

Fe-Mg mixing in cordierite: Constraints from natural data and implications for cordierite-garnet geothermometry in granulites

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ABSTRACT

From chemical data on 108 pairs of naturally occurring garnet and cordierite, the interchange energy of Fe-Mg mixing in cordierite ($W_{\text{Fe-Mg}}$) and the free-energy change of the exchange equilibrium $\frac{1}{3}\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \frac{1}{2}\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18} = \frac{1}{3}\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \frac{1}{2}\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ in the temperature range of 700–850 °C have been extracted using standard methods of linear regression analysis. The input thermochemical parameters for multicomponent Ca-Mg-Fe-Mn garnet solid solutions are based on the updated and revised values after Ganguly and Saxena (1984), e.g., $W_{\text{Fe-Mg}} = 2500$ cal, $W_{\text{Ca}} = W_{\text{Mn}} = 3000$ cal calculated on the basis of one-third formula unit. On the basis of the derived values at 710, 760, 800, and 850 °C, Fe-Mg mixing in cordierite has been approximated to a symmetric regular solution. The Fe-Mg substitution shows positive deviation from ideality in cordierite, with $W_{\text{Fe-Mg}}^{\text{crd}} = 9.34 \pm 4.54$ kJ/mol of divalent cation. The values derived for the free energy of mixing, at $X_{\text{Fe}}^{\text{crd}} = X_{\text{Mg}}^{\text{crd}} = 0.5$, are -3.26 kJ at 700 °C and -4.39 kJ at 900 °C. The $\Delta G_{1,T}$ value (in joules) for the above equilibrium can be expressed as $15079 - 8.55T$. Incorporating these parameters, the geothermometric expression for the exchange equilibrium is

$$T = \frac{1814 + 0.0152P + 1122(X_{\text{Mg}}^{\text{crd}} - X_{\text{Fe}}^{\text{crd}}) - 1258(X_{\text{Mg}}^{\text{gt}} - X_{\text{Fe}}^{\text{gt}}) + 1510(X_{\text{Ca}}^{\text{gt}} + X_{\text{Mn}}^{\text{gt}})}{1.028 - \ln(X_{\text{Fe}}/X_{\text{Mg}})^{\text{crd}}/(X_{\text{Fe}}/X_{\text{Mg}})^{\text{gt}}},$$

where T is in kelvins and P is in bars. When applied to natural assemblages, the predicted temperatures, over the wide compositional range $0.38 < X_{\text{Mg}} < 0.92$, are found to be from 620 °C to 860 °C—a reasonable span for granulite-facies rocks. Although the “accuracy” of the computed T values is of the order of ± 65 °C, the “precision” of the proposed geothermometer is higher by 30% to 60% than for earlier calibrations. The refinement in the mixing models of cordierite and garnet results in temperatures that are more reliable than those from the earlier formulations postulating ideal mixing in both phases.

INTRODUCTION

The T - X dependence of Mg-Fe partitioning between coexisting garnet and cordierite has been a subject of much debate. Experimental studies on the exchange equilibrium yield contradictory results regarding the nature of the T vs. $\ln K_D$ slope (Currie, 1971, 1974; Hensen and Green, 1973; Holdaway, 1976; Perchuk and Lavrent'eva, 1983). This contradiction has been often attributed to difficulties in attaining equilibrium and determining compositional homogeneity of the phases from hydrothermal runs. On the other hand, studies based on natural samples show that $\ln K_D$ decreases with increasing temperature (Thompson, 1976; Holdaway and Lee, 1977).

It is important to note that the existing formulations of the cordierite-garnet thermometer assume ideal mixing in both phases. Natural and experimental studies on multicomponent Ca-Mg-Fe-Mn garnets indicate departure from ideality at granulite P - T conditions. Regarding mixing in binary Mg-Fe cordierites, no unequivocal inferences have emerged from experimental studies and phase-equilibrium relations. As a consequence, in our attempt

to refine the cordierite-garnet thermometer, we were prompted to examine compositional data from naturally occurring cordierite-garnet pairs in search of evidence on the nature of Fe-Mg mixing in cordierite. The present communication is directed toward an analysis of the energetics of Fe-Mg mixing in cordierite with the ultimate goal of refining the cordierite-garnet geothermometer.

THEORETICAL CONSIDERATIONS

The equilibrium conditions at P and T for the reaction



can be written as

$$0 = \Delta G_{1,T} + P\Delta V + RT \ln K_D + RT \ln(\gamma_{\text{Mg}}/\gamma_{\text{Fe}})^{\text{gt}} + RT \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{crd}} \quad (1)$$

where $K_D = (X_{\text{Fe}}/X_{\text{Mg}})^{\text{crd}} / (X_{\text{Fe}}/X_{\text{Mg}})^{\text{gt}}$. X_i^p and γ_i^p are the mole fraction and activity coefficient of component i in phase p . $\Delta G_{1,T}$ denotes the free-energy change of the reaction at 1 bar and T (in kelvins) and can be expressed

