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The thermal-compositional dependence of Fe^{2+}-Mg distributions between coexisting garnet and pyroxene: applications to geothermometry[1]

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Abstract

The thermal-compositional dependence of Fe^{2+}-Mg distributions between coexisting garnet and pyroxene in diverse metamorphic lithologies from two small areas in the Ruby Range, southwestern Montana, has been studied by electron microprobe and multiple linear regression techniques. For coexisting garnet-clinopyroxene, this dependence, which is inferred from independent metamorphic P–T estimates for two areas and thirteen mineral-pair analyses, is summarized by the equation

$$RT \ln K_D = (2482 \pm 845) + (1509 \pm 1392)(X_{Fe} - X_{Mg})^{Gar} + (2810 \pm 954)(X_{Ca}^{Gar}) + (2855 \pm 792)(X_{Mn}^{Gar})$$

where $K_D = (X_{Fe}/X_{Mg})^{Gar}/(X_{Fe}/X_{Mg})^{Cpx}$, X = mole fraction, $2482 = 2324 + 0.022P = -\Delta G_T^P$(cal) for the gar–cpx Fe–Mg exchange reaction, and the coefficients represent regressed values for garnet mixing parameters (w_{ij}^{Gar}). The regressed parameters for Ca and Mn agree well with those calculated by Ganguly (1979); however, the regressed value of w_{FeMg}^{Gar} is intermediate to those of Ganguly and O'Neill and Wood (1979).

For nine garnet-orthopyroxene pairs, the best-fit equation is identical to that given above except that $-\Delta G_T^P = 1391 \pm 288$ cal for the gar–opx Fe–Mg exchange reaction.

The garnet-clinopyroxene geothermometers of Ganguly (1979) and Saxena (1979) yield anomalously high temperatures for the Ruby Range. If this result is observed in other upper-amphibolite to lower-granulite facies terrains, more realistic temperatures may be obtained from the gar–cpx equation presented here. The gar–opx equation can be used as a relative (but not absolute) geothermometer.

Introduction

The temperature dependence of Fe^{2+}–Mg distributions between coexisting ferromagnesian silicates has been used extensively in the calibration of mineral-pair geothermometers. Such distributions are a function not only of temperature, however, but depend also upon composition of the exchanging minerals and—to a lesser extent—upon load pressure. This paper examines the compositional dependence of Fe^{2+}–Mg distributions for garnet–clinopyroxene and garnet–orthopyroxene pairs in natural assemblages from the Ruby Range, southwestern Montana (Fig. 1). Potentially the most useful field areas for such a study are those that contain a diversity of lithologic units, yet are sufficiently small that uniformity of metamorphic P–T conditions can be reasonably assumed. If, in addition, coexisting garnets and pyroxenes crystallized under equilibrium conditions, then it follows that any variation in Fe^{2+}–Mg distributions between these minerals must be compositionally controlled. With these considerations in mind, two small areas in the Ruby Range were chosen for study. These areas, designated in Figure 1 as the Kelly and Carter Creek areas, are 1 km^2 and 9 km^2, respectively.

Coexisting garnets and pyroxenes in 17 rocks representing six metamorphic lithologies in the Kelly and Carter Creek areas were analyzed by electron microprobe. The distribution of Fe^{2+} and Mg between coexisting minerals, usually expressed by a distribution coefficient K_D, is defined here as

$$K_D\ (\mathrm{Fe/Mg;\ gar\text{–}pyrox}) = (X_{Fe}/X_{Mg})^{Gar}/(X_{Fe}/X_{Mg})^{Pyrox} \quad (1)$$

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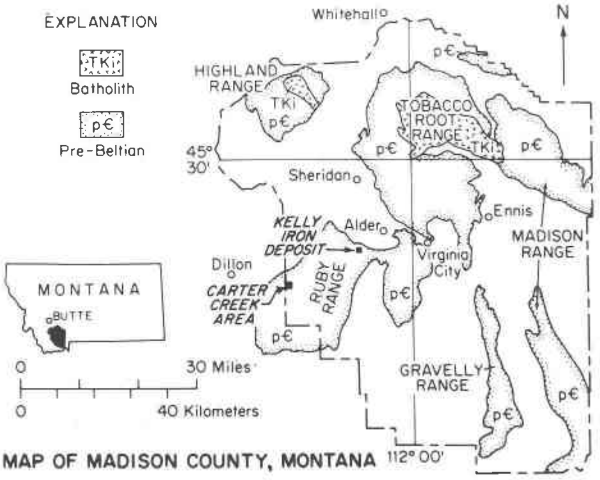


Fig. 1. Map showing exposures of Precambrian metamorphic rocks and Tertiary intrusives in Madison County, Montana (after Cordua, 1973). The Kelly and Carter Creek areas of the Ruby Range are the primary sample sites for this study. One sample is from the Stone Creek area, located approximately halfway between the two main areas.

where the X terms denote mole fractions. In this paper, thermodynamic modeling of thermal and compositional effects on K_D is done by two methods. The first approach utilizes Ganguly's (1979) binary mixing parameters for garnet and Dahl's (1979) estimates of peak metamorphic temperatures in the Kelly and Carter Creek areas; the second approach involves multiple linear and step-wise regression techniques, utilizing the 17 Montana samples as the data base. The results are evaluated in terms of earlier studies by Banno (1970), Berg (1975, 1977), Davidson (1969), Davidson and Mathison (1973), Dougan (1974), Ganguly (1979), O'Neill and Wood (1979), Råheim and Green (1974), and Saxena (1968, 1969, 1976, 1979).

Methods of study

Garnet–pyroxene-bearing rocks collected in the Ruby Range were studied by standard optical and electron microprobe techniques. Mineral assemblages and compositional data for these rocks are summarized in Tables 1 and 2, respectively. Chemical analyses of all minerals were performed on polished thin sections using a 3-spectrometer ETEC Autoprobe; operating conditions and analytical conditions were identical to those described by Klein (1974). Only mean analyses, based on 3–10 individual analyses and generally uncorrected for small amounts of Fe^{3+}, were used in the calculation of distribution coefficients (K_D) and graphical data points. The averaging procedure did not significantly alter trends observed by plotting data from single analyses, but served only to reduce analytical scatter. Core and rim analyses of mineral grains, although not significantly different in most cases, were averaged separately; only rim analyses were used in this study, however.

Multiple linear and step-wise regressions were performed using a Hewlett-Packard model 9845A computer.

Geologic setting

The Precambrian metamorphic core of the Ruby Range is underlain by sillimanite–K feldspar-zone assemblages, except in the extreme northeast, where the orthopyroxene isograd is exceeded. Both the Kelly and Carter Creek areas contain a thick sequence of marbles, mafic gneisses, iron-formations, pelitic and semi-pelitic rocks, and quartzites. These rocks, collectively termed "Cherry Creek" rocks by Heinrich (1960), probably attained their high-grade metamorphic character approximately 2750 m.y. ago, during the Beartooth orogeny (James and Hedge, 1980).

Table 1. Summary of iron-formation and mafic gneiss assemblages in samples from the Ruby Range

Sample	Unit	gar	cpx	opx	hb	bi	plag	qtz	ilm	mag	other
RMK-13	GN	x	x		x		x	x	–		(zirc)
RMK-17	GN	x	x				x	x			
RMS-22	GN	x	x	x	x		x	x	–		
RMK-26	GN	x	x		x		x		–		
RMK-27_1	GN	x	x		x	x	x	x	–		
RMK-27_2	GN	x	x			–	x	x	x	–	(apa)
RMK-27_3	GN	x	–	x	x	–	x	x	x	–	
RMK-77	GN	x	x		x		x		x	–	
RMK-122	GN		x	x	x		x				
RMK-51	GQ	x	–	x	x	x	x	x	–		(zirc)
RMK-46	GIF	x	x	x				x		x	
RMK-76	GIF	x	x	x				x		x	(cal)
RMK-82	GIF	x	x	x				x		x	
RMK-37_1	QIF	x	x	x				x	–	–	
RMK-37_2	QIF	x	x	x				x		–	
RMK-48	QIF	–		x				x		x	
RMC-1_1	DGN	x	x		x			–			mic, sph, cal, scp, (zirc)
RMC-1_2	DGN	x	x		x			–			
RMC-71	AM	x	x				x				cal, scp

RMK and RMC samples are from the Kelly and Carter Creek areas, respectively. Subscripts on sample numbers denote compositional bands within a polished thin section. Sample RMS-22 is from the Stone Creek area, located directly between the two main sample areas. Lithologic designations (James et al., 1969; James and Wier, 1972a, 1972b) : GN = mafic granulite gneiss; GQ = garnet quartzite; GIF = garnet iron-formation; QIF = quartz iron-formation; DGN = diopside gneiss; AM = amphibolite. The term mafic gneiss (in table title and text) includes all lithologies except GIF and QIF. Symbols: x = major constituent; ( ) or - = minor or trace component (less than 3 modal %). Abbreviations: hb = hornblende; cum = cummingtonite; mag = magnetite; apa = apatite; mic = microcline; sph = sphene; cal = calcite; scp = scapolite; bi = biotite; plag = andesine or labradorite.

