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Eliminating closure in mineral formulae with specific application to amphiboles

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Abstract

Competition among atomic or molecular species for occupancy of crystallographic sites exaggerates correlations among chemical elements in suites of mineral chemical data, a phenomenon known as closure. Such exaggerated correlations can lead to incorrect conclusions about ionic substitution mechanisms and the petrological forces that drive them. Expressing mineral compositions in terms of a single additive component and molar concentrations of exchange components, eliminates the effects of closure. Statistical analysis of data so transformed can, in some instances, lead to conclusions distinct from analysis of the same data expressed in terms of ionic abundances. The chemical variability of fictive and naturally occurring amphiboles serves to illustrate the potential difficulties brought about by closure and the benefits of its elimination.

Introduction

In this paper we examine the petrological meaning of correlations among elemental concentrations in minerals. As a corollary, the distinction between ionic substitutions and proportions of exchange components is elucidated.

Spurious correlations that arise among geochemical variables where the variables represent portions of a single whole are well known (e.g., Chayes 1962). Their cause is straightforward: An increase in the proportion of one major component of the whole requires decreases in the proportions of the other major components. Identification of such correlations is often less straightforward. Known collectively as closure, they are considered spurious because they mask the more interesting interrelations that are products of geological phenomena, and it is demonstration of the latter that is a primary motivation for studying the chemistry of rocks and minerals. There has been considerable discussion of the effects of closure on whole-rock chemical data in recent years (e.g., Nicholls 1988; Russell and Nicholls 1988). The effects of closure on mineral chemical data have been largely ignored.

Bragg (1937) recognized that several conceptual pitfalls could be avoided by describing mineral structures and mineral compositions separately. He suggested that ideal formulae be used to convey crystal structure and that chemical variability, which is most often isomorphous or approximately so, be described by a set of independent operations that act on an ideal structural formula (Bragg 1937, p. 38). In this way crystal structure and chemical variations are decoupled. Stressing that the customary practice of using end-member formulae to describe mineral composition was inherently flawed, Bragg wrote that use of end-members

> "... implies the existence of a chemical 'molecule' in which a definite number of atoms form a characteristic subgroup in the structure."

He indicated that his scheme for confining structural information to a single formula and expressing compositions in terms of deviations from that formula should supplant the use of end-members; his scheme would eliminate the flawed concept of molecular mixing that end-members connote.

Thompson (1982) formalized Bragg's ideas (see also Burt 1976 and Burt 1988). In Thompson's approach, mineral chemical compositions are cast into a single ideal formula, or additive component, and a linearly independent set of operators, referred to as exchange components, that express deviations from the additive component. The purpose of the additive component is to characterize the structure of the mineral group. The exchange components depict changes in chemistry that leave the extensive amount of additive component unchanged.

A powerful yet commonly overlooked attribute of the Bragg-Thompson method for representing mineral compositions is that formulae so transformed are free from closure. In this paper we illustrate the utility of closure-free variables for elucidating the petrological significance of chemical variability in minerals that possess multiple crystallographic sites. The approach is used to investigate the important ionic substitutions in some natural amphiboles.

Closure in mineral formulae

Principles

Amphiboles are composed of numerous crystallographic sites that host a large variety of elements and are well-

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suited for illustrating the complexities associated with interpreting some mineral chemical data.

Amphibole formulae described in terms of end-member mole fractions are subject to the effects of closure. Closure in turn will tend to obscure petrologically meaningful trends in a suite of chemical compositions. Consider an amphibole composition defined in terms of the end-member components $Ca_2Mg_5Si_8O_{22}(OH)_2$ (tremolite), $Ca_2Mg_4AlAlSi_7O_{22}(OH)_2$ (magnesio-hornblende), and $NaCa_2MgFe_4Al_2Si_6O_{22}(OH)_2$ (hastingsite). As the mole fractions of tremolite (X_{trem}) and magnesio-hornblende (X_{mghbl}) increase, the mole fraction of hastingsite (X_{hast}) must decrease because the sum of the three fractions is always one by definition. Constant sums such as this cause closure, and elimination of closure requires their removal.

Constant sums are removed from whole-rock chemical analyses by identifying a conserved element (an element that has retained a constant absolute abundance throughout the geological process under consideration) from among the data and by using this element as the denominator for element ratios (e.g., so-called Pearce element ratios; Nicholls 1988). This approach is not practicable for mineral compositions in part because identification of an analogous conserved quantity for mineral compositional data is complicated by the presence of distinct crystallographic sites.

Crystal-chemical descriptions of mineral phases include mole fractions of elements occupying particular crystallographic sites with due consideration to order-disorder relations. In the case of hastingsite, for example, the mole fraction of Fe occupying the five octahedrally coordinated M1, M2, and M3 sites is $4/5$ and the mole fraction of Mg is $1/5$ assuming disordered mixing of Fe and Mg. Site-specific mole fractions offer no relief from closure. Rather, each site is associated with a constant sum (e.g., five in the present example) so the problem is in some ways more insidious. What is more, coupling of elemental exchanges on distinct sites imposed by charge balance (as well as ionic size, crystal-field effects, and so on) is another form of closure affecting site-specific mole fractions.

Unlike these other variables, the parameters used in the Bragg-Thompson representation of mineral formulae are entirely free of closure. Recall that the root cause of closure is the presence of constant sums prevalent in virtually all forms of concentration data. Yet Thompson (1982) observed that the intensive molar amounts of exchange components are free of constant sums.

Because the single additive component and the exchange components are formulated to account for charge neutrality, molar amounts of exchange components may vary independently from one another without violating charge balance. Put another way, exchange-component molar concentrations are free of covariations imposed by charge neutrality because any combination of components with zero net charge will itself have a net charge of zero.

All the crystal-chemical constraints that give rise to closure are transferred to molar amounts of exchange components. The latter can be thought of as devices that filter out the effects of closure mathematically, leaving what remains free to vary completely independently from one another. Any covariations in the amounts of exchange components can thus be ascribed confidently to physicochemical processes rather than to the definition of the parameters themselves.

Definition of closure-free variables

Positive and negative subscripts are used to represent ionic substitutions within exchange component formulae. A positive subscript indicates that the labeled species enters the mineral structure. A negative subscript signifies replacement of the labeled element or element group. True to convention, subscript notation in this paper is used to denote both extant substitutions (i.e., ionic substitutions that actually occurred or may occur in a real mineral) and exchange components that simply describe the chemical composition of a mineral. An essential conclusion of the present work is that the two are not always synonymous. The meaning of each instance of subscript notation should be evident from context.

Thompson (1982) favored omission of crystallographic sites and valence states in exchange component formulae. His terminology was necessitated by the intended application in which the same exchange components are used to describe variations in the chemistry of different mineral groups (see Thompson et al. 1982). Thus, $MnFe_{-1}$, when written as here with no crystallographic site specificity, is independently variable in both olivine and epidote minerals but with different charge and structural connotations. For olivine, $MnFe_{-1}$ can represent substitution of Mn^{2+} for Fe^{2+} in both the Ml and M2 octahedral sites or in the smaller M1 site alone. When applied to epidote it describes substitution of Mn^{3+} for Fe^{3+} or Mn^{2+} for Fe^{2+} in the M1 and M3 octahedral sites (Dollase 1971).

The flexibility sought by Thompson leads to ambiguity when describing the crystal chemistry of an individual mineral group. For this reason, Burt (1988) found it useful to augment exchange component formulae with coordination numbers and, in some instances, valence states. We adopt the practice of designating coordination numbers where site assignments may not be clear from the formulae themselves. For example, $^{[6]}Al\,^{[4]}Al$ is used instead of Al_2 to denote octahedral-site Al and tetrahedral-site Al in the same component. For simplicity, valences are given explicitly in the exchange component formulae sparingly but in all cases can be deduced from stoichiometry.

Methods for calculating moles of a single additive component and moles of exchange components from moles of an equal number of ionic species per formula unit are described in detail by Thompson (1982). Equations for the number of moles of ionic species prescribed by unit moles of exchange components and an additive component are solved simultaneously to yield a new set of equations that give the number of moles of exchange components and additive component in terms of ionic

species per formula unit. Coefficients for the former equations are collected into a square matrix **J** (the symbol emphasizes that the transformation matrix is a Jacobian). Rows i of **J** correspond to ions, columns j correspond to exchange components and the single additive component, and elements J_{ij} are moles of ion i per exchange or additive component j. The system of linear equations is solved by inversion of **J** to yield

$$\mathbf{M}^{ex} = \mathbf{J}^{-1} \cdot \mathbf{M}^{ion} \quad (1)$$

where $\mathbf{M}^{ex}$ is the vector (or matrix of vectors) composed of moles of exchange components and the additive component and $\mathbf{M}^{ion}$ is the vector (or matrix of vectors) containing the moles of ionic species per formula unit. When the formula unit and additive component are written on the basis of equal numbers of anions, Equation 1 results in a unit mole of additive component for every formula. If the original formula unit and the additive component are referred to different numbers of anions, the moles of additive component per formula will deviate from one.

The symbol X_j^{ex} is used to represent the molar concentration of exchange component j obtained by dividing the moles of each exchange component per formula unit, elements $\mathbf{M}_j^{ex}$ of $\mathbf{M}^{ex}$, by the associated moles of additive component (the total moles of mineral to which the $\mathbf{M}_j^{ex}$ refer). This definition of the molar concentration (also referred to as molar amount or molar proportion) of an exchange component is consistent with the definition of other molar, or so-called proper, properties. The extensive moles of exchange components per formula unit are numerically equivalent to their corresponding intensive molar concentrations when the transformation is made to unit moles of additive component. Quantities X_j^{ex} are closely analogous to mole fractions in being without units, but differ in that their sum for an individual phase is not unity. In this last respect they bear some similarity to the solute-solvent mole ratios that describe dilute solutions, as they are all independently variable. It is important to recognize, however, that the fixed amount of additive component reflects that, as with other sorts of proportions, only $n - 1$ of the total n components required to specify the chemical composition of the phase can vary independently.

Example

Amphiboles that are described by the mole fractions of magnesio-hornblende, tremolite, and hastingsite cited above can be described equally well by one mole of the magnesio-hornblende additive component, $Ca_2Mg_4AlAlSi_7O_{22}(OH)_2$, and variable molar amounts of the exchange components $^{[6]}Al\,^{[4]}Al\,Mg_{-1}Si_{-1}$ (tschermakite) and $NaFe_4Al_2^{[12]}\square_{-1}Mg_{-4}Si_{-2}$ (hastingsite). In this form the moles of tschermakite and hastingsite exchange components per formula unit are numerically equivalent to molar concentrations X_{tsch}^{ex} and X_{hast}^{ex}, respectively (the denominator in the molar quantities is always one mole of magnesio-hornblende additive component).