as $\Delta H - T\Delta S$. ΔV is the volume change of the exchange reaction at 298 K and 1 bar. It is assumed that the hydration of cordierite is independent of $(X_{\text{Fe}}/X_{\text{Mg}})$ in cordierite (cf. Thompson, 1976; Lonker, 1981). Ganguly and Kennedy (1974) have used the expression $RT \ln(\gamma_i/\gamma_j) = W_{ij}(X_j - X_i) + (W_{ik} - W_{jk})X_k$ for multicomponent $(\text{Fe}, \text{Mg}, \text{Mn}, \text{Ca})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ garnets that follow the "simple mixture model" (Guggenheim, 1967). However, there is little unanimity regarding the magnitude of the binary interaction parameters, especially in the $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ join. From a review of available experimental and natural data, Ganguly and Saxena (1984) proposed that the expression

$$RT \ln(\gamma_{\text{Mg}}/\gamma_{\text{Fe}})^{\text{gt}} = 2500(X_{\text{Fe}} - X_{\text{Mg}}) + 3000(X_{\text{Ca}} + X_{\text{Mn}}) \quad (2)$$

adequately describes the activity-composition relations in the almandine-pyropite binary join in quaternary garnet solid solutions. In the present communication, we have adopted their formulation.

The composition of cordierites coexisting with garnets is represented by the two end members $\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ and $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$. The small amounts of Mn in cordierites (<1 mol%) have been neglected. The previous workers assumed an ideal-solution model for cordierites. If the Fe-Mg substitution is nonideal (as is known to be true for many silicates), in the simplest case, i.e., a random mixing approximation, the binary can be treated as a regular solution where the activity coefficient is related to the mole fraction as

$$\ln \gamma_i = W/[RT(1 - X_i)^2]. \quad (3)$$

In the absence of any thermochemical determination, the adjustable energy parameter, $W_{\text{Fe-Mg}}^{\text{rd}}$ has been taken to be independent of temperature and pressure, i.e., the entropy change for excess mixing, $S_m^{\text{e}} = 0$ (Guggenheim, 1967; Saxena, 1973). From these considerations, we derive, for the last term in Equation 1,

$$RT \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{rd}} = W_{\text{Fe-Mg}}^{\text{rd}}(X_{\text{Mg}}^{\text{rd}} - X_{\text{Fe}}^{\text{rd}}). \quad (4)$$

Substituting Equations 2 and 4 in 1 and transposing, one obtains

$$\Delta G_{1,T} + W_{\text{Fe-Mg}}^{\text{rd}}(X_{\text{Mg}}^{\text{rd}} - X_{\text{Fe}}^{\text{rd}}) = \phi \quad (5)$$

where $\phi = -P\Delta V + RT \ln K_D + 2500(X_{\text{Fe}}^{\text{gt}} - X_{\text{Mg}}^{\text{gt}}) + 3000(X_{\text{Ca}}^{\text{gt}} + X_{\text{Mn}}^{\text{gt}})$. It is evident that a plot of $(X_{\text{Mg}}^{\text{rd}} - X_{\text{Fe}}^{\text{rd}})$ vs. ϕ in Equation 5 would yield a straight line if $W_{\text{Fe-Mg}}^{\text{rd}}$ is independent of composition at an assumed T . The slope of the straight line is a measure of $W_{\text{Fe-Mg}}^{\text{rd}}$ and its intersection at $(X_{\text{Mg}}^{\text{rd}} - X_{\text{Fe}}^{\text{rd}}) = 0$ yields ΔG at T . It is important to note that if the Fe-Mg binary in cordierite is asymmetric and W is dependent on composition, a nonlinear plot should result.

SELECTION OF SAMPLES

In order to extract reliable data on ΔG and W , it is necessary to (1) consider only those samples that have compositional homogeneity and are thought to represent

equilibrium conditions; (2) evaluate correctly the temperatures of equilibration; (3) have a large spread in terms of $(X_{\text{Mg}}^{\text{rd}} - X_{\text{Fe}}^{\text{rd}})$, which would minimize errors in statistical analyses and extrapolations thereof; and (4) determine the pressure effect with reasonable accuracy. For a few samples reported to have zoned garnet and cordierite, the core compositions were used in the computations.

With these criteria in view, 108 pairs of analyses of coexisting cordierites and garnets were scrutinized in the first phase. The geographic distribution is as follows: Nain Complex—16 (Berg, 1977); South India—9 (Harris and Jayaram, 1982; Harris et al., 1982); Snyder Group, Kiglapait—12 (Speer, 1982; unpub. data); Scottish Caledonides—7 (Ashworth and Chinner, 1978); Egersund-Ogna—6 (Henry, 1974); Ganoque area, Ontario—5 (Reinhardt, 1968); Lilesville pluton—6 (Evans and Speer, 1984); Liberty Hill pluton—8 (Speer, 1981); central Massachusetts—4 (Tracy et al., 1976); Limpopo belt—4 (van Reenen and du Toit, 1975); Daly Bay Complex—3 (Hutcheon et al., 1974); Inari Complex—12 (Ackermann, cited in Newton, 1983); Frontenac axis—5 (Lonker, 1980); Namaqualand—4 (Clifford et al., 1981); Hara Lake—4 (Kays and Medaris, 1976); Enderby Land and Gage Ridge—3 (Ellis et al., 1980; Grew, 1982a). Among these, the analytical data of the Daly Bay Complex, Ganoque area, Hara Lake, and Egersund-Ogna region were not considered. First, the P and T of equilibration for these areas had been determined from cordierite-garnet systematics, and independent estimates of P and T were not available. Second, most of the analyses were done by wet-chemical methods. Furthermore, the four sets of analysis from zone IV of central Massachusetts were not considered owing to the absence of an independent check on the P and T values (680 °C and 6.4 kbar) advocated by Tracy et al. (1976). Also, there are not enough data to constrain Equation 5 at this temperature.

