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Distribution of Fe and Mg between garnet and biotite in Scottish Barrovian metamorphic zones

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SUMMARY. The distribution coefficient $K_D = (Mg/Fe)_{garnet}/(Mg/Fe)_{biotite}$ has been calculated for eight garnet-biotite pairs from rocks ranging from the garnet isograd to the staurolite zone along the Stonehaven coast of NE Scotland. This distribution coefficient depends upon metamorphic temperature and is not dependent upon the Mn and Ca content of garnet. Garnet-biotite geothermometer yields temperatures of about 500, 550, and 575-620 °C for the garnet, chloritoid + staurolite, and staurolite zones respectively.

PARTITIONING of elements between coexisting minerals is extensively used in geothermometry and for measuring the attainment of chemical equilibrium. The Mg-Fe distribution between coexisting garnet and biotite, for example, can be treated from the viewpoint of equilibrium for the reaction:

$$\underset{\text{Fe garnet}}{Fe_3Al_2Si_3O_{12}} + \underset{\text{Mg biotite}}{KMg_3AlSi_3O_{10}(OH)_2} \rightleftarrows \underset{\text{Mg garnet}}{Mg_3Al_2Si_3O_{12}} + \underset{\text{Fe biotite}}{KFe_3AlSi_3O_{10}(OH)_2}$$

If the two minerals behave as ideal solid solutions we have the equation:

$$\ln K_D = \ln (Mg/Fe)\ \text{garnet}/(Mg/Fe)\ \text{biotite} = -\tfrac{1}{3}\Delta G^\circ/RT$$

where K_D = distribution coefficient; ΔG° = the change in the standard free energy of the reaction; R = Gas constant; T = Temperature in °K.

Systematic studies of $K_{D_{gt\text{-}biot}}^{Fe\text{-}Mg}$ (Lambert, 1959; Miyashiro, 1953, 1973; Phinney, 1963; Albee, 1965, 1968; Hietanen, 1969; Kretz, 1964; Saxena, 1968, 1969, 1973; Sen and Chakraborty, 1968; Lyons and Morse, 1970; Goldman and Albee, 1977) have indicated that the distribution coefficient is primarily dependent upon temperature and thus metamorphic grade, but it is also dependent upon compositional variation in either phase, especially when this variation is pronounced. The effect of pressure upon the distribution coefficient is negligible in comparison with the temperature dependence. Tilley (1926), Kretz (1959), Albee (1965), and Sen and Chakraborty (1968) noted that the distribution coefficient is also related to the Mn content of the garnet, such that $K_{D_{gt\text{-}biot}}^{Mg\text{-}Fe}$ becomes more in those garnet-biotite pairs where the garnet is Mn-rich than in the case of Mn-poor garnet coexisting with biotite of the same composition, so that projection to an arbitrary value of X_{gt}^{Mn} (generally zero) is necessary before making comparison between data for different metamorphic grades.

Albee (1965) suggested the following average values of $K_D(Mg/Fe)$ after projection to $X_{gt}^{Mn} = 0$: garnet zone 0.20; staurolite zone 0.215; kyanite zone 0.23; sillimanite + K-feldspar zone 0.3-0.37. Hietanen (1969) gives $K_D(Mg/Fe)$ values 0.107-0.122, 0.106, 0.137, 0.312, and 0.224 for garnet-biotite pairs from the garnet, staurolite, kyanite, kyanite-sillimanite, and sillimanite-muscovite zones respectively from north of the Idaho batholith. Lyons and Morse (1970) compiled previously published data and suggested for garnet, staurolite, sillimanite, and sillimanite-orthoclase zones the values of 0.13, 0.151, and 0.274 respectively for a Mn-free system.

Mineral analyses (Table I) were completed in the University of Manchester on a Cambridge Instruments Geoscan using wavelength-dispersive techniques and using a Link Systems Model 290-2KX energy-dispersive spectrometer, attached to a Cambridge Instruments Geoscan. Pure-metal standards were used for Fe and Mn and synthetic or natural minerals for the other elements. Full ZAF corrections were made. The samples come from a traverse indicated on fig. 1 of Baltatzis and Wood (1977).