Table 2. Fe–Mg K_D values and compositional data for the subassemblage garnet±clinopyroxene±orthopyroxene in samples from the Ruby Range

		K_D(Fe/Mg)			Cations per 12 oxygens in garnet				Cations per 6 oxygens in clinopyroxene				Cations per 6 oxygens in orthopyroxene			
Sample	Unit	gar-cpx	gar-opx	cpx-opx	Fe	Mg	Ca	Mn	Fe	Mg	Ca	Mn	Fe	Mg	Ca	Mn
RMK-27_2	GN	6.80			1.890	0.453	0.697	0.038	0.445	0.621	0.861	0.003				
RMK-13	GN	6.48			1.720	0.511	0.778	0.042	0.352	0.678	0.878	0.002				
RMK-27_3	GN	*	3.52	0.53	1.927	0.526	0.559	0.056	0.364	0.660	0.828	0.005	0.995	0.957	0.020	0.012
RMK-17	GN	7.33			1.734	0.277	1.059	0.060	0.461	0.540	0.951	0.005				
RMS-22	GN	*	3.65	0.55	1.965	0.411	0.578	0.062	0.461	0.597	0.844	0.012	1.071	0.877	0.023	0.017
RMK-51	GQ	*	3.87	0.51	1.763	0.671	0.557	0.063	0.265	0.764	0.907	0.003	0.807	1.187	0.019	0.010
RMK-122	GN			0.55					0.260	0.761	0.888	0.012	0.740	1.201	0.017	0.019
RMK-77	GN	7.17			1.785	0.462	0.766	0.080	0.359	0.666	0.901	0.005				
RMK-26	GN	6.84			1.710	0.458	0.810	0.099	0.368	0.674	0.872	0.006				
RMK-76	GIF	7.29	4.37	0.60	1.920	0.322	0.574	0.269	0.475	0.581	0.862	0.022	1.103	0.808	0.026	0.053
RMK-82	GIF	7.65	4.34	0.57	2.021	0.173	0.613	0.313	0.655	0.429	0.882	0.029	1.390	0.516	0.033	0.066
RMK-46	GIF	8.45	4.96	0.60	1.710	0.297	0.533	0.563	0.432	0.634	0.827	0.042	0.999	0.874	0.027	0.110
RMK-37_2	QIF	9.08	5.40	0.60	1.486	0.137	0.517	0.978	0.576	0.482	0.821	0.120	1.147	0.571	0.040	0.235
RMK-37_1	QIF	8.95	5.79	0.65	1.499	0.125	0.497	1.006	0.618	0.461	0.796	0.124	1.190	0.575	0.034	0.235
RMK-48	QIF		5.61		**1.078	0.109	0.482	1.315					0.985	0.555	0.046	0.411
RMC-71	AM	11.54			**1.037	0.121	1.632	0.229	0.390	0.525	0.958	0.016				
RMC-1_1	DGN	11.47			1.566	0.113	1.073	0.280	0.545	0.451	0.904	0.022				
RMC-1_2	DGN	11.41			1.503	0.168	1.083	0.311	0.446	0.569	0.970	0.019				

*Subscripts on sample numbers denote compositional bands within a polished thin section. See Table 1 for explanation of lithologic symbols. *K_D not reported because gar and cpx were not found in contact. **These values have been corrected for relatively large amounts of Fe^{3+} using the computer program of Friberg (1976). All other Fe values are uncorrected for Fe^{3+}. Although not discussed in the text, cpx-opx K_D values (calculated from gar-cpx and gar-opx K_D values) approximately correlate with Fe^{cpx} and Mn^{cpx}. The Fe trend parallels a similar trend observed and explained by Davidson (1968) for Australian pyroxene pairs.*

Estimated *P–T* conditions of metamorphism for the two areas, based upon geothermometric and mineral assemblage data, are shown in Figure 2. Assemblage data and six mineral-pair geothermometers yielded concordant temperature estimates of 745±50°C (Kelly) and 675±45°C (Carter Creek) (Dahl, 1979). Because sillimanite is the stable aluminosilicate polymorph in pelitic rocks throughout the Ruby Range (Dahl, 1977), these estimates, coupled with Holdaway's (1971) determination of aluminosilicate *P–T* stabilities, constrain the maximum load pressures for the two areas (see Fig. 2). Minimum load pressures cannot have been too far below the sillimanite–kyanite univariant, or kyanite—a metastable relict in some pelitic rocks—would probably not have persisted. Thus, load pressures for the two areas are tentatively estimated at 7.2±1.2 kbar (Kelly) and 6.2±1.2 kbar (Carter Creek). The *P–T* ranges shown in Figure 2 are consistent with geothermal gradients of 30° to 35°C/km.

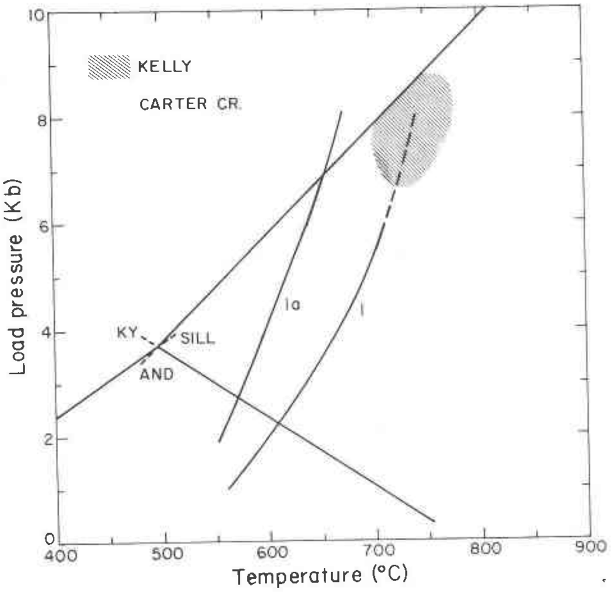


Fig. 2. *P–T* diagram showing probable peak metamorphic conditions for the Kelly and Carter Creek areas. Curves 1 and 1a represent the reaction mu + qtz $\rightleftarrows$ Al_2SiO_5 + ksp + H_2O at X_{H_2O} = 1 (Chatterjee and Johannes, 1974) and X_{H_2O} = 0.5 (Kerrick, 1972), respectively. Wintsch (1975) has calculated that Kerrick's experimental X_{H_2O} may correspond to $a_{H_2O} \simeq 0.25$.

The common association of microcline and sillimanite in metapelites indicates muscovite breakdown, and it appears from Figure 2 that the activity of water a_{H_2O} was significantly less than 1—and perhaps as low as or lower than 0.25—for pelitic rocks in the Carter Creek area; such was probably also the case for the higher-temperature pelitic rocks in the Kelly area. These conclusions are consistent with the lack of widespread partial melting in pelitic rocks throughout the Ruby Range.

Local alteration of prograde assemblages indicates that Precambrian greenschist to lower amphibolite facies metamorphism occurred in the Ruby Range

(1) during the waning stages of the 2750 m.y. event and/or (2) during a separate event at 1600 m.y., inferred from mineral dates of Giletti (1966).

Additional details on the stratigraphy, structure, and petrology of the "Cherry Creek" rocks in the Ruby Range are given in Garihan (1979), Heinrich (1960), James *et al.* (1969), James and Wier (1972a,b), Okuma (1971), and Dahl (1977, 1979).

Attainment of chemical equilibrium

The thermodynamic models presented in the following section assume that (1) chemical equilibrium between garnet and coexisting pyroxene was attained during the 2750 m.y. metamorphism, (2) garnet–pyroxene pairs within a given area equilibrated at the same (or similar) temperature regardless of lithology, and (3) evidence of this equilibrium was preserved (*i.e.*, was not partly obliterated by local retrograde effects). Evidence supporting the validity of these assumptions is presented below.

In support of assumption (1), no assemblage in Table 1 has negative variance; most assemblages are either di- or tri-variant. Second, coexisting garnets and pyroxenes typically exhibit smooth grain boundaries, suggesting textural equilibrium (Dahl, 1977). Third, element distributions between grain edges of coexisting garnets and pyroxenes are orderly, as exemplified by Mn and Al distributions in Figures 3A, B, C. Orderly element distributions also support assumption (2).

Assumption (3) is supported by the general lack of retrograde zoning among coexisting garnets and pyroxenes (Dahl, 1977). Furthermore, these minerals are typically free of retrograde alteration products; some grains, however, exhibit incipient alteration to minerals such as chlorite or actinolitic hornblende. Only pyroxenes in mafic granulite gneisses (the GN unit) from the Kelly area exhibit slight zoning. The GN unit may have originated as a gabbroic magma (Dahl, in preparation); zoning in Na, Al, Fe^{2+}, and Mg, therefore, is thought to reflect re-equilibration of the pyroxenes from igneous to high-grade metamorphic conditions. Rim compositions of coexisting garnets and pyroxenes in this unit are thus thought to reflect the latter conditions.