Samples from all other areas were then classified into four groups, depending on their temperature of equilibration, e.g., 685–730 °C, 730–780 °C, 780–825 °C, and 825–875 °C. These values were advocated on the basis of convergence of phase-equilibrium relations reported by the respective authors and correspond to natural clusters observed in the spread of temperatures. It is important to note that these temperatures exclude those obtained from cordierite-garnet thermometry and avoid, as far as possible, biotite-garnet thermometry owing to problems of Al and Ti solubility in biotites (Ferry and Spear, 1978; Ganguly and Saxena, 1984; Indares and Martignole, 1985). In some cases, the temperatures so estimated from petrogenetic grids show a large spread across these well-defined clusters; for these samples, independent temperature estimates from orthopyroxene-garnet and clinopyroxene-garnet thermometry were made from spatially associated quartzofeldspathic and mafic rocks. For example, the temperature for the granulites of South India, Inari Complex, and Antarctica were determined from these thermometers. Analytical data that did not meet these requirements were discarded.

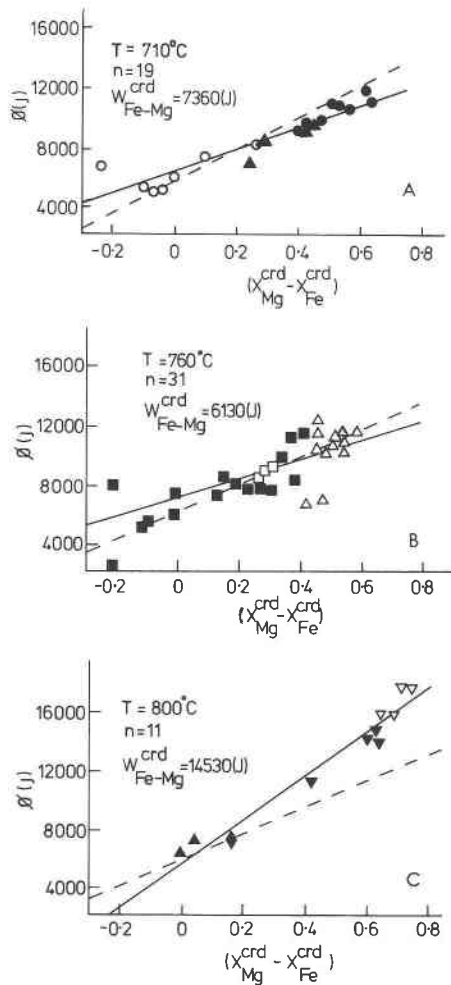


Fig. 1. Relation between ϕ and $(X_{Mg}^{crd} - X_{Fe}^{crd})$ at three different temperatures. Symbols: \circ —South India; \blacktriangle —Scottish Caledonides; \bullet —Snyder Group (zone III); \triangle —Finnish Lapland; \blacksquare —Nain Complex; \square —Lillesville pluton; \blacklozenge —Snyder Group (border breccia); \blacktriangledown —Enderby Land; ∇ —Namaqualand.

Some ambiguity remains regarding the 13 pairs of garnet and cordierite analyses in the temperature range of 825–875 °C. For the eight pairs of cordierite-garnet from xenoliths in the innermost aureoles at Liberty Hill, no estimates from phase-equilibrium relations are available. Although temperatures of 825 ± 119 °C (Ferry and Spear, 1978) and 911 ± 125 °C (Goldman and Albee, 1977) are predicted, Spear (1981) argued that at such high temperatures, aluminous orthopyroxene-bearing assemblages are expected to be stable. Hence the “real” temperatures of equilibration are presumably lower. Similar problems affect the temperature estimates of the three samples from the Antarctica granulites. The “consensus” temperature values for this area lie between 850 and 900 °C, but according to Grew (1982b), these cordierites are secondary; therefore, the cordierite-garnet paragenesis possibly bears a lower P - T imprint. Harley (1985) has estimated tem-

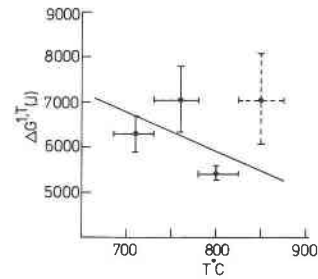


Fig. 2. Dependence of ΔG on T . (Bars represent the uncertainty, expressed as $\pm 1\sigma$).

peratures of 650–700 °C for the Enderby Land rocks from cordierite-garnet and biotite-garnet geothermometers.