TABLE I. *Microprobe analyses of garnet-biotite pairs*

	Garnet Zone		Chloritoid + Staurolite Zone										Staurolite Zone			
	St17		D31		D32		D33		D34		D35		St21/A		St21/3	
	Gt	Bte	Gt	Bte	Gt	Bte	Gt	Bte	Gt	Bte	Gt	Bte	Gt	Bte	Gt	Bte
SiO_2	37.73	35.51	37.53	33.50	37.56	33.75	37.49	33.88	36.41	33.01	36.76	34.19	37.60	35.04	37.34	34.51
TiO_2	—	1.78	—	1.59	—	1.62	—	1.45	—	1.45	—	2.01	—	1.94	—	1.80
Al_2O_3	21.84	19.35	21.48	19.36	21.49	19.75	21.17	20.05	21.73	19.29	21.58	18.82	21.03	19.66	21.11	18.85
FeO	34.69	21.34	32.42	24.12	32.78	22.61	32.21	23.44	32.94	24.28	32.60	22.63	34.43	21.58	33.45	21.94
MnO	3.93	—	7.24	0.21	6.77	0.26	7.78	—	7.54	0.21	7.69	—	4.00	0.08	3.80	—
MgO	1.48	8.92	1.57	7.73	1.84	7.66	1.84	7.97	1.96	7.99	1.93	7.43	2.60	8.93	2.33	8.86
CaO	0.95	—	1.26	—	1.38	—	1.29	—	1.16	—	1.30	—	1.64	—	1.32	—
Na_2O	—	0.28	—	—	—	—	—	—	—	0.04	—	—	—	0.13	—	—
K_2O	—	9.34	—	7.64	—	8.45	—	7.86	—	8.43	—	8.89	—	9.05	—	9.00
Total	101.12	96.52	101.51	94.14	101.82	94.10	101.78	94.83	101.75	94.71	101.86	93.96	101.30	96.41	99.35	94.98
Ions	12(0)	22(0)	12(0)	22(0)	12(0)	22(0)	12(0)	22(0)	12(0)	22(0)	12(0)	22(0)	12(0)	22(0)	12(0)	22(0)
Si	3.011	5.377	3.003	5.250	2.995	5.273	2.998	5.246	2.925	5.183	2.982	5.360	3.003	5.313	3.026	5.333
Al^{iv}	—	2.623	—	2.750	0.005	2.727	0.002	2.754	0.075	2.817	0.018	2.640	—	2.687	—	2.667
Al^{vi}	2.054	0.831	2.026	0.827	2.015	0.911	1.993	0.905	1.983	0.752	1.949	0.836	1.981	0.827	2.016	0.766
Ti	—	0.202	—	0.187	—	0.190	—	0.168	—	0.171	—	0.236	—	0.211	—	0.209
Fe^{+2}	2.315	2.702	2.169	3.161	2.186	2.955	2.148	3.036	2.198	3.187	2.165	2.967	2.284	2.737	2.267	2.835
Mn	0.265	—	0.490	0.028	0.457	0.034	0.527	—	0.513	0.028	0.529	—	0.271	0.010	0.261	—
Mg	0.235	2.013	0.187	1.805	0.218	1.785	0.219	1.839	0.234	1.871	0.234	1.736	0.310	2.018	0.281	2.042
Ca	0.081	—	0.108	—	0.118	—	0.111	—	0.100	—	0.113	—	0.141	—	0.115	—
Na	—	0.084	—	—	—	—	—	—	—	0.014	—	—	—	0.038	—	—
K	—	1.804	—	1.528	—	1.684	—	1.553	—	1.688	—	1.778	—	1.750	—	1.775
Mg/Fe	0.102	0.745	0.086	0.571	0.100	0.604	0.102	0.606	0.106	0.587	0.108	0.585	0.136	0.737	0.124	0.720

Discussion

The distribution of Mg/Fe for the garnet-biotite pairs of the present study is shown in fig. 1. The ratio Mg/Fe of the garnets has been calculated from analyses of the rims of the crystals. The mean values obtained from the rocks studied are: garnet zone 0.136, chloritoid + staurolite zone 0.170, and staurolite zone 0.180.

Provided that the pressure dependence of the distribution coefficient is small and oxygen fugacities were similar, values obtained from the rocks studied should be similar to those presented by Albee (1965*a*) and Lyons and Morse (1970). The K_D(Mg/Fe) values for the garnet-biotite pairs of this study are higher than those of Lyons and Morse (1970) and lower than those of Albee (1965*a*). This suggests that the rocks of this study have formed at temperatures higher than those of Lyons and Morse and at temperatures lower than those of Albee.