Thermodynamic models

Garnet–clinopyroxene

The exchange of Fe^{2+} and Mg between garnet and clinopyroxene can be represented by the equilibrium

$$\underset{\text{HD}}{CaFeSi_2O_6} + \underset{\text{PY}}{1/3Mg_3Al_2Si_3O_{12}} \leftrightarrows \underset{\text{DI}}{CaMgSi_2O_6} + \underset{\text{ALM}}{1/3Fe_3Al_2Si_3O_{12}} \quad (2)$$

Assuming (1) a substitutional solution model [*cf.* Kerrick and Darken (1975)] and (2) no Fe^{2+} or Mg in the *M2* site of clinopyroxene, the equilibrium constant $K(P,T)$ in terms of activities a, mole fractions X, and activity coefficients γ is given by

$$K(P,T) = \frac{(a_{Fe}^{Gar})^{1/3}(a_{Mg}^{Cpx})}{(a_{Mg}^{Gar})^{1/3}(a_{Fe}^{Cpx})} = \frac{(X_{Fe}^{Gar})(X_{Mg}^{Cpx})}{(X_{Mg}^{Gar})(X_{Fe}^{Cpx})} \cdot \frac{(\gamma_{Fe}^{Gar})(\gamma_{Mg}^{Cpx})}{(\gamma_{Mg}^{Gar})(\gamma_{Fe}^{Cpx})} \quad (3)$$

where the term composed of mole fractions is equivalent to the Fe–Mg distribution coefficient K_D. The equilibrium constant $K(P,T)$ is related to the Gibbs free energy change ΔG_T^P for the exchange reaction by the expression

$$\Delta G_T^P = -RT \ln K(P,T) \quad (4)$$

where R is the gas constant. Substitution of equation (4) into equation (3) and rearrangement of terms yields the relationship

$$RT \ln K_D = -\Delta G_T^P - RT \ln (\gamma_{Fe}^{Gar}/\gamma_{Mg}^{Gar}) + RT \ln (\gamma_{Fe}^{Cpx}/\gamma_{Mg}^{Cpx}) \quad (5)$$

Ganguly and Kennedy (1974) used the "simple mixture" approximation of Guggenheim (1967, p. 54–57) to derive the following expression for the activity coefficients of Fe^{2+} and Mg in garnet:

$$RT \ln (\gamma_{Fe}^{Gar}/\gamma_{Mg}^{Gar}) \simeq w_{FeMg}(X_{Mg}^{Gar} - X_{Fe}^{Gar}) + (w_{FeCa} - w_{MgCa})(X_{Ca}^{Gar}) + (w_{FeMn} - w_{MgMn})(X_{Mn}^{Gar}) \quad (6)$$

The w_{ij} are binary solution interaction parameters which express the non-ideality of mixing between components i and j in garnet. Applying multivariate regression methods to published analyses of garnet and coexisting biotite in staurolite-zone assemblages, Ganguly and Kennedy derived w_{ij} values for garnet. Revised values presented by Ganguly (1979) are: $w_{FeMg} = 2710$ cal/mole; $w_{FeCa} - w_{MgCa} = -3152$ cal/mole; and $w_{FeMn} - w_{MgMn} = -2600$ cal/mole. Substitution of these values into equation (6) permits calculation of the activity term for garnet in equation (5). Equation (5) thus becomes

$$RT \ln K_D = -\Delta G_T^P + 2710(X_{Fe}^{Gar} - X_{Mg}^{Gar}) + 3152(X_{Ca}^{Gar}) + 2600(X_{Mn}^{Gar}) + RT \ln (\gamma_{Fe}^{Cpx}/\gamma_{Mg}^{Cpx}) \quad (7)$$

Table 3. Compositional effects on K_D (Fe–Mg) predicted by equation (9) for garnet–clinopyroxene pairs in samples from the Ruby Range

Sample	$2710(X_{Fe} - X_{Mg})^{Gar}$ (cal/mole)	+	$3152(X_{Ca}^{Gar})$ (cal/mole)	+	$2600(X_{Mn}^{Gar})$ (cal/mole)	=	$Sum(X)$ (cal/mole)	K_D predicted	K_D measured
RMK-27_2	1266		712		31		2009	6.82	6.80
RMK-13	1073		804		36		1913	6.50	6.48
RMK-17	1260		1065		49		2374	8.17	7.33
RMK-77	1160		782		68		2010	6.82	7.17
RMK-26	1103		829		83		2015	6.84	6.84
RMK-76	1404		586		226		2216	7.55	7.29
RMK-82	1604		618		260		2482	8.61	7.65
RMK-46	1233		542		471		2246	7.67	8.45
RMK-37_2	1173		523		816		2512	8.74	9.08
RMK-37_1	1190		501		837		2528	8.81	8.95
RMC-71	821		1705		198		2724	11.48	11.54
RMC-1_1	1298		1116		239		2653	11.06	11.47
RMC-1_2	1182		1113		263		2658	11.09	11.41

Ganguly (1979) has used a simplified activity term for clinopyroxene of the form

$$RT \ln (\gamma_{Fe}^{Cpx}/\gamma_{Mg}^{Cpx}) = \Delta w (X^{Jd} + X^{Ac})^{Cpx} \quad (8)$$

where Δw is the difference between the simple-mixture interaction parameters in the jadeite–hedenbergite and jadeite–diopside joins and the X terms represent mole fractions of jadeite and acmite in clinopyroxene. Although a reliable estimate for Δw is lacking in the 700–800°C range ($\Delta w \simeq 0$ at 1000°C; Ganguly, 1979), the magnitude of the activity term is probably near zero for clinopyroxenes from the Kelly area, judging from their extremely low and uniform Na contents ($X_{Na}^{M2-Cpx} = 0.02$–0.06 at grain edges). With this approximation, equation (7) can be simplified to the form

$$RT \ln K_D = -\Delta G_T^P + 2710(X_{Fe}^{Gar} - X_{Mg}^{Gar}) + 3152(X_{Ca}^{Gar}) + 2600(X_{Mn}^{Gar}) \quad (9)$$

Equation (9) approximates the dependence of K_D(Fe/Mg; gar–cpx) on mineral composition and temperature. Calculated values for the compositional terms in equation (9) are presented in Table 3 for garnet–clinopyroxene-bearing samples from the Ruby Range; for a given sample, the sum of the three compositional terms is denoted by the quantity *sum*(X).

The approximate validity of equation (9) can be tested in several ways. First, the equation predicts that increases in X_{Fe}^{Gar}, X_{Ca}^{Gar}, or X_{Mn}^{Gar} cause sympathetic increases in K_D(Fe/Mg; gar–cpx). Indeed, all three effects have been reported in the literature; data of D. H. Green plotted by Banno (1970) indicate very weak Fe and Ca effects, whereas Saxena (1968, 1969) infers a strong Mn and relatively weak Ca effect.

Second, equation (9) predicts that any increase in *sum*(X) effects a corresponding increase in K_D, all other factors equal. Indeed, for samples RMK-27_2 through RMK-37_1 (listed in Table 3 in order of increasing Mn content in garnet), the general trend of increasing *sum*(X) values is paralleled by an increase in measured K_D values. Note that the *sum*(X) values for the Carter Creek samples are distinctly higher than those for the Kelly samples. These higher values, which are due partly to increased Ca concentrations in garnet (Table 3, column 3), are consistent with the higher K_D values measured in the Carter Creek samples. The other factor contributing to the higher K_D values is the lower metamorphic temperature for the Carter Creek area (see Fig. 2).

The most rigorous test involves a comparison of K_D values predicted from equation (9) and values actually measured for the 13 samples from the Ruby Range. The first step in predicting K_D values is the calculation of ΔG_T^P for equation (2). A mean value of -1874 ± 240 cal (95 percent confidence limits) for ΔG_T^P is obtained from equation (9) by averaging the 13 values obtained for the difference between $RT \ln K_D$ and *sum*(X). Despite the inferred P–T difference between the Kelly and Carter Creek areas (Fig. 2), ΔG_T^P values calculated for the two areas by the above method are not significantly different. Furthermore, values for ΔG_{1018}^{7200} ($P = 7200$ bars and $T = 1018$°K) and ΔG_{948}^{6200}—calculated from molar enthalpy, entropy, heat capacity, and volume data in Robie *et al.* (1978), Helgeson *et al.* (1978), and Zen (1973)—are different by only 0.8 percent. Hence, the -1874 cal value is retained for all 13 samples from the Ruby

Range (Table 3). Inferred values for ΔG^P_T, *sum*(X), and T can now be substituted into equation (9) to predict K_D.