REGRESSION ANALYSES

Figure 1 depicts the variations of $(X_{Mg}^{crd} - X_{Fe}^{crd})$ vs. ϕ (in joules) at the three temperatures 710, 760, and 800 °C that represent the median values of the ranges chosen. It is evident that within the limits of uncertainty, the plots can be adequately described to be linear at each T value. The linear regression analysis, based on the analytical data (Table 1) has been carried out following the standard method of least squares. The confidence interval of the random variable has been computed by assuming a t distribution with $n - 2$ degrees of freedom (Cramer, 1963; Kreyszig, 1971). The computed values are presented in Table 2. The straight line fit at 850 \pm 25 °C is not shown owing to the large scatter of the sample population. This is evident from the generally higher level of uncertainty associated with the computed values of ΔG and W (Table 2).

A straight line fit to the ΔG values at 710, 760, and 800 °C yields the following expression: $\Delta G_{1,T} = 15079 - 8.55T$ (where ΔG is in joules) for the exchange equilibrium (Fig. 2). The derived values for the change in entropy ($8.55 \text{ J} \cdot \text{K}^{-1}$) and enthalpy (15079 J) compare favorably with those computed by others (Thompson, 1976; Holdaway and Lee, 1977; Perchuk and Lavrent'eva, 1983). It may be noted that the free-energy change of the reaction at 850 °C, extrapolated from the relation above, is 5481 J; this value is just outside the lower limit of the ΔG value obtained from the statistical analysis.

The results of our calculation suggest a symmetric, positive deviation from ideality along the $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ - $\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ join. Even if the limits of uncertainties are considered, there are real differences in the magnitude of $W_{\text{Fe-Mg}}^{crd}$. This could possibly indicate the influence of temperature on the interaction parameter. In the present study, the influence of temperature has been neglected and an average value of 9.34 ± 4.54 kJ/mol of divalent cation adopted. The weighted average of the binary interaction parameter for the Fe-Mg mixing in cordierites turns out to be 8.71 kJ; however, as the difference is small, 9.34 kJ has been used in the computations. Using this value, the various Fe-Mg mixing parameters of cordierite have been calculated and depicted in Figure 3.

TABLE 1. Analytical data used in the regression analyses

Area	Sample	Cordierite		Garnet				Assumed T (°C)	Assumed P (kbar)
		X _{Fe}	X _{Mg}	X _{Fe}	X _{Mg}	X _{Ca}	X _{Mn}		
South India	732	0.183	0.817	0.492	0.404	0.046	0.058	710	6.0
	601	0.221	0.779	0.586	0.326	0.030	0.059	710	6.0
	731	0.189	0.811	0.576	0.347	0.041	0.036	710	6.0
	P-3	0.237	0.763	0.643	0.301	0.030	0.026	710	6.0
	104°	0.242	0.758	0.638	0.326	0.023	0.013	710	6.0
	107°	0.298	0.702	0.664	0.259	0.053	0.023	710	6.0
	110°	0.363	0.637	0.747	0.196	0.037	0.020	710	6.0
	112°	0.264	0.736	0.661	0.288	0.031	0.020	710	6.0
	114°	0.284	0.716	0.673	0.296	0.020	0.010	710	6.0
	Scottish Caledonides	105765	0.363	0.637	0.760	0.210	0.030	—	710
105557		0.285	0.715	0.664	0.274	0.038	0.025	710	5.5
105570		0.269	0.731	0.649	0.254	0.054	0.043	710	5.5
189°		0.379	0.621	0.707	0.236	0.040	0.017	710	5.5
Snyder Group (Kiglapait)	SN-211	0.498	0.501	0.822	0.155	—	0.024	710	4.0
	SN-263	0.617	0.383	0.899	0.077	—	0.024	710	4.0
	SN-287	0.548	0.452	0.851	0.137	—	0.012	710	4.0
	SN-288	0.456	0.544	0.831	0.155	—	0.014	710	4.0
	SN-309	0.533	0.467	0.835	0.155	—	0.010	710	4.0
	SN-374	0.531	0.469	0.831	0.143	—	0.026	710	4.0
Inari Complex	194 III	0.270	0.730	0.632	0.323	0.032	0.013	760	5.0
	162 II	0.233	0.767	0.603	0.358	0.029	0.010	760	5.0
	161 I	0.260	0.740	0.649	0.319	0.024	0.008	760	5.0
	158 I	0.233	0.767	0.622	0.350	0.022	0.006	760	5.0
	158 II	0.270	0.730	0.701	0.263	0.030	0.006	760	5.0
	89 V	0.226	0.774	0.531	0.427	0.032	0.010	760	5.0
	93 VI	0.271	0.729	0.642	0.298	0.038	0.020	760	5.0
	24 II	0.289	0.711	0.730	0.217	0.027	0.023	760	5.0
	177 I	0.228	0.772	0.576	0.374	0.036	0.014	760	5.0
	110 III	0.206	0.794	0.540	0.426	0.028	0.006	760	5.0
	119 I	0.244	0.756	0.592	0.374	0.028	0.006	760	5.0
Lillesville pluton	LV-31	0.349	0.651	0.719	0.224	0.027	0.031	760	5.5
	S-7-38	0.356	0.644	0.714	0.222	0.031	0.033	760	5.5
	S-7-38A	0.346	0.654	0.722	0.218	0.028	0.032	760	5.5
	LV-38	0.501	0.499	0.681	0.079	0.026	0.212	760	5.5
Nain Complex	2-1729	0.605	0.395	0.813	0.069	0.032	0.067	760	3.5
	KI-3557	0.555	0.445	0.810	0.140	0.040	0.010	760	3.5
	74-980	0.492	0.508	0.835	0.147	0.011	0.008	760	3.5
	2-893	0.436	0.564	0.765	0.188	0.027	0.019	760	3.5
	2-1637	0.406	0.594	0.736	0.207	0.034	0.024	760	3.5
	2-1726	0.404	0.596	0.775	0.172	0.027	0.026	760	3.5
	2-1578	0.386	0.614	0.721	0.244	0.025	0.009	760	3.5
	2-1572	0.362	0.638	0.672	0.292	0.025	0.011	760	3.5
	2-1480	0.360	0.640	0.678	0.285	0.024	0.012	760	3.5
	NK-420B	0.330	0.670	0.712	0.224	0.042	0.021	760	3.5
	2-275	0.315	0.685	0.718	0.231	0.033	0.016	760	3.5
	2-1455	0.311	0.689	0.623	0.335	0.030	0.013	760	3.5
	NU-69	0.296	0.704	0.710	0.213	0.041	0.035	760	3.5
	LRD-72-01	0.241	0.759	0.618	0.347	0.030	0.004	760	3.5
	KI-3909	0.506	0.494	0.795	0.163	0.027	0.015	760	3.5
	2-625	0.425	0.575	0.793	0.165	0.024	0.017	760	3.5
Scottish Caledonides	82891	0.478	0.522	0.772	0.154	0.035	0.039	800	5.5
	99376	0.499	0.501	0.754	0.149	0.043	0.053	800	5.5
Snyder Group (Kiglapait)	SN-175	0.120	0.580	0.731	0.230	—	0.039	800	4.0
Limpopo belt	DR-10	0.132	0.868	0.593	0.355	0.039	0.013	800	7.5
	DR-19	0.157	0.843	0.586	0.378	0.027	0.008	800	7.5
	DR 73	0.179	0.821	0.644	0.306	0.037	0.013	800	7.5
	DR 54	0.139	0.861	0.550	0.408	0.029	0.014	800	7.5
Namaqualand	46	0.274	0.276	0.610	0.368	0.006	0.016	800	7.7
	47A	0.182	0.818	0.585	0.383	0.018	0.015	800	7.7
	47B	0.194	0.806	0.637	0.344	0.018	—	800	7.7
	47	0.184	0.816	0.631	0.349	0.014	0.006	800	7.7

