

GEOCHEMICAL CONTROLS ON MANGANESE DISTRIBUTION IN AMPHIBOLITE-GRADE METAMORPHIC ROCKS*

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The geochemical distribution of manganese in metamorphic rocks is explicable in terms of crystal field theory by comparison with other transition metals. We shall apply this theory to interpret crystal chemical controls on manganese fractionation as shown by distribution coefficient values for 13 mineral pairs. Among these, the silicate pair, clinopyroxene/amphibole is used as a detailed example.

Recent applications of crystal field theory to trace element distribution in metamorphic rocks, such as by SCHWARTZ [1967] or BURNS [1970], have provided explanations of crystal chemical mechanisms for fractionation phenomena which previously were limited only to thermodynamic considerations. In general, crystal field theory is based on electrostatic interactions between a metal ion and its neighboring anions or, more specifically, ligands. For a specific number and geometry of coordinating ligands, an electrostatic field of unique symmetry and intensity is produced which affects the d-orbital electrons of the metal ion. The differential effect of this crystal field on the energies of these bonding electrons is quantitatively described as crystal field stabilization energy, or simply "CFSE".

Silicates are predominantly ionic structures to which crystal field theory is particularly applicable. Most transition metals occur in silicates on sites with octahedral coordination. However, the ligand fields may cause some site distortion for the metals from the ideal octahedral symmetry to a somewhat more tetrahedral, perhaps trigonal, or even monoclinic symmetry. The corresponding change in CFSE may have a noticeable effect on transition metal ion distribution among competitive sites. Fortunately, most site distortions are consistent for any given type of silicate crystal structure. Besides the effects of distortion, a size factor may also operate on transition metal ion distribution. Site sizes and cationic radii vary with the nature of surrounding ligands and the crystal structure. Using average metal-oxygen bond distances to express site size, we find that larger transition metal ions (relative to a major host cation such as Mg^{2+} or Ca^{2+} in ferromagnesian silicates) will prefer coordination sites with larger average dimensions. Conversely, though, CFSE is greater in sites with smaller average dimensions. Thus, transition metal ions which possess a stabilization energy as a result of their electronic configurations, should prefer the smallest site which will accommodate their ionic radii. These competing factors, along with site distortion effects, determine the transition metal distribution between different sites of a single phase and also between sites of coexisting phases.

* Lecture delivered at the technical session of the Commission on Manganese (IAGOD) during the XXIV IGC, 23 August, 1972, Montreal, Canada.

Consider, for example, the effects of site distortion, site size and CFSE on the distribution of Mn^{2+} , relative to Fe^{2+} , Mg^{2+} and Ca^{2+} , in coexisting clinopyroxenes and amphiboles (*Tables 1 to 3*). Within the octahedral layer of the clinopyroxenes, there are two crystallographically distinct cation sites designated M_1 and M_2 . For M_1 , which approximates a regular octahedron, the average metal-oxygen distance is 2.12 Å [CLARK, APPLEMAN, and PAPIKE, 1969]. The M_2 site is highly distorted and metal-oxygen distances, although much greater than for M_1 , range from 2.34 to 2.75 Å depending on the resident cation. The Mn^{2+} ion, due to its electron configuration, possesses no CFSE and has a relatively large ionic radius. Consequently, it strongly prefers the M_2 sites. The Mg^{2+} and Ca^{2+} ions which have no d-electrons, and thus no CFSE, also are distributed according to size; the smaller Mg^{2+} ions prefer M_1 sites while the larger Ca^{2+} ions prefer the M_2 sites. Ferrous iron has a relatively small effective ionic radius of 0.86 Å (*Table 1*) and should prefer the M_1 site; however, the stabilization energy for Fe^{2+} is often slightly higher for the distorted M_2 site so that it is preferred. These relations are summarized in *Table 2*.

TABLE 1

Crystal chemical properties of the important metal ions

Ion	Ionic Radius (Å) ¹	d-electrons	CFSE
Na ⁺	1.24	0	0
Ca ²⁺	1.20	0	0
Mg ²⁺	0.80	0	0
Mn ²⁺	0.91	5	0
Fe ²⁺	0.86	6	+
Fe ³⁺	0.73	5	0

¹ From WHITTAKER and MUNTIS (1970) based on radius ratio criteria.