K_D values predicted thereby are presented in Table 3 for garnet–clinopyroxene-bearing mafic gneisses and iron-formations from the Ruby Range. The model appears to over-correct for the high Ca and Fe contents in samples RMK-17 and RMK-82, respectively, but for most other samples there is good agreement between predicted and measured K_D values. Linear regression of predicted *vs.* measured K_D values in Table 3 yields a line of slope 0.90 and a correlation coefficient (r) of 0.97. This level of correlation lends credence to Ganguly's (1979) mixing parameters for garnet and to the temperature estimates inferred for the Kelly and Carter Creek areas. Furthermore, it indicates—for the Montana clinopyroxenes at least—that any clinopyroxene mixing terms have nearly constant, or negligible, value.

Although equation (9) closely defines the thermal and compositional dependence on K_D observed in garnet–clinopyroxene pairs from the Ruby Range, it is possible to use the 13 Ruby Range samples themselves as the data base for multiple linear regression. Accordingly, regression was performed by computer on 13 equations in the form of equation (9), where $RT \ln K_D$ was chosen as the dependent variable, the three X terms as the independent variables, and ΔG^P_T as the regression constant. Regressed coefficients derived from the Ruby Range samples are included in Table 4; substitution of these values into equation (9) yields

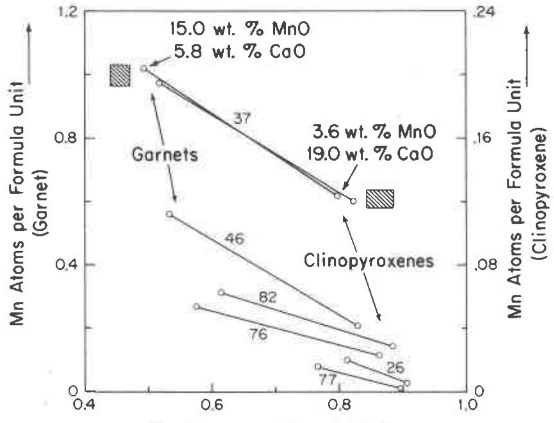
$$RT \ln K_D = 2482 + 1509(X^{Gar}_{Fe} - X^{Gar}_{Mg}) + 2810(X^{Gar}_{Ca}) + 2855(X^{Gar}_{Mn}) \qquad (10)$$

Measured K_D values and values predicted from equation (10) are compared in Table 5. Linear regression (as before) yields a line slope of 0.89 (*cf.* unity for a perfect model) and an r value of 0.97. This regression is plotted in Figure 4.

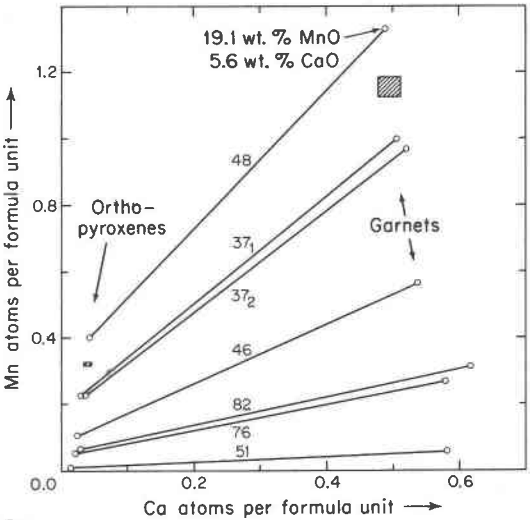
In Table 4, the regressed coefficients and thermal–compositional data base of this study are compared to data of Ganguly and Kennedy (1974), Ganguly (1979), and O'Neill and Wood (1979). Despite its relatively small size, the Montana data base comprises a broader range of composition—particularly for X^{Gar}_{Ca}—than that of Ganguly and Kennedy. Furthermore, analysis of variance indicates that equation (10)—derived from the 13 Montana samples—accounts for 89 percent of the total variance in $RT \ln K_D$ actually observed in this data base, whereas similar analysis (by this writer) of Ganguly and Kennedy's (1974) model (data base of 30 samples) reveals a 55 percent accounting of the total variance they observed in $RT \ln K_D$. The remaining 45 percent of variance is probably explained by (1) temperature differences among samples included in their data base, (2) the effects of variable Al^{3+}, Fe^{2+}, Fe^{3+}, and Ti^{4+} in biotite on K_D [see Goldman and Albee (1977)], and (3) the analytical uncertainty in determining Fe^{2+} and Fe^{3+} concentrations in biotites. The Montana model, on the other hand, is based on samples from two very small areas whose respective peak temperatures were probably uniform (see Dahl, 1979). Also, points (2) and (3) above are much less of a problem for the Montana clinopyroxenes, as they contain very low amounts of Na, Al^{3+}, Fe^{3+}, and Ti^{4+} (Dahl, 1977). Furthermore, mixing of Fe^{2+} and Mg in the clinopyroxenes is confined largely to a single site (*M1*), unlike in biotite. The remaining 11 percent of variance in the Montana model may be explained by (1) analytical error, (2) non-ideal mixing among Fe^{2+}, Mg, Ca, and Mn in clinopyroxenes, and (3) small yet variable amounts of Fe^{3+} among garnets. However, the small data base precludes meaningful consideration of more than the three independent variables.

The first three sets of interaction parameters w_{ij} given in Table 4 all correctly predict the effects of X^{Gar}_{Ca} and X^{Gar}_{Mn} on K_D, but the relatively low value of w_{FeMg} derived from the Montana data base suggests a lesser effect of X^{Gar}_{Fe} on K_D than that predicted by Ganguly's (1979) revised model. Furthermore, the low value and high uncertainty in w_{FeMg}, relative to the other w_{ij} computed from the Montana data base, indicate that variable X^{Gar}_{Fe} has a lesser effect on K_D than comparable variations in X^{Gar}_{Ca} or X^{Gar}_{Mn}. This conclusion is supported by a stepwise linear regression of $RT \ln K_D$ for the Montana data base. In this regression, variation in X^{Gar}_{Mn} alone is found to explain 33 percent of the variance observed in $RT \ln K_D$; X^{Gar}_{Mn} and X^{Gar}_{Ca} together explain 82 percent of the variance, and all three variables together account for 89 percent of the total variance. This result indicates that X^{Gar}_{Mn} is the most important variable affecting K_D in the Montana samples, whereas $X^{Gar}_{Fe} - X^{Gar}_{Mg}$ is the least important (of the three considered).

Data in Table 4 suggest that the value of w_{FeMg} may be temperature dependent. However, this observation contradicts Ganguly and Kennedy (1974), who concluded on the basis of thermodynamic and crystal-chemical reasoning that the w_{ij} for garnet should be insensitive to temperature. For equilibration temperatures greater than 675°C, I believe that only w_{FeMg} values significantly lower than 2710 cal/



(A)



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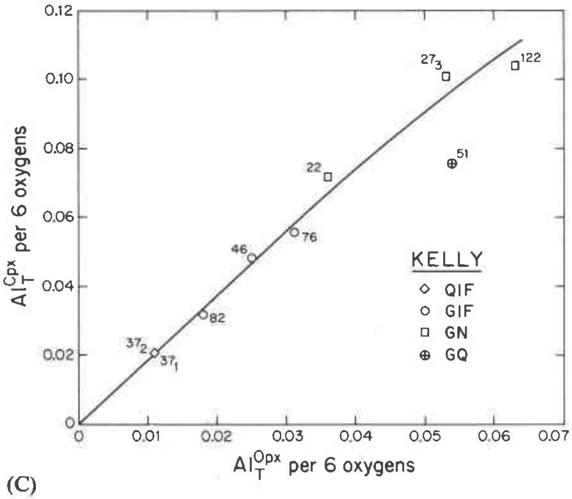

(C)

Fig. 3. (A, B) Partitioning of Mn and Ca between coexisting garnet and pyroxene in iron-formations (GIF, QIF) and mafic granulite gneiss (GN) from the Kelly area of the Ruby Range. Formula units based upon 12 oxygens for garnet and 6 oxygens for pyroxene. Error blocks (2σ) are given for the data points of sample RMK-37 (Fig. 3A) and sample RMK-48 (Fig. 3B). Errors for other data points are comparable. (C) Roozeboom plot of total Al (Al_T) between coexisting pyroxenes from the Kelly and Stone Creek areas. Lithologic abbreviations are defined in Table 1. RMK (or RMS) sample numbers are adjacent to tie lines and data points. All data points are computed from averaged electron microprobe analyses.

mole are realistic, for two reasons: (1) variable $X_{Fe}^{Gar} - X_{Mg}^{Gar}$ explains only a small percentage of the total variance observed in $RT \ln K_D$ for the Montana samples, and (2) neither experimental studies (*e.g.*, Råheim and Green, 1974) nor statistical studies (*e.g.*, Saxena, 1969) concerning *P*, *T*, or *X* dependences of K_D(Fe/Mg; gar–cpx) reveal significant effects of variable X_{Fe}^{Gar} or X_{Mg}^{Gar} on K_D.

There is, however, good agreement between Ganguly's (1979) w_{ij} for Ca and Mn and those calculated in this study, and despite the discrepancy in w_{FeMg} values both equations (9) and (10) closely approximate the thermal–compositional dependence of K_D(Fe/Mg; gar–cpx) for the Ruby Range samples.