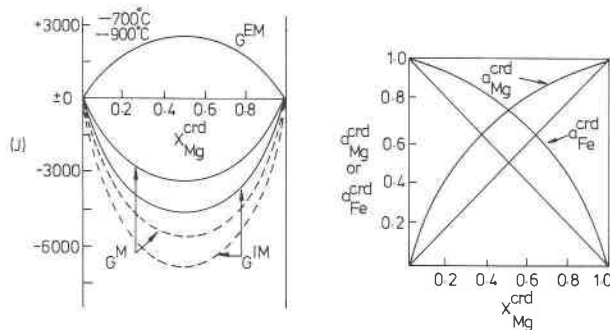


Fig. 3. Mixing parameters in Fe-Mg cordierites: G^M = free energy of mixing, G^{IM} = free energy of ideal mixing, G^{EM} = excess free energy of mixing.

COMPARISON WITH EXPERIMENTAL RESULTS

The ΔG and W_{Fe-Mg} values derived here may be incorporated into Equation 1 to obtain the geothermometric expression

$$T = \frac{1814 + 0.0152P + 1122(X_{Mg}^{crd} - X_{Fe}^{crd}) - 1258(X_{Mg}^{gt} - X_{Fe}^{gt}) + 1510(X_{Ca}^{gt} + X_{Mn}^{gt})}{1.028 - \ln[(X_{Fe}/X_{Mg})^{crd}/(X_{Fe}/X_{Mg})^{gt}]},$$

for the Mg-Fe partitioning between cordierite and garnet (T in kelvins, P in bars). Figure 4 depicts the curves obtained from Equation 6 and compares it with those generated by Currie's (1971) and Perchuk and Lavrent'eva's (1983) experimental data. It is important to note that uncertainties regarding the composition of the phases in their experiments exist. The compositions of the run products in Currie's work are suspect: first, they probably do not represent equilibrium owing to very short run times; second, the determinative techniques (X-ray diffraction and refractive index) are not accurate enough. Perchuk and Lavrent'eva observed large variations in the compositions of garnet and cordierite even within single grains. The analytical data of the latter authors show that for individual grains, the minimum and the maximum values of $(X_{Mg}^{crd} - X_{Fe}^{crd})$ are 0.25 and 0.77—the corresponding values for garnets are 0.19 and 0.59, respectively. This implies that homogenization was not achieved. In fact, the dashed curves in Figure 4 represent smoothed curves calculated by Perchuk and Lavrent'eva using the method of projective correspondence developed by Korzhinskii (1959). In spite of these shortcomings, there is a surprisingly good correspondence between the three sets at 700 °C, above which there are large discrepancies especially with Currie's formulation. At temperatures significantly higher than 700 °C, our thermometric formulation registers higher temperatures, whereas around 700 °C there is good agreement between the computed T values. Also, our formulation and that of Perchuk and Lavrent'eva predict that at fixed X_{Mg}^{crd} , X_{Mg}^{gt} should decrease with increasing temperature—a trend observed by several workers. Currie's data, however, show an opposite trend.

