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Mg/Fe PARTITIONING IN GARNET AND BIOTITE FROM SOME GRANITIC, PELITIC, AND CALCIC ROCKS

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ABSTRACT

K_D Mg/Fe for garnet-biotite pairs in calcium-rich metamorphic rocks from New Hampshire of the garnet to kyanite zones is significantly lower (0.10 ± 0.01) than that in isogradic pelitic schists (0.16 ± 0.02). Sillimanite zone pelitic rocks show a wide range of K_D ($0.16 \pm .03$), but much lower values than those in the enclosed Kinsman Quartz Monzonite ($K_D = 0.28 \pm .03$), which has been variously described as a magmatic, granitized, or metamorphic rock. The Kinsman and the enclosing pelitic rocks have closely similar chemical compositions and mineral assemblages, and formed under high load pressure (>5 kbar), low to intermediate oxygen fugacity, and (probably) similar H_2O fugacity. Thus the higher K_D of the Kinsman rocks is taken as evidence of higher temperature of formation, and of probable magmatic origin.

In these rocks CaO and MnO in garnet is not directly related to metamorphic grade, as several investigators have proposed in other areas.

INTRODUCTION

Several attempts have been made to establish an interrelationship between the partitioning of Mg and Fe in coexisting garnet and biotite, and the known or inferred geologic temperature and pressure. The pressure effect should be relatively inconsequential for reactions of the type: Fe garnet+Mg biotite$\rightleftharpoons$Mg garnet+Fe biotite, and if these minerals behave as ideal solid solutions, it follows (Kretz, 1961, p. 367) that:

$$\ln K_D = \frac{-\Delta G^\circ}{RT} \qquad (1)$$

ΔG° = change in standard free energy for the reaction
R = gas constant
T = °Kelvin
K_D = distribution coefficient = atomic $\dfrac{(\mathrm{Mg/Fe})}{(\mathrm{Mg/Fe})}\ \dfrac{\text{garnet}}{\text{biotite}}$

The literature on Mg/Fe partitioning in biotite and garnet has been surveyed by Albee (1965a), who concluded on the basis of 70 pairs of analyses that: (1) K_D in Mn-free garnets ranges from 0.2 in garnet-zone rocks to 0.37 in sillimanite-orthoclase zone rocks, but that (2) K_D is reduced in proportion to the atom percent of [Mn/(Mn+Fe+Mg)] in garnet. Frost (1962) had previously shown an increase in K_D with inferred temperature increase, but found it necessary to introduce an arbitrary correction for both Mn and Ca in garnet in order to introduce some regularity into his data. Sen and Chakraborty (1968) using 87 pairs of analyses concluded that K_D is a systematic function of both metamorphic grade and of Ca/Mn ratio in garnets. This result is not quite what might have been predicted from earlier literature surveys by Sturt (1962) and Nandi (1967) which show that a plot of weight percent (CaO+MnO) against (FeO+MgO) in garnet is nearly linear, (as it should be because of diadochy) and that the latter two oxides systematically increase at the expense of the former with increasing metamorphism. This generalization with respect to temperature probably is valid only for nearly isochemical rocks.

Mn zoning in garnet is nearly ubiquitous (Hollister, 1962; Atherton, 1968; Drake, 1968), with Mn usually decreasing and Fe usually increasing from core toward rim. Even though Mg/Fe in the garnet rim is somewhat higher than in the core, the effect on K_D in individual samples is generally not large (Albee, 1968), and is often masked by other variables such as differences in bulk rock composition, or differences in mineral phase assemblages.

Chinner (1960) has established a relationship between rock oxidation ratio (defined as mol. $2Fe_2O_3 \times 100/2Fe_2O_3+FeO$) and suites of opaque oxides, showing that as oxidation ratios rise above 43, there is a major increase in biotite MgO/FeO ratio, and in garnet MnO/FeO ratio. This implies the possibility of non-ideality of Fe-Mg substitution in one or both phases, and that at a given grade of metamorphism K_D might be decreased in rocks of high oxidation. Because his garnet analyses are incomplete, it is not possible to confirm this deduction from Chinner's data, but Hounslow and Moore (1967) have shown in coexisting biotite-garnet-staurolite assemblages that strong variations in FeO:MgO ratios in these minerals do correlate with rock oxidation ratios, as do variations in the opaque mineral suites. It is interesting, however, that their K_D for Mg/Fe in garnet-biotite pairs is fairly consistent (see Table 1), and independent of rock oxidation ratios.