Garnet-orthopyroxene

The exchange of Fe^{2+} and Mg between garnet and orthopyroxene can be represented by the equilibrium

$$\underset{FS}{FeSiO_3} + \underset{PY}{1/3Mg_3Al_2Si_3O_{12}} \rightleftarrows \underset{EN}{MgSiO_3} + \underset{ALM}{1/3Fe_3Al_2Si_3O_{12}} \qquad (11)$$

Treatment of this exchange equilibrium in a manner similar to that of the garnet–clinopyroxene equilibrium yields an expression analogous to equation (10) that approximates the thermal–compositional dependence of the distribution coefficient K_D(Fe/Mg; gar–opx). This expression is

$$RT \ln K_D = -\Delta G_T^P + sum(X) \qquad (12)$$

where *sum(X)* is the sum of the three compositional terms in equation (10) and incorporates the same w_{ij} values derived earlier from the Montana garnet–clinopyroxene data base. The term ΔG_T^P is the Gibbs free energy change for equation (11) at the *P* and *T* of interest.

One limitation inherent in equation (12), in addition to those cited earlier for equation (10), is its failure to account for non-ideality of mixing between

Table 4. Thermal–compositional data bases and regressed thermochemical values from different studies

Parameter	Ganguly and Kennedy (1974)	Ganguly (1979)	This study	O'Neill and Wood (1979)
number of samples	30		13	
$(X_{Fe}-X_{Mg})^{Gar}$	0.348-0.665		0.303-0.592	
X_{Ca}^{Gar}	0.004-0.24		0.159-0.541	
X_{Mn}^{Gar}	0.04-0.27		0.012-0.322	
T(°C)	630±40		745±50** 675±45***	1150±250
w_{FeMg}	2979±369	2710±200	1509±1392	195±430
$w_{MgCa}-w_{FeCa}$	4603±2117	3152±720	2810±954	2676±402
$w_{MgMn}-w_{FeMn}$	2308±1508	2600±850	2855±792	
ΔG_{1018}^{7200}		-1874±240*	-2482±845	

*The term $\Delta\underline{G}(\underline{P},\underline{T})$ refers to the Fe-Mg exchange reaction (equation (2)). Values for $\Delta\underline{G}(\underline{P},\underline{T})$ and the $\underline{w}_{ij}$ are expressed in cal and cal/mole, respectively, and quoted uncertainties reflect 95 percent confidence limits. *calculated in this study using data from Ganguly (1979) (see text for explanation). Temperature estimates for the Kelly (**) and Carter Creek (***) areas are from Dahl (1979).*

Fe^{2+} and Mg in the *M1* site of orthopyroxene; Saxena and Ghose (1971) reported a value of 1956 cal/mole (at 700°C) for the Fe–Mg interaction parameter for this site. However, site occupancies of Fe and Mg in the Montana orthopyroxenes were not determined in this study. Mixing between Fe^{2+} and Mg in these pyroxenes is probably further complicated by their high Mn^{2+} contents (Table 2). For these reasons, and given the small data base, compositional terms for orthopyroxene are not considered in equation (13), and the distribution coefficient K_D(Fe/Mg; gar–opx) is based on total Fe and Mg in orthopyroxene. The consequences of these simplifications are discussed further in this and later sections.

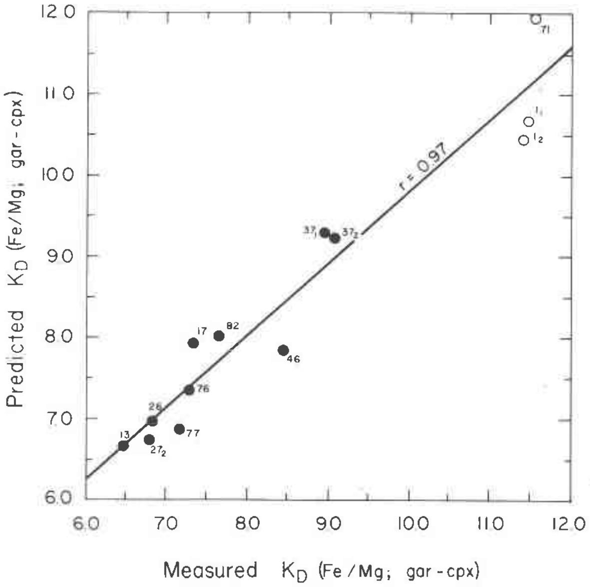

Fig. 4. Correlation between K_D(Fe/Mg; gar–cpx) values predicted from equation (10) and values measured in samples from the Ruby Range (see Table 5). RMK and RMC sample numbers are adjacent to data points. Solid circles represent Kelly samples; open circles represent Carter Creek samples.

A mean value for ΔG_T^P in equation (12) can be obtained from the difference between known values of $RT \ln K_D$ and *sum*(*X*) for the nine garnet–orthopyroxene pairs from the Kelly area, using the same procedure described earlier for garnet–clinopyroxene pairs. For the Kelly area, the computed value of ΔG_{1018}^{7200} is -1391 ± 288 cal (95 percent confidence limits). Equation (12) can now be rewritten in the form

$$RT \ln K_D = 1391 + 1509(X_{Fe}^{Gar} - X_{Mg}^{Gar}) + 2810(X_{Ca}^{Gar}) + 2855(X_{Mn}^{Gar}) \quad (13)$$

Table 5. Compositional effects on K_D (Fe,Mg) predicted by equation (10) for garnet–clinopyroxene pairs in samples from the Ruby Range

Sample	$1509(X_{Fe}-X_{Mg})^{Gar}$ (cal/mole)	+	$2810(X_{Ca}^{Gar})$ (cal/mole)	+	$2855(X_{Mn}^{Gar})$ (cal/mole)	=	*Sum(X)* (cal/mole)	K_D predicted	K_D measured
RMK-27$_2$	705		635		34		1374	6.73	6.80
RMK-13	598		717		40		1355	6.66	6.48
RMK-17	702		950		54		1706	7.93	7.33
RMK-77	646		697		74		1417	6.87	7.17
RMK-26	614		739		91		1444	6.97	6.84
RMK-76	782		523		248		1553	7.35	7.29
RMK-82	893		551		286		1730	8.02	7.65
RMK-46	687		483		517		1687	7.85	8.45
RMK-37$_2$	653		467		897		2017	9.25	9.08
RMK-37$_1$	663		447		919		2029	9.30	8.95
RMC-71	457		1520		217		2194	11.98	11.54
RMC-1$_1$	723		995		263		1981	10.69	11.47
RMC-1$_2$	658		992		288		1938	10.45	11.41

Table 6. Compositional effects on K_D (Fe,Mg) predicted by equation (13) for garnet–orthopyroxene pairs in samples from the Ruby Range

Sample	$1509(X_{Fe}-X_{Mg})^{Gar}$ (cal/mole)	+	$2810(X_{Ca}^{Gar})$ (cal/mole)	+	$2855(X_{Mn}^{Gar})$ (cal/mole)	=	Sum(X) (cal/mole)	K_D predicted	K_D measured
RMK-27_3	690		511		51		1252	3.69	3.52
RMS-22	779		540		60		1379	3.93	3.65
RMK-51	539		511		60		1110	3.44	3.87
RMK-76	782		523		248		1553	4.29	4.37
RMK-82	893		551		286		1730	4.68	4.34
RMK-46	687		483		517		1687	4.58	4.96
RMK-37_2	653		467		897		2017	5.39	5.40
RMK-37_1	663		447		919		2029	5.42	5.79
RMK-48	489		455		1259		2203	5.91	5.61

This expression permits an independent check on the validity of the three compositional terms derived earlier, insofar as K_D(Fe/Mg; gar–opx) values predicted by equation (13) can be compared to values actually measured for the nine garnet–orthopyroxene-bearing samples from the Kelly area. Predicted and measured K_D values, as well as compositional trends in the garnets, are presented in Table 6. Linear regression of predicted *vs.* measured K_D values yields a line of slope 0.92 and a correlation coefficient r of 0.93. This regression is plotted in Figure 5. The near-unity slope and high level of correlation in Figure 5 not only corroborate the w_{ij} used in equations (10) and (12), but also suggest that any mixing terms for orthopyroxene in equation (12) have nearly constant or negligible value for the nine samples of the data base. Furthermore, the w_{ij} appear to be applicable beyond the X_{Mn}^{Gar} range of the original data base, to at least X_{Mn}^{Gar} equal to 0.441. This level of Mn content, found in sample RMK-48, is the highest yet reported in the literature for garnet coexisting with orthopyroxene (*cf.* Davidson and Mathison, 1973).