TABLE 2. Thermodynamic parameters extracted from the statistical analysis

Mean T (°C)	Compositional range ($X_{Mg}^{crd} - X_{Fe}^{crd}$)	$\Delta G_{1,r}$ (J)	W_{Fe-Mg}^{crd} (kJ)
710	-0.234 to 0.634	6305(406)	7.36(1.41)
760	-0.210 to 0.588	7079(753)	6.13(2.44)
800	0.002 to 0.722	5443(151)	14.53(0.03)
850	0.014 to 0.836	7079(1013)	11.92(3.27)

Note: Values in parentheses indicate confidence intervals for the derived data. The ΔV of the exchange equilibrium was taken as 0.1264 J·bar⁻¹ (Holdaway and Lee, 1977).

ACCURACY AND PRECISION OF THE GEOTHERMOMETER

Temperatures have been calculated from the granulite areas mentioned earlier from Equation 6 as well as from two other geothermometric formulations that have been constrained from natural data (Thompson, 1976; Holdaway and Lee, 1977). The temperatures obtained from

all areas fall in the range 620–860 °C and hence broadly correspond to granulite-facies conditions. A perusal of Table 3 indicates that the statistical mean of the temperatures from our thermometric formulation for any area is always within ± 30 °C of the temperatures registered by one of the two other thermometers and often within ± 30 °C of both of them. The differences in mean temperatures compared with the Holdaway and Lee thermometer are ± 55 °C for all areas. If the samples from the contact aureoles are excluded, the differences with Thompson's thermometer are ± 30 °C. Considering that the "true" temperature values adopted in this study in reality represent a range, it is not possible to assess the accuracy of the proposed geothermometer beyond a limit. It can, however, be stated that the "accuracy" of our formulation, calculated as the difference between the "true" value and the arithmetic mean of the computed T values, is within ± 65 °C (Fig. 5).

The "precision" of a geothermometer, measured by the degree of scatter obtained on replication of analysis, can only be assessed with difficulty owing to complexities caused by geothermal gradients, disequilibrium, and effects of minor constituents on the T - X dependence of the exchange equilibrium. The effect of geothermal gradients are pronounced in some metamorphic terranes, as in the granulites around intrusives in the Liberty Hill and Lilesville areas. According to Berg and Docka (1983) the geothermal gradient around the Kiglapait intrusion was of the order of 110 °C/km. In regionally metamorphosed granulite terranes, geothermal gradients are much shallower (~ 30 – 40 °C/km), and hence their effects on dispersion of T values are minimal. Assuming that the distri-

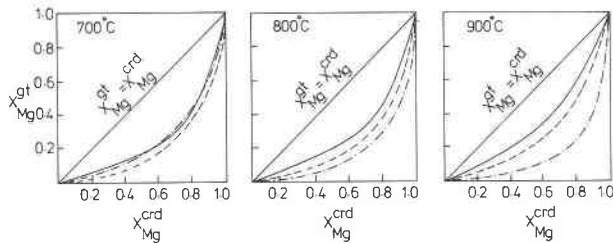


Fig. 4 Partitioning pattern of Mg between cordierite and garnet; solid line after Equation 6, dash and dot line from the data of Currie (1971), dashed line from the data of Perchuk and Lavrent'eva (1983).

bution of the computed T values is symmetric at $x = c$ with a discrete or continuous distribution,¹ the spread or dispersion of the computed T values can be best expressed by the standard deviation (σ), calculated as $[(x_i - c)^2 F(x_i)]^{1/2}$. It follows then that the thermometric formulation that registers T values with the smallest σ , has a better "precision" than the other formulations of the same geothermometer. Other effects like disequilibrium and effects of minor constituents notwithstanding, improved modeling of the energetics of exchange equilibrium should be reflected in a better precision of the geothermometer. The results of our calculation show that our thermometric formulation registers the lowest spread among the three formulations in each area (Table 3). This is true even when temperatures are computed from different P - T zones demarcated from the granulites around intrusives (Speer, 1981, 1982; Evans and Speer, 1984). For all areas, the

¹ c = the mean value of a symmetric distribution; $F(x_i)$ is the probability function of the random variable x .

TABLE 3. Comparison of mean temperatures obtained from cordierite-garnet geothermometers in granulite terranes

Area	No. of samples	Temperatures (°C)		
		H. + L.	T.	t.s.
Nain Complex	16	768(74)	809(92)	778(48)
Inari Complex	12	779(75)	804(89)	778(36)
South India	9	727(27)	758(31)	756(9)
Frontenac axis	5	733(110)	765(131)	754(72)
Namaqualand	4	721(91)	754(111)	738(61)
Hara Lake	4	698(50)	725(60)	740(16)
Egersund-Ogna	6	721(25)	752(30)	755(19)
Liberty Hill	4	728(10)	759(13)	763(6)
Lillesville pluton	8	735(40)	908(55)	746(30)
Snyder Group: Zone III	7	741(66)	777(80)	710(58)
Zone II	3	702(104)	731(125)	700(76)
border breccia	1	841	900	824
Central Massachusetts	4	683(21)	707(25)	738(15)
Enderby Land	5*	717(67)	748(80)	721(35)
Daly Bay Complex	3	745(16)	781(20)	788(23)
Scottish Caledonides:				
Glen Scaddle	4	731(26)	764(31)	764(9)
Huntly Portsoy	2	798(10)	838(25)	795(18)

Note: All temperatures computed at pressures recommended by the respective authors. H. + L., Holdaway and Lee (1977); T., Thompson (1976); t.s., this study. Values in parentheses are $\pm 1 \sigma$. Wet-chemical data on cordierite-garnet pairs from Ganoque area (Reinhardt, 1968) excluded.

