CORRELATION OF Mg/Fe PARTITIONING BETWEEN GARNET AND BIOTITE WITH $^{18}O/^{16}O$ PARTITIONING BETWEEN QUARTZ AND MAGNETITE*

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ABSTRACT. Isotopic and chemical data for thirteen metamorphic rocks containing garnet and biotite are used to investigate the dependence of the Mg–Fe partition upon temperature, expressed as the $^{18}O/^{16}O$ fractionation between quartz and magnetite, and upon chemical variation in both phases. Additional sets of samples considered to have equilibrated at nearly the same temperature are utilized to improve the least-squares solution of the compositional coefficients. The most acceptable least-squares solution, using the singular-value decomposition algorithm, is: $K_D{}^{Mg-Fe}{}_{G-B} = -0.177(\pm0.010)1000 \ln\alpha{}^Q{}_M \quad -1.22(\pm0.14)X^G{}_{Mn} \quad -2.14(\pm0.13)X^G{}_{Ca} \quad +1.40(\pm0.09)X^B{}_{Fe} \quad +0.942(\pm0.109)X^B{}_{Ti} \quad -1.59(\pm0.21)X^B{}_{Al^{vi}} \quad -0.492(\pm0.068)$. K_D is primarily dependent upon temperature but is also dependent upon compositional variation, particularly upon $X^B{}_{Fe}$, although $X^G{}_{Ca}$ becomes significant at higher concentrations.

INTRODUCTION

Partitioning of elements and isotopes between coexisting mineral phases has been extensively studied for use in geothermometry and as a measure of the attainment of chemical and isotopic equilibrium. Both partitions depend strongly upon temperature, but elemental partitioning is also generally dependent upon compositional variation in the ex-changing phases. Correlating the isotopic and elemental data on co-existing natural minerals makes it possible (1) to study compositional dependencies in natural systems that are presently too complex to study experimentally, (2) to calculate a model $^{18}O/^{16}O$ partition value from chemical data, and (3) to estimate a temperature based on experimentally calibrated isotopic fractionations.

This paper examines the correlation of Mg–Fe partitioning between garnet and biotite with the $^{18}O/^{16}O$ partitioning between quartz and magnetite. A detailed understanding of the distribution of Mg and Fe between coexisting garnet and biotite would be particularly useful in metamorphic studies because this mineral pair commonly occurs over a wide range of metamorphic grade in rocks having a wide range of bulk-chemical composition. As a result, many studies have been undertaken (Albee, 1965a, b; Dahl, 1969; Dallmeyer, 1974; Evans, 1965; Frost, 1962; Hietanen, 1969; Kano and Kuroda, 1973; Kretz, 1959, 1964; Lyons and Morse, 1970; Miyashiro, 1953; Perchuk, 1970; Phinney, 1963; Saxena, 1968, 1969, 1973, and; Sen and Chakraborty, 1968). However, these studies have reached quite different conclusions regarding the composi-tional dependencies of the Mg–Fe partition.

Thirteen metamorphic rocks have been selected, based upon the availability of published isotopic data, and garnet and biotite were ana-lyzed by electron microprobe. Multivariate least-squares analysis, utilizing

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the singular-value decomposition algorithm (SVD) described by Boggs (1972), is used to examine the functional dependency of the Mg–Fe partition between garnet and biotite upon temperature, in terms of the $^{18}O/^{16}O$ partition, and upon compositional variation.

DATA

Taylor, Albee, and Epstein (1963), Garlick (ms), Garlick and Epstein (1967), and Shieh and Taylor (1969) reported oxygen isotopic data for metamorphic rocks representing a wide range of metamorphic grade. Their samples, which contain ferromagnesium phases, were studied in thin section, and the silicate and opaque phases were analyzed with the electron microprobe. Garnet and biotite were chosen for this study, despite the problem of the ubiquitous zoning in garnet, because this pair occurs in more samples and over a larger range of metamorphic grade than any other mineral pair. However, only 13 samples contain both garnet and biotite in apparent textural equilibrium (table 1). Sample descriptions are given in Albee (1965a), Garlick (ms), Garlick and Epstein (1967), and Hietanen (1969).

Elemental analyses were made on a three-channel Applied Research Laboratory (EMX) electron microprobe using the general technique of Bence and Albee (1968). The triads Mn–Fe–Mg, Ca–Al–Si, K–Ba–Na, and Zn–Ti–F were analyzed at 15 kV with constant integrated beam current and pulse height selection. The beam current, spot size, and counting time were adjusted to obtain maximum counting rates with minimal sample damage and contamination.

Several analyses of each phase were made on each of a number of adjacent grains in small areas that contain all of the phases in the rock. Garnet zoning was sampled by analyzing the rim and the center of the garnet porphyroblast. However, this discussion is based upon the aver-aged analyses of the biotite grains and of the garnet rims adjacent to the biotite. It is assumed that the garnet rim, but not necessarily the garnet core, is in chemical equilibrium with the adjacent biotite grain (Hollister, 1966). In several samples, erratic analyses were excluded from the average. The garnet and biotite chemical data used in this paper are given in table 1. A computer printout of all analyses may be obtained from A. Albee.

The oxygen isotope data for the 13 samples is given in terms of the quartz-magnetite partition.

$$\alpha^Q_M = (^{18}O/^{16}O)_Q/(^{18}O/^{16}O)_M$$

because experimental temperature calibrations are available for this partition (O'Neil and Clayton, 1964; Becker, ms; and see also, Bottinga and Javoy, 1973). α^Q_M has been directly measured in only five samples (table 2). It has been calculated from the quartz-ilmenite partition (α^Q_I) for five additional samples using the relation, $\alpha^Q_M = 1.000696 \, \alpha^Q_I$, based on the magnetite-ilmenite fractionation measured in sample D-6 (see Garlick and Epstein, 1967, p. 206 for discussion). It has been calculated

TABLE 1

Averaged microprobe analyses of garnet* and biotite**

Sample	ln K_D	K_D	X^G_{Mn}	X^G_{Ca}	X^B_{Fe}	X^B_{Ti}	$X^B_{Al^{vi}}$	Assemblage†	Locality
A64G	−1.21	0.298	0.035	0.036	0.57	0.073	0.157	Si-I	Central Connecticut
A56J	−1.77	0.171	0.037	0.043	0.466	0.023	0.163	Si-St	Central Connecticut
AH243	−1.69	0.185	0.062	0.043	0.57	0.047	0.167	Si-I	Northern Idaho
F22B	−2.00	0.135	0.009	0.139	0.372	0.030	0.147	Ky-St	Southern Vermont
D-12	−1.69	0.184	0.070	0.048	0.55	0.040	0.177	St-M	Duchess County, N.Y.
D-47	−1.59	0.203	0.044	0.072	0.58	0.051	0.148	St-M	Duchess County, N.Y.
D-7	−1.81	0.164	0.026	0.081	0.55	0.040	0.152	St-M	Duchess County, N.Y.
S35J	−1.98	0.137	0.011	0.068	0.386	0.026	0.129	St	Southern Vermont
AH2096	−2.07	0.126	0.020	0.099	0.43	0.027	0.154	St-I	Northern Idaho
D-6	−1.78	0.169	0.043	0.055	0.53	0.040	0.150	Si-St-I-M	Duchess County, N.Y.
A66a	−1.80	0.165	0.057	0.009	0.66	0.030	0.157	M	Central Connecticut
LA10Q	−2.31	0.099	0.117	0.182	0.47	0.034	0.144	Ch-I	Central Vermont
D-18	−2.01	0.133	0.027	0.061	0.53	0.027	0.164	St-I	Duchess County, N.Y.
Mean			0.043	0.072	0.516	0.038	0.155		