Examination of amphibole compositions within the two-dimensional space described by the variables X_{hast}^{ex} and X_{tsch}^{ex} demonstrates the unique characteristics of exchange components relative to other expressions of mineral chemical data. Experiments show that amphibole compositions are sensitive to intensive variables that characterize the environment in which they grow. It is therefore reasonable to assume that changes in parameters of state such as temperature (T), pressure (P), hydrogen fugacity (f_{H_2}), and phase assemblage will produce a sequence of compositions that define a particular path in this section of amphibole composition space. Identification of such a path requires preservation of a sequence of suspended states represented by multiple mineral parageneses or zonate compositions. Conversely, we expect a random distribution of compositions to result from indiscriminate (i.e., irrespective of physicochemical environment) sampling of amphiboles from within this space. We accept as self-evident that departures from random dispositions of data in composition space signal the presence of underlying physicochemical controls to be discovered through petrological investigation. Clear distinction between random and non-random distributions in composition space, and thus characterization of the petrological significance of a set of compositions, is facilitated by using exchange components precisely because they are free of closure.

To illustrate, we drew at random ten amphibole formulas that fall within the two-dimensional section of amphibole composition space described above (Table 1, see Appendix for method). The ten random compositions are plotted in terms of X_{tsch}^{ex} and X_{hast}^{ex} relative to the $Ca_2Mg_4AlAlSi_7O_{22}(OH)_2$ origin in Figure 1. As these data were chosen at random, the lack of a trend in of $X_{tsch}^{ex} - X_{hast}^{ex}$ space accurately reflects the fact that there was no physical or chemical cause for the variability in chemical composition. Also shown in Figure 1 are ten compositions drawn at random from the one-dimensional space defined by the of X_{hast}^{ex} axis alone. The one-dimensional and two-dimensional data sets shown in Figure 1 exhibit similar correlations among elemental abundances (Fig. 2). This similarity results from the closure imparted by crystal chemistry. Indeed, Figures 1 and 2 show that element-element plots are of little value in distinguishing between data that exhibit variation in both the of X_{tsch}^{ex} and X_{hast}^{ex} parameters and those that vary in of X_{hast}^{ex} only. This is a simplified example of a general result indicating that the petrological significance of trends in element-element plots of mineral data is dubious.

Statistical effects of closure

The purpose of statistical analysis of mineral chemical data is most often to identify trends that are indicative of petrological processes, although it is important to recognize also that in some cases statistics are applied for the purpose of elucidating the poorly known crystal chemistry of a phase (e.g., Saxena and Ekström 1970). Closure adversely affects statistical analyses of mineral chemical

TABLE 1. Random draws from a portion of amphibole composition space defined by the $CaMg_4AlAlSi_7O_{22}(OH)_2$ origin and exchange-component axes X^{ex}_{hast} (range 0 to 1) and X^{ex}_{tsch} (range −1 to 0)

	Ions (pfu)									
Species	1	2	3	4	5	6	7	8	9	10
Si	6.966	6.684	6.707	7.440	6.050	6.355	7.425	6.764	6.035	5.958
Al	1.728	2.017	2.186	0.874	2.811	2.319	0.959	2.037	2.220	2.344
Fe	0.682	1.227	0.802	0.493	2.180	1.943	0.381	0.869	3.421	3.478
Mg	3.624	3.071	3.306	4.193	1.960	2.384	4.235	3.330	1.325	1.219
Ca	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.171	0.307	0.200	0.123	0.545	0.486	0.095	0.217	0.855	0.869
OH	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
O	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000	22.000
	Molar concentrations									
X^{ex}_{hast}	0.169	0.310	0.198	0.123	0.542	0.483	0.096	0.218	0.853	0.873
X^{ex}_{tsch}	−0.308	−0.296	−0.109	−0.686	−0.142	−0.329	−0.615	−0.198	−0.747	−0.694

compositions where the goal is to extract petrological information.

In practice, the minimum number of components used to depict variable mineral compositions depends on the goal of the investigation and the analytical precision with which differences in elemental concentrations can be determined. Principal components analysis is a statistical method that allows chemical compositions (or any other multivariate parameters) to be recast in terms of the fewest number of linearly independent components necessary to account for a prescribed portion of the total variability of the data. It is therefore well-suited for quantifying the importance of chemical differences among natural mineral compositions in a manner consistent within the thermodynamic formalism often used in petrological studies (Labotka 1983).

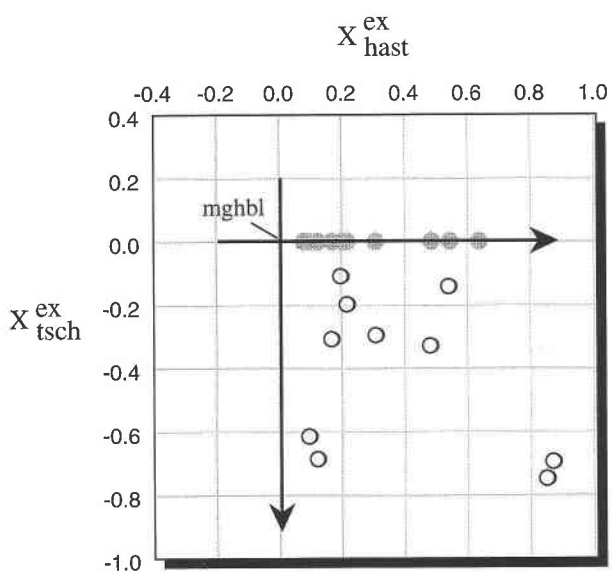

FIGURE 1. Ten amphibole compositions (open circles) selected at random from the two-dimensional composition space defined by the $Ca_2Mg_4AlAlSi_7O_{22}(OH)_2$ origin (mghbl) and exchange component axes X^{ex}_{tsch} and X^{ex}_{hast}. Also shown are ten compositions drawn at random from the one-dimensional space defined by X^{ex}_{hast} only (grey circles).

Principal components analysis is used here to illustrate the effects of closure.

In the present case, principal components are a set of new coordinate axes or new components equal in number to the original components, that define amphibole composition space. They are unique to each data set and are derived from the original chemical components comprising the axes of amphibole space by orthogonal rotation such that each principal component axis is geometrically and statistically independent (the origin of the new axes is shifted to the centroid of the data, but this shift has no bearing on the issues at hand). The first principal component is chosen to correspond to the direction of greatest variance exhibited by the data, the second principal component corresponds to the next greatest variance subject to the condition of orthogonality, and so forth. The advantage of this rotation of axes is the parsimony afforded by considering only those new components (principal components) that account for the largest portions of the variance of the data. In many cases no more than two principal components are necessary to characterize a set of mineral chemistry data originally described in terms of many more variables.

Principal components are obtained by diagonalizing the covariance matrix $\mathbf{S}_x$ of the data of interest according to the relationship:

$$\mathbf{S}_y = \mathbf{P}' \, \mathbf{S}_x \mathbf{P} \tag{2}$$

where $\mathbf{S}_y$ is a diagonal matrix composed of the eigenvalues of $\mathbf{S}_x$ and $\mathbf{P}$ is a matrix with columns comprising orthonormal eigenvectors of $\mathbf{S}_x$. The distinct eigenvalues of $\mathbf{S}_x$ are the variances associated with the new principal components, i.e., $\mathbf{S}_y$ is the covariance matrix for the data expressed in terms of their principal components. The elements of $\mathbf{P}$, p_{ij}, are the direction cosines relating principal component i to original component j; p_{ij} are the coefficients that define the new principal components in terms of the original components. Accordingly, $\mathbf{P}$ also serves as the matrix that transforms the data expressed in terms of the original components to representation in terms of the new principal components (i.e., $\mathbf{P}$ effects the shift in coordinate axes).

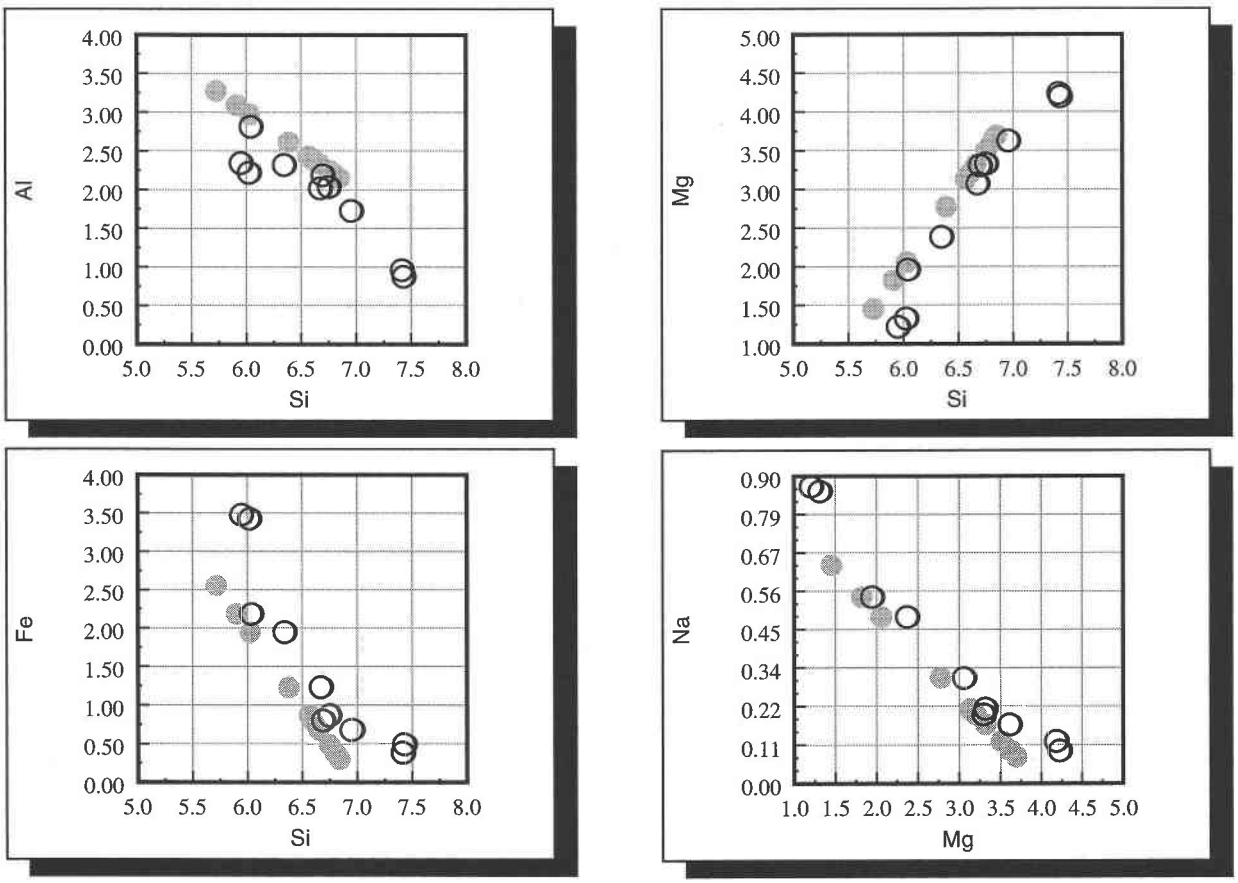

FIGURE 2. Plots illustrating variations in cation abundances per 24 anions for amphibole compositions shown in Figure 1. Note similarities between two-dimensional (open circles) and one-dimensional (grey circles) data sets.