* Three sets of analysis from Harley (1985) included.

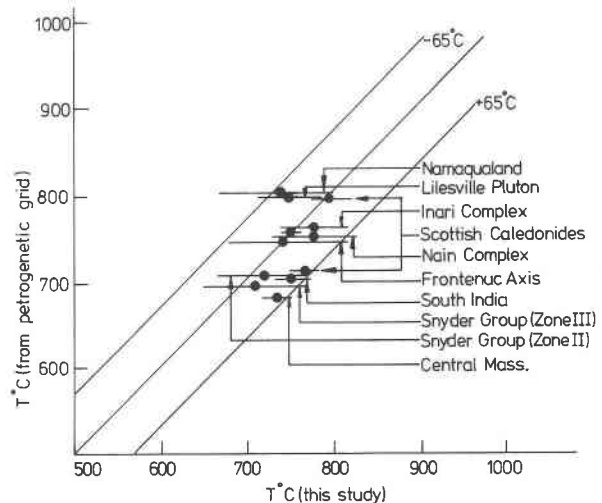


Fig. 5. Comparison of temperatures derived from Equation 6 with those estimated from "petrogenetic grid." Samples from Enderby Land and Liberty Hill pluton excluded because of large uncertainties in temperatures of equilibration (see text).

standard deviation of the T values obtained from Equation 6 is better by 30% to 60% than those for the formulations of Thompson (1976) and Holdaway and Lee (1977). The higher precision warrants that it is more justified to use nonideal mixing models for garnet and cordierite, rather than ideal mixing as postulated by previous workers. To this extent the present formulation is an improvement over earlier formulations of cordierite-garnet thermometry.

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REFERENCES CITED

- Ashworth, J.R., and Chinner, G.A. (1978) Coexisting garnet and cordierite in migmatites from the Scottish Caledonides. *Contributions to Mineralogy and Petrology*, 65, 379-394.
- Berg, J.R. (1977) Regional geobarometry in the contact aureoles of the anorthositic Nain Complex, Labrador. *Journal of Petrology*, 18, 399-430.
- Berg, J.H., and Docka, J.A. (1983) Geothermometry in the Kiglapait contact aureole, Labrador. *American Journal of Science*, 283, 414-434.
- Clifford, T.N., Stumpf, E.F., Burger, A.J., McCarthy, T.S., and Rex, D.C. (1981) Geological-chemical and isotopic studies of Namaqualand granulites, South Africa: Grenville analogue. *Contributions to Mineralogy and Petrology*, 77, 225-250.
- Cramer, H. (1963) *Mathematical methods of statistics* (8th edition). Princeton University Press, Princeton, New Jersey.
- Currie, K.L. (1971) The reaction $3 \text{ cordierite} = 2 \text{ garnet} + 4 \text{ sillimanite} + 5 \text{ quartz}$ as a geological thermometer in the Opinicon Lake region, Ontario. *Contributions to Mineralogy and Petrology*, 33, 215-226.
- (1974) A note on the calibration of the garnet-cordierite geothermometer and geobarometer. *Contributions to Mineralogy and Petrology*, 44, 35-44.
- Ellis, D.J., Sheraton, J.M., England, R.N., and Dallwitz, W.B. (1980) Osumilite-sapphirine-quartz granulites from Enderby Land, Antarctica—Mineral assemblages and reactions. *Contributions to Mineralogy and Petrology*, 72, 123-143.
- Evans, N.H., and Speer, J.A. (1984) Low pressure metamorphism and