*Garnet rim analyses are normalized to Σ cations = 8

**Biotite analyses are normalized to (Σ cations − Na − K − Ca) = 7

†All assemblages contain garnet, biotite, quartz, muscovite (except A56J and A64G), plagioclase (except S35J, A66a and AH243). Other phases are St − staurolite, Si − sillimanite, Ky − kyanite, Ch − chlorite, I − ilmenite, and M − magnetite

$$K_D = \frac{(Mg/Fe)g}{(Mg/Fe)b}$$

$$X^B_{Fe} = \frac{Fe}{Fe + Mg}$$

$$X^G_{Mn} = \frac{Mn}{Fe + Mg + Mn + Ca}$$

$$X^G_{Ca} = \frac{Ca}{Fe + Mg + Mn + Ca}$$

$$X^B_{Ti} = \frac{Ti}{Fe + Mg + Mn + Ti + Al^{vi}}$$

$$X^B_{Al^{vi}} = \frac{Al^{vi}}{Fe + Mg + Mn + Ti + Al^{vi}}$$

TABLE 2
Isotopic data

Sample	α^Q_M	α^Q_I	α^Q_G	$1000 \ln \alpha^Q_M$
A64G	—	1.0067514	1.0033640	7.42†
A56J	—	—	1.0038702	8.64††
AH243	—	1.0073500	—	8.02†
F22B	—	—	1.0043560	9.13††
D-12	1.0090448	—	1.0042536	9.00
D-47	1.0091469	—	1.0049505	9.11
D-7	1.0091415	—	1.0047487	9.10
S35J	—	1.0087475	1.0045540	9.32††
AH2096	—	1.0086421	1.0044540	9.40†
D-6	1.0093439	—	1.0046502	9.30
A66a	1.0097512	—	1.0037587	9.70
LA10Q	—	1.0091379	—	9.79†
D-18	—	1.0099433	1.0047482	10.59†

† calculated from quartz–ilmenite.
†† calculated from quartz–garnet.
α values have been calculated from the measured δ values. All data are from Garlick and Epstein, 1967, except for LA10Q which are from Taylor, Albee, and Epstein, 1963.

from the quartz-garnet partition (α^Q_G) for the three remaining samples using the relation, $\alpha^Q_M = 1.00479 \, \alpha^Q_G$ based on a least-squares solution for five samples containing isotopic data for quartz, magnetite, and garnet. The compositional zoning in garnet does not demonstrate the presence of $^{18}O/^{16}O$ zoning, since such chemical zoning is more indicative of Mn depletion, rather than temperature change, during growth (Hollister, 1966). The isotopic data from the hydrous minerals were not utilized because the fractionations among quartz, magnetite, ilmenite, and garnet and among quartz, muscovite, and biotite are each internally consistent, but fractionations between these two groups are irregular. Garlick and Epstein (1967) concluded from this observation that micas tend partially to reequilibrate during cooling so that their isotopic fractionations do not represent the peak metamorphic grade as accurately as do those of the anhydrous phases.

The correlation model, errors, and least-squares solution.—The partitioning of Mg and Fe between garnet and biotite can be expressed by an exchange equation, which specifies the number of exchangeable sites in the two phases, for example:

$$8 \, [Fe_3 \, Al_2 \, SiO_4)_3] + 9 \, [K \, Mg_{2\,2/3} \, Al_{1/3} \, (Al_{1\,1/3} \, Si_{2\,2/3} \, O_{10}) \, (OH)_2] \rightleftharpoons$$
$$8 \, [Mg_3 \, Al_2 \, SiO_4)_3] + 9 \, [K \, Fe_{2\,2/3} \, Al_{1/3} \, (Al_{1\,1/3} \, Si_{2\,2/3} \, O_{10}) \, (OH)_2] \, . \tag{1}$$
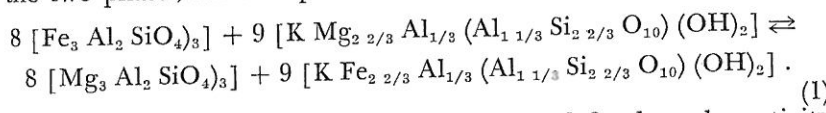
The equilibrium constant, K, for this reaction, defined as the activity product, is:

$$K \equiv \frac{(a^G_{Mg\text{-}G})^8 \, (a^B_{Fe\text{-}B})^9}{(a^G_{Fe\text{-}G})^8 \, (a^B_{Mg\text{-}B})^9} \equiv \exp\left[\frac{-\Delta G^\circ}{RT}\right] \tag{2}$$

where $a^G_{Mg\text{-}G}$ is the activity of Mg-garnet with three exchangeable Mg-atoms in a garnet phase containing 3 exchangeable sites $[Mg_3 \, Al_2 \, (SiO_4)_3]$,

				Duchess County, N.Y.
				Central Connecticut
				Central Vermont
				Duchess County, N.Y.

	Si-St-I-M
	M
	Ch-I
	St-I

$$X^B_{Ti} = \frac{Ti}{Fe + Mg + Mn + Ti + Al^{vi}}$$

$$X^B_{Al^{vi}} = \frac{Al^{vi}}{Fe + Mg + Mn + Ti + Al^{vi}}$$

		Ti
	0.150
	0.157
	0.144
	0.164
	0.155

	0.040
	0.030
	0.034
	0.027
	0.038

	0.533
	0.668
	0.474
	0.532
	0.516

$$X^a_{Mn} = \frac{Mn}{Fe + Mg + Mn + Ca}$$

$$X^a_{Ca} = \frac{Ca}{Fe + Mg + Mn + Ca}$$

	0.055
	0.009
	0.182
	0.061
	0.072

	0.043
	0.057
	0.117
	0.027
	0.043

	0.169
	0.165
	0.099
	0.133

*Garnet rim analyses are normalized to Σ cations = 8

**Biotite analyses are normalized to (Σ cations – Na – K – Ca) = 7

†All assemblages contain garnet, biotite, quartz, muscovite (except S35J, A66a and AH243). Other phases are St – staurolite, Si – sillimanite, Ky – kyanite, Ch – chlorite, I – ilmenite, and M – magnetite

$$K_D = \frac{(Mg/Fe)g}{(Mg/Fe)b}$$

$$X^B_{Fe} = \frac{Fe}{Fe + Mg}$$

| | |
| -1.78 |
| -1.80 |
| -2.31 |
| -2.01 |

(Garnet rim margin table values partially legible: D-6, A66a, LA10Q, D-18, Mean)