Table 1 is a compilation of K_D Mg/Fe in garnet-biotite pairs published since Albee's (1965a) review of 70 older analyzed pairs. Not shown in Table 1 are 40 additional new analyses by Albee (1968) which have been presented graphically, and for which the calculation of K_D has not been made.

From Table 1 and from earlier literature surveys, the conclusion is inescapable that K_D Mg/Fe for garnet-biotite assemblages increases with metamorphic grade. Perturbations, however, are severe and may be

Table 1. Some Recent Determinations of $K_D[\mathrm{Mg}/(\mathrm{Fe}^{+2}+\mathrm{Fe}^{+3})]$ in Garnet-Biotite Pairs

Approximate Grade	K_D	Reference
Garnet	0.187, .173, .077, .089, .094, .097	Atherton, 1968
Av. = 0.130	.112, .115	Hietanen, 1969
(n=10)	.160, .200	Sen and Chakraborty, 1968
	0.150, .137, .150, .114, .127, .141	Atherton, 1968
Staurolite and kyanite	.132, .163, .215, .217, .188	Gorbatschev, 1968
	.132, .134, .155	Hietanen, 1969
Av. = 0.151 (n=33)	.125, .115, .133, .139, .127, .139, .155	Hounslow and Moore, 1967
	.095, .156, .131, .114, .152, .208	Saxena, 1968a
	.173, .143, .178, .177	Saxena and Hollander, 1969
	.190, .190	Sen and Chakraborty, 1968
Sillimanite and sillimanite-orthoclase	0.196, .359, .194	Gobatschev, 1968
	.224, .227	Hietanen, 1969
Av. = .274	.329, .259, .230, .338	Saxena, 1968b
(n=23)	.360, .400, .400, .250, .180, .320, .330, .250, .280, .300, .200, .190, .200, .240	Sen and Chakraborty, 1968

caused by factors such as disequilibrium, zoning in garnet, analytical and mineral separation errors, differing load pressure, and significant differences other than Fe/Mg in the composition of garnet and/or biotite (cf. Albee, 1965b, p. 277–278). Many of the variables may be estimated or circumscribed, and it is with this in mind that the determination of partitioning coefficients is applied here to (1) the estimation of temperature differences between the Kinsman Quartz Monzonite and its wallrocks, and (2) the determination of differences in K_D in isogradic pelitic and calcareous schists.

Geologic Relations of the Kinsman Quartz Monzonite

The Kinsman Quartz Monzonite forms several stocks and batholiths in western New Hampshire (Billings, 1956, Plate 1) and in everywhere in contact with pelitic wallrocks. The formation is generally gneissic and is characterized by striking megacrysts of potash feldspar up to 12 cm in length. In most exposures the Kinsman is of quartz monzonitic composition, consisting of approximately 30% potash feldspar, 30% quartz, 25% oligoclase-andesine, 12% biotite, and 3% muscovite. The rock is "two-textured," and has a generally coarse grained aspect, but all of the major minerals are strained and deformed, and the groundmass is a fine-grained mosaic-textured aggregate of the same mineralogy as that of the main rock, except that myrmekite and micrographic intergrowths are extraordinarily well developed. Garnet is locally abundant, sillimanite is not uncommon, and cordierite is often noted, particularly near contacts. Although most investigators have concluded that the rock is of magmatic origin, Chapman (1952) has argued that it is a granitized pelite, and Barker (1961) has described it as a metamorphosed plutonic rock which has undergone a reaction such as: (1) biotite+muscovite=cordierite +garnet+microcline or (2) biotite+sillimanite=cordierite+garnet+ potash feldspar. Barker concludes that the Kinsman is of higher metamorphic grade than the adjacent schist, either because of a higher temperature, or a lower H_2O fugacity (thus explaining its lower biotite content).

PETROGENETIC PARAMETERS

The Kinsman Quartz Monzonite was formed in the late stages of the Acadian orogeny (Billings, 1956) and its areal distribution is restricted to the high-temperature side of the sillimanite isogradic surface in west-central New England (Thompson *et al.*, 1968, p. 216). Most of the samples whose analyses are reported here for the first time (Tables 2, 3, 4) lie on the high-pressure side of an areal boundary separating kyanite-sillimanite from andalusite-sillimanite assemblages (Thompson and Norton, 1968, Fig. 1). This suggests that the Kinsman Quartz Monzonite and the enclosing pelitic schists formed at a load pressure generally in excess of 5 kbar (Richardson *et al.*, 1969). There is no geologic indication that degree of deformation or inferred intensity of shearing stress is related to grade of metamorphism.