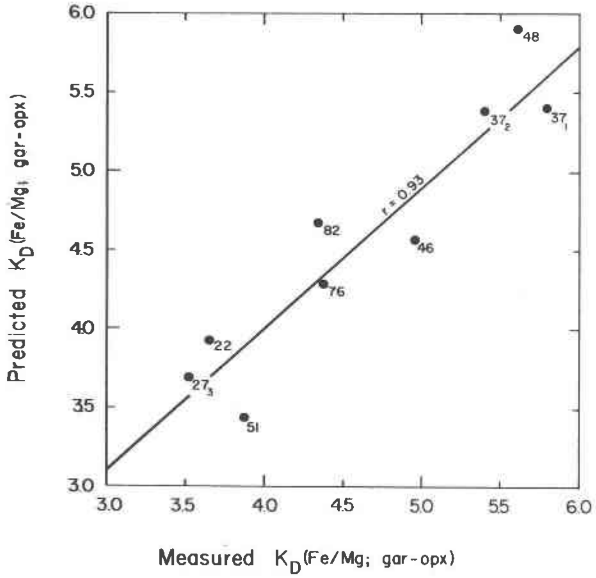

Fig. 5. Correlation between K_D(Fe/Mg; gar–opx) values predicted from equation (13) and values measured in samples from the Ruby Range (see Table 6). RMK (and RMS) sample numbers are adjacent to data points.

I conclude that equation (13) closely approximates the thermal–compositional dependence of K_D(Fe/Mg; gar–opx) for the Ruby Range samples. This dependence is comparable to that of garnet–clinopyroxene K_D values.

Similar analysis using Ganguly's (1979) interaction parameters in equation (13) yields a ΔG_{1018}^{7200} value of -896 ± 425 cal for equation (11) (95 percent confidence limits); linear regression of predicted *vs.* measured K_D(Fe/Mg; gar–opx) values results in a line with a slope of only 0.70 and a correlation coefficient r of 0.85.

Accuracy of ΔG_T^P *calculations*

The ΔG_T^P values for garnet–pyroxene Fe–Mg exchange reactions, calculated from the thermodynamic models presented in earlier sections, vary widely from values calculated using thermochemical data in Robie *et al.* (1978), Helgeson *et al.* (1978), and Zen (1973). For example, for gar–cpx pairs [equation (2)], the model yielded $\Delta G_{1018}^{7200} \simeq \Delta G_{948}^{6200} = -2482 \pm 845$ cal. The published thermochemical data, on the other hand, when applied to the equation

$$\Delta G_T^P = \Delta H_{298}^\circ - T\Delta S_{298}^\circ + \int_{298}^{T} \Delta C_p^\circ dT - T\int_{298}^{T} \frac{\Delta C_p^\circ}{T} dT + \int_{1}^{P} \Delta V^\circ dP \tag{14}$$

yield $\Delta G_{1018}^{7290} = -14018 \pm 4000$ cal and $\Delta G_{948}^{6200} = -13905 \pm 4000$ cal. Substitution of the latter values into equation (10) yields metamorphic temperatures that are completely unreasonable for the Kelly area (*ca.* 3700°C!). It is highly unlikely that additional compositional terms (*e.g.*, for clinopyroxene) in equation (10) could account for the -11500 cal/mole that would be necessary in this case to render the equation a reliable temperature indicator, since (1) the sum of all compositional terms for garnet accounts for only 1000 to 2000 cal/mole (ee Table 5) and (2) the model presented earlier accounts for 89 percent of the compositional variance observed in $RT \ln K_D$. Thus, I conclude that the discrepancy in ΔG_T^P values is due at least partly to inaccuracies in some of the published enthalpy and entropy values for garnet and clinopyroxene end-members. For garnet–orthopyroxene pairs, the discrepancy is even greater, and the conclusion is the same.

The validity of the regressed ΔG_T^P values for equations (2) and (11) can be tested by determining the degree of internal consistency among K_D and ΔG_{1018}^{7200} values for gar–cpx, gar–opx, and cpx–opx Fe–Mg exchange equilibria. Because the cpx–opx exchange reaction

$$\begin{array}{ccccccc} FeSiO_3 & + & CaMgSi_2O_6 & \rightleftarrows & MgSiO_3 & + & CaFeSi_2O_6 \\ \mathrm{FS} & & \mathrm{DI} & & \mathrm{EN} & & \mathrm{HD} \end{array} \qquad (15)$$

is obtained by subtraction of equations (2) and (11), the ΔG_{1018}^{7200} values for the three equilibria must be related by

$$(\Delta G_{1018}^{7200})_{\text{gar-opx}} - (\Delta G_{1018}^{7200})_{\text{gar-cpx}} = (\Delta G_{1018}^{7200})_{\text{cpx-opx}}$$

$$(-1391 \pm 288 \text{ cal}) - (-2482 \pm 845 \text{ cal}) \qquad (16)$$
$$= (1091 \pm 893 \text{ cal})$$

where $(\Delta G_{1018}^{7200})_{\text{cpx-opx}}$ refers to equation (15). We can state that

$$(\Delta G_T^P)_{\text{cpx-opx}} \simeq -RT \ln K_D(\text{Fe/Mg; cpx-opx}) \qquad (17)$$

Now, if the calculated value of 1091 cal for $(\Delta G_{1018}^{7200})_{\text{cpx-opx}}$ in equation (17) is accurate, then the K_D(Fe/Mg; cpx–opx) value we can compute from this equation must agree with K_D values observed in natural assemblages at 1018°K (745°C). Indeed, equation (17) yields a K_D value of 0.58, which compares with the mean K_D(Fe/Mg; cpx–opx) value of 0.57 for nine pyroxene pairs reported in Table 2. This internal consistency corroborates not only the three ΔG_T^P values, but also the validity of equations (10) and (13) and the basic correctness of the interaction parameters w_{ij} contained therein.

However, internal consistency of ΔG_T^P values calculated using Ganguly's (1979) mixing parameters can also be demonstrated by equations (16) and (17). In this case, the computed value of ΔG_{1018}^{7200} for equation (15) is 1042 cal [*i.e.*, -896 cal $-$ (-1938 cal)], and for K_D (Fe/Mg; cpx–opx) a value of 0.60 is obtained. Thus I conclude that only the *difference* in calculated ΔG_T^P values for equations (2) and (11) can truly be tested by the above method, and *not* their absolute values.

Applications to geothermometry

Garnet–clinopyroxene

Measured ln K_D (Fe/Mg; gar–cpx) and calculated *sum*(X) values from Table 5 are plotted in Figure 6. The line representing garnet–clinopyroxene pairs from the Kelly area defines a 745°C isotherm. Because the Carter Creek samples plot at significantly higher K_D than the Kelly samples at equivalent *sum*(X) values, the former probably represent part of a lower-temperature isotherm. This conclusion is consistent with (1) the known divergence of K_D (Fe/Mg; gar–cpx) from unity with declining temperature (*e.g.*, see Banno, 1970, and Råheim and Green, 1974) and (2) the lower peak temperature estimate of 675±45°C inferred for the Carter Creek area by Dahl (1979).

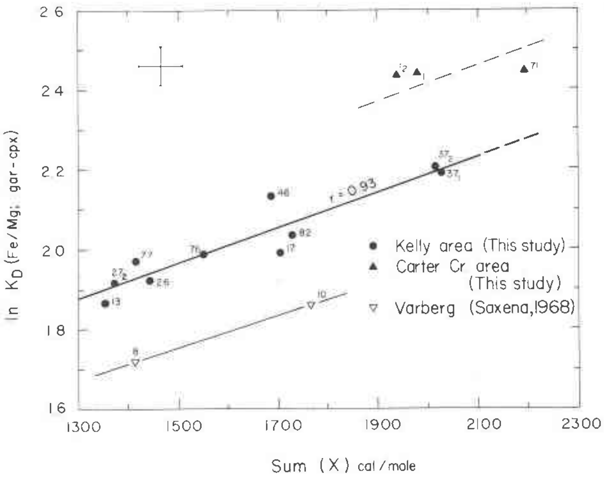

Fig. 6. Variations in ln K_D(Fe/Mg; gar–cpx) as a function of *sum*(X) [as defined in equation (10)] for gar–cpx pairs in samples from the Ruby Range and from Varberg, Sweden (Saxena, 1968; only unzoned samples plotted). Kelly and Carter Creek samples define two distinct isotherms for the Ruby Range, with the Carter Creek samples indicating the lower apparent temperature (higher K_D). K_D = $(\text{Fe/Mg})^{\text{Gar}}/(\text{Fe/Mg})^{\text{Cpx}}$. Total Fe used to calculate K_D except for sample RMC-71, whose garnets contain relatively high Fe^{3+}. Cross in upper left represents uncertainties (2σ) in the data points for sample RMK-37; uncertainties in all other Ruby Range data points are smaller.

Similar reasoning suggests that the charnockites from Varberg, Sweden (Saxena, 1968), reached metamorphic temperatures higher than the 745±50°C for the Kelly area. Indeed, Saxena (1976, p. 651) has estimated temperatures of 801±60°C for the Varberg area, using pyroxene geothermometry.