T is the absolute temperature, and $\Delta G°$ is the free energy of this reaction at a standard state. Substitution of $a^G_{Mg-G} = (\gamma^G_{Mg-G} \cdot X^G_{Mg-G})^3$, $a^B_{Mg-B} = (\gamma^B_{Mg-B} \cdot X^B_{Mg-B})^{2\frac{2}{3}}$, et cetera (Albee, 1965a, p. 275; 1972, p. 3262) gives:

$$K = \left[\frac{\gamma^G_{Mg-G}}{\gamma^G_{Fe-G}} \cdot \frac{\gamma^B_{Fe-B}}{\gamma^B_{Mg-B}} \right]^{24} \cdot \left[\frac{X^G_{Mg}}{X^G_{Fe}} \cdot \frac{X^B_{Fe}}{X^B_{Mg}} \right]^{24} . \quad (3)$$

The latter term within the brackets is defined as the distribution coefficient, K_D. Henceforth in this paper, K_D will refer specifically to this exchange equation. For ideal solution of the Mg and Fe components in both phases (that is, $\gamma^G_{Mg-G} = 1$, et cetera)

$$K = K_D{}^{24} = \exp \left[\frac{-\Delta G°}{RT} \right] \quad (4)$$
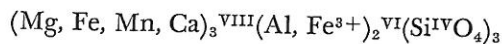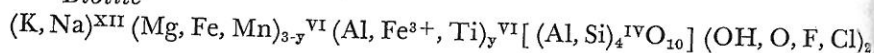
and,

$$24 \cdot \ln K_D = \frac{-\Delta G°}{RT}$$

where 24 is the least-common denominator of the number of exchangeable sites in the two phases. K, the activity coefficients, and the least-common denominator are defined in terms of $\Delta G°$ for a specific exchange reaction between two phases having fixed compositions of the non-exchangeable elements. Hence, K_D, the measurable parameter, can vary with temperature and with changes in the composition of either phase. Because of the small ΔV of the exchange reaction, Albee (1965b) and Perchuk (1970) indicated that the pressure dependence of K_D is not significant unless the depth of metamorphism is extremely great.

Garnet and biotite compositions are considerably more complex than the formulae used above, and can be considered as:

Garnet

$$(Mg, Fe, Mn, Ca)_3{}^{VIII}(Al, Fe^{3+})_2{}^{VI}(Si^{IV}O_4)_3$$

Biotite

$$(K, Na)^{XII} (Mg, Fe, Mn)_{3-y}{}^{VI} (Al, Fe^{3+}, Ti)_y{}^{VI} [(Al, Si)_4{}^{IV}O_{10}] (OH, O, F, Cl)_2$$

where the Roman numerals represent cation coordination numbers. In garnet, K_D depends upon the ideality of the Mg-Fe exchange, on the amount of Mn and Ca in the VIII-fold position, and to a lesser extent, upon the Fe^{3+} content in the VI-fold position.

The stoichiometry in biotite requires a balancing of the charge from the XII-fold position and any charge in excess of six from the VI-fold positions by Al replacing Si in the IV-fold position or by dehydroxylation. K_D will depend upon the ideality of the Mg-Fe exchange and on the number of exchangeable Mg-Fe sites (that is, on VI-fold Al, Fe^{3+}, et cetera).

Other compositional dependencies, such as the Cr or Ti content of garnet, could be important in some rocks, but such elements are absent or show little variation in these samples. Fe^{+3} was not utilized as an

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bee, 1965a, p. 275; 1972, p. 3262) gives:

$$\bigg]^{24} \cdot \left[\frac{X^G_{Mg}}{X^G_{Fe}} \cdot \frac{X^B_{Fe}}{X^B_{Mg}} \right]^{24} . \quad (3)$$

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cetera)

$$= \exp\left[\frac{-\Delta G°}{RT} \right] \quad (4)$$

$$K_D = \frac{-\Delta G°}{RT}$$

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$^{VIII}(Al, Fe^{3+})_2 {}^{VI}(Si^{IV}O_4)_3$
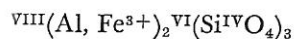
$^{3+}, Ti)_y {}^{VI}[(Al, Si)_4 {}^{IV}O_{10}] (OH, O, F, Cl)_2$

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samples. Fe^{+3} was not utilized as an

additional variable, because it cannot be determined in biotite with the electron microprobe. In garnet, charge balance considerations indicate that the concentration of Fe^{3+} is small and nearly constant.

In addition to K_D, X^G_{Mn}, X^G_{Ca}, X^B_{Fe}, X^B_{Ti}, and $X^B_{Al^{vi}}$ are defined as compositional variables following the reasoning indicated above and are tabulated in table 1. It is essential to minimize the number of correlated variables to solve the statistical model. Hence, X^B_{Mn}, X^B_{Mg}, X^G_{Mg}, X^G_{Fe}, and $X^B_{Al^{vi}}$ are not used, since they can, in theory at least, be calculated from the tabulated variables, utilizing the stoichiometry of the phases and the presumed functional dependencies of the various partition coefficients upon temperature.

Elemental and isotopic partitioning do not have the same temperature dependency since $\ln K_D$ is a function of $1/T$ whereas $\ln \alpha^Q_M$ [1] is expressed as a function of $1/T^2$ (Bottinga and Javoy, 1973). However, there is little difference in the departure from linearity of $1/T$ or $1/T^2$ with $1000 \ln \alpha^Q_M$ over the metamorphic temperature range (400-750°C). Hence, we will use the following simplest linear model among $\ln K_D$, $1000 \ln \alpha^Q_M$, and the compositional variables:

$$\ln K_D = a\ 1000 \ln \alpha^Q_M + b\ X^G_{Mn} + c\ X^G_{Ca} + d\ X^B_{Fe} + e\ X^B_{Ti} +$$
$$f\ X^B_{Al^{vi}} + g. \quad (5)$$

Ln K_D is used as the dependent parameter in eq 5 because of its functional dependence upon the other variables. The error in K_D for each sample is about 4 percent, based upon microprobe counting statistics, yielding a 0.04 error for each $\ln K_D$ value. Hence, all 13 samples were equally weighted in obtaining a solution. The other variables in eq 5 are assumed to be well-defined and to have a zero error (see discussion in Reid, Gancarz, and Albee, 1973).