Whether $P_{H_2O} \rightarrow P_{fluid} = P_{load}$ is uncertain. Avaliable analyses of middle and high-grade pelitic metamorphic rocks in New Hampshire (Billings and Wilson, 1964) show that these have slightly higher H_2O contents than the Kinsman. On the other hand, potash feldspars in the pelitic schists are generally less "triclinic" than those in the Kinsman, and the higher degree of annealing in the latter may reflect higher H_2O fugacities. Oxidation ratios in 9 analyzed sillimanite-zone schists from areas near the Kinsman plutons (Billings and Wilson, 1964) range from 2 to 45 (one sample having an anomalously high value of 61). Eight available analyses of Kinsman have oxidation ratios between 9 and 42, and like most pelitic schists belong to Chinners' (1960) low to intermediate oxidation groups. As determined by polished section study, ilmenite-pyrrhotite-chalcopyrite is almost a universal assemblage in both

TABLE 2. CHEMICAL ANALYSES OF GARNETS AND BIOTITES FROM NEW HAMPSHIRE AND VERMONT

	Garnets									
Sample	L-12[a]	S-14[a]	S-15[a]	S-16[a]	S-17[a]	Mo-6[a]	BF-10[a]	H-10[b]	H-23[b]	H-27[b]
SiO_2	39.84	36.93	36.63	36.61	36.96	36.97	37.51	55.47	39.27	37.89
Al_2O_3	19.92	21.30	21.24	20.71	20.53	21.13	20.62	15.36	20.11	20.22
TiO_2	.41	.13	.14	.08	.07	.11	.07	.16	.48	1.42
Fe_2O_3	.80	.79	.71	1.36	2.61	1.02	.49	1.04	1.13	1.50
FeO	29.54	33.97	34.53	27.44	27.70	32.89	28.22	20.77	24.51	24.17
MnO	5.42	3.74	3.27	12.03	10.70	4.57	8.70	.58	4.14	4.22
MgO	2.17	2.05	2.24	.74	.64	2.40	1.75	.55	2.15	1.51
CaO	1.54	1.09	1.04	.81	.53	.86	2.21	6.33	8.18	9.38
Na_2O	.05	n.d.	n.d.	n.d.	.05	.03	.04	.09	.08	.15
K_2O	.07	n.d.	n.d.	n.d.	.07	.01	.02	.02	.04	.02
H_2O+	.09	n.d.	.14	n.d.	.16	.03	.11	—	.04	.05
H_2O-	.00	.00	.00	.00	.00	.00	.00	.03	.00	.00
	99.85	100.00	99.94	99.78	100.02	100.02	99.74	100.40	100.13	100.53

[a] Analyst C. O. Ingamells

[b] Analyst H. Dehn

Formulae:

L-12 $(Mg_{.54}\overset{+2}{Fe}_{4.16}Mn_{7.7}Ca_{.28})_{5.75}(Al_{3.93}\overset{+3}{Fe}_{.10}Ti_{.05})_{4.08}Si_{6.04}O_{24}$

S-14 $(Mg_{.49}\overset{+2}{Fe}_{4.58}Mn_{.51}Ca_{.19})_{5.77}(Al_{4.01}\overset{+3}{Fe}_{.09}Ti_{.04})_{4.04}(Al_{.04}Si_{5.96})_{6.00}O_{24}$

S-15 $(Mg_{.54}\overset{+2}{Fe}_{4.65}Mn_{.45}Ca_{.18})_{5.83}(Al_{3.99}\overset{+3}{Fe}_{.08}Ti_{.04})_{4.11}(Al_{.04}Si_{5.96})_{6.00}O_{24}$

S-16 $(Mg_{.18}\overset{+2}{Fe}_{3.74}Mn_{1.66}Ca_{.14})_{5.72}(Al_{3.95}\overset{+3}{Fe}_{.18}Ti_{.01})_{4.14}(Al_{.03}Si_{5.97})_{6.00}O_{24}$

S-17 $(Mg_{.16}\overset{+2}{Fe}_{3.77}Mn_{1.47}Ca_{.17})_{5.50}(Al_{3.94}\overset{+3}{Fe}_{.31}Ti_{.01})_{4.26}Si_{6.03}O_{24}$

Mo-6 $(Mg_{.56}\overset{+2}{Fe}_{4.43}Mn_{.62}Ca_{.58})_{5.78}(Al_{3.98}\overset{+3}{Fe}_{.12}Ti_{.01})_{4.11}(Al_{.03}Si_{5.97})_{6.00}O_{24}$