TABLE 2

Clinopyroxene site preferences

Ion	Site Preference	Criteria
Mg ²⁺	$M_1 \gg M_2$	Size
Fe ²⁺	$M_1 \cong M_2$	CFSE, Site Distortion ²
Mn ²⁺	$M_1 < M_2$	Size
Ca ²⁺	$M_1 \ll M_2$	Size

¹ For site sizes based on average metal-oxygen distances: $M_1 = 2.12$ Å and $M_2 = 2.34$ to 2.75 Å.

² Most other transition metal ions will distribute according to these criteria.

In the general amphibole structure, there are four distinct cation sites (*Table 3*). The relatively undistorted octahedral M_1 , M_2 and M_3 sites are small, having average metal-oxygen distances of 2.075, 2.065 and 2.080 Å respectively [PAPIKE, *et al.*, 1969], and accommodate the smaller cations including Mg^{2+} and Fe^{2+} . The larger M_4 site (see *Table 3*) with distorted six to eight-fold coordination prefers the larger cations such as Mn^{2+} , Ca^{2+} , Na^+ and sometimes Fe^{2+} . Ferrous iron, however, should distribute between M_4 and the smaller M_1 , M_2 and M_3 sites much the same as between the clinopyroxene M_2 and M_1 . This is because the basic structures are very similar and the amphibole M_4 site is almost equal in size to the M_2 of the clinopyroxene.

Amphibole site preferences

Ion	Site preference	Criteria
Mg ²⁺ Fe ²⁺	M ₂ ≻ M ₁ ~ M ₃ ≻ M ₄ ¹ M ₁ ≻ M ₃ ~ M ₁ ≻ M ₂	Size CFSE, Site distortion
Mn ²⁺	or M ₃ ~ M ₁ ≻ M ₂ ≻ M ₄ ² M ₄ ≻ M ₃ ~ M ₁ ≻ M ₂	CFSE, Site distortion Size
Ca ²⁺ Na ⁺	M ₄ ≻ M ₁ , M ₂ , M ₃ M ₃ ≻ M ₁ , M ₂ , M ₃	Size Size Size

¹ For site sizes based on average metal-oxygen distances, M₁ = 2.075; M₂ = 2.065; M₃ = 2.080; and M₄ = 2.30 to 2.75 Å.

² If Fe²⁺ is not concentrated in the M₁ site, it is very depleted (See text).

When Mn²⁺ is compared to other transition metal ions, all of which are sensitive to crystal field parameters (except Fe³⁺), manganese appears anomalous in its distribution among sites in clinopyroxene and amphibole. The reason is that it responds only to size criteria. (The exception, Fe³⁺, is an extremely small ion (0.73 Å) compared to Mn²⁺ (0.91 Å) and does not compete for the same sites.) Consequently, Mn²⁺ ions can be expected to predominate in the amphibole M₄ and clinopyroxene M₂ sites by about equal proportions. However, in some amphiboles, such as actinolite or hornblende, the M₄ site is considerably more distorted, contracting its size and leaving the clinopyroxene M₂, or even M₁, sites more attractive. The effects of these minor size variations among potential sites is illustrated by the observed Mn²⁺ distribution between clinopyroxenes and amphiboles (some examples are given later in this paper). Size differences between the smaller, more

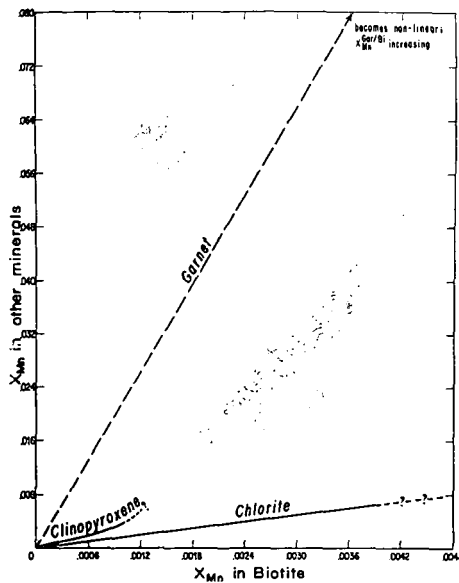


Fig. 1. Distribution of Mn between biotite and garnet, clinopyroxene, and chlorite. Concentrations are in atomic percent.

cramped sites of coexisting phases become important only if Mn^{2+} concentration in the environment is greater than can be accommodated in the primary sites. The clinopyroxene M_2 site, being significantly larger than the amphibole M_1 , M_2 and M_3 sites, will preferentially accept the excess Mn^{2+} ions — producing an even greater fractionation towards clinopyroxene with increasing Mn concentration. In other words, an enrichment of manganese in clinopyroxene relative to amphibole greatly in excess of 1:1 correlates with a manganese-rich environment.