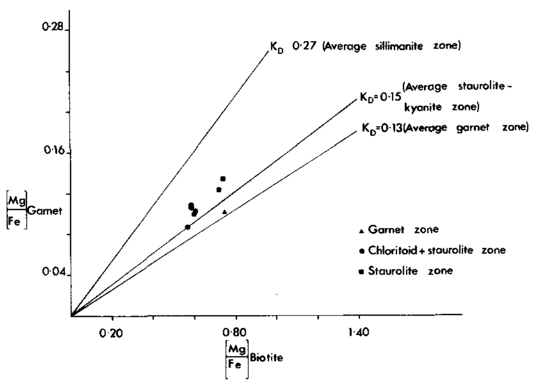
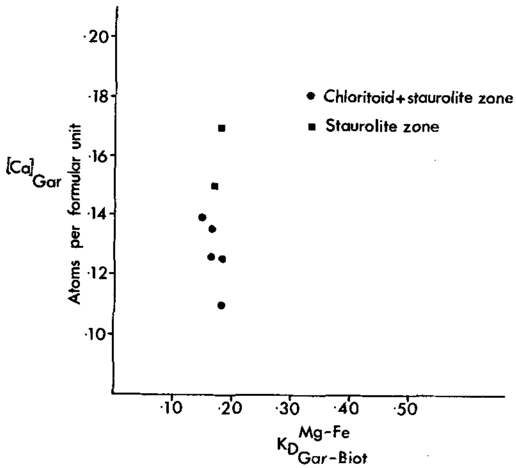
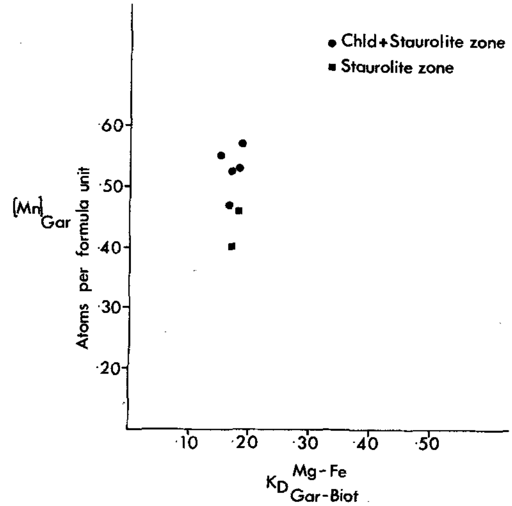


FIG. 1. Distribution of Mg/Fe^{2+} for the garnet-biotite pairs from different metamorphic zones. K_D values for various metamorphic zones as delimited by Lyons and Morse (1970) shown.

The effects of the Mn and Ca in the garnet on $K_{D_{gt\text{-}biot}}$ have been tested with the present chloritoid + staurolite and staurolite zones samples by plotting K_D against Mn in garnet and Ca in garnet (figs. 2, 3). There is apparently no relationship between the Mn content in garnet and K_D (fig. 2), possibly because of the low Mn in the garnets. No influence of Ca in garnet on the distribution of Fe and Mg between coexisting garnet and biotite has been observed (fig. 3). Phinney (1963) and Kretz (1959) have obtained the same results from their observations.

Using the Fig. 1B of Thompson (1976, p. 429; a plot of ln K_D(Fe–Mg) between garnet and biotite against temperature) temperatures 500, 550, and 575 °C for the garnet, chloritoid + staurolite, and staurolite zones respectively have been obtained. These values are in reasonable agreement with the





FIGS. 2 and 3: FIG. 2 (*left*). Relation between Mn in garnet and $K_D{}^{Mg\text{-}Fe}_{garnet\text{-}biotite}$ of the chloritoid + staurolite and staurolite zone samples. FIG. 3 (*right*). Relation between Ca in garnet and $K_D{}^{Mg\text{-}Fe}_{garnet\text{-}biotite}$ of the chloritoid + staurolite and staurolite zone samples.

result obtained for rocks close to the staurolite isograd using the muscovite-paragonite solvus (Baltatzis and Wood, 1977), although temperatures derived by $^{18}O/^{16}O$ quartz-magnetite isotopic thermometers were found to be 50 °C lower than those obtained from fig. 1B, by Goldman and Albee (1977).

Using, also, the garnet-biotite geothermometer of Perchuk (1970) the temperatures obtained for the garnet, chloritoid + staurolite, and staurolite zones are 500, 550, and 620 °C respectively.

Conclusions

The following K_D values were obtained from the studied rocks of the Stonehaven coast: garnet zone 0.136, chloritoid + staurolite zone 0.170, and staurolite zone 0.180 giving temperatures of metamorphism of about 500, 550, and 575-620 °C for the garnet, chloritoid + staurolite, and staurolite zones respectively.

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