BF-10 $(Mg_{.43}\overset{+2}{Fe}_{3.93}Mn_{1.18}Ca_{.43})_{5.92}(Al_{3.91}\overset{+3}{Fe}_{.06}Ti_{.01})_{3.98}Si_{6.06}O_{24}$

H-10 $(Mg_{.19}\overset{+2}{Fe}_{3.96}Mn_{.11}Ca_{1.54}Na_{.06})_{5.85}(Al_{3.94}\overset{+3}{Fe}_{.16}Ti_{.03})_{4.13}(Al_{.20}Si_{5.80})_{6.00}O_{24}$

H-23 $(Mg_{.14}\overset{+2}{Fe}_{3.50}Mn_{.60}Ca_{1.50}Na_{.02})_{5.76}(Al_{3.94}\overset{+3}{Fe}_{.14}Ti_{.06})_{4.14}(Al_{.12}Si_{5.88})_{6.00}O_{24}$

H-27 $(Mg_{.36}\overset{+2}{Fe}_{3.19}Mn_{.56}Ca_{1.58}Na_{.04})_{5.73}(Al_{3.75}\overset{+3}{Fe}_{.17}Ti_{.34})_{4.26}(Al_{.01}Si_{5.99})_{6.00}O_{24}$

L-12	Littleton schist; staurolite zone; contains 5% quartz.
S-14	Littleton schist; sillimanite zone.
S-15	Kinsman quartz monzonite.
S-16	Aplite; intrusive into S-15.
S-16	Pegmatite; intrusive into S-15.
Mo-6	Littleton schist; staurolite zone.
BF-10	Littleton schist; sillimanite zone.
H-10	Standing Pond amphibolite member; Waits River formation; garnet zone; contains 30% quartz.
H-23	Standing Pond amphibolite member; Waits River formation; kyanite zone; contains 5% quartz.
H-27	Standing Pond amphibolite member; Waits River formation; kyanite zone.

TABLE 2—(*Continued*)

Biotites			
Sample	L-12	S-14	Mo-6
SiO_2	37.80	36.49	37.10
Al_2O_3	20.66	22.69	19.81
TiO_2	1.14	2.36	1.44
Fe_2O_3	1.59	.77	1.10
FeO	16.33	20.05	18.43
MnO	.07	.08	.05
MgO	9.54	5.49	8.91
Li_2O	.02	.06	.02
CaO	.08	.07	.09
Na_2O	.39	.22	.38
K_2O	7.64	7.74	7.67
Rb_2O	.05	.03	.04
F	.22	.04	.21
Cl	n.d.	.03	.00
H_2O+	4.25	3.32	4.08
H_2O-	.17	.09	.02
Less O=F & Cl	99.95	99.53	99.35
	.09	.02	.09
	99.86	99.51	99.26

Analyst C. O. Ingamells

Formulae:

(Half-cell, calculated by method of Foster, 1960)

L-12 $(Al_{.59}Ti_{.06}\overset{+3}{Fe}_{.09}\overset{+2}{Fe}_{1.00}Mn_{.01}Mg_{1.05})(Si_{2.79}Al_{1.21})(O_{10})(OH)_2(K_{.72}Na_{.06}Ca_{.01})$

$\beta = 1.638$

S-14 $(Al_{.74}Ti_{.14}\overset{+3}{Fe}_{.04}\overset{+2}{Fe}_{1.25}Mg_{.62})(Si_{2.73}Al_{1.27})(O_{10})(OH)_2(K_{.74}Na_{.03}Ca_{.01})$

$\beta = 1.648$

Mo-6 $(Al_{.53}Ti_{.08}\overset{+3}{Fe}_{.06}\overset{+2}{Fe}_{1.16}Mg_{1.00})(Si_{2.78}Al_{1.22})(O_{10})(OH)_2(K_{.74}Na_{.05}Ca_{.01})$

$\beta = 1.636$

groups of rocks and there are variable but never large amounts of magnetite, pyrite, and hematite in some. Graphite is common in many schists, and in the garnetiferous phases of the Kinsman. The chemical and mineralogical evidence thus points to low but somewhat variable f_{O_2} and f_{H_2O} conditions during the crystallization of both groups of rocks. Similarly, because of the presence of graphite, it is probable that $P_{H_2O} \ll P_{fluid}$ (cf. French, 1966), but there is no basis for concluding that P_{H_2O} for the Kinsman was greatly different than P_{H_2O} in the pelitic schists.