Abundances of Si, $^{[4]}$Al, $^{[6]}$Al, Fe, Mg, and Na per formula unit for the ten randomly chosen amphibole compositions described in the previous section (Table 1) yield the following 6 × 6 covariance matrix (Ca, OH, and O do not vary in these data.):

$$\mathbf{S}_x = \begin{pmatrix} \sigma^2_{Si} & \sigma_{Si\,[4]Al} & \sigma_{Si\,[6]Al} & \sigma_{SiFe} & \sigma_{SiMg} & \sigma_{SiNa} \\ \vdots & \sigma^2_{[4]Al} & \sigma_{[4]Al\,[6]Al} & \sigma_{[4]AlFe} & \sigma_{[4]AlMg} & \sigma_{[4]AlNa} \\ & \vdots & \sigma^2_{[6]Al} & \sigma_{[6]AlFe} & \sigma_{[6]AlMg} & \sigma_{[6]AlNa} \\ & & \vdots & \sigma^2_{Fe} & \sigma_{FeMg} & \sigma_{FeNa} \\ & & & \vdots & \sigma^2_{Mg} & \sigma_{MgNa} \\ & & & & \cdots & \sigma^2_{Na} \end{pmatrix}$$

$$= \begin{pmatrix} 0.294 & -0.294 & -0.009 & -0.570 & 0.579 & -0.142 \\ -0.294 & 0.294 & 0.009 & 0.570 & -0.579 & 0.142 \\ -0.009 & 0.009 & 0.062 & -0.105 & 0.043 & -0.026 \\ -0.570 & 0.570 & -0.105 & 1.348 & -1.243 & 0.337 \\ 0.579 & -0.579 & 0.043 & -1.243 & 1.200 & -0.311 \\ -0.142 & 0.142 & -0.026 & 0.337 & -0.311 & 0.084 \end{pmatrix}. \quad (3)$$

The total variance associated with these fictive data is 3.282 and is obtained by summing the diagonal terms of $\mathbf{S}_x$ (i.e., computing the trace of $\mathbf{S}_x$). The diagonalized covariance matrix is

$$\mathbf{S}_y = \begin{pmatrix} \sigma^2_{pc1} & \sigma_{pc1pc2} & \sigma_{pc1pc3} & \sigma_{pc1pc4} & \sigma_{pc1pc5} & \sigma_{pc1pc6} \\ \vdots & \sigma^2_{pc2} & \sigma_{pc2pc3} & \sigma_{pc2pc4} & \sigma_{pc2pc5} & \sigma_{pc2pc6} \\ & \vdots & \sigma^2_{pc3} & \sigma_{pc3pc4} & \sigma_{pc3pc5} & \sigma_{pc3pc6} \\ & & \vdots & \sigma^2_{pc4} & \sigma_{pc4pc5} & \sigma_{pc4pc6} \\ & & & \vdots & \sigma^2_{pc5} & \sigma_{pc5pc6} \\ & & & & \cdots & \sigma^2_{pc6} \end{pmatrix}$$

$$= \begin{pmatrix} 3.139 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.143 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (4)$$

Note that total variance is unaffected by diagonalization (i.e., the trace of $\mathbf{S}_x$ is equal to the trace of $\mathbf{S}_y$) and is accounted for by only two principal components because only two non-zero eigenvalues for $\mathbf{S}_x$ (diagonals of $\mathbf{S}_y$) exist. What is more, the vast majority of the total variance (96%) is accommodated by the first principal component (pc1) alone, as indicated by the magnitudes of the diag-

onals of $\mathbf{S}_y$ (i.e., 3.139/(3.139 + 0.143) × 100 = 96%). The identities of the principal components in terms of the original cation abundances are given by matrix **P**:

$$\mathbf{P} = \begin{pmatrix} \cos\theta_{pc1Si} & \cos\theta_{pc2Si} \\ \cos\theta_{pc1^{[4]}Al} & \cos\theta_{pc2^{[4]}Al} \\ \cos\theta_{pc1^{[6]}Al} & \cos\theta_{pc2^{[6]}Al} \\ \cos\theta_{pc1Fe} & \cos\theta_{pc2Fe} \\ \cos\theta_{pc1Mg} & \cos\theta_{pc2Mg} \\ \cos\theta_{pc1Na} & \cos\theta_{pc2Na} \end{pmatrix} = \begin{pmatrix} 0.294 & -0.402 \\ -0.294 & 0.402 \\ 0.030 & 0.642 \\ -0.648 & -0.470 \\ 0.617 & -0.172 \\ -0.162 & -0.119 \end{pmatrix} \quad (5)$$

where only non-zero columns of **P** are shown for clarity. From inspection of the coefficients of **P** it is seen that principal component 1 corresponds to the substitution (rewritten in terms of positive Na)

$$Na_{0.162}Fe_{0.648}{}^{[4]}Al_{0.294}Mg_{-0.617}{}^{[6]}Al_{-0.030}Si_{-0.294} \quad (6)$$

or

$$NaFe_4{}^{[4]}Al_{1.8}Mg_{-3.8}{}^{[6]}Al_{-0.2}Si_{-1.8} \quad (7)$$

when normalized to unit (and positive) Na.

Principal component 1 is essentially equivalent to the $NaFe_4Al_2{}^{[12]}\square_{-1}Mg_{-4}Si_{-2}$ (hastingsite) exchange component. One concludes from this analysis of elemental abundances that variation in these fictive amphibole compositions is essentially one-dimensional, with fully 96% of the total variation accounted for by a hastingsite exchange mechanism and the remaining 4% being accommodated by a tschermakitic exchange mechanism (pc2, Eq. 5).

However recall that these data were constructed by drawing at random from a two-dimensional section of amphibole composition space defined by the independently variable components $NaFe_4Al_2{}^{[12]}\square_{-1}Mg_{-4}Si_{-2}$ and $^{[6]}Al^{[4]}AlMg_{-1}Si_{-1}$ acting on the formula $Ca_2Mg_4AlAlSi_7O_{22}(OH)_2$, and that there is significant uncorrelated variability along both exchange vectors as verified by inspection of Figure 1. Why then does this statistical analysis suggest that the variability of the data is essentially one-dimensional along $NaFe_4Al_2{}^{[12]}\square_{-1}Mg_{-4}Si_{-2}$?

The answer is closure. The influence of closure on the covariance structure of the elemental data is seen in matrix $\mathbf{S}_x$ (Eq. 2). As described by Chayes and Trochimczyk (1978), closure imparts strong dependencies among variances and covariances such that sums of elements of individual columns in the covariance matrix are zero or nearly so. In the case of closure on individual crystallographic sites, zero variance-covariance sums result among elements that occupy the same sites. The reader may verify that in Equation 3 the sum of variances and covariances for tetrahedral site cations is zero as is the sum of variances and covariances corresponding to octahedral site cations.

Closure and its effects are removed if the elemental abundances per formula unit are replaced by molar concentrations of exchange components. The 2 × 2 covariance matrix for the ten random compositions expressed in terms of X^{ex}_{hast} and X^{ex}_{tsch} relative to the $Ca_2Mg_4AlAlSi_7O_{22}(OH)_2$ origin is

$$\mathbf{S}_x = \begin{pmatrix} \sigma^2_{X^{ex}_{hast}} & \sigma_{X^{ex}_{hast}X^{ex}_{tsch}} \\ \sigma_{X^{ex}_{tsch}X^{ex}_{hast}} & \sigma^2_{X^{ex}_{tsch}} \end{pmatrix} = \begin{pmatrix} 0.084 & -0.026 \\ -0.026 & 0.061 \end{pmatrix}. \quad (8)$$

Elimination of closure is evidenced by non-zero column (and row) sums in $\mathbf{S}_x$; variances and corresponding covariances do not sum to zero. The diagonalized covariance matrix

$$\mathbf{S}_y = \begin{pmatrix} \sigma^2_{pc1} & \sigma_{pc1pc2} \\ \sigma_{pc2pc1} & \sigma^2_{pc2} \end{pmatrix} = \begin{pmatrix} 0.101 & 0 \\ 0 & 0.044 \end{pmatrix} \quad (9)$$

shows that 70% of the total variance is explained by principal component 1 and 30% by principal component 2. Unlike for cation abundances, statistical analysis of exchange components correctly reveals that these data exhibit significant variability in two dimensions (cf. Fig. 1). The exact percentages of variance accounted for by each of the two principal components is a function of the specific random amphibole compositions sampled but they are always of comparable magnitude. Subequal partitioning of variance among principal components is indeed characteristic of randomly distributed data where the ranges of the parameters that describe the data are similar.

The identities of the two principal components derived from analysis of exchange components are given by matrix **P**:

$$\mathbf{P} = \begin{pmatrix} \cos\theta_{pc1X^{ex}_{hast}} & \cos\theta_{pc2X^{ex}_{hast}} \\ \cos\theta_{pc1X^{ex}_{tsch}} & \cos\theta_{pc2X^{ex}_{tsch}} \end{pmatrix} = \begin{pmatrix} -0.838 & 0.546 \\ 0.546 & 0.838 \end{pmatrix}. \quad (10)$$

Because molar concentrations of exchange components are numerically equivalent to moles of exchange components (recall that the denominators are unit moles of additive component), it is a simple matter to rewrite the principal components in terms of the net transfer of atomic species, referred to hereafter as substitutions. The first principal component net substitution is a linear sum of $NaFe_4Al_2{}^{[12]}\square_{-1}Mg_{-4}Si_{-2}$ and $^{[6]}Al^{[4]}AlMg_{-1}Si_{-1}$ according to the equation $pc1 = -0.838(NaFe_4Al_2{}^{[12]}\square_{-1}Mg_{-4}Si_{-2}) + 0.546(^{[6]}Al^{[4]}AlMg_{-1}Si_{-1})$ and the second principal component net substitution is given by the relation $pc2 = 0.546NaFe_4Al_2{}^{[12]}\square_{-1}Mg_{-4}Si_{-2}) + 0.838(^{[6]}Al^{[4]}AlMg_{-1}Si_{-1})$, yielding

$$NaFe_4{}^{[4]}Al_{1.4}Mg_{-3.3}{}^{[6]}Al_{-0.7}Si_{-1.4} \quad (11)$$

and

$$NaFe_4{}^{[6]}Al_{1.5}{}^{[4]}Al_{3.5}Mg_{-5.5}Si_{-3.5} \quad (12)$$

for *pc*1 and *pc2,* respectively, normalized to one (positive) Na ion. Because the numbers comprising **P** are cosines of angles between the principal components and the original exchange components in composition space, their magnitudes quantify the degrees of similarity between the various principal components and the exchange components from which the principal components derive. A value of 0 for element p_{ij} of **P** indicates that principal component i is perpendicular to exchange component j in composition space. A value of 1 or −1 signifies that principal component i is parallel to exchange component j.

It follows that if the absolute value of a number in the first column of **P**, p_{ij}, approaches 1, then the greatest variation in the data occurs along a substitution similar to exchange component j. This is treacherous ground, however, because although the significance of the numbers p_{ij} is a truism geometrically, it is all too easy to attach undue physical significance to the exchange components themselves, as discussed in the section to follow. Errors are avoided by using exchange components solely as means for removing closure in statistical analyses while using the resultant net substitutions to interpret the final results.