The conventional least-squares method (Hamilton, 1964) did not provide an acceptable solution due to correlations among the data. As an alternative, least-squares solutions were obtained using the singular-value decomposition algorithm (SVD), which is described in the appendix. Commonly, correlations among the variables in a multi-parameter problem, especially those with small ranges of variation, make it difficult to obtain a valid solution by the conventional least-squares technique. Any strong correlation between two variables makes it difficult to distinguish completely between them. Inaccurate solutions for these variables, in turn, affects the solutions for all other variables. SVD is a selective method from which a number of least-squares solutions to the same problem can be obtained based upon the sensitivity of the de-

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[1] $^{18}O/^{16}O$ fractionations are conventionally reported as $1000 \ln \alpha^Q_M$ based upon the substitution of $\ln \alpha^Q_M \approx (\alpha^Q_M - 1)$, which is an approximation for numbers close to unity, into the following

$$\frac{\delta_Q - \delta_M}{1000} \approx (\alpha^Q_M - 1)$$

where $(\delta_Q - \delta_M)$ is the per mil fractionation between quartz and magnetite relative to a standard. This approximation is less accurate for δ values that are widely different, and in this study, $1000 \ln \alpha^Q_M$ was calculated from the reported δ measurements.

pendent variable to the various correlations that exist among the data. By systematically eliminating portions of the variation in the data that are responsible for creating undesirable linear combinations that do not add useful information, a more representative solution is obtained.

Results and discussion.—Isotopic and chemical partition data for the 13 samples are shown in figure 1. The temperature values are given by (Bottinga and Javoy, 1973):

$$1000 \ln \alpha^Q_M = 5.57 \ (10^6/T^2).$$

The error bar in figure 1 represents analytical error. Typical uncertainties in a $1000 \ln \alpha^Q_M$ measurement are about $\pm 0.15\%_o$ indicating that isotopic temperatures can be estimated with uncertainties of about $\pm 15°C$ (see discussion by Deines, 1975).

The distribution of points in figure 1 indicates that as $\ln K_D$ (and K_D) increases, $1000 \ln \alpha^Q_M$ decreases (temperature increases). As expected, the extent of both isotopic and elemental partitioning becomes smaller at higher temperatures.
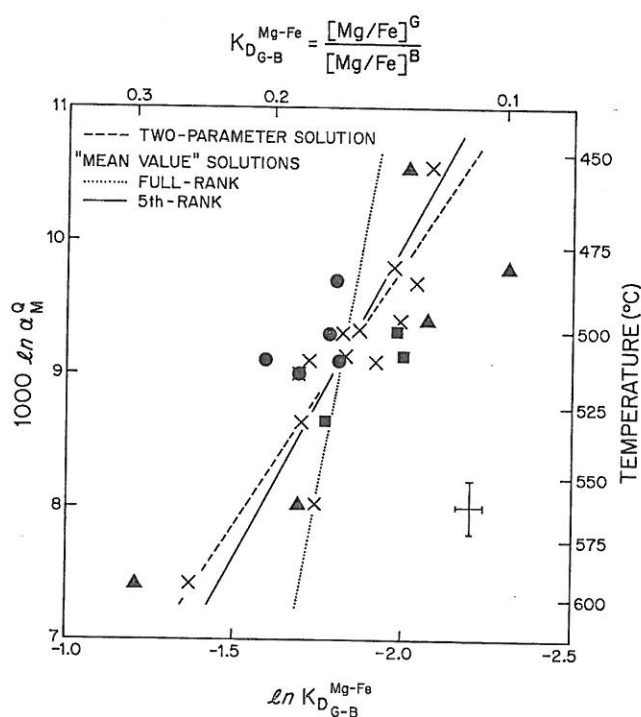

Fig. 1. Isotopic and elemental partition data. The circles represent samples having measured quartz–magnetite fractionations. The squares and triangles represent samples having quartz–magnetite fractionations that are derived from measured quartz–garnet and quartz–ilmenite fractionations, respectively. The x's represent $\ln K^*_D$ values calculated from eq 6 (see text for explanation).

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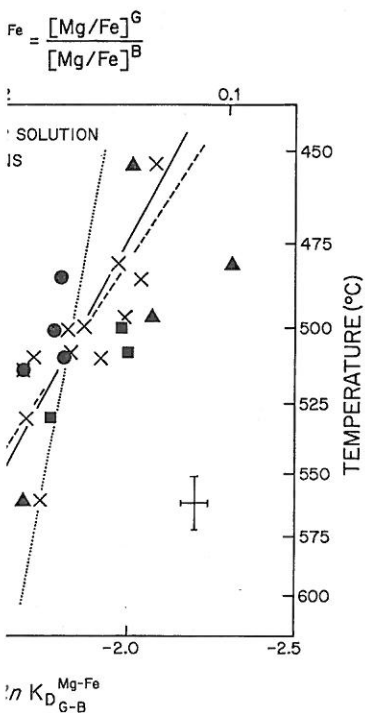
$$_{Fe} = \frac{[Mg/Fe]^G}{[Mg/Fe]^B}$$

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1s. The squares and triangles represent samples
that are derived from measured quartz–garnet
ectively. The x's represent $\ln K*_D$ values calcu-

The coefficients and the formal errors obtained from SVD for the full-rank and for the sixth- and fifth-rank solutions are shown in figure 2. As discussed in the appendix, the full-rank solution utilizes the true inverse of the information matrix; it is therefore identical to the conventional Gaussian least-squares method described by Hamilton (1964). In the full-rank solution of this seven parameter problem, seven eigenvalue-eigenvector combinations are extracted from the information matrix (table 3). The model is least sensitive to the linear combination of variables that characterizes the smallest eigenvector. In table 3, the smallest eigenvector (VII) is almost entirely dominated by X^B_{Ti}, which has the smallest range of variation of any variable in the data. In addition, X^B_{Ti} strongly correlates with $1000 \ln \alpha^Q_M$ (correlation coefficient, ρ, of 0.85), and hence, the technique is unable to distinguish between these variables, which affects their solutions and the solutions for the other
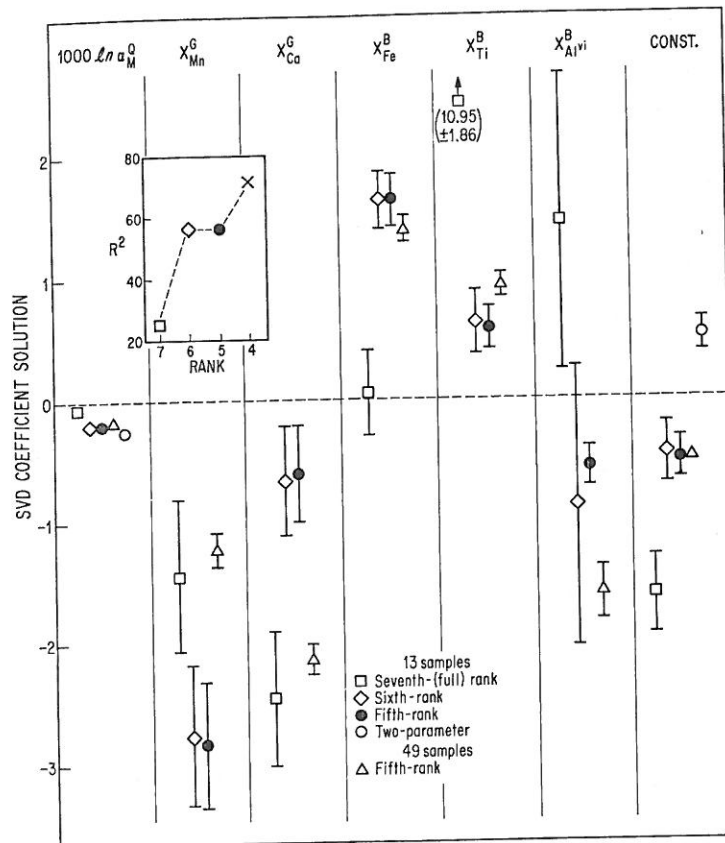