Because the Carter Creek, Kelly, and Varberg garnet–clinopyroxene pairs define isotherms or parts of isotherms whose temperatures have been independently estimated, Figure 6 provides the basis for geothermometry in other upper-amphibolite to granulite facies terrains. As more chemical data from other localities become available, additional isotherms can be added to Figure 6.

Reconstruction (not shown) of Figure 6, using instead Ganguly's (1979) mixing parameters for garnet, results in no change in the relative positions of isotherms and data points shown.

Figure 6 illustrates the marked effects of composition on K_D (Fe/Mg; gar–cpx) and underscores the danger inherent in the application of any mineral-pair geothermometer without due consideration of this potential complication. For example, routine application of Råheim and Green's (1974) calibrated garnet–clinopyroxene geothermometer to the Kelly area results in temperatures ranging from 653°C [low K_D, low *sum*(X)] down to 584°C [high K_D, high *sum*(X)]. These estimates are low and falsely indicate variations in peak temperature for the Kelly area. Application of this calibration to the Kelly area is valid only if, along the Kelly isotherm, a range of K_D values is chosen that corresponds to the range of *sum*(X) values characteristic of Råheim and Green's experimentally-derived garnets. Their chemical analyses indicate a *sum*(X) value of 379±200 cal/mole (95 percent confidence limits), which, upon substitution into the line equation for the Kelly isotherm

$$\ln K_D = 0.00044\, sum(X) + 1.30010 \qquad (18)$$

yields a compositionally corrected K_D value of 4.34±0.40. This value, in turn, when applied to Råheim and Green's calibration, gives a temperature estimate of 752±44°C (at $P = 7200 \pm 1200$ bars) for the Kelly area. This estimate is concordant with the independent estimate of 745±50°C reported earlier. Thus, by correcting for compositional effects on K_D, a reliable temperature estimate is obtained. Clearly, the application of this technique to other localities requires samples sufficient to define adequately an isothermal line equation.

Yet a third approach to geothermometry involves solution of equation (10) for T. A pressure term can be incorporated by first evaluating the volume term in equation (14), using garnet–clinopyroxene volume data from Takahashi and Liu (1970) and Rutstein and Yund (1969). For a load pressure of 7200 bars (Kelly area), the volume term for the Fe–Mg exchange reaction [equation (2)] equals −158 cal. Thus, included in the calculated ΔG^{7200}_{1018} value of −2482 cal is −2324 cal (ΔG°_T) and a volume term of −158 cal [*i.e.*, $-0.022P$(bars) for the Kelly area]. Equation (10) can now be rewritten in the form

$$T(^\circ\mathrm{K}) = [2324 + 0.022P(\mathrm{bars}) + 1509(X^{\mathrm{Gar}}_{\mathrm{Fe}} - X^{\mathrm{Gar}}_{\mathrm{Mg}}) + 2810(X^{\mathrm{Gar}}_{\mathrm{Ca}}) + 2855(X^{\mathrm{Gar}}_{\mathrm{Mn}})]/(1.987 \ln K_D) \qquad (19)$$

Recent gar–cpx geothermometers of Ganguly (1979) and Saxena (1979) work very well for peridotites, high-temperature eclogites, and upper-granulite facies rocks. However, both methods yield temperatures for the Kelly and Carter Creek areas that are significantly higher than the consensus estimates reported earlier (see Table 7). Equation (19) may find general application to (1) upper-amphibolite and lower-granulite facies rocks in which pyroxenes are low in Na and Al and (2) rocks that are high in Mn. Reliable application of equation (19) to other localities is based upon the assumption that ΔG°_T is nearly constant over a broad temperature range. This assumption is reasonable because (1) the heat capacity integrals in equation (14) virtually cancel out, regardless of temperature, and (2) the value of ΔS°_{298} for equation (2) is nearly zero; a value of +1.013 cal/°K is obtained using S°_{298} data from Robie *et al.* (1978)

Table 7. Peak metamorphic temperature estimates for the Ruby Range

Sample	Ganguly (1979) T°C	Saxena (1979) T°C	this paper (eqn. 10) T°C	Råheim and Green (1974) T°C	
RMK-27$_2$	811	809	739	643	Kelly area
RMK-13	832	792	760	653	
RMK-17	833	827	785	627	
RMK-77	810	812	723	632	
RMK-26	827	800	755	641	
RMK-76	803	791	749	628	
RMK-82	799	803	769	618	
RMK-46	791	836	710	598	
RMK-37$_2$	809	790	753	584	
RMK-37$_1$	811	795	763	587	
mean T =	813±14	806±16	751±22	621±24	
RMC-71	811	671	685	536	Carter Creek area
RMC-1$_1$	761	671	643	536	
RMC-1$_2$	764	674	636	537	
mean T =	779±28	672±2	655±27	536±1	

Equation (18) yields an independent temperature estimate of 752±22°C for the Kelly area. Consensus estimates for the Ruby Range are 745±50°C (Kelly) and 675±45°C (Carter Creek). (Dahl, 1979).

and Helgeson *et al.* (1978). If this value is correct, then a 100°K change in temperature results in only a 101 cal (or 4.6 percent) change in ΔG_T° (= −2324 cal).

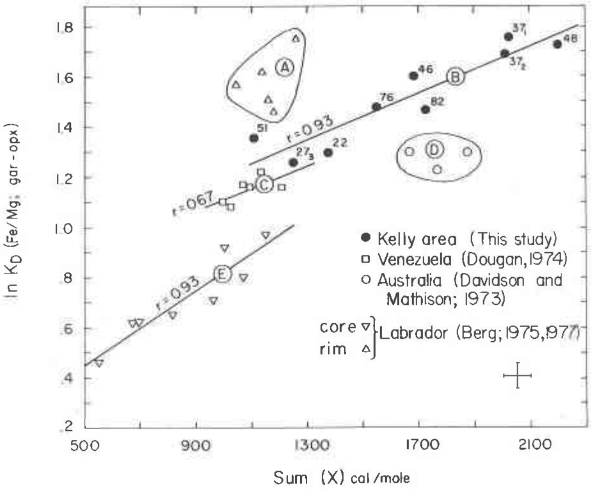

Fig. 7. Dependence of K_D(Fe/Mg; gar–opx) on *sum*(X) [as defined in equation (13)] for garnet–orthopyroxene pairs from several localities. Labeled lines delineate trends for each locality. Lines B, C, and E represent distinct isotherms; groups A and D represent parts thereof (see text). Lower K_D isotherms probably represent higher metamorphic temperatures. K_D = $(Fe/Mg)^{Gar}/(Fe/Mg)^{Opx}$. Ruby Range samples are all from the Kelly area except for sample RMS-22, which is from Stone Creek. Total Fe was used in the K_D calculations for Labrador and Ruby Range samples, except for sample RMK-48. All other K_D values were corrected for Fe^{3+} in the published analyses. Cross in lower right represents uncertainties (2σ) in the data point for sample RMK-48; uncertainties in all other data points in line B are smaller.

Garnet-orthopyroxene

Measured ln K_D (Fe/Mg; gar–opx) and calculated *sum*(X) values for garnet–orthopyroxene pairs from the Kelly area (Table 6) and other localities are plotted in Figure 7. The relative positions of the data points representative of these localities should, in principle, permit tentative determination of their relative metamorphic temperatures. Line B represents the Kelly isotherm (745±50°C). Line C is an isotherm defined by compositions in garnet–orthopyroxene–cordierite gneisses from a 43-km² area in the Guayana Shield region, Venezuela (Dougan, 1974). The proximity of lines B and C suggests little or no temperature difference between the Kelly and Venezuelan localities. On the basis of several geothermometers, Dougan inferred a metamorphic temperature of 760±40°C for the Venezuelan locality, which indeed is concordant with estimates for the Kelly area.

The three points comprising group D in Figure 7 define part of an isotherm for highly metamorphosed iron-formations from a small area near Quairading, Western Australia (Davidson and Mathison, 1973). Group D plots at significantly lower ln K_D than line B, suggesting that peak temperatures in the Quairading area exceeded 745°C. To test this conclusion, coexisting pyroxenes from the two localities are compared in the pyroxene quadrilateral shown in Figure 8. The Quairading pyroxenes plot at a higher temperature (*ca.* 800°C) on the pyroxene solvus than those from the Kelly area. Thus, two independent methods result in the same relative temperature estimate for the two localities.

Line E in Figure 7 represents core compositions for garnet–orthopyroxene–cordierite-bearing anorthosites from a 10000-km² area in the Nain Province, Labrador (Berg, 1975, 1977). The eight samples included in Figure 7 represent those for which Berg obtained his highest (concordant) garnet–cordierite and garnet–biotite temperatures—858±60°C. Lines E and B barely overlap, so that thermal comparison of the Kelly and Nain areas is possible only at *sum*(X) values near 1100 cal/mole. The lower ln K_D for line E at this *sum*(X) is consistent with the higher temperatures inferred by Berg for the Nain area.