Chapman (1952) pointed out that the pelitic schists have somewhat lower CaO (0.2 to 2.0 percent) and Na_2O (0.14 to 2.6 percent) contents than Kinsman rocks (2.0 to 3.0 percent CaO: 2.4 to 2.8 percent Na_2O) and that this is the major chemical distinction between the two. MnO

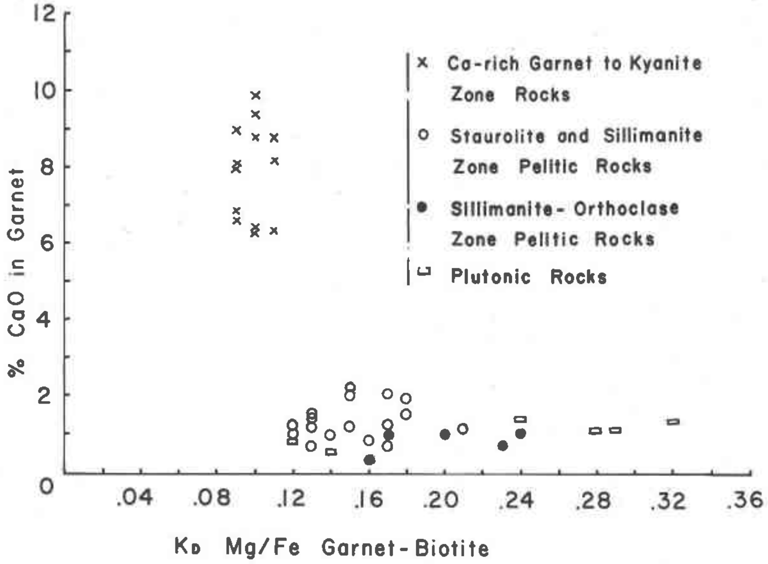

FIG. 1. Weight percent CaO in garnet vs. K_D Mg/Fe for garnet-biotite pairs of Table 3.

differences are generally small, the totals ranging up to 0.12 percent for the Kinsman, and up to 0.25 percent for pelitic schists. A notable exception is a coticule rock (spessartite-rich) in the sillimanite zone with 9.20 percent MnO (Clifford, 1960); garnet from this rock has 56 mole percent spessartite.

Some of the samples (the H series) are hornblende or chlorite-bearing assemblages which are non-pelitic, and of high CaO content (Table 6). Garnets in these rocks are also of high CaO content (5.7 to 11 percent), in contrast to the pelitic and granitic garnets (0.5 to 2.1 percent CaO). The calcic rocks, as well as some pelitic rocks, are from the garnet to kyanite regional metamorphic zones, and therefore represent lower temperature assemblages than the plutonic rocks and their enclosing sillimanite-zone pelites.

In summary, rocks, reported upon in this study appear to have formed under load pressures above 5 kbar, under low to intermediate H_2O and O_2 fugacity conditions, and over a span of temperatures ranging from that of the garnet zone to that of the plutonic rocks. Chemically and geologically they fall into three groups, granitic and pelitic groups in which chemical differences appear to be unimportant, and a more calcic group in which the bulk chemistry may have a significant effect on the partitioning coefficient.

Rocks assigned to the New Hampshire Plutonic series of Billings

(1956), of which the Kinsman is a member, show a striking areal correlation with the highest grade regional metamorphic zones, so that a genetic relationship seems likely even though, "it is by no means clear which is the primary and which is the secondary feature" (Thompson and Norton, 1968, p. 325).

The phase assemblage common to all rocks whose analyses are reported here is garnet+biotite+quartz+plagioclase+Fe-Ti oxide±Fe sulfide. Additional mineral phases are as indicated in the Table 5. As shown by Barker (1961) muscovite constitutes an excess phase in the Kinsman, and is probably of retrogressive origin. Its persistence in sillimanite-orthoclase zone rocks (Table 5) may, however, possibly be accounted for on other grounds (Evans and Guidotti, 1966).

Analytical Data

Analyses reported here are both chemical (Table 2) and spectrographic. Approximately half the spectrographic determinations were made by O. Joensuu using emission techniques which have an estimated accuracy (Joensuu, verbal communictaion) of 5 percent to 7 percent of the amount of the element reported. The remaining spectrographic analyses were made in our laboratory by atomic absorption spectrophotometry. Tests for precision and accuracy against G-1 and W-1 standards are within 6 percent of the accepted values. With few exceptions, duplicate and cross-check analyses in Tables 3 and 4 are in good agreement.[1] Table 5 includes a few previously published analyses for comparative purposes.