Fig. 2. Coefficient solutions from SVD including the formal 1σ errors for the 13 samples given in table 1. The sum of the squares of the weighted residuals, R^2, is also presented for the full-rank and for the sixth-, fifth-, and fourth-rank SVD solutions. The fifth-rank SVD solution for the 13 samples given in table 1 with the samples from Dahl (1969) and Phinney (1963) is also shown.

variables. The strong correlation of X^B_{Ti} and $1000 \ln \alpha^Q_M$ supports the use of X^B_{Ti} as a geothermometer. Excluding eigenvalue-eigenvector pair VII by dropping to the sixth-rank results in better-determined coefficients for all variables as evidenced by the reduction of their absolute errors (fig. 2). It also results in more acceptable values for the coefficients, especially for $1000 \ln \alpha^Q_M$, as will be discussed later.

The smallest eigenvalue-eigenvector pair (VI) that is utilized in the sixth-rank solution is almost entirely dominated by $X^B_{Al^{vi}}$, which strongly correlates with X^B_{Ti} ($\rho \backsim -0.84$). Similarly, exclusion of this eigenvalue-eigenvector combination by dropping to the fifth-rank improves the coefficients of X^B_{Ti} and $X^B_{Al^{vi}}$. Except for a small change in the coefficients of $X^B_{Al^{vi}}$, the other coefficients remain about the same indicating that a stable solution is obtained in the fifth-rank. R^2, the sum of the squares of the weighted residuals, gives an indication of the predictive capability of each solution to model the data. As shown in figure 2, R^2 increases from the full-rank to the sixth-rank solution, remains about the same from the sixth- to the fifth-rank, and increases from the fifth- to the fourth-rank. An SVD solution is selected by the quality of all coefficients, which usually improve after decorrelating part of the data upon dropping rank, while maintaining the smallest value of R^2 possible. It will be shown that the full-rank solution cannot be correct, due to the correlation of $1000 \ln \alpha^Q_M$ and X^B_{Ti}. Note that the coefficient of $1000 \ln \alpha^Q_M$ (fig. 2) does not change in dropping from the sixth-rank to the fifth-rank solution. We conclude that the fifth-rank solution is the best solution that can be obtained for these data because it sufficiently decorrelates the data without significantly impairing the predictive capability of the solution. The fifth-rank solution is:

$$\ln K_D = -0.213(\pm 0.015)\ 1000 \ln \alpha^Q_M - 2.82(\pm 0.52)\ X^G_{Mn}$$
$$-0.603(\pm 0.387)\ X^G_{Ca} + 1.64(\pm 0.22)\ X^G_{Fe}$$
$$+0.579(\pm 0.173)\ X^B_{Ti} - 0.561(\pm 0.162)\ X^B_{Al^{vi}} \qquad (6)$$
$$-0.496(\pm 0.168)$$

TABLE 3

Eigenvalue-eigenvector results of SVD for the 13 samples

	Eigenvalues						
	690460.0	109.351	31.782	11.457	2.375	0.675	0.262
	Eigenvectors						
	I	II	III	IV	V	VI	VII
$1000 \ln \alpha^Q_M$	0.992	0.106	0.061	0.008	0.001	0.002	0.013
X^G_{Mn}	0.005	−0.066	0.081	−0.613	0.744	0.212	0.120
X^G_{Ca}	0.008	0.201	−0.330	−0.746	−0.481	−0.189	−0.162
X^B_{Fe}	0.056	−0.778	0.501	−0.216	−0.269	−0.037	−0.143
X^B_{Ti}	0.004	−0.110	−0.064	−0.076	−0.263	0.162	0.940
$X^B_{Al^{vi}}$	0.017	−0.132	0.070	0.026	0.249	−0.933	0.212
const.	0.108	−0.557	−0.788	0.116	0.107	0.148	−0.106

Left column (partially cut off at spine):

1 of X^B_{Ti} and 1000 ln α^Q_M supports the
r. Excluding eigenvalue-eigenvector pair
k results in better-determined coefficients
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pairing the predictive capability of the
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$$(^B_{Ti} -0.561(\pm 0.162)\, X^B_{Al^{vi}} \tag{6}$$

ABLE 3

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782	11.457	2.375	0.675	0.262

nvectors				
III	IV	V	VI	VII
061	0.008	0.001	0.002	0.013
081	−0.613	0.744	0.212	0.120
330	−0.746	−0.481	−0.189	−0.162
501	−0.216	−0.269	−0.037	−0.143
064	−0.076	−0.263	0.162	0.940
070	0.026	0.249	−0.933	0.212
788	0.116	0.107	0.148	−0.106

Right column:

The method used to define the compositional variables assumes that compositional variation is a perturbation on an exchange equation involving $(Mg,Fe)_3Al_2(SiO_3)_4$ and $K(Mg,Fe)_3(Si_3AlO_{10})(OH)_2$. Eq 6 allows this treatment to be extended to real garnet and biotite compositions. The combined effect of all compositional variation can be examined by considering an exchange equation written for the average composition of each phase and by considering deviations from these mean values. Figure 1 shows a "mean value" equation for both the full- and fifth-rank solutions; they were obtained by substituting the mean value for each compositional variable (table 1) into eq 6 and combining the products into the constant term. The fifth-rank "mean-value" equation represents the relationship between K_D and 1000 ln α^Q_M (or temperature) for the average compositions of garnet and biotite. The scatter of points about this line, in part, expresses the effect of compositions differing from the average.