The five scattered points labelled group A in Figure 7 represent rim compositions for some of the eight high-temperature Nain samples. Berg concluded, on the basis of antithetic Fe–Mg profiles at grain edges of both garnets and coexisting orthopyroxenes, that the rim K_D values reflect retrograde metamorphic conditions; for these conditions, he estimated temperatures in the range of 547±25°C. It is not surprising, therefore, that the group A data points cluster well above all isotherms in Figure 7.

Reconstruction (not shown) of Figure 7, using instead Ganguly's (1979) mixing parameters for garnet, results in no change in the relative positions of isotherms and data points shown, although the slope for line E parallels the other lines better.

The ΔG_T° component of ΔG_T^P in equation (13) is not constant over a broad range of temperature, inasmuch as a ΔS_{298}° value of +13.9 cal/°K is obtained for equation (13), using S_{298}° data from Robie *et al.* (1978) and Helgeson *et al.* (1978). This shortcoming precludes the use of equation (13) as an absolute geothermometer, but does not affect the use of K_D (Fe/Mg; gar–opx) as a relative geothermometer, as in Figure 7.

Limitations

Figures 6 and 7 represent attempts to normalize the compositional effects on ln K_D (Fe/Mg; gar–cpx) and ln K_D (Fe/Mg; gar–opx) so that meaningful geothermometry can be done. However, there are several limitations inherent in their application. First, thermal comparisons between areas may be invalid unless their respective isotherms (or portions thereof) overlap in *sum*(X) values. Thus in Figure 7 direct comparison of lines C or E with group D is not advisable.

Second, in both figures the effects of load pressure P on ln K_D are ignored. All samples plotted in these figures were metamorphosed to pressures in the range 4.5–8.5 kbar, according to estimates available from the literature. Råheim and Green's (1974) experiments suggest that an increase in P from 4.5 to 8.5 kbar results in a 4 percent increase in ln K_D (Fe/Mg; gar–cpx) at 750°C. Thus, normalization for pressure effects in Figures 6 and 7 may result in slight shifts among the isotherms, but these shifts are probably not significant enough to alter the relative temperatures inferred earlier.

Third, and perhaps most important, the reliability of Figures 6 and 7 is contingent on the inherent correctness of the respective thermodynamic models [*i.e.,* equations (10) and (13)]. Although the models do account for most of the variance in RT ln K_D observed for the Montana garnet–pyroxene pairs, they do not account for the possible effects of variable Fe^{3+} in garnet or variable Na, Al, Ca, or Mn in pyroxene; nor do they account for the non-ideality of mixing between Fe and Mg in pyroxene *M1–M2*

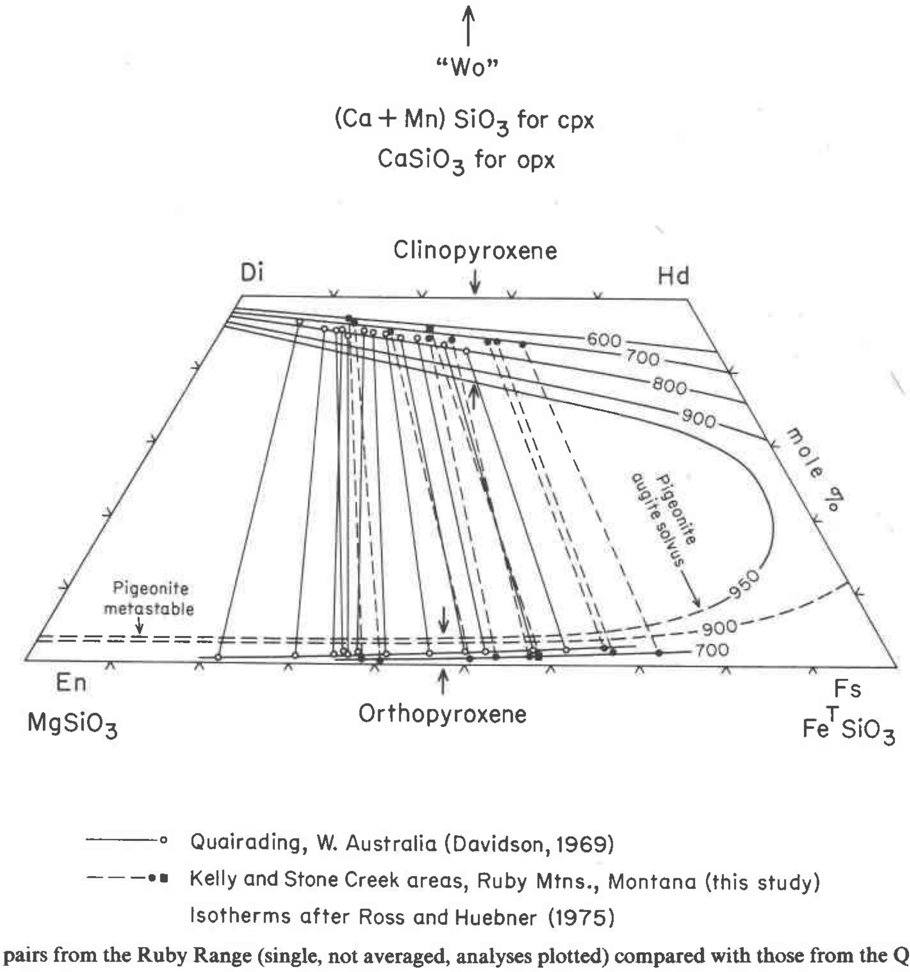

Fig. 8. Pyroxene pairs from the Ruby Range (single, not averaged, analyses plotted) compared with those from the Quairading district of Western Australia (Davidson, 1969). Superimposed is the experimentally-determined pyroxene solvus of Ross and Huebner (1975). It is assumed that Ca and Mn occupy the *M2* site of clinopyroxene; the relative position of the two curves is not changed, however, if Mn is plotted with Fe^T (total iron) instead of with Ca. Ross and Huebner place a ±100°C uncertainty on temperatures estimated by their method.

sites. These limitations can be removed only when larger data bases incorporating broad variations in diverse components are studied. Such data bases are most likely to be found in highly metamorphosed terrains containing garnet–pyroxene pairs in diverse lithologies.

Conclusions

The Ruby Range, southwestern Montana, has been used as a natural laboratory to model the *P–T–X* dependences of garnet-pyroxene K_D (Fe/Mg) values. The major conclusions of this study are summarized below.

(1) Petrographic and geothermometric data indicate that peak metamorphic *P–T* conditions for the Kelly and Carter Creek areas were 7.2±1.2 kbar, 745±50°C and 6.2±1.2 kbar, 675±45°C, respectively.

(2) The excellent correlation between measured garnet–clinopyroxene K_D values and those predicted using Ganguly's (1979) garnet mixing parameters (Table 3) supports the general validity of his parameters and confirms the temperature difference inferred between the Kelly and Carter Creek areas. The correlation also indicates that within a given area, garnet–pyroxene pairs in diverse lithologies last equilibrated at the same or nearly the same temperature.

(3) Garnet–pyroxene K_D (Fe/Mg) values are highly dependent on composition—particularly on X^{Gar}_{Mn} and X^{Gar}_{Ca}. Meaningful geothermometry, therefore, requires that such compositional effects be taken into account, such as is done in equations (9), (10), (13), (18), and (19), and in Figures 6 and 7.

(4) Multiple linear regression of the Ruby Range data base in conjunction with known temperatures of metamorphism yields new and internally consistent values of $\Delta G^{6200-7200}_{948-1018}$ for Fe^{2+}–Mg exchange reactions involving garnet–clinopyroxene [equation (2)], garnet–orthopyroxene [equation (11)], and clinopyroxene–orthopyroxene [equation (15)]. Because all three values are much closer to zero than values obtained using thermochemical data from Robie *et al.* (1978), Helgeson *et al.* (1978), and Zen (1973), they are more compatible with the known dependences of K_D values on temperature.

The regression also yields new values for the garnet mixing parameters (Table 4). These results corroborate those reported by Ganguly (1979), except that the w_{FeMg} inferred in my study is intermediate to Ganguly's and O'Neill and Wood's (1979) values. This discrepancy may reflect a temperature dependence for this parameter.

(5) Equation (19) may be applied as a geothermometer to upper-amphibolite and lower-granulite facies rocks or to rocks high in Mn. Both Ganguly's (1979) and Saxena's (1979) garnet–clinopyroxene thermometers yield high temperatures for such rocks (Table 7), although they appear to work extremely well for eclogites, peridotites, and upper-granulite facies rocks.

(6) Larger data bases from the Ruby Range and other terrains are required in order to evaluate the possible effects on K_D of components other than those considered in this study. Such components include Fe^{3+} in garnet and Na, Al, Ca, and Mn in pyroxene. Also, an accounting for the non-ideal mixing of Fe and Mg in pyroxene *M1–M2* sites is desired. Despite these omissions, the thermodynamic models presented in this paper explain up to 89 percent of the variance actually observed in K_D (Fe/Mg) values for garnet–pyroxene-bearing mafic gneisses and iron-formations from the Ruby Range.

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