- anatexis of Carolina Slate Belt phyllites in the contact aureole of Lilesville pluton, North Carolina, USA. *Contributions to Mineralogy and Petrology*, 84, 297–309.
- Ferry, J.M., and Spear, F.S. (1978) Experimental calibration of partitioning of Fe and Mg between biotite and garnet. *Contributions to Mineralogy and Petrology*, 66, 113–117.
- Ganguly, J., and Kennedy, G.C. (1974) The energetics of natural garnet solid solutions. I. Mixing of the aluminosilicate end-members. *Contributions to Mineralogy and Petrology*, 48, 137–148.
- Ganguly, J., and Saxena, S.K. (1984) Mixing properties in aluminosilicate garnets: Constraints from natural and experimental data, and applications to geothermobarometry. *American Mineralogist*, 69, 88–97.
- Goldman, D.S., and Albee, A.L. (1977) Correlation of Mg/Fe partitioning between garnet and biotite with $^{18}\text{O}/^{16}\text{O}$ partitioning between quartz and magnetite. *American Journal of Science*, 277, 750–767.
- Grew, E.S. (1982a) Osumilite in the sapphirine-quartz terrane of Enderby Land, Antarctica: Implications for osumilite petrogenesis in the granulite facies. *American Mineralogist*, 67, 762–787.
- (1982b) A review of Antarctica granulite-facies rocks. *Tectonophysics*, 105, 177–191.
- Guggenheim, E.A. (1967) *Thermodynamics*. North-Holland, Amsterdam.
- Harley, S.L. (1985) Paragenetic and mineral-chemical relationships in orthoamphibole-bearing gneisses from Enderby Land, east Antarctica: A record of Proterozoic uplift. *Journal of Metamorphic Petrology*, 3, 179–200.
- Harris, N.B.W., and Jayaram, S. (1982) Metamorphism of cordierite-gneisses from the Bangalore region of the Indian Archean. *Lithos*, 15, 89–98.
- Harris, N.B.W., Holt, R.W., and Drury, S.A. (1982) Geobarometry and geothermometry and late Archean geotherms from the granulite facies terrain of South India. *Journal of Geology*, 90, 509–527.
- Hensen, B.J., and Green, D.H. (1973) Experimental study of the stability of cordierite and garnet at high pressures and temperatures. III. Synthesis of experimental data and geological applications. *Contributions to Mineralogy and Petrology*, 38, 151–166.
- Henry, J. (1974) Cordierite-garnet gneisses near the Egersund-Ogna anorthositic intrusion, southwestern Norway. *Lithos*, 7, 207–216.
- Holdaway, M.J. (1976) Mutual compatibility relations of the Fe^{2+} -Mg-Al silicates at 800°C and 3 kb. *American Journal of Science*, 276, 285–308.
- Holdaway, M.J., and Lee, S.M. (1977) Fe-Mg cordierite stability in high grade pelitic rocks based on experimental, theoretical and natural observations. *Contributions to Mineralogy and Petrology*, 63, 175–198.
- Hutcheon, I., Froese, E., and Gordon, T.M. (1974) The assemblage quartz-sillimanite-garnet-cordierite as an indicator of metamorphic conditions in the Daly Bay Complex, N.W.T. *Contributions to Mineralogy and Petrology*, 44, 29–34.
- Indares, A., and Martignole, J. (1985) Biotite-garnet geothermometry in granulite facies: The influence of Ti and Al in biotite. *American Mineralogist*, 70, 272–278.
- Kays, M.A., and Medaris, L.G. (1976) Petrology of the Hara Lake paragenesis, northwestern Saskatchewan, Canada. *Contributions to Mineralogy and Petrology*, 59, 141–159.
- Kreyszig, E. (1971) *Advanced engineering mathematics*. Wiley, New York.
- Korzhinskii, D.S. (1959) *Physicochemical basis of the analysis of paragenesis of minerals*. Consultants Bureau, New York.
- Lonker, S.W. (1980) Conditions of metamorphism in high grade pelites from the Frontenac Axis, Ontario, Canada. *Canadian Journal of Earth Sciences*, 17, 1666–1684.
- (1981) The P - T - X relations of the cordierite-garnet-sillimanite-quartz equilibrium. *American Journal of Science*, 281, 1056–1090.
- Newton, R.C. (1983) Geobarometry of high grade metamorphic rocks. *American Journal of Science*, 283-A, 1–28.
- Perchuk, L.L., and Lavrent'eva, I.V. (1983) Experimental investigation of exchange equilibria in the system cordierite-garnet-biotite. In S.K. Saxena, Ed., *Kinetics and equilibrium in mineral reactions*, p. 199–239. Springer-Verlag, New York.
- Reinhardt, E.W. (1968) Phase relations in cordierite-bearing gneisses from the Ganoque area, Ontario. *Canadian Journal of Earth Sciences*, 5, 455–482.
- Saxena, S.K. (1973) *Thermodynamics of rock-forming crystalline solutions*. Springer-Verlag, New York.
- Speer, J.A. (1981) The nature and magnetic expression of isograds in the contact aureole of the Liberty Hill Pluton, South Carolina, pt II. *Geological Society of America Bulletin*, 92, 1262–1358.
- (1982) Metamorphism of the pelitic rocks of the Snyder Group in the contact aureole of the Kiglapait layered intrusion, Labrador: Effects of buffering partial pressures of water. *Canadian Journal of Earth Sciences*, 19, 1888–1909.
- Thompson, A.B. (1976) Mineral reactions in pelitic rocks. II. Calculation of some P - T - X (Fe-Mg) phase relations. *American Journal of Sciences*, 276, 425–444.
- Tracy, R.J., Robinson, P., and Thompson, A.B. (1976) Garnet composition and zoning in the determination of temperature and pressure of metamorphism, central Massachusetts. *American Mineralogist*, 61, 762–775.
- van Reenen, D.D., and du Toit, M.C. (1975) The reaction garnet + quartz = cordierite + hypersthene in granulites of the Limpopo metamorphic complex in northern Transvaal. In W.J. Verwood, Ed., *Mineralisation in metamorphic terranes*, p. 149–178. Geological Society of South Africa Special Publication no. 4.

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