Ferrous iron (and other transition metal ions) sensitive to site distortion and crystal field effects, in addition to size criteria, can be expected to display a more complex distribution pattern between different clinopyroxenes and amphiboles. For example, acute distortion of the M_4 site of a particular amphibole may sufficiently affect the crystal field parameters to make this site more attractive for Fe^{2+} ions than the clinopyroxene M_2 site; alternatively, the presence of considerable Mn^{2+} in the clinopyroxene M_2 and amphibole M_4 sites could be enough to make the smaller sites more amenable to Fe^{2+} occupancy (see Table 3). We begin to see, then, how the very different crystal chemical behaviors of Mn^{2+} and other transition metal ions affect their distribution patterns in many ferromagnesian rock-forming silicates.

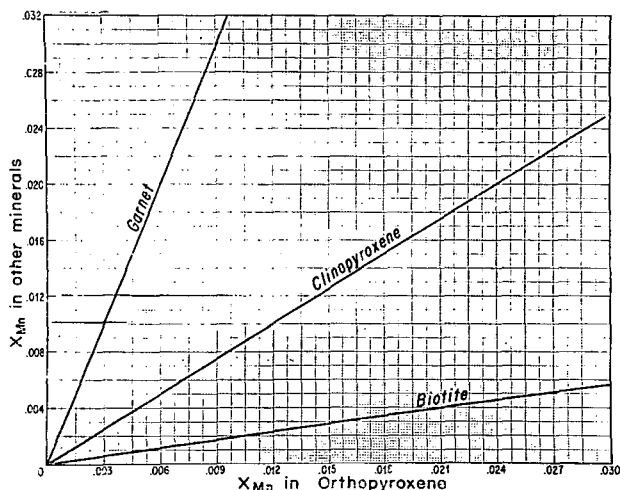


Fig. 2. Distribution of Mn between orthopyroxene and garnet, clinopyroxene, and biotite. Concentrations are in atomic percent.

Trace element distribution between coexisting phases is conveniently expressed by the distribution coefficient, K_D , which is the slope of a curve, near its origin, defined by the equation:

$$K_D = X_i^A / X_i^B$$

where, X_i^A is the atomic fraction of element i in mineral A

X_i^B is the atomic fraction of the same element i in coexisting mineral B .

For equilibrium between the two minerals, the data points should lie either on a straight line (ideal mixing) or a smooth curve (non-ideal mixing). In the ferromagnesian silicates, major cations competing for the same coordination sites are Ca^{2+} ,

Mg^{2+} , Fe^{2+} and Mn^{2+} . Other cations, usually present in trace amounts, do not noticeably affect Mn^{2+} distribution. Thus, rewriting K_D in terms of Mn^{2+} and competing ions:

$$K_D = \frac{X_{Mn}^A}{X_{Mn}^B} = \frac{(Mn/Mn + Fe + Mg + Ca)^A}{(Mn/Mn + Fe + Mg + Ca)^B}$$

where the metals are divalent ions. The data used for calculation of average K_D values are from a variety of sources as given in Appendix 1. Most were available as chemical analyses of coexisting phases; equilibrium conditions stated by the authors were accepted unless the data failed to produce either a straight line or smooth curve, whereupon the data were rejected. Except for the mineral pair garnet/biotite for which the values are especially inconsistent, scatter in the data is about 20%. Distribution curves for Mn^{2+} are presented for 13 silicate mineral pairs common to protore assemblages surrounding metamorphic manganese deposits in Figures 1, 2 and 3. The results suggest an increasing affinity for Mn^{2+} through the sequence biotite-chlorite-hornblende-actinolite-clinopyroxene, cummingtonite-orthopyroxene-garnet. Theoretical evaluations of manganese distribution in similar silicates by BURNS [1970] and WHITE [1971] add further support to this observation. Average numerical K_D values taken from the curves are tabulated in an appendix to this paper.