In general, net substitutions in terms of ionic species can be derived from principal components expressed as sums of exchange-component proportions with the relation

$$\mathbf{N} = \mathbf{J}^{ex} \cdot \mathbf{P}. \quad (13)$$

Matrix $\mathbf{J}^{ex}$ in Equation 13 is a submatrix of **J** in Equation 1 in which the column for the additive component has been removed. The columns of matrix **N** are the eigenvectors (principal components) expressed in terms of relative numbers of ions such that the first element of **N**, for example, is

$$N_{11} = \sum_j J_{1j} \cos \theta_{pc1X_j^{ex}}.$$

It should be clear that closure can alter not only the apparent identity and relative importance of net substitutions but also the implied chemical degrees of freedom. If for example, 96% of the variance is considered sufficient for accurate representation of the dispersion in the data (e.g., Labotka 1983), then the principal components analysis of elemental abundances incorrectly suggests that amphiboles shown in Figure 1 comprise a two component system while the analysis of exchange component proportions reveals that the same amphibole system is actually defined by a minimum of three components. In each case the requisite number of components depends on the amount of variance to be explained. Differences in analytical and petrological uncertainties associated with real data (and absent in this simple example) make it difficult to provide a generally applicable statement as to the fraction of total variance that must be included to capture the essence of petrological histories.

Significance of proportions of exchange components

Hewitt and Abrecht (1986) argued that using exchange components to describe mineral compositions can give ambiguous or misleading indications of the relative importance of ionic substitutions. Lest confusion reign regarding the significance of exchange component proportions, it is shown below that the misgivings harbored by Hewitt and Abrecht are misplaced. Proportions of exchange components should not be expected to correspond one-to-one with ionic substitutions when used to define the chemical composition of a mineral.

As evidence for their conclusion, Hewitt and Abrecht presented the compositions of well-characterized biotites in terms of two different sets of exchange components relative to the phlogopite additive component. For example, their biotite sample FD-12 is described by the coordinate matrix

$$\mathbf{V} = \begin{pmatrix} X^{ex}_{NaK_{-1}} \\ X^{ex}_{FeMg_{-1}} \\ X^{ex}_{MnMg_{-1}} \\ X^{ex}_{F(OH)_{-1}} \\ X^{ex}_{Cl(OH)_{-1}} \\ X^{ex}_{[12]\square SiK_{-1}Al_{-1}} \\ X^{ex}_{AlAlFe_{-1}Si_{-1}} \\ X^{ex}_{Fe^{3+}OFe_{-1}OH_{-1}} \\ X^{ex}_{Ti^{[6]}\square Fe_{-2}} \\ X^{ex}_{TiAl_2Fe_{-1}Si_{-2}} \\ X^{ex}_{TiO_2Fe_{-1}(OH)_{-2}} \end{pmatrix} = \begin{pmatrix} 0.15 \\ 4.64 \\ 0.14 \\ 0.39 \\ 0.02 \\ -0.01 \\ 0.67 \\ 0.44 \\ 0.40 \\ -0.04 \\ -0.01 \end{pmatrix} \quad (14)$$

and by the matrix

$$\mathbf{V}' = \begin{pmatrix} X^{ex}_{NaK_{-1}} \\ X^{ex}_{FeMg_{-1}} \\ X^{ex}_{MnMg_{-1}} \\ X^{ex}_{F(OH)_{-1}} \\ X^{ex}_{Cl(OH)_{-1}} \\ X^{ex}_{[12]\square SiK_{-1}Al_{-1}} \\ X^{ex}_{AlAlFe_{-1}Si_{-1}} \\ X^{ex}_{Fe^{3+}OFe_{-1}OH_{-1}} \\ X^{ex}_{Al_2{}^{[6]}\square Fe_{-3}} \\ X^{ex}_{TiAl_2Fe_{-1}Si_{-2}} \\ X^{ex}_{AlOFe_{-1}(OH)_{-1}} \end{pmatrix} = \begin{pmatrix} 0.15 \\ 4.64 \\ 0.14 \\ 0.39 \\ 0.02 \\ -0.01 \\ -0.11 \\ 0.44 \\ 0.40 \\ 0.35 \\ -0.02 \end{pmatrix}. \quad (15)$$

The identities of the ninth and eleventh variables that describe FD-12 in **V** and **V′** are different. For **V** they are $X^{ex}_{Ti\square Fe_{-2}}$ and $X^{ex}_{TiO_2Fe_{-1}(OH)_{-2}}$ while for **V′** they are $X^{ex}_{Al_2\square Fe_{-3}}$ and $X^{ex}_{AlOFe_{-1}(OH)_{-1}}$, respectively. Hewitt and Abrecht focused on the fact that this use of different exchange components to describe the mineral composition gives rise to different coefficients for two components common to both descriptions, $AlAlFe_{-1}Si_{-1}$ and $TiAl_2Fe_{-1}Si_{-2}$, the seventh and tenth components, respectively. They posited that the different coefficients for the components in common give inconsistent indications of the importance of the respective ionic substitutions. Their interpretation, however, assumes that proportions of exchange components have immutable physical meaning. They do not.

In terms of the geometry of composition space, Hewitt and Abrecht (1986) examined a single compositional vector that can be thought of as a line connecting the origin and the composition of biotite FD-12. The orientation of this vector is fixed in composition space. They compared the coordinates of the vector relative to two different sets of coordinate axes (basis vectors) related to one another by orthogonal rotation about the origin and being composed of exchange components. Replacing one or more of the components with another as was done by Hewitt and Abrecht (1986), is equivalent to rotation because of the constraint that all axes must remain perpendicular. The coordinates themselves are the elements of the matrices **V** and **V′** and are defined as $\cos\theta_i|\mathbf{V}|$ and $\cos\theta_i|\mathbf{V'}|$, respectively, where θ_i are the angles between the biotite vector and exchange components i and $|\mathbf{V}|$ and $|\mathbf{V'}|$ are the lengths of the biotite vector relative to the two sets of coordinate axes (calculated as the sum of the squares of elements of **V** and **V′**). It is impossible to rotate just one axis and still retain an orthogonal set, thus it is inescapable that more than one of the angles θ_i between the fixed biotite vector and the coordinate axes are altered by changing the identity of a single exchange component. The exact number of altered angles depends on the number of axes that are forced to rotate to preserve orthogonality. Thus several elements of the coordinate matrices **V** and **V′**, being determined by θ_i, must be altered by axis rotation effected by changing only two of the exchange components used to describe the biotite data. A paradox arises in which one mineral possesses distinct molar concentrations of the same exchange components.

Molar proportions of the two components $AlAlFe_{-1}Si_{-1}$ and $TiAl_2Fe_{-1}Si_{-2}$ are different in the two descriptions of biotite FD-12 because rotation of the axes to which these components refer changes their identities. Identities of exchange-component axes are altered by rotation because their positions relative to the fixed reference frame defined by ionic abundances change. Consider the equations that define $X^{ex}_{AlAlFe_{-1}Si_{-1}}$, $X^{ex}_{TiAl_2Fe_{-1}Si_{-2}}$, $X^{ex}_{Ti\square^{VI}Fe_{-2}}$, and $X^{ex}_{Al_2\square^{VI}Fe_{-3}}$ in terms of ionic species Si, $^{[4]}$Al, $^{[6]}$Al, Ti, Fe^{3+}, Fe^{2+}, Mg, Mn, Na, K, Cl, and F (as determined using methods described by Thompson 1982). For coordinate matrix **V** the equations are

$$X^{ex}_{AlAlFe_{-1}Si_{-1}} = M_{^{[4]}Al} \tag{16}$$

$$X^{ex}_{TiAl_2Fe_{-1}Si_{-2}} = 0.5M_{^{[4]}Al} - 0.5M_{^{[6]}Al} - 0.5M_{Na} - 0.5M_K \tag{17}$$

$$X^{ex}_{Ti^{[6]}\square Fe_{-2}} = 0.75M_{Si} + 0.75M_{^{[4]}Al} - 1.0M_{^{[6]}Al} - 1.0M_{Ti} - 1.0M_{Fe^{3+}} - 1.0M_{Fe^{2+}} - 1.0M_{Mg} - 1.0M_{Mn} \tag{18}$$

while for coordinate matrix **V′** they are

$$X^{ex}_{AlAlFe_{-1}Si_{-1}} = 1.0M_{^{[4]}Al} - 2.0M_{Ti} - 1.0M_{Na} - 1.0M_K \tag{19}$$

$$X^{ex}_{TiAl_2Fe_{-1}Si_{-2}} = M_{Ti} \tag{20}$$

$$X^{ex}_{Al_2\square Fe_{-3}} = 0.75M_{Si} + 0.75M_{^{[4]}Al} - 1.0M_{^{[6]}Al} - 1.0M_{Ti} - 1.0M_{Fe^{3+}} - 1.0M_{Fe^{2+}} - 1.0M_{Mg} - 1.0M_{Mn} \tag{21}$$

where M_i refers to moles of ionic species i per formula unit. Equations 16, 17, 19, and 20 show that exchange components common to both coordinate systems are defined differently. Equations 18 and 21 show that the same definition applies to two different exchange components in the two coordinate systems. Because exchange component axes are not always in the same position relative to ionic components in composition space, proportions of a given exchange component can have different meanings in different coordinate systems.

There are a multitude of positions for exchange-component axes in composition space. Accordingly, there are an equal number of different sets of exchange-component molar concentrations that define the composition of a particular mineral. How then, can one choose which position of the axes or which set of molar concentrations is most meaningful physically? The answer is that one cannot, and to try constitutes an inappropriate interpretation of the data. Instead it must be recognized that exchange components as basis vectors are merely devices for defining composition space.

In contrast, coordinate axes defined by ionic abundances per formula unit are fixed in composition space because they refer to measurable quantities with independent, a priori physical significance. For this reason, closure-free manipulations of data afforded by conversion to exchange components are more easily (although not necessarily more correctly) interpreted if results are presented in terms of net substitutions of ionic species (e.g., Eq. 12).

Returning to the example of Hewitt and Abrecht, both representations of biotite FD-12, **V** and **V′**, yield the same net substitution relative to phlogopite:

$$Na_{0.15}Fe^{2+}_{2.78}Fe^{3+}_{0.44}Mn_{0.14}Ti_{0.35}{}^{[6]}Al_{0.67}{}^{[4]}Al_{0.60}O_{0.42}F_{0.39}Cl_{0.02} K_{-0.15}Mg_{-4.78}Si_{-0.60}OH_{-0.83} \tag{22}$$

illustrating that the two coordinate matrices describe the same mineral composition with equal precision. One concludes that there is nothing ambiguous or misleading about mineral compositions described in terms of exchange components if it is recognized that their proportions cannot be interpreted as relative amounts of the namesake ionic substitutions.