The effect of the compositional terms in eq 6 can be illustrated by considering a new variable, ln K_D^*, which represents a value of ln K_D extrapolated to mean compositions of garnet and biotite. This variable was calculated for each of the 13 samples using the following expression:

$$\ln K_D^* = \ln K_D \quad - \sum_{i=1}^{5} \beta_i(X_i - \overline{X}_i) \tag{7}$$

where β_i is the least-squares coefficient of the compositional variable, X_i, in eq 6, and $\overline{X}_i$ is the mean value of that compositional variable (table 1). The ln K_D^* values in figure 1 (shown by the X's) converge about the "mean-value" line from the fifth-rank solution and show less scatter than does ln K_D. From eq 7, the difference between ln K_D and ln K_D^* is determined by both the magnitude of the least-squares coefficient and the deviation from mean composition. Differences between ln K_D and ln K_D^* arise chiefly from variations in X^B_{Fe} although X^G_{Mn} and X^G_{Ca} become significant at higher concentrations (particularly in LA-10Q).

The slopes of the "mean-value" equations in figure 1 are coefficients of 1000 ln α^Q_M. As was discussed earlier, 1000 ln α^Q_M is correlated with X^B_{Ti} in the full-rank solution, and the steep slope of the full-rank "mean value" equation results from this correlation. The full-rank solution indicates that ln K_D is nearly independent of temperature, which contradicts both the theoretical treatment of elemental partitioning and the available petrologic evidence. Many high-grade metamorphic rocks, such as those studied by Dahl (1969) and Kretz (1959), have ln K_D values to −1.0 ($K_D \sim 0.37$) and would not be explained by the full-rank "mean-value" line in figure 1. Hence, this solution is not acceptable, and we conclude that the fifth-rank solution provides a much more reasonable solution for the data.

For comparison, a two-parameter solution of these data (figs. 1 and 2) which excludes the compositional variables is:

$$\ln K_D = -0.257(\pm 0.015) \, 1000 \ln \alpha^Q_M + 0.522(\pm 0.134). \tag{8}$$

This solution is very similar to the fifth-rank "mean-value" equation and could be used for samples with compositions similar to the mean values of these data.

The solution for the compositional coefficients can be improved by incorporating two additional data sets. Each set consists of samples, considered to have formed at about the same temperature, for which chemical, but not isotopic, data have been published. Phinney (1963) studied 18 staurolite schist samples from a 1 x 3 km area on St. Paul Island, Nova Scotia. Dahl (1969) studied 18 quartz-feldspathic gneiss samples from a 10 x 15 km area in central Sweden. K_D and the compositional parameters for garnet and biotite were calculated from the bulk-chemical analyses of Phinney and the electron microprobe analyses of Dahl in the same manner as used for the data in table 1. The samples of Dahl are particularly important due to a paucity of data in the high temperature region. A single value of $1000 \ln \alpha^Q_M$, calculated from the two-parameter solution (eq 8) using the average value of K_D, was used for all samples in each data set. The average K_D is 0.151 for the Phinney data and 0.275 for the Dahl data, corresponding to temperatures of 495° and 615°C, respectively.

Independent solutions of each data set produced coefficients similar to those in eq 6, and we concluded that the assumption of constant temperature and the use of bulk analyses for garnet did not invalidate their use. Thus, in addition to the 13 samples listed in table 1, each of the 18 Phinney samples was entered into SVD with a $1000 \ln \alpha^Q_M$ value of 9.37, and each of the 18 Dahl samples was entered with a value of 7.07 to produce a combined solution. Similar correlation problems were encountered, and again, the fifth-rank solution for the 49 samples (also shown in fig. 2) is selected as the most representative solution:

$$\ln K_D = -0.177(\pm 0.010) \, 1000 \ln \alpha^Q_M - 1.22(\pm 0.14) \, X^G_{Mn}$$
$$-2.14(\pm 0.13) \, X^G_{Ca} + 1.40(\pm 0.09) \, X^B_{Fe} + 0.942(\pm 0.109) \, X^B_{Ti}$$
$$-1.59(\pm 0.21) \, X^B_{Al^{vi}} - 0.492 \, (\pm 0.068). \tag{9}$$

It can be seen from figure 2 that the signs of all coefficients remain the same and that only the coefficients of X^G_{Ca}, X^G_{Mn}, and $X^B_{Al^{vi}}$ are distinctly different from eq 6.

The validity of eq 9 can be tested by comparing samples with quite different bulk-chemical compositions, but which formed at a similar P and T. A set of 15 gneissic samples studied by Kretz (1959) meets these criteria but are bulk-chemical analyses. The samples are from a 25 x 30 km area in the Grenville Province of Quebec, Canada and are considered to have attained a uniform grade of metamorphism. Six samples have the assemblage sillimanite–garnet–biotite, and the remaining nine

.meter solution of these data (figs. 1 and
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(9)

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m grade of metamorphism. Six samples
garnet–biotite, and the remaining nine

samples have the assemblage hornblende–garnet–biotite. Although the
contrasting assemblages occur close together in the field, they have quite
different values of K_D and of the other compositional variables, par-
ticularly in X^{G}_{Ca}. Eq 9 was used to calculate a $1000 \ln \alpha^{Q}_{M}$ value from
the bulk-chemical data for each sample, and the results are shown in
figure 3. The $1000 \ln \alpha^{Q}_{M}$ values that would be obtained from K_D using
eq 8, without the compositional adjustments, fall along the two-para-
meter line.

The $1000 \ln \alpha^{Q}_{M}$ values calculated from the two-parameter solution
are distinctly different for the two assemblages. Hence, it would be
inferred that the sillimanite samples formed at higher temperatures
(~650°-700°C) than the hornblende samples (~550°-600°C), despite the
close field occurrence of the two sample types. However, the compo-
sitional adjustments produce a convergence and an overlapping of
temperatures. These adjustments are largest for the hornblende-bearing
samples primarily due to the high values of X^{G}_{Ca}. The effect of higher
calcium content in garnet is to reduce the value of K_D, so that it indi-
cates a temperature that is lower than the "true" value. Although
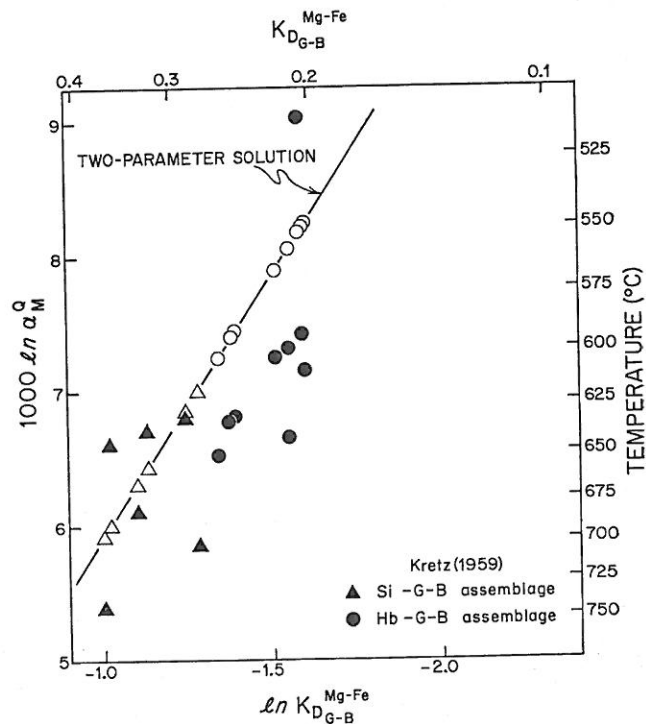further data are needed, especially considering that the bulk-chemical

Fig. 3. Temperature estimates for the sillimanite–garnet–biotite (Si–G–B) and the
hornblende–garnet–biotite (Hb–G–B) rocks of Kretz (1959) using eq 9. The open circles
and triangles are the temperatures calculated from the two-parameter solution (eq 8).

analyses of the Kretz garnets include compositional zonation, this test does suggest that the signs of the coefficients have been correctly determined.

