the various phases in the assemblage. The ultimate microscopic explanations lie in the crystal chemistry of biotite. Guidotti *et al.* (1977) observed that the Ti-content in biotite from aluminous assemblages decreased and Si-content increased as Mg/Fe increased. They explained these observations by necessity of the lateral fit of octahedral and tetrahedral sheets. Hewitt and Wones (1975) showed that the size of the octahedral sheet decreases with substitution of Mg for Fe and the size of the tetrahedral sheet decreases with substitution of Si for ^{IV}Al . Guidotti *et al.* (1977) suggested that the best fit between octahedral and tetrahedral layers can be maintained in Mg-rich biotite by reduction of ^{IV}Al because of the constraint imposed by interlayer K on the rotation of the tetrahedral sheet. The compositions of biotite from the Rove Formation completely support this explanation. In fact, the data of Hewitt and Wones (their Figs. 4 and 5, 1975) suggest that the stable compositions of biotite from the Rove Formation are strongly constrained, if not completely controlled by the volume of the unit cell. Hewitt and Wones show a significant relationship among unit cell volume, $Mg/(Mg + Fe)$, and ^{IV}Al for biotites synthesized at $T > 700^\circ C$, $P = 1000$ bars. The relationship shows that for constant volume, there is a positive correlation between Fe and ^{IV}Al ($= 1 + ^{VI}Al$ in their experiments). The results are consistent with the stable biotite compositions being those that reflect small changes in unit cell volume over the prevailing temperature range. The principal components, that is, the multiple cation correlations, reflect substitutions that minimize distortions of the biotite structure. This view is very simplistic; nevertheless, the cation correlations exhibited by biotite from the Rove Formation suggest a strong crystal-chemical control.

The pressure dependence of the equilibrium constants for the reaction in Table 1 is given by $(\partial \ln K / \partial P)T = \Delta V / RT$. Estimates of ΔV for these reactions are *phlogopite*: 171 cm^3 , *talc*: 166 cm^3 , *muscovite*: ~ 0 , *siderophyllite*: 95 cm^3 , *annite*: 180 cm^3 , and *Ti-mica*: -50 cm^3 for which the molar volume of *siderophyllite* was extrapolated from the data of Hewitt and Wones (1975), and the molar volume of *Ti-mica* was estimated from the volume of *muscovite*- $Al_2O_3 + 1\frac{1}{2} TiO_2$, and the volume of H_2O at 1500 bars, $550^\circ C$ (Burnham *et al.*, 1969) was used. These results suggest that for the constant assemblage quartz + muscovite + biotite + cordierite + K-feldspar + ilmenite the relative proportions of the components in biotite, particularly *Ti-mica* and to a lesser extent *siderophyllite*, depend on the pressure. Thus the abundances of minor components in biotite from a constant assemblage might be sensitive gauges of pressure.

Conclusions

The compositions of biotite from the Rove Formation, northeastern Minnesota, show strong dependences on

mineral assemblage and metamorphic grade. Application of the multivariate technique of principal components analysis shows that biotite from muscovite-bearing assemblages contains more dioctahedral components and less Ti-component than those from muscovite-free assemblages. Biotite from the assemblage quartz + muscovite + biotite + cordierite + K-feldspar + ilmenite has a composition that is strongly dependent on metamorphic grade. The composition is reasonably accurately described by: *phlogopite* and the substitutions ${}^{\text{IV}}\text{Al}_{0.45} + \text{Fe}_{2.29} + {}^{\text{VI}}\text{Al}_{0.21} + \text{Ti}_{0.31} + {}^{\text{VI}}\square_{0.19} \rightleftharpoons \text{Si}_{0.45} + \text{Mg}_3$, and $\text{Ti}_{1.5} + {}^{\text{VI}}\square_{0.5} \rightleftharpoons {}^{\text{VI}}\text{Al}_2$.

An analysis of the thermodynamic variance of the constant assemblage shows that the observed range in biotite composition and the order of magnitude of the partition coefficient K_D (Mg/Fe, cord/bio) can be reproduced using these three components and assuming ideal mixing. In detail, the three-component description fails to describe the Ti, ${}^{\text{VI}}\text{Al}$, and ${}^{\text{VI}}\square$ contents, particularly for Mg-rich compositions. The absolute value of the partition coefficient is also underestimated. These result from the fact that biotite from the Rove Formation is rigorously a six-component phase. The observed cation correlations are consistent with the suggestion of Guidotti *et al.* (1977) that compositions of biotite are constrained by crystal chemistry. The suggestion of this study is that for a constant assemblage, the crystal-chemical constraints on stable biotite compositions are dependent on the prevailing pressure. If so, the cation correlations in biotite composition might be sensitive indicators of the geothermal gradient.

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Appendix 1

SAMPLE	LOCATION ¹	ASSEMBLAGE ²	T ³ (°C)	f _{H₂O} (bars)
Low Grade				
3, 43d	Cross River	A	-	-
41e, 41s	South Round Lake	A	-	-
Medium Grade				
35f	Mayhew Lake	B	548	252
35g	"	B	484	83
39a	Loon Lake	B	620	903
39b	"	B	613	1126
39c	"	B	627	954
39d	"	B	568	422
39r	"	B	570	423
48f	Gunflint Palisades	E	544	379
22a	Gunflint Trail	B	-	-
26	"	C	-	-
35a	Mayhew Lake	D	-	-
39i	Loon Lake	D	-	-
39m	"	D	-	-
High Grade				
16b	Kakakebic Trail	F	-	-
16i	"	G	-	-
16j	"	F	-	-
18e	"	C	-	-

¹ Sample localities are shown on Figure 1 of Labotka et al. (1981)

- ²
- A. qtz + musc + chl + bio + plag + ilm
 - B. qtz + musc + bio + cord + Kfeld + plag + ilm
 - C. qtz + bio + cord + Kfeld + plag + ilm
 - D. qtz + bio + cumm + plag + ilm
 - E. qtz + musc + bio + cord + Kfeld + And + plag + ilm
 - F. qtz + bio + cord + Kfeld + hyp + plag + ilm
 - G. qtz + bio + cord + plag + rut

³ Values from Labotka et al (1981)