Examples

Igneous calcic amphiboles

Empirical and experimental studies indicate that the total aluminum concentration in calcic amphiboles, Al^{hbl}_{tot}, equilibrated with appropriate buffering mineral assemblages within calc-alkaline granitoid plutons correlates with temperature and pressure (Hammarstrom and Zen 1986; Hollister et al. 1987; Johnson and Rutherford 1989; Thomas and Ernst 1990; Blundy and Holland 1990;

Schmidt 1992). In particular, it has been proposed that Al_{tot}^{hbl} can serve as a geobarometer if sufficient care is taken to account for other factors that might affect amphibole Al concentrations such as T, f_{O_2}, and bulk composition (Anderson and Smith 1995). Although thermodynamic equilibrium constants for individual reactions suffice to parameterize the behavior of ratios of concentrations, the concentration of a single element in a phase is the net result of all linearly independent reactions that drive ionic substitutions during equilibration. The many independent reactions that characterize magmatic systems can cause complicated net substitutions in amphiboles. Assessment of the applicability of the Al_{tot}^{hbl} geobarometer thus depends on identification of ionic substitutions that control Al concentrations in natural calcic amphiboles and the forces that drive them.

Based largely on experimental data, a consensus is emerging that, for appropriate phase assemblages, the pressure dependency of Al_{tot}^{hbl} derives primarily from operation of the generalized tschermakite substitution $AlAlR^{2+}_{-1}Si_{-1}$ (where R^{2+} represents divalent cations) while temperature affects Al_{tot}^{hbl} through operation of the edenite substitutions $Na^{[4]}Al^{[12]}\square_{-1}Si_{-1}$ and $K^{[4]}Al^{[12]}\square_{-1}Si_{-1}$ (Spear 1981; Johnson and Rutherford 1989; Blundy and Holland 1990; Schmidt 1992). Evidence for the importance of tschermakite and edenite substitutions in the evolution of calcic amphiboles of igneous origin would justify direct application of the experimental calibrations for T and P dependence of these exchange mechanisms. Anderson and Smith (1995) argued that strong correlation between $^{[12]}Na + {}^{[12]}K + {}^{[4]}Al$ and Si and between $^{[6]}Al + {}^{[4]}Al$ and R^{2+} + Si is evidence that the edenite and tschermakite substitutions were important during compositional evolution of amphiboles from the Mount Stuart batholith. If these two mechanisms are not generally dominant then factors giving rise to other substitutions that combine to influence Al_{tot}^{hbl} in igneous amphiboles must also be considered.

In what follows the reliability of element-element correlations as indicators of substitutional mechanisms in calcic amphiboles is evaluated using the methods described above. For this purpose we chose 88 analyses of amphiboles from the Hill Creek granodiorite, part of the Pioneer Batholith of southwestern Montana, reported by Hammarstrom (1984). These data are among those used originally by Hammarstrom and Zen (1986) to calibrate the empirically based Al_{tot}^{hbl} geobarometer. Hydrogen contents were not reported by Hammarstrom (1984) and so our analysis is necessarily incomplete in that it could not include substitutions involving anions.

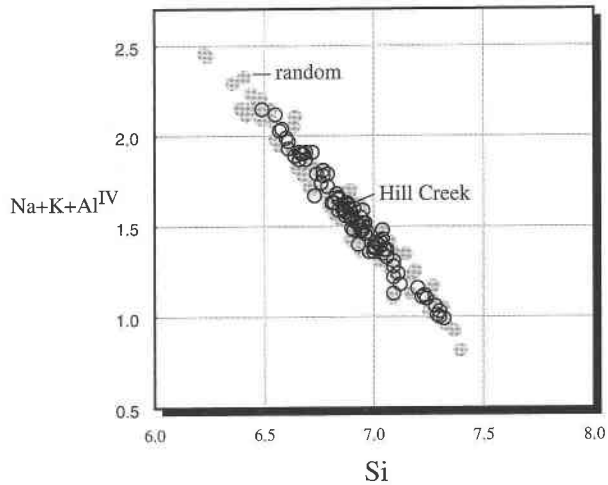

Figure 3. Plot showing high degree of correlation between Na+K+$^{[4]}$Al and Si in amphiboles from the Hill Creek granodiorite (open circles, data from Hammarstrom 1984). Also shown are an equal number of amphibole compositions drawn at random from the volume of amphibole space spanned by the Hill Creek data (grey circles). The similarity in trends between the random data and the Hill Creek data shows that the correlation in the latter is not attributable to petrological forces.

Figure 3 shows that among amphiboles of the Hill Creek granodiorite, $^{[12]}(Na + K) + {}^{[4]}Al$ exhibits significant correlation with Si, the same trend that has been interpreted to be indicative of the importance of $Na^{[4]}Al^{[12]}\square_{-1}Si_{-1}$ and $K^{[4]}Al^{[12]}\square_{-1}Si_{-1}$ exchange mechanisms. However, Figure 3 also shows that an equal number of fictive amphibole compositions chosen at random from the space spanned by the Hill Creek data possess a similar correlation. As with the simple example shown in Figure 2, the trend in Figure 3 is imposed by the crystal chemistry of calcic amphiboles and has no other petrological significance. If the Hill Creek data are related principally by operation of an edenite exchange mechanism, then so are all calcic amphiboles from this section of composition space, a conclusion that is shown to be false in what follows.

Cation abundances of Si, $^{[4]}Al$, $^{[6]}Al$, Ti, Fe, Mg, Ca, Na, and K per formula unit yield the following covariance matrix for the Hill Creek amphiboles (variances and covariances are scaled upward for numerical precision):

$$\mathbf{S}_x = \begin{pmatrix} 3.075 & -3.075 & -0.565 & -0.310 & -2.382 & 3.156 & -0.207 & -0.749 & -0.533 \\ -3.075 & 3.075 & 0.565 & 0.310 & 2.382 & -3.156 & 0.207 & 0.749 & 0.533 \\ -0.565 & 0.565 & 0.381 & 0.064 & 0.474 & -1.081 & 0.065 & 0.154 & 0.112 \\ -0.310 & 0.310 & 0.064 & 0.063 & 0.186 & -0.315 & -0.010 & 0.103 & 0.053 \\ -2.382 & 2.382 & 0.474 & 0.186 & 2.647 & -3.155 & 0.133 & 0.492 & 0.445 \\ 3.156 & -3.156 & -1.081 & -0.315 & -3.155 & 4.903 & -0.349 & -0.764 & -0.621 \\ -0.207 & 0.207 & 0.065 & -0.010 & 0.133 & -0.349 & 0.224 & -0.010 & 0.034 \\ -0.749 & 0.749 & 0.154 & 0.103 & 0.492 & -0.764 & -0.010 & 0.312 & 0.139 \\ -0.533 & 0.533 & 0.112 & 0.053 & 0.445 & -0.621 & 0.034 & 0.139 & 0.138 \end{pmatrix}.$$

Closure is evident in the covariance matrix for these data in the form of nearly zero sums of variances and covariances for tetrahedral-site cations and octahedral-site cations, respectively. The diagonalized covariance matrix

$$\mathbf{S}_y = \begin{pmatrix} 12.706 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1.156 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0.542 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.242 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.093 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0.041 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0.034 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0.003 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

and the matrix of associated eigenvectors (only the first four columns are significant)

$$\mathbf{P} = \begin{pmatrix} \cos\theta_{pc1Si} & \cos\theta_{pc2Si} & \cos\theta_{pc3Si} & \cos\theta_{pc4Si} & \cdots \\ \cos\theta_{pc1^{[4]}Al} & \cos\theta_{pc2^{[4]}Al} & \cos\theta_{pc3^{[4]}Al} & \cos\theta_{pc4^{[4]}Al} & \cdots \\ \cos\theta_{pc1^{[6]}Al} & \cos\theta_{pc2^{[6]}Al} & \cos\theta_{pc3^{[6]}Al} & \cos\theta_{pc4^{[6]}Al} & \cdots \\ \cos\theta_{pc1Ti} & \cos\theta_{pc2Ti} & \cos\theta_{pc3Ti} & \cos\theta_{pc4Ti} & \cdots \\ \cos\theta_{pc1Fe} & \cos\theta_{pc2Fe} & \cos\theta_{pc3Fe} & \cos\theta_{pc4Fe} & \cdots \\ \cos\theta_{pc1Mg} & \cos\theta_{pc2Mg} & \cos\theta_{pc3Mg} & \cos\theta_{pc4Mg} & \cdots \\ \cos\theta_{pc1Ca} & \cos\theta_{pc2Ca} & \cos\theta_{pc3Ca} & \cos\theta_{pc4Ca} & \cdots \\ \cos\theta_{pc1Na} & \cos\theta_{pc2Na} & \cos\theta_{pc3Na} & \cos\theta_{pc4Na} & \cdots \\ \cos\theta_{pc1K} & \cos\theta_{pc2K} & \cos\theta_{pc3K} & \cos\theta_{pc4K} & \cdots \end{pmatrix}$$

$$= \begin{pmatrix} 0.469 & 0.481 & -0.123 & 0.080 & \cdots \\ -0.469 & -0.481 & 0.123 & -0.080 & \cdots \\ -0.113 & 0.257 & 0.424 & 0.164 & \cdots \\ -0.046 & -0.063 & 0.105 & 0.169 & \cdots \\ -0.422 & 0.148 & -0.806 & 0.033 & \cdots \\ 0.587 & -0.647 & -0.240 & -0.021 & \cdots \\ -0.037 & 0.068 & 0.166 & -0.851 & \cdots \\ -0.112 & -0.149 & 0.209 & 0.453 & \cdots \\ -0.086 & -0.037 & 0.021 & 0.037 & \cdots \end{pmatrix}$$

show that 86% of the variance among these data is described by the first principal component comprising the net substitution

$$Na_{0.5}K_{0.4}Ca_{0.15}Fe_{1.9}Ti_{0.2}{}^{[6]}Al_{0.5}{}^{[4]}Al_{2.1}Mg_{-2.6}Si_{-2.1}. \quad (23)$$

For purposes of comparison with simple substitutions, we have multiplied the coefficients of P by a constant value. This step is permissible because it is the stoichiometry of the net substitutions that is of interest.

Equation 23 closely resembles the pargasite substitution $Na^{[6]}Al^{[4]}Al_2{}^{[12]}\square_{-1}R^{2+}{}_{-1}Si_{-2}$ (notice the *net* amount of R^{2+} transferred in Eq. 23) and so can also be described as being composed of equal parts of the edenite and tschermakite substitutions. Since experiments indicate that the edenite and tschermakite substitutions operate in response to changes in temperature and pressure, respectively (Schmidt 1992), statistical analysis of the cation data is consistent with the hypothesis that temperature and pressure were the principal factors that controlled the composition of amphiboles as they grew in the Hill Creek granodiorite (the phase assemblage of the pluton is analogous to the experiments cited).

Conclusions drawn from Equation 23 are suspect, however, because the correlations that give rise to the first principal component in this instance are attributable primarily to closure. A comparison with results of an analogous statistical analysis of amphibole compositions drawn at random from the same volume of composition space as that occupied by the Hill Creek data can be used to show that this is so. The premise is that if the stoichiometry of the net substitution in Equation 23 is mainly the product of closure then the same stoichiometry will be exhibited by the random data (see section "Example").