The dependence of the Mg–Fe partition between garnet and biotite upon compositional variation has been examined in many studies, particularly with emphasis on the calcium and manganese content of garnet. Eqs 6 and 9 provide a quantitative basis for evaluating these dependencies. Negative coefficients to X^G_{Mn} and X^G_{Ca} indicate that an inverse relationship exists between these variables in $\ln K_D$ (and also K_D). These results corroborate the findings of Albee, 1965a,b), Kretz (1959), Miyashiro (1953), and Saxena (1968) for manganese and of Sen and Chakraborty (1968) for calcium.

Garnet–biotite geothermometers developed by Perchuk (1970) and Thompson (1976) permit temperatures to be calculated for the 13 samples (table 1) so that these results can be compared with measured isotopic temperatures and those calculated from eq 9. Perchuk derived isotherms based upon estimated garnet–amphibole equilibria temperatures (Perchuk, 1967). Thompson presents a correlation between $\ln K_D$ and $1/T$ for many rocks using temperatures estimated from their mineral assemblage. Temperatures are derived from the measured and calculated $1000 \ln \alpha^Q_M$ values using the proposed calibration of Bottinga and Javoy (1973). The comparison is presented in figure 4 in which samples having calculated temperatures that match those derived from the measured isotopic data will fall on the line. Typical uncertainties in the isotopic measurements result in temperature uncertainties of about 15°C. The temperatures from eq 9 show the least scatter about the line because this equation is based upon the same isotopic measurements. The scatter reflects the same scatter shown in figure 1. In general, sample points in figure 1 that lie above the "mean-value" fifth-rank line also lie above their measured isotopic temperatures in figure 4 and vice versa. A notable exception to this observation is sample LA-10Q, which would be expected to fall below its measured isotopic temperature but falls on the line due to compositional adjustments, particularly from X^G_{Ca}. The compositional adjustments have been applied to all 13 samples, but scatter in these data that cannot be explained by analytical error or compositional variation still remains. This scatter may result from gross chemical or isotopic disequilibrium, or it may result from the attainment and quenching of chemical and isotopic equilibria in different phases at different temperatures. As emphasized by Bottinga and Javoy (1973, 1975) and Deines (1975), isotopic equilibria can be tested by measuring the isotopic composition of three cogenetic minerals and by evaluating the concordance of temperatures resulting from the three possible mineral pairs. Similarly, chemical equilibria can be tested using the various elemental partitions among the coexisting phases. Additional samples are needed in which the questions of chemical and isotopic equilibria have been tested.
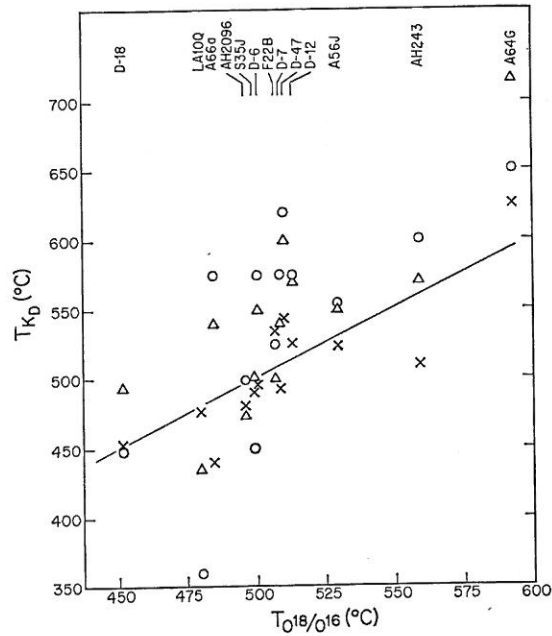
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Fig. 4. Comparison of the temperatures for the 13 samples in table 1 obtained from eq 9 (x), from Perchuk (1970) (o), and from Thompson (1976) (△) with the temperatures obtained from measured isotopic data using the quartz–magnetite calibration given in Bottinga and Javoy (1973). Samples falling on the line have the same temperature value determined from both methods.

The temperatures derived from the Perchuk and Thompson geothermometers are higher for most samples than those calculated from eq 9 and from the measured isotopic data. In particular, the isotopic temperature of sample A64G of 593°C appears to be low for a sillimanite-grade metamorphic rock in which muscovite has broken down. Experimental work on the stability field of muscovite (Day, 1973) indicates that the Thompson estimate of 715° for A64G is much more reasonable. Although this result may suggest that isotopic equilibration continues during cooling after elemental equilibration has ceased, the overall consistency of this pattern more likely suggests that the proposed quartz–magnetite calibration of Bottinga and Javoy (1973) is incorrect, especially in the higher temperature region. It is important to realize that the correlation presented in this paper is independent of the choice of the isotopic mineral pair and its calibration with temperature, but it does rely on the attainment of chemical and isotopic equilibria at the same temperature.

Finally, it was indicated that X^B_{Fe} is the most important compositional parameter in most samples (except for those with significant variations in X^G_{Ca}) that affects the ln K_D-1000 ln α^Q_M relationship. If the Mg–Fe partition between garnet and biotite represents ideal solution, the

coefficient of X^B_{Fe} would be zero. However, the non-zero value of this coefficient and the importance of X^B_{Fe} in eqs 6 and 9 may suggest that this partition is non-ideal. Alternatively, this coefficient may result from failure to decouple the various correlations in the data, since SVD finds a solution weighted by the variation exhibited by each variable. X^B_{Fe} has the largest compositional variation, and hence, its coefficient may include undesirable linear combinations that result from these correlations. Extension of the data base, especially in the high temperature region, is needed to examine this possibility using samples that have been tested for isotopic and chemical equilibria.

CONCLUSION

The correlation of isotopic and chemical partition data in eq 9 provides a quantitative basis for understanding the compositional and temperature dependencies of Fe–Mg partitioning in the complex garnet– biotite system. It has been shown that the partitioning of Mg and Fe between garnet and biotite primarily depends upon temperature, but it also depends upon compositional variation in either phase, especially when this variation is pronounced. From this relationship, it is possible to derive pseudo-ternary phase diagrams (that is, Fe–Mg–Mn or Fe–Mg–Ca) showing the tie lines between garnet and biotite as a function of composition and temperature. Eq 9 also makes it possible to calculate a model oxygen isotopic partition value from chemical data and to infer an equilibration temperature based on the experimentally calibrated quartz–magnetite fractionation.