In the sample lists the S, LM, BF, Clifford (1960) and some of the L series samples come from southwestern New Hampshire. The H series and the Crawford (1966) samples lie 25 miles to the north, and the P, Mo, and the remainder of the L series, 40 miles still further north, near the Al_2SiO_5 triple-point map boundary (Thompson and Norton, 1968). Green's (1963) samples lie 60 miles north-northeasterly of the boundary, in a lower pressure environment.

For most garnets, unit cell sizes were determined by a Bradley-Jay extrapolation in the back reflection region of a 57.3 mm. radius X-ray powder camera, and indices of refraction were measured at room temperature by the dispersion method. These numbers along with MnO and density were plotted on a Philipsborn tetrahedron as a cross-check (successful) of analytical accuracy (cf. Levin, 1950; Skinner, 1956), and are listed in Table 3.

Four rock samples (L12, L29, L49, L62) which have been chemically analyzed (Shaw, 1956) have compositions similar to those cited earlier for the pelitic schists. Two new analyses are listed in Table 6 for rocks typical of the range of the H series. In these rocks, garnet CaO is appreciably higher than in garnets from granitic or pelitic rocks (Table 3), and is evidently a function of bulk rock chemistry. Mineral assemblages for all rocks are listed in Table 5.

Discussion

Means and standard deviations of the partition coefficients in Table 5 show, as anticipated, that the values for the plutonic group are higher

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[1] Tables 3 and 4 have been deposited with the National Auxiliary Publication Service. To obtain a copy, order NAPS Document No. 00709 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001, remitting $1.00 for microfiche or $3.00 for photocopies payable to ASIS-NAPS.

Table 5. Assemblages Mg/Fe Ratios for Garnet-Biotite Mineral Pairs
Q+Pl+B+G+Fe−Ti Lxide±Fe Sulfides

Sample	Formation	Other phases	Garnet $Mg/(Fe^{+2}+Fe^{+3})$	Biotite $Mg/(Fe^{+2}+Fe^{+3})$	Garnet/biotite $Mg/(Fe^{+2}+Fe^{+3})$
		Plutonic Rocks			
S-6	Kqm	M, Si, Kf	.155	.651	.24
S-7	Kqm	M, Si, Kf	.240	.752	.32
S-15	Kqm	M, Kf	.113	.408	.28
LM-1	Kqm	M, Kf	.237	.799	.29
LM-1 (Heald, 1950)	Kqm	M, Kf	.238	.834	.29
S-12	Aplite	M, Kf	.061	.337	.18
S-16	Aplite	M, Kf	.045	.371	.12
S-17	Pegmatite	M, Kf	.036	.265	.14
			$K_D=.28\pm0.3$ (Kqm)		
			$K_D=.24\pm.08$ (All plutonics)		
		Sillimanite or Sillimanite-Orthoclase Zone Rocks			
S-9 (Or. zone)	Dl	M, Si	.107	.534	.20
S-13 (Or. zone)	Dl	M, Si	.089	.532	.17
S-14 (Or. zone)	Dl	M, Si	.105	.434	.24
S-18 (Or. zone)	Dl	M, Si	.070	.481	.16
BF-6	Dl	M, Si	.105	.765	.14
BF-8	Dl	M	.094	.543	.17
BF-10	Dl	M	.098	.666	.15
P-3	Dl	M, Si	.090	.729	.12
L-27	Dl	M?, Si?	.085	.741	.12
L-29 (Or. zone)	Dl	M, Si, (Ch)	.128	.618	.21
L-58	Dl	M, Si, (Ch)	.087	.735	.12
L-80	Dl	M, Si	.157	.694	.23
ER-142 (Green, 1963)	ꞒOa	M, Si	.111	.854	.13
Clifford (1960)	Dl	M	.562	3.23	.17
			$K_D=.16\pm.03$		
			K_D (Or. Zone) $=.20\pm.03$		
		Garnet to Kyanite Zone Rocks			
a. With staurolite					
Mo-6	Dl	M, St	.126	.815	.16
Mo-8	Dl	M, St	.063	.358	.18
L-12	Dl	M, St, (Ch)	.126	.955	.13
L-60	Dl	M? St?	.102	.685	.15
L-62	Dl	M, St	.087	.522	.17
D-2 (Green, 1963)	ꞒOa	M, St, Ch	.156	.889	.18
Er-101b (Green, 1963)	Oal	M, St, Ch	.150	.836	.18
			$K_D=.16\pm.02$		