Several studies have implied a temperature-dependence of Mn^{2+} distribution between mineral pairs. Although such a "geothermometer" has been used with some success for Fe^{2+} , the available data do not show that Mn^{2+} distribution correlates well with temperature. It is conceivable that a manganese geothermometer the more promising examples is garnet/biotite partitioning, but more work is needed to verify the temperature dependency.

There is clear evidence that manganese content decreases with increasing temperature in both garnet and biotite. In garnet, for example, higher temperatures

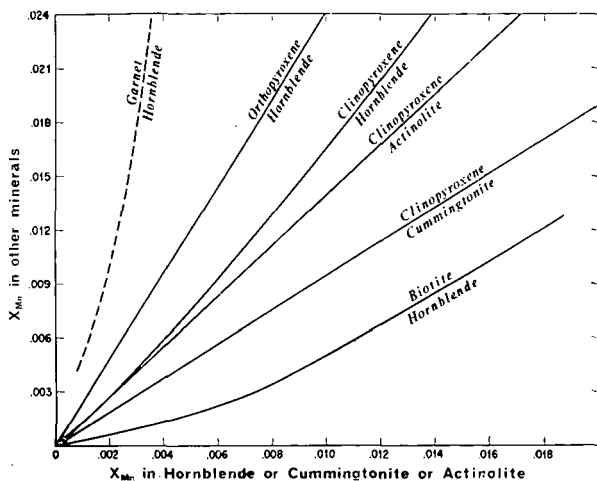


Fig. 3. Distribution of Mn between mineral pairs. Concentrations, in atomic percent, are given on the ordinate for Mn in garnet, orthopyroxene, clinopyroxene, and biotite, and on the abscissa for hornblende, cummingtonite, and actinolite for respective mineral pairs.

shrink cation sites to cause a decrease in manganese content [MIYASHIRO, 1953; LAMBERT, 1959; ENGEL and ENGEL, 1960; STURT, 1962]. In fact, STURT found that Mn-content of garnets was a very sensitive index of metamorphic grade throughout a section of pelitic schists. Although SEN and CHAKRABORTY [1968] found an opposite correlation with temperature, they attribute this to disequilibrium and inhomogeneity but other variables may also affect the Mn content of silicates. SAXENA [1968] cautions that high manganese concentrations in garnet contribute to diadochic Ca^{2+} effects — leading to somewhat unpredictable K_D values. Similar to that of garnet, there is apparently a coincident decrease in manganese content in biotite with increasing temperature. This decreases the temperature dependence of K_D for garnet/biotite but suggests an important, yet imperfectly known, function of temperature of manganese content in garnet and biotite. Other functional relations between K_D and temperature for the remaining mineral pairs presented in this paper cannot be resolved without much more detailed data than now available. These include metamorphic grade, temperatures, and concentrations of elements competing for manganese-containing sites.

In summary, a clearer chemical understanding of causes of manganese distribution in ferromagnesian silicates, relative to other transition metals, has become possible through the use of crystal field theory. Values of K_D for Mn^{2+} in 13 coexisting silicate pairs suggest two important relationships: (1) manganese distribution is affected by temperature and (2) manganese partitioning is sensitive to total manganese concentration. A "manganese geothermometer" based on distribution coefficients cannot be reliably evaluated until considerably more data are available. There is a distinct correlation, however, between total manganese content in the host rock and manganese distribution in coexisting silicates, so that we may soon be able to predict the minimum concentration levels at which formation of primary manganese silicates, such as rhodonite, will begin in metamorphic assemblages.