ACKNOWLEDGMENTS

APPENDIX

The least-squares solution (after Hamilton, 1964, and Reid, Gancarz, and Albee, 1973) to the set observational equations written in matrix notation as

$$S = CX + E \tag{10}$$

is

$$\hat{X} = (C^T M_s^{-1} C)^{-1} C^T M_s^{-1} S \tag{11}$$

$\hat{X}$ is the least-squares estimate of $X(m \times 1)$, S is the $(n \times 1)$ column vector containing n observations of the dependent variable, C is the $(n \geq m)$ data matrix, and E is the $(n \times 1)$ column vector containing n experimentally determined errors on the associated observations of S. All elements in the data matrix, C, are assumed to be rigidly

ro. However, the non-zero value of this
of X^B_{Fe} in eqs 6 and 9 may suggest that
rnatively, this coefficient may result from
correlations in the data, since SVD finds
:iation exhibited by each variable. X^B_{Fe}
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; between garnet and biotite as a function
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)n value from chemical data and to infer
based on the experimentally calibrated

IOWLEDGMENTS

the assistance of Drs. D. O. Muhleman
Reid in discussing many aspects of the
problem. In addition, we wish to thank
)r, Jr. for supplying the samples used in
for most of the microprobe data. This
om the detailed comments of Professor

APPENDIX

Hamilton, 1964, and Reid, Gancarz, and Albee,
ıs written in matrix notation as

$$ = CX + E \qquad (10)$$

$$M_s^{-1}C)^{-1} C^T M_s^{-1} S \qquad (11)$$

$\times$ 1), S is the (n $\times$ 1) column vector containing
ble, C is the (n $\geqq$ m) data matrix, and E is the
perimentally determined errors on the associated
he data matrix, C, are assumed to be rigidly

defined and therefore have zero error. The observational (n $\times$ n) error matrix used
to weight the model (assuming that all measurements on S are mutually independent) is

$$M^{-1}_s = \begin{bmatrix} 1/e^2_1 & \cdots & \cdots & 0 \\ \vdots & & & \vdots \\ \vdots & & & 1/ \\ 0 & \cdots & \cdots & e^2_n \end{bmatrix}$$

By dividing each C_1 and S_1 by e_1, the weighted matrices, C^* and S^* are formed, and
eq 11 can be rewritten as

$$\hat{X} = (C^{*T}C^*)^{-1} C^{*T}S^* \qquad (12)$$

The singular-value decomposition algorithm (SVD) is presented in Boggs (1972),
Golub and Reinsch (1970), and Hanson and Lawson (1969). SVD finds the true inverse
and a series of pseudo-inverses of the data information matrix, $(C^{*T}C^*)$. Let

$$C^* = VP^{1/2}U^T \qquad \text{and} \qquad C^{*T} = UP^{1/2}V^T \qquad (13)$$

where the U consists of the m orthogonal, unitized eigenvectors arranged in decreasing
order of their associated eigenvalues, V is the transpose of U, and P is the diagonal
matrix containing m eigenvalues. The information matrix is therefore

$$C^{*T}C^* = UPU^T \qquad (14)$$

and

$$(C^{*T}C^*)^{-1} = UP^{-1}U^T. \qquad (15)$$

The rank of an SVD solution, k ($\leqq$ m), indicates the number of eigenvalue-eigenvector
combinations excluded in obtaining that solution as m — k. In eq 15, U, P^{-1}, and U^T
are m x k, k x k, and k x m matrices, respectively. The eigenvalues, λ, of P^{-1} where

$$P^{-1} = \begin{bmatrix} 1/\lambda_1 & & \\ & \ddots & \\ & & 1/\lambda_k \end{bmatrix}$$

have been rearranged such that $\lambda_1 \geqq \lambda_2 \cdots \geqq \lambda_k$ and, as stated above, the eigen-
vector columns of U and rows of U^T have been rearranged accordingly. The process
of dropping rank proceeds by excluding the smallest eigenvalue and its associated
eigenvector. Note that $(C^{*T}C^*)^{-1}$ will always be an mxm matrix in each SVD solution.
In addition, it is important to realize that the true inverse of $(C^{*T}C^*)$ will only be
utilized in the full-rank solution.

Boggs (1972) indicated that if a system of linear equations is ill-conditioned (that
is, the C matrix), the resulting information matrix becomes even more ill-conditioned.
The degree of ill-conditioning is measured by the condition number of the matrix and
is defined as the ratio of the largest to the smallest eigenvalue. Hence, a large condi-
tion number reflects a large eigenvalue range. The accuracy of the inverse matrix,
from which the coefficient errors are determined, inversely depends upon the condition
number of the information matrix. In addition, variable correlations, represented by
strong similarities among the data columns, also increase the condition number.
Therefore, the degree of ill-conditioning in the data can only be increased in the
statistical procedure. The rank-deficient solutions generally minimize these problems
by decreasing the eigenvalue range (that is, decreasing the condition number) of the
information matrix and by decorrelating the system by excluding the more insensitive
linear combinations of variables that characterize the smallest eigenvectors.

A small value for λ_1 in P results in a large value for $1/\lambda_1$ in P^{-1}. A large value
for $1/\lambda_1$, in turn, results in large formal errors for the variables that dominate the ith
eigenvector because the error (variance-covariance) matrix is obtained using P^{-1} as

shown in eq 15. Therefore, the model is least sensitive to the linear combination of variables in the eigenvector that has the smallest eigenvalue and, hence, the largest error. For example, eigenvector VII in table 3 is associated with the smallest eigenvalue. This eigenvector is dominated almost entirely by X^B_{Ti}, which has the smallest range of variation of any variable in the data. The full-rank solution shown in figure 2 indicates that the largest error in the data is associated with X^B_{Ti}. This results from the insensitivity of the model to the linear combination in eigenvector VII due to the small value for eigenvalue VII. It is important to note that SVD does not eliminate a variable from the problem. It systematically eliminates a portion of the variation of that variable that does not add useful information in obtaining a solution.

The m eigenvectors are the orthogonal axes, whose lengths are defined by the magnitude of their eigenvalues, of the solid volume that encompasses the data in hyperspace (m > 3). Eliminating the smallest eigenvalue-eigenvector pair to obtain a more representative solution indicates that the distribution of data can be adequately explained without this axis (that is, without this information). These results are also achieved by obtaining a least-squares solution on the transformed variables from principal component analysis (Davis, 1973; Saxena, 1969). An SVD computer program is available upon request from A. Albee.

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man and A. L. Albee

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