TABLE 5—(*Continued*)

b. With chlorite

		Other Phases	Zone	%CaO			
H-2	Dws	K, Ch, Ru	Kyanite		.106	1.185	.09
H-10	Dws	M, Ep. Ch, Ru	Garnet		.044	.393	.11
H-13	Dws	M, Ep. Ch	Garnet		.050	.510	.10
37 (Crawford, 1966)	Dgm	M, Ch	Garnet	6.61	.098	1.102	.09
39 (Crawford, 1966)	Dgm	M, Ch	Garnet	6.36	.103	.992	.10
40 (Crawford, 1966)	Dgm	M, Ch, Cc?	Garnet	6.36	.128	1.358	.09
44 (Crawford, 1966)	Dgm	M, Ch, Cc?	Garnet	6.40	.138	1.402	.10
67 (Crawford, 1966)	Dgm	M, Ch	Garnet	8.04	.131	1.475	.09

$K_D = .10 \pm .01$

c. With hornblende

		Other Phases	Zone			
H-5	Dws	Hb, Ep, Cc, Ch	Kyanite	.090	1.060	.09
H-17	Dws	Hb, Ep, Ch, Ru	Garnet	.107	1.032	.10
H-23	Dws	Hb, Ep, Cc	Kyanite	.149	1.375	.11
H-27	Dws	Hb, Ep, Cc, (Ch)	Kyanite	.105	1.024	.10

$K_D = .10 \pm .01$

ЄOa—Aziscohos formation.
Dgm—Gile Mountain formation.
Dws—Standing Pond Member; waits River Formation
Dl—Littleton schist
Kgm—Kinsman Quartz Monzonite
± values are standard deviations of the means.

Key:

B—Biotite
Cc—Carbonate
Ch—Chlorite
Ep—Epidote; Clinozoisite
G—Garnet
Hb—Hornblende
K—Kyanite
Kf—K-feldspar
M—Muscovite, sericite
Q—Quartz
Pl—Plagioclase
Ru—Rutile
St—Staurolite
St—Sillimanite

than for the metamorphics, supporting the inference that the former represents a higher temperature assemblage. Because the effects of CaO and MnO on the partitioning coefficients are known to be significant, it is instructive to examine plots of these components in garnet against the K_D Mg/Fe Garnet-Biotite (Fig. 1 and 2). Several conclusions are apparent:

1. High-calcium garnets of the garnet to kyanite zones have uniformly low distribution coefficients (0.10±.01) despite the fact that temperature-wise they overlap higher K_D (0.16±.02) pelitic rocks of the staurolite zone. A similar effect was noted by Albee (1965b.

TABLE 6. CHEMICAL ANALYSES OF GARNETIFEROUS SCHIST AND GNEISS HANOVER QUADRANGLE, VERMONT-NEW HAMPSHIRE

SiO_2	79.22	39.79
TiO_2	.29	2.54
Al_2O_3	10.96	18.33
Fe_2O_3	.92	1.48
FeO	3.42	13.41
MgO	.21	5.57
MnO	.10	.97
CaO	2.00	9.72
Na_2O	.60	3.00
K_2O	1.45	1.92
H_2O^+	.87	.90
H_2O^-	.07	.10
CO_2	n.d.	2.05
P_2O_5	.04	.68
Totals	100.15	100.45
Oxidation Ratio	20	9

Analyst: H. Dehn.
H-10 Garnet-biotite-chlorite-muscovite-albite-epidote-quartz schist
H-27 Hornblende-garnet-biotite-plagioclose-epidote-calcite-quartz gneiss

p. 159) for higher grade rocks but a question raised by him, and unresolvable on the basis of available data, is whether the effect is due to Ca in the garnet or to variations in biotite composition in different assemblages. The effect of MnO in calcic garnets is apparently inconsequential.