For this exercise we drew at random 88 amphibole compositions from the volume of composition space spanned by the Hill Creek data. Cation abundances of Si, $^{[4]}$Al, $^{[6]}$Al, Ti, Fe, Mg, Ca, Na, and K per formula for the random compositions yield the covariance matrix (scaled for numerical precision)

$$\mathbf{S}_x = \begin{pmatrix} 6.202 & -6.202 & -3.131 & -0.478 & -2.554 & 6.031 & 0.136 & -1.995 & -0.124 \\ -6.202 & 6.202 & 3.131 & 0.478 & 2.554 & -6.031 & -0.136 & 1.995 & 0.124 \\ -3.131 & 3.131 & 3.729 & -0.436 & -0.789 & -2.297 & -0.210 & 0.461 & -0.088 \\ -0.478 & 0.478 & -0.436 & 1.461 & 0.445 & -1.660 & 0.190 & 0.165 & -0.031 \\ -2.544 & 2.554 & -0.789 & 0.445 & 6.816 & -6.574 & 0.098 & 1.656 & -0.100 \\ 6.031 & -6.031 & -2.297 & -1.660 & -6.574 & 11.198 & -0.661 & -2.244 & 0.244 \\ 0.136 & -0.136 & -0.210 & 0.190 & 0.098 & -0.661 & 0.582 & -0.040 & -0.026 \\ -1.995 & 1.995 & 0.461 & 0.165 & 1.656 & -2.244 & -0.040 & 1.125 & -0.069 \\ -0.124 & 0.124 & -0.088 & -0.031 & -0.100 & 0.244 & -0.026 & -0.069 & 0.209 \end{pmatrix}.$$

As with the natural data, the presence of closure is evidenced in the random cation data by nearly zero sums of variances and covariances among cations of like coordination numbers. Diagonalization of $\mathbf{S}_x$ yields

$$\mathbf{S}_y = \begin{pmatrix} 25.030 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 7.635 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2.234 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1.652 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.540 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0.365 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0.070 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}.$$

and the eigenvectors

$$\mathbf{P} = \begin{pmatrix} 0.450 & 0.342 & -0.229 & -0.273 & -0.070 & \cdots \\ -0.450 & -0.342 & 0.229 & 0.273 & 0.070 & \cdots \\ -1.89 & -0.530 & -0.184 & -0.592 & -0.235 & \cdots \\ -0.067 & 0.105 & -0.507 & 0.604 & -0.397 & \cdots \\ -0.362 & 0.629 & 0.431 & -0.214 & -0.166 & \cdots \\ 0.631 & -0.270 & 0.526 & 0.202 & -0.051 & \cdots \\ -0.012 & 0.066 & -0.265 & -0.001 & 0.847 & \cdots \\ -0.163 & 0.008 & 0.257 & 0.121 & 0.159 & \cdots \\ 0.004 & -0.023 & 0.080 & 0.110 & 0.065 & \cdots \end{pmatrix}.$$

Inspection of $\mathbf{S}_y$ and $\mathbf{P}$ for the randomly chosen compositions shows that 67% of the total variance among these data is accounted for by the first principal component:

$$Na_{0.75}Ca_{0.1}Fe_{1.65}Ti_{0.3}{}^{[6]}Al_{0.9}{}^{[4]}Al_{2.1}Mg_{-2.95}Si_{-2.1}. \quad (24)$$

Equation 24 closely resembles the first principal component for the Hill Creek data (Eq. 23). Since there can be no petrological explanation for Equation 24, the resemblance between Equations 23 and 24 shows that closure dominates both sets of data in similar fashion.

Conversion of the Hill Creek data and the random data to descriptions in terms of a single addition component and molar concentrations of exchange components affords analysis free from closure and eliminates the similarity between their respective principal exchange vectors. The choice of additive and exchange components is arbitrary so long as they adequately describe the composition of the amphiboles of interest. The additive component $Ca_2Mg_4AlAlSi_7O_{22}(OH)_2$ and exchange components $FeMg_{-1}$, $MgCa_{-1}$, $Na^{[6]}Al^{[4]}Al_2{}^{[12]}\square_{-1}Mg_{-1}Si_{-2}$, $NaFe_4Al_2{}^{[12]}\square_{-1}Mg_{-4}Si_{-2}$, ${}^{[6]}Al^{[4]}Al_2Mg_{-1}Si_{-1}$, $K^{[6]}Al^{[12]}\square_{-1}Si_{-1}$, $TiO^{[6]}Al_{-1}OH_{-1}$, and $TiO_2Mg_{-1}OH_{-2}$ suffice in this instance. The scaled covariance matrix for Hill Creek amphiboles recast as molar concentrations of these exchange components is

$$\mathbf{S}_x = \begin{pmatrix} 0.149 & -0.001 & 0.027 & -0.024 & -0.188 & 0.010 & -0.315 & 0.332 \\ -0.001 & 0.207 & 0.021 & -0.017 & -0.120 & -0.029 & -0.014 & 0.022 \\ 0.027 & 0.021 & 0.229 & -0.040 & -0.294 & 0.031 & -0.152 & 0.226 \\ -0.024 & -0.017 & -0.040 & 0.163 & 0.278 & 0.108 & 0.167 & -0.133 \\ -0.188 & -0.120 & -0.294 & 0.278 & 1.023 & 0.120 & 0.661 & -0.665 \\ 0.010 & -0.029 & 0.031 & 0.108 & 0.120 & 0.138 & 0.044 & 0.006 \\ -0.315 & -0.014 & -0.152 & 0.167 & 0.661 & 0.044 & 0.779 & -0.798 \\ 0.332 & 0.022 & 0.226 & -0.133 & -0.665 & 0.006 & -0.798 & 0.889 \end{pmatrix}.$$

Absence of closure in the exchange-component form for the data is evidenced by the lack of zero sums in the columns of $\mathbf{S}_x$. Diagonalization yields

$$\mathbf{S}_y = \begin{pmatrix} 2.537 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.500 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0.249 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.187 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.067 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0.025 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0.011 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}.$$

The net substitutions corresponding to the first four principal components for these recast data, accounting for more than 97% of the total variance, are given by matrix $\mathbf{N}$ (Eq. 13):

$$\mathbf{N} = \begin{pmatrix} \sum_j J_{\mathrm{Si}j}\cos\theta_{\mathrm{pc1}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{Si}j}\cos\theta_{\mathrm{pc2}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{Si}j}\cos\theta_{\mathrm{pc3}X_j^{\mathrm{ex}}} & \cdots \\ \sum_j J_{[4]\mathrm{Al}j}\cos\theta_{\mathrm{pc1}X_j^{\mathrm{ex}}} & \sum_j J_{[4]\mathrm{Al}j}\cos\theta_{\mathrm{pc2}X_j^{\mathrm{ex}}} & \sum_j J_{[4]\mathrm{Al}j}\cos\theta_{\mathrm{pc3}X_j^{\mathrm{ex}}} & \cdots \\ \sum_j J_{[6]\mathrm{Al}j}\cos\theta_{\mathrm{pc1}X_j^{\mathrm{ex}}} & \sum_j J_{[6]\mathrm{Al}j}\cos\theta_{\mathrm{pc2}X_j^{\mathrm{ex}}} & \sum_j J_{[6]\mathrm{Al}j}\cos\theta_{\mathrm{pc3}X_j^{\mathrm{ex}}} & \cdots \\ \sum_j J_{\mathrm{Ti}j}\cos\theta_{\mathrm{pc1}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{Ti}j}\cos\theta_{\mathrm{pc2}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{Ti}j}\cos\theta_{\mathrm{pc3}X_j^{\mathrm{ex}}} & \cdots \\ \sum_j J_{\mathrm{Fe}j}\cos\theta_{\mathrm{pc1}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{Fe}j}\cos\theta_{\mathrm{pc2}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{Fe}j}\cos\theta_{\mathrm{pc3}X_j^{\mathrm{ex}}} & \cdots \\ \sum_j J_{\mathrm{Mg}j}\cos\theta_{\mathrm{pc1}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{Mg}j}\cos\theta_{\mathrm{pc2}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{Mg}j}\cos\theta_{\mathrm{pc3}X_j^{\mathrm{ex}}} & \cdots \\ \sum_j J_{\mathrm{Ca}j}\cos\theta_{\mathrm{pc1}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{Ca}j}\cos\theta_{\mathrm{pc2}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{Ca}j}\cos\theta_{\mathrm{pc3}X_j^{\mathrm{ex}}} & \cdots \\ \sum_j J_{\mathrm{Na}j}\cos\theta_{\mathrm{pc1}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{Na}j}\cos\theta_{\mathrm{pc2}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{Na}j}\cos\theta_{\mathrm{pc3}X_j^{\mathrm{ex}}} & \cdots \\ \sum_j J_{\mathrm{K}j}\cos\theta_{\mathrm{pc1}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{K}j}\cos\theta_{\mathrm{pc2}X_j^{\mathrm{ex}}} & \sum_j J_{\mathrm{K}j}\cos\theta_{\mathrm{pc3}X_j^{\mathrm{ex}}} & \cdots \end{pmatrix} = \begin{pmatrix} 0.556 & 1.176 & 2.554 & -0.120 & \cdots \\ -0.556 & -1.176 & -2.544 & 0.120 & \cdots \\ 0.131 & -0.750 & -0.329 & -0.087 & \cdots \\ 0.028 & -0.110 & -0.376 & 0.054 & \cdots \\ -0.371 & -1.515 & -1.386 & 0.968 & \cdots \\ 0.252 & 2.643 & 2.010 & 0 & \cdots \\ -0.041 & -0.267 & 0.081 & -0.935 & \cdots \\ 0.024 & -0.137 & -1.063 & -0.005 & \cdots \\ -0.041 & -0.282 & -0.526 & 0.030 & \cdots \end{pmatrix}.$$

Inspection of $\mathbf{S}_y$ and $\mathbf{N}$ derived from the closure-free form of the data shows that 71% of the total variance exhibited by the Hill Creek amphiboles is explained by the net substitution

$$\mathrm{Na}_{0.1}\mathrm{Mg}_{0.95}\mathrm{Ti}_{0.1}{}^{[6]}\mathrm{Al}_{0.5}\mathrm{Si}_{2.1}\mathrm{K}_{-0.15}\mathrm{Ca}_{-0.15}\mathrm{Fe}_{-1.4}{}^{[4]}\mathrm{Al}_{-2.1}. \quad (25)$$

The closure-free first principal component represented by Equation 25 differs significantly from the first principal component derived from the cation form of the Hill Creek data (Eq. 23) and indicates that the evolution of these amphiboles cannot be described simply as a linear sum of the tschermakite and edenite substitutions as the cation data might suggest. Analysis of the data in the absence of closure implies that changes in pressure and temperature were not the only important factors that controlled amphibole chemistry during crystallization of the Hill Creek granodiorite.