REFERENCES

- ATHERTON, M. P. [1968]: The variation in garnet, biotite and chlorite composition in medium grade pelitic rocks from the Dalradian, Scotland, with particular reference to the zonation in garnet: *Contr. Miner. and Petrol.* 18, 347—371.
- BLACK BURN, W. H. [1968]: The spatial extent of chemical equilibrium in some high-grade metamorphic rocks from Grenville of Southeastern Ontario: *Contr. Miner. and Petrol.* 19, 72—92.
- BUDDINGTON, A. F. [1964]: Distribution of MnO between coexisting ilmenite and magnetite: in *Advancing Frontiers in Geology and Geophysics*: Subramanian, A. P., Ed. Ind. Geophys. Union, Hyderabad, India.
- BURNS, R. G. [1970]: *Mineralogical Applications of Crystal Field Theory*, Cambridge Univ. Press.
- BURNS, R. G. [1970]: Site preferences of transition metal ions in silicate crystal structures: *Chem. Geol.* 5, 275—283.
- CLARK, J. R., APPLEMAN, D. E. and PAPIKE, J. J. [1969]: Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements: *Crystal Chemistry and Phase Petrology*, M.S.A. Spec. Paper 2, Ed. J. J. Papike, pp. 31—50.
- CLIFFORD, T. N. [1960]: Spessartine and magnesium biotite in cotecule-bearing rocks from Mill Hollow, Alstead Township, N. H., U.S.A. — A contribution to the petrology of metamorphosed manganiferous sediments — *N. Jb. Min. Abh.* 94, (II), 1369—1400.
- ENGEL, A. E. and ENGEL, C. G. [1962]: Progressive metamorphism and granitization of the major paragneiss, northwest Adirondack Mtns., New York: *Geol. Soc. America, Buddington Vol.*, 37—82.
- GORBATSHEV, ROLAND [1968]: Distribution of elements between cordierite, biotite, and garnet: *N. Jb. Miner. Abh.* 110 (1) 57—80.

- KRETZ, RALPH [1959]: Chemical study of garnet, biotite and hornblende from gneisses of south-western Quebec, with emphasis on distribution of elements in co-existing minerals: *J. Geol.* 67, 371—402.
- KRETZ, RALPH [1960]: The distribution of certain elements among coexisting calcic pyroxenes, calcic amphiboles and biotites in skarns: *Geochim. Cosmochim. Acta* 20, 161—191.
- KRETZ, RALPH [1961]: Some applications of thermodynamics to coexisting minerals of variable composition. Examples: Orthopyroxene-Clinopyroxene and Orthopyroxene-Garnet: *J. Geol.* 69 (4), 361—387.
- KRETZ, RALPH [1963]: Distribution of magnesium and iron between orthopyroxene and calcic pyroxene in natural mineral assemblages: *J. Geol.* 71, 773—784.
- KRETZ, RALPH [1964]: Analysis of equilibrium in garnet-biotite-sillimanite gneisses from Quebec: *J. Petrol.* 5, 1—20.
- LAMBERT, R. ST. J. [1959]: The mineralogy and metamorphism of the Moine schists of the Morar and Knoydart districts of Inverness-shire: *Roy. Soc. Edin. Trans.* 63 (3) 553—588.
- LEELANANDAM, C. [1967]: Chemical study of pyroxenes from the charnockitic rocks of Kondapalli (Andhra Pradesh), India, with emphasis on the distribution of elements in coexisting pyroxenes: *Min. Mag.* 36, 153—179.
- MATEJOVSKA, O. [1970]: Composition of coexisting garnet and biotite from some granulites of Moldanubicum, Czechoslovakia: *N. Jahrb. Miner. Monatsh.* 6, 249—262.
- MIYASHIRO, A. [1953]: Progressive metamorphism of calcium-rich rocks of the Gosaisyo-Takanuki district, Abukuma, Japan: *Jap. Jour. Geol. Geog.* 23, 81—107.
- MUELLER, R. F. [1961]: Analysis of relations among Mg Fe and Mn in certain metamorphic minerals: *Geochimica et Cosmochimica Acta* 25, 267—296.
- PAPIKE, J. J., ROSS, M. and CLARK, J. R. [1969]: Crystal-chemical characterization of clinopyroxenes: *Crystal Chemistry and Phase Petrology*, M. S. A. Spec. Paper 2, Ed. J. J. Papike, pp. 117—136.
- RAY, S. and SEN, S. K. [1970]: Partitioning of major exchangeable cations among orthopyroxene, calcic pyroxene and hornblende in basic granulites from Madras: *N. Jb. Miner. Abh.* 114, 61—88.
- SAXENA, S. K. [1966]: Distribution of elements between coexisting biotite and hornblende in metamorphic caledonides, lying to the west and northwest of Trondheim, Norway: *Neues Jahrb. Min. Monatsh.* 3, 67—80.
- SAXENA, S. K. [1968]: Chemical study of phase equilibria in charnockites, Varberg, Sweden: *Amer. Min.* 53, 1674—1695.
- SAXENA, S. K. [1968]: Distribution of elements among coexisting minerals and the nature of solid solution in garnet: *Am. Min.* 53, 994—1014.
- SAXENA, S. K. [1968]: Crystal-chemical aspects of distribution of elements among certain coexisting rock-forming silicates: *N. Jb. Miner., Abh.* 108, 292—323.
- SAXENA, S. K. [1968]: Nature of mixing in ferromagnesian silicates and the significance of the distribution coefficient: *Neues Jahrb. Miner. Monats.* 8, 275—286.
- SAXENA, S. K. [1968]: Distribution of elements between coexisting minerals and the nature of solid solution in garnet: *Amer. Min.* 53, 994—1015.
- SAXENA, S. K. [1969]: Distribution of elements in coexisting minerals and the problem of chemical disequilibrium in metamorphosed basic rocks: *Contr. Miner. and Petrol.* 20, 177—197.
- SCHWARCZ, HENRY P. [1967]: The effect of crystal field stabilization on the distribution of transition metals between metamorphic minerals: *Geochimica et Cosmochimica Acta* 31, 503—517.
- SEN, S. K. and CHAKRABORTY, K. R. [1968]: Magnesium-iron exchange equilibrium in garnet biotite and metamorphic grade: *N. Jb. Miner. Abh.* 108, 181—207.
- STURT, BRIAN [1962]: The composition of garnets from pelitic schists in relation to the grade of regional metamorphism: *J. of Petrology* 3, Part 2, 181—191.
- WHITE, W. B. [1971]: Electronic properties of minerals: *Lecture Notes*, Dept. of Geosciences, Pennsylvania State Univ.
- WYNNE-EDWARDS, H. R. and HAY, P. W. [1963]: Coexisting cordierite and garnet in regionally metamorphosed rocks from the Westport area, Ontario: *Can. Min.* 7, 453—478.