2. Pelitic rocks of the staurolite and sillimanite zone have the same range of Ca contents and roughly equivalent partitioning coefficients, but the variability is more extreme in the sillimanite zone (0.16 ± 0.03). Sillimanite-orthoclase zone rocks (0.20 ± 0.03) are distinctly lower than the plutonics (0.24 ± 0.08) or the Kinsman alone (0.28 ± 0.03). Average values for the partitioning coefficients are decreased by MnO in the garnet (Fig. 2) and the value for K_D for a group of rocks can best be estimated by extrapolating values to zero percent MnO. On this basis, K_D for all plutonic rocks would lie in the range of 0.32 to 0.34, sillimanite-orthoclase rocks 0.23 to 0.27, and sillimanite or staurolite zone rocks 0.15 to 0.27. Clifford's (1960) sample [65 percent $Mn/(Mn+Fe+Mg)$; K_D 0.17] plots far off the top of Figure 2, and implies that at high Mn concentration, the visually extrapolated curves of Figure 2 (cf. Albee, 1965a) may become vertical, as with the Ca-rich garnets. Because of this, it is not certain whether pegmatites and aplites cutting the Kinsman

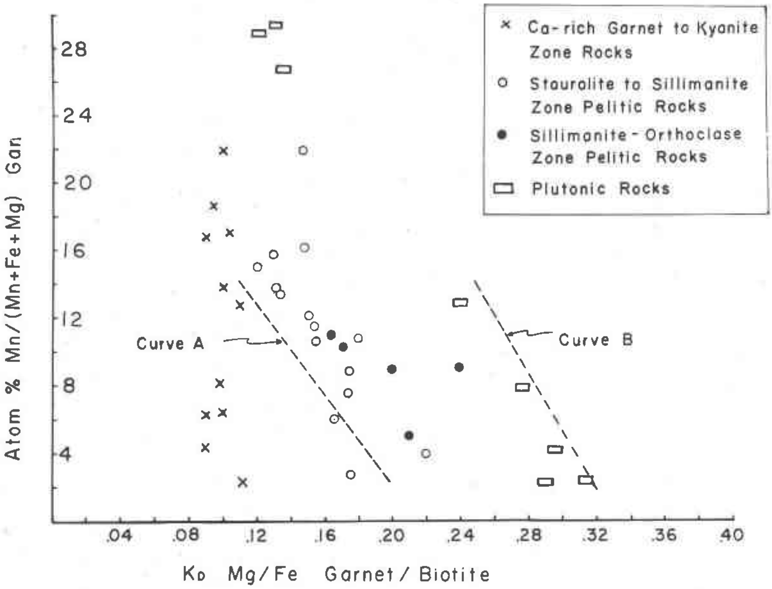

FIG. 2. Atom percent Mn/(Mn+Fe+Mg) of garnet vs. K_D Mg/Fe for garnet-biotite pairs of Table 3. Curves A and B are empirical curves of Albee (1965a) for gar-bio-stau-musc-qtz-plag. and gar-bio-sill-Kfs.-qtz-plag assemblages respectively.

crystallized at the same or at somewhat lower temperatures than it.

Experimental data of Evans (1965) and Richardson et al. (1969) imply a minimum temperature of 700° C for the sillimanite-orthoclase zone at 5.5 kbar. This is 75° above the minimum melting curve for granite at that pressure (Tuttle and Bowen, 1958) and thus may be unrealistically high. How much higher the temperature would have to be to produce the K_D of the plutonic rocks is, of course, uncertain, but the range (0.32 to 0.34 at zero percent MnO) of K_D is characteristic of many granulite facies rocks (cf. Table 1). If the Kinsman and associated plutonic rocks are granulite-facies metamorphic rocks there is a problem in explaining the source of the heat for the metamorphism. If they are magmatic, there is no heat problem, and the somewhat abnormal mineralogy may be accounted for by the effects of crystallization under low oxygen and H_2O fugacity conditions (Hsu, 1968; Barker, 1961). We cannot, on the basis of K_D or temperature conditions, rule out the granitization hypothesis, but convincing evidence in its favor is lacking.

3. Ca^{2+} and Mn^{2+}, being large ions, are favored over Fe^{2+} and Mg^{2+} in the 8-fold coordination sites in garnet, but whereas Mn^{2+} behaves

ideally, Ca^{2+} shows strong departures from ideality (Saxena, 1968a; Atherton, 1968). Because of this there is no systematic relation in our data between plots of garnet (CaO+MnO) vs. (FeO+MgO) and metamorphic grade (Sturt, 1962; Nandi, 1967); nor between Ca/Mn in garnet vs. K_D and metamorphic grade (Sen and Chakraborty, 1968).

4. Finally, the use of Mg/Fe partitioning coefficients in garnet-biotite pairs to estimate temperatures may be beset by several other problems not considered here such as analytical errors, the effects of Al, Ti, and varying FeO/Fe_2O_3 ratios in biotite, etc. The geological complexities are such that the establishment of a linear relationship between metamorphic grade and K_D similar to that recently described by Hietanen (1969) will continue to be the exception, rather than the rule.

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