Results of principal components analysis of the 88 random compositions recast in terms of exchange components are significantly different from those of the Hill Creek data. The dissimilarity verifies that Equation 25 is free of the effects of closure. The diagonalized covariance matrix for the exchange-component form of the randomly chosen data is

$$\mathbf{S}_y = \begin{pmatrix} 2.429 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1.125 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0.818 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.705 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.476 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0.367 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0.175 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}.$$

The relative magnitudes of the covariances of $\mathbf{S}_y$ show that the total variance defined by the random data is distributed more evenly among the principal components than it is for the Hill Creek data. For example, only 40% of the total random variance is accounted for by the first principal component. What is more, the net substitution corresponding to the first principal component:

$$\mathrm{Na}_{0.2}\mathrm{Ca}_{0.02}\mathrm{Fe}_{0.6}\mathrm{Mg}_{1.4}\mathrm{Si}_{1.7}\mathrm{K}_{-0.4}\mathrm{Ti}_{-0.2}{}^{[6]}\mathrm{Al}_{-1.9}{}^{[4]}\mathrm{Al}_{-1.7} \quad (26)$$

is significantly different from that obtained from the analysis of the exchange-component form of the Hill Creek data (compare Eq. 25 and Eq. 26) and from edenite substitution (compare with Fig. 3).

Kaersutitic amphiboles

A concerted effort in recent years has been put forth to correlate observed variability in elemental concentrations in mantle-derived amphibole megacrysts to changes in *T*, *P*, and oxidation state (Helz 1982; Dyar et al. 1992; Huckenholz et al. 1992). At issue in the present example is what mantle-derived kaersutitic and titanian pargasitic amphibole megacrysts tell us about the oxidation state of the upper mantle in view of the potential effects of closure. Three sets of data relevant to the evolution of mantle-derived kaersutitic amphiboles are examined with the methods described above. Results illustrate the validity of using molar concentrations of exchange components as variables for statistical analysis.

The first data set subjected to statistical analysis is that of Popp et al. (1995a). These data represent the results of experiments on a single titanian pargasite megacryst from Vulcan's Throne, Arizona, that demonstrate the effects of *T*, *P*, and f_{H_2} on the substitution $Fe^{3+}OFe^{2+}_{-1}(OH, F, Cl)_{-1}$. For these data, except for the correlations involving Fe^{2+}, Fe^{3+}, O and H, all other correlations among ionic species are unity. They are of particular value because they include precise measurements of both H concentration and Fe^{3+}/Fe^{2+}.

The second data set chosen for analysis is that of Popp and Bryndzia (1992). Their study is among several investigations of amphibole megacrysts that document negative correlations between the concentrations of Fe^{3+} and

total univalent anions OH, F, and Cl (e.g., Boettcher and O'Neil 1980; Dyar et al. 1993). The correlation has been interpreted to mean that progressive oxidation of amphibole in the upper mantle proceeds according to the substitution

$$Fe^{3+}OFe^{2+}_{-1}(OH,F,Cl)_{-1} \quad (27)$$

by which O^{2-} replaces the univalent anions $(OH,F,C)^-$ on the O3 crystallographic site. However, Popp and Bryndzia (1992) concluded that Equation 27 alone cannot explain H^+ deficiencies in kaersutitic amphiboles. They proposed that the complete oxy substitution involves a combination of Equation 27 and the Ti-oxy substitution

$$Ti^{4+}OAl_{-1}(OH,F,Cl)_{-1}. \quad (28)$$

The exchange mechanisms represented by Equations 27 and 28 were proposed on the basis of statistical analysis of relative amounts of ionic species. Popp and Bryndzia suggested that closure may have augmented the negative correlations upon which their conclusions are based. Using the methods described above it is possible to quantify the influence that closure may have had on the substitution mechanisms proposed.

The data compiled by Popp and Bryndzia represent a wide variety of analytical methods and petrological settings. Because analytical errors in compilations such as this are variable and because amphiboles from such diverse petrological environments delimit a large portion of amphibole composition space without necessarily being linked to one another by any evolutionary path, we assume that the Popp and Bryndzia data exhibit a substantial element of random noise. To obviate the difficulties associated with such pooled data, we also apply the methods described herein to data presented by Dyar et al. (1993). The random element in these data is likely to be less than in the Popp and Bryndzia data in that the former were analyzed with consistently more precise methods (Mössbauer spectroscopy, vacuum fusion extraction of H^+) and come from a comparatively restricted petrological setting; they derive from megacrysts in basalts from continental rift environments.

Experimental data. Figure 4 is a comparison between the elemental variations exhibited by the Vulcan's Throne experimental data and random draws from the volume of composition space spanned by the data. Perfect correlation between $Fe^{3+} + O^{2-}$ and Fe^{2+} + (OH+F+C1) among the experimental compositions and lack of correlation among the randomly distributed compositions indicates that the trend in the experimental compositions is not a result of closure. The substitution mechanism that controlled the evolution of the experimental charges is therefore known a priori (Fig. 4), and these compositions serve as a control that demonstrates the validity of combining principal components analysis with exchange components to derive meaningful substitution mechanisms; principal components analysis of the data transformed into proportions of exchange components should yield the substitution $Fe^{3+}OFe^{2+}_{-1}(OH, F, C1)_{-1}$.

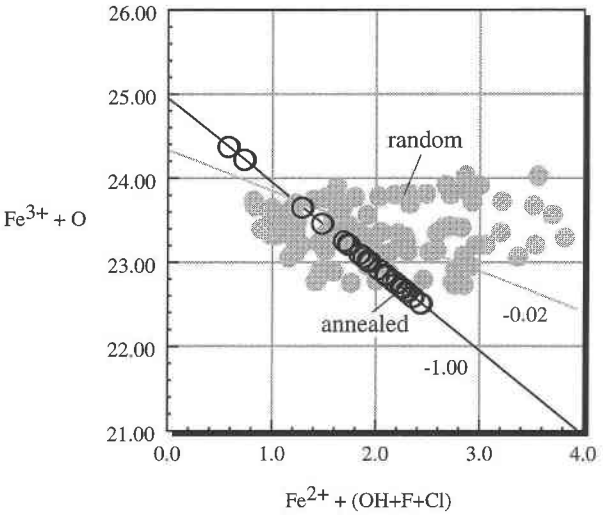

FIGURE 4. Plot of amphibole Fe^{3+} +O vs. Fe^{2+} + (OH+F+Cl) showing that the high degree of correlation present in the experimental data (open circles) of Popp et al. (1995a) is absent from randomly distributed data (grey circles) from the same volume of amphibole space occupied by the experimental data. The trend in the experimental data is thus correctly interpreted as being the product of petrological forces. Lines are reduced major axis fits (Till 1974). Numbers adjacent lines indicate correlation coefficients.

For this test, the Vulcan's Throne experimental results were transformed from abundances of ionic species to unit moles of the additive component $Ca_2Mg_4AlAlSi_7O_{22}(OH)_2$ and molar concentrations of the exchange components $FeMg_{-1}$, $Na^{M4[6]}Al\,Ca_{-1}Mg_{-1}$, $MgCa_{-1}$, $Na^{[6]}Al^{[4]}Al_2^{[12]}\square_{-1}Mg_{-4}Si_{-2}$, $NaFe_4Al_2^{[12]}\square_{-1}Mg_{-4}Si_{-2}$, $^{[6]}Al^{[4]}AlMg_{-1}Si_{-1}$, $Ti^{[4]}Al_2Mg_{-1}Si_{-2}$, $TiSi_{-1}$, $K^{[4]}Al^{[12]}\square_{-1}Si_{-1}$, and $TiO^{[6]}Al_{-1}OH_{-1}$. Note charge balance mandates that Fe refers to Fe^{2+} and to $3Fe^{2+} + Fe^{3+}$ in the first and fifth components, respectively. Principal components analysis of the transformed data shows that 99.6% of the total variance is accommodated by the net substitution

$$Fe^{3+}_{0.20}O_{0.22}\ Fe^{2+}_{-0.20}OH_{-0.22}. \quad (29)$$

Despite the fact that it does not appear in the list of exchange components used, and notwithstanding the complexity of the mathematical manipulations involved, statistical analysis of exchange components correctly identifies the Fe-oxy substitution as the sole exchange mechanism that relates the experimental compositions.

Natural data. Having shown that statistical analysis of closure-free variables provides the means to identify correctly substitutions in annealed amphiboles that operated in response to petrological factors, we extend application of the method to the analysis of compositions of natural kaersutites. Figure 5 compares the elemental correlations for kaersutites cited by Popp and Bryndzia (1992) and Dyar et al. (1993) with fictive amphiboles drawn at random from uniform distributions of amphibole substitutions spanning the same volume of composition space as

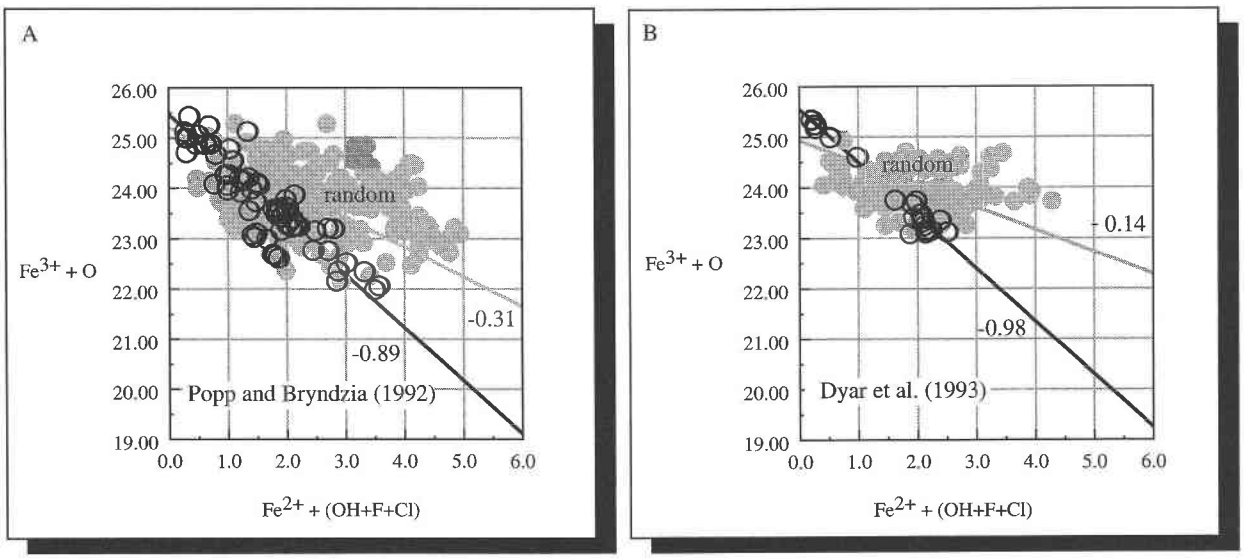

FIGURE 5. Plots of Fe^{3+} + O vs. Fe^{2+}+(OH+F+Cl) for natural (open circles) and fictive randomly distributed (grey circles) amphiboles. The natural data are from the compilations of Popp and Bryndzia (1992) and Dyar et al. (1993) The fictive compositions include 200 and 100 analyses from the range of chemical compositions spanned by the Popp and Bryndzia (1992) and Dyar et al (1993) data sets, respectively. Lines are reduced major axis fits (Till 1974) to the natural (black) and fictive (grey) data. Numbers are correlation coefficients.

the natural data. For both groups of natural samples, there are statistically significant (at the 99% confidence level) inverse correlations between the reactants and products of the Fe-oxy substitution (Eq. 27). The fictive compositions also show statistically significant correlations at the 99% level, but the correlation coefficients are small, signifying that the correlations comprise a relatively small proportion of the total variance. The presence of any correlations among the random data in Figure 5 raises the possibility that closure influences the trends exhibited by the natural data although the statistics of the correlations in the random data suggest that closure is not dominant.