Manuscript received, June 15, 1972.

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APPENDIX I

Distribution Coefficient Data (primarily for the amphibolite facies)

Mineral Pair	K_D	Qualifying Remarks	Sources of Data
Garnet/Biotite	22 (X_{Mn}^{Bt} reaches max. at. 015)	considerable scatter in data; some T, X dependence	KRETZ [1959, 1964]; WYNNE-EDWARDS & HAY [1963]; GORBATSCHEV [1968]; SEN & CHAKRABORTY [1968]; BLACKBURN [1968]; MATEJOVSKA [1970], CLIFFORD [1960]
Hornblende/Biotite	3.0 (at low ΣMn) 1.5 (at higher ΣMn)	data slim but good; some T, X dependence	KRETZ [1959, 1960]; MOXHAM [1964]; SAXENA [1968, 1969]
Chlorite/Biotite	1.6 (different from original source due to recalculations)	very little good data; T, X dependence uncertain	ATHERTON [1968]
Clinopyroxene/Biotite	3.1 (increasing but not definite)	not enough data to substantiate results	KRETZ [1960]; SAXENA [1969]
Orthopyroxene/Biotite	5.25 (linear)	not enough data to resolve P, T, X dependence	SAXENA [1969]
Garnet/Orthopyroxene	3.3 (linear)	good data, but only from one area	KRETZ [1961]
Orthopyroxene/Clinopyroxene	1.2 (linear)	differs from sources due to recalculation	SAXENA [1968]; BURNS [1970] MUELLER [1961]; RAY & SEN [1970]; SAXENA [1969]; KRETZ [1963]; LEELANANDAM [1967]
Garnet/Hornblende	5?	data is scarce and poor; line only dashed and approximated	KRETZ [1959]; SAXENA [1968]
Clinopyroxene/Hornblende	1.3 (at low ΣMn) 1.4 (at higher ΣMn)	data suggests compositional dependence	SAXENA [1968a, b, 1969]; KRETZ [1960]; RAY & SEN [1970]
Orthopyroxene/Hornblende	2.4 (essentially linear)	more scatter; data probably quite good	SAXENA [1968a, b, 1969]; RAY & SEN [1970]
Cummingtonite/Clinopyroxene	1.05 (linear)	very little data; probably good though	MUELLER [1961]
Clinopyroxene/Actinolite	1.4 (linear)	may be non-linear but not enough data	MUELLER [1961]
Ilmenite/Magnetite	8 (linear)	only one source; limited ΣMn range	BUDDINGTON [1964]