A test of the potential influence of closure on the conclusions drawn from the trends in Figure 5 is afforded by converting the natural data to molar concentrations of exchange components and a single additive component in the same way that the Vulcan's Throne data were treated. Principal components analysis of the converted Popp and Bryndzia data shows that 84% of the total variance exists by virtue of the net substitution

$$Fe^{3+}_{0.20}O_{0.21}\ Fe^{2+}_{-0.20}OH_{-0.21} \qquad (30)$$

where coefficients less than 0.03 have been ignored. Similarly, again ignoring coefficients less than 0.03, 96% of the total variance exhibited by the Dyar et al. (1993) samples in closure-free form is attributable to the net substitution

$$Fe^{3+}_{0.21}O_{0.19}\ Fe^{2+}_{-0.19}OH_{-0.19}. \qquad (31)$$

Clearly, the Fe-oxy substitution dominated the variability in these natural kaersutites. Because this analysis is free of closure, it can be stated that operation of this component was due solely to petrological factors.

The possible influence of the Ti-oxy substitution shown in Equation 28 is also revealed by closure-free principal components analysis. Statistically significant negative correlations (99% confidence level) between the variables that describe Equation 28 are observed not only for the natural data (Popp and Bryndzia 1992) but also for fictive random compositions from the same volume of composition space (Fig. 6). These results suggest the possibility that the importance of the regression and correlation analysis reported by Popp and Bryndzia (1992) may be overestimated because of closure.

For this test, attention is directed to the net substitutions defined by the second principal components of the kaersutite data. The second principal components comprise 14 and 3% of the total variance in the data sets of Popp and Bryndzia (1992) and Dyar et al. (1993), respectively. These low proportions of the total variances are themselves significant because a subequal partitioning of variance among two principal components that correspond to the Fe and Ti-oxy reactions is suggested by Popp et al. (1995b). The higher percentage of variance found for Popp and Bryndzia's data suggests that the second principal components may contain a significant component of noise because the relative errors in their compilation are greater by at least a factor of two. If so, a distinct variance structure indicative of the Ti-oxy substitution in these amphiboles may be masked by the effect of pooling the data from various igneous suites. Pooling should not be a significant problem for the data set of

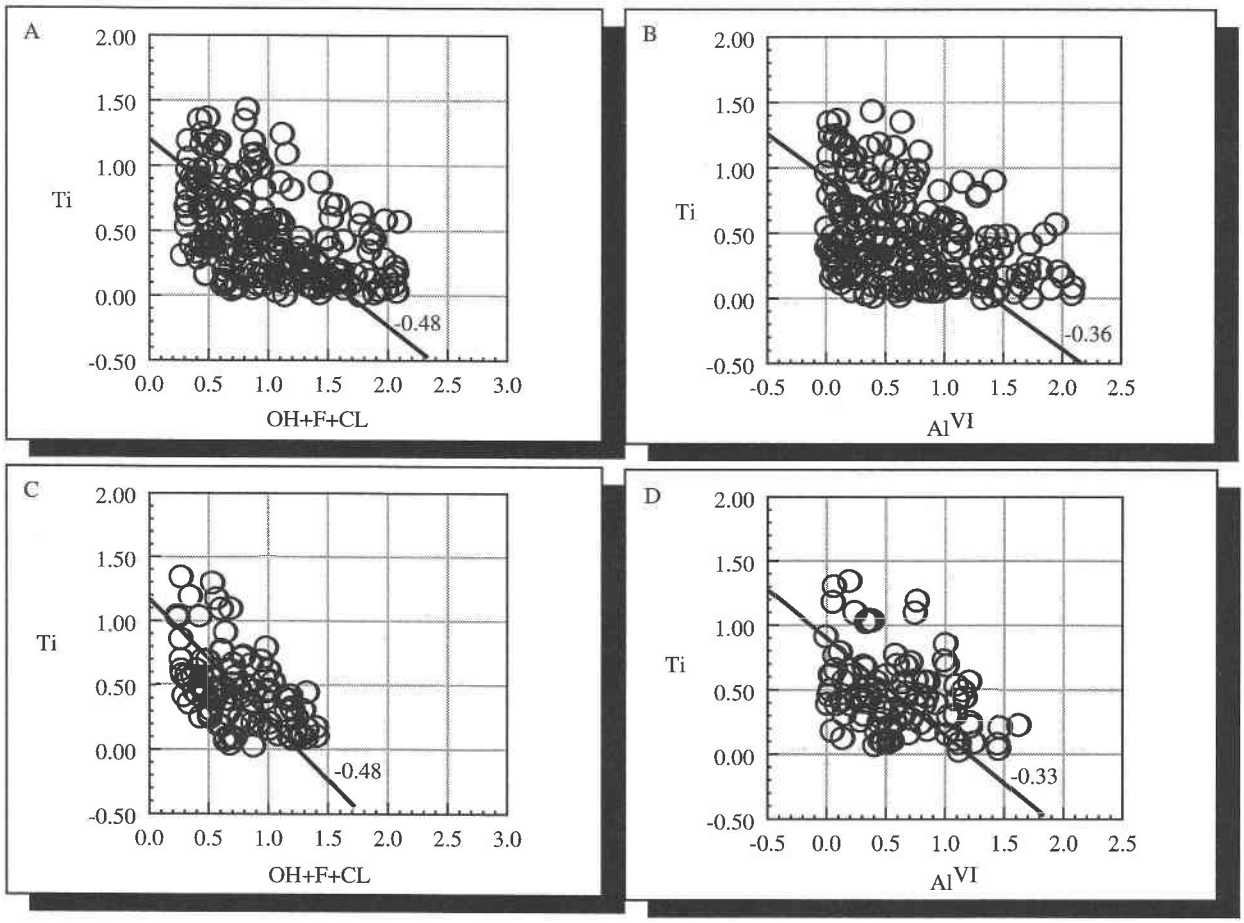

FIGURE 6. Plots showing correlations among atomic species for fictive amphibole compositions drawn at random from the range of chemical compositions spanned by natural megacrysts. Two hundred randomly drawn compositions from the volume of composition space spanned by the data set of Popp and Bryndria (1992) are shown in A and B. One hundred randomly drawn compositions from the space occupied by the data of Dyar et al. (1993) are shown in C and D. Lines are reduced major axis fits (Till 1974). Numbers adjacent lines are correlation coefficients at 99% confidence:

Dyar et al., however, and there is a greater likelihood that the second principal component for these data is meaningful. The net substitution associated with the second principal component of the Dyar et al. data is

$$^{[12]}Na_{0.52}Mg_{0.04}{}^{[6]}Al_{0.37}Ti^{4+}_{0.40}\,O^{[12]}K_{-0.37}Ca_{-0.15}Na_{-0.17}$$
$$Fe^{3+}_{-0.19}{}^{[4]}Al_{-0.29}Si_{-0.02}(OH)_{-1}. \qquad (32)$$

Equation 32 is significantly different from the substitution proposed by Popp and Bryndzia (1992). We propose that a unique Ti-oxy substitution for the natural amphiboles may not exist. Instead, different generalized substitutions involving Ti and O broadly similar in form to Equation 32 may accommodate H deficiencies in different ways depending upon petrological environment. Bulk composition of the magma may be an important factor that determines the precise stoichiometry of the Ti-oxy substitution.

CONCLUSIONS

Through examination of amphibole compositions generated by computer, compositions induced by experiment in the laboratory, and those occurring in nature we have shown that correlations among elemental abundances in these minerals are sometimes exaggerated by competition for a fixed number of crystallographic sites, a manifestation of the statistical phenomenon known as closure. Enhanced correlations caused by closure mask covariations among elements produced by chemical reactions. Expressions of mineral compositions in terms of a single additive component and molar concentrations of exchange components are free from closure and can be analyzed statistically to elucidate ionic substitution mechanisms that represent progress of reactions. Statistical analysis of closed data, such as those expressed in terms of relative concentrations of ions, are not necessarily reflective of chemical processes.

We propose that their unique capacity for removing closure makes exchange component proportions useful variables for elucidation of petrological processes through analysis of the chemical variability of multi-site minerals. At the same time it must be remembered that, unlike the ionic substitutions for which they are named, molar concentrations of exchange components by themselves have no physical significance. Statistical analyses of exchange components must always be interpreted in terms of the net ionic substitutions defined by the results.

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Appendix

Throughout this paper reference has been made to amphibole compositions drawn at random from various volumes of composition space. The volumes of amphibole space were defined by transforming the data of interest into unit moles of the $Ca_2Mg_4AlAlSi_7O_{22}(OH)_2$ additive component and molar concentrations of the exchange components $FeMg_{-1}$, $NaAlCa_{-1}Mg_{-1}$, $MgCa_{-1}$, $Na^{[6]}Al^{[4]}Al_2^{[12]}\square_{-1}Mg_{-1}Si_{-2}$, $NaFe_4Al_2^{[12]}\square_{-1}Mg_{-4}Si_{-2}$, $^{[6]}Al^{[4]}AlMg_{-1}Si_{-1}$, $K^{[4]}Al^{[12]}\square_{-1}Si_{-1}$, $TiO^{[6]}Al_{-1}OH_{-1}$, and $TiO_2Mg_{-1}OH_{-2}$. Ranges in values exhibited by the data for each of the exchange component molar proportions were used to define uniform distributions of molar concentrations from which random numbers were drawn. Random numbers were generated using a FORTRAN routine described by Press et al. (1986, p. 196) that effectively eliminates sequential correlations. Following random draws for each of the nine exchange component molar proportions, five test criteria were applied to avoid (1) compositions with less than 5.5 Si atoms per 23 O atoms per formula unit (an arbitrary but practical lower limit for igneous amphiboles suggested by the literature), (2) compositions with greater than eight Si per formula

unit, (3) compositions with greater than five Mg atoms per formula unit, (4) compositions with more than three Na atoms per formula unit, and (5) compositions with negative abundances of ions. These tests were required to ensure that each random draw conforms to amphibole crystal chemistry. The precise criteria used in the tests are dictated by the choice of origin in amphibole space and would be different for some other origin.

A set of random exchange component molar concentrations drawn in this way and applied to one unit mole of the magnesio-hornblende additive component comprises a crystal chemically viable amphibole composition. By collectively spanning the total range of molar concentrations defined by the data for each exchange component irrespective of any extant correlations, the fictive, randomly distributed amphibole compositions encompass the volume of amphibole composition space occupied by the original data. The random compositions were routinely converted to their expressions in terms of ionic species for comparison with real amphibole formulae.