

# Some geobarometers involving cordierite in the $\text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 (\pm \text{H}_2\text{O})$ system: refinements, thermodynamic calibration, and applicability in granulite facies rocks

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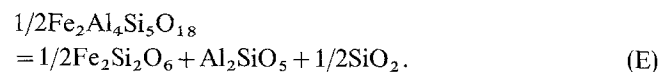
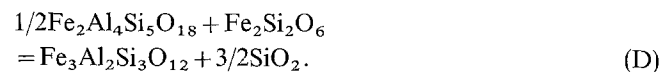
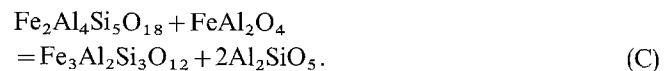
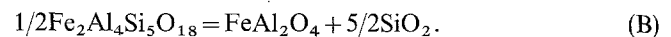
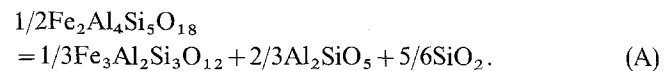
**Abstract.** Five geobarometers involving cordierite have been formulated for quantitative pressure sensing in high grade metapelites. The relevant reactions in the  $\text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 (\pm \text{H}_2\text{O})$  system are based on the assemblages (A) cordierite-garnet-sillimanite-quartz, (B) cordierite-spinel-quartz, (C) cordierite-garnet-spinel-sillimanite, (D) cordierite-garnet-orthopyroxene-quartz and (E) cordierite-orthopyroxene-sillimanite-quartz. Application of the barometric formulations to a large number of granulite grade rocks indicates that the cordierite-garnet-sillimanite-quartz equilibrium is widely applicable and registers pressures which are in good agreement with the “consensus” pressure estimates. The dispersion in the computed  $P$  values, expressed as one standard deviation, is within  $\pm 1.2$  kbar. The geobarometers (B) and (C) also yield pressures which are reasonable and compare well with those computed from equilibrium (A). The estimated pressures from (D) and (E), both involving orthopyroxene, are at variance with these estimates. It has been argued that the discrepancy in pressures obtained from these geobarometers stems from an inadequate knowledge of activity-composition relations and/or errors in input thermodynamic data of aluminous orthopyroxene. The convergence of pressure values estimated from the barometric formulations, especially (A), (B) and (C), implies that the present formulations are more dependable than the existing formulations and are also capable of setting limits on  $P$  values in response to varying  $a_{\text{H}_2\text{O}}$ .

## Introduction

Breakdown reactions involving cordierite have been employed to estimate equilibration pressures of peraluminous rocks over a wide range of temperature values in high grade terranes. Notable in this context are the geobarometers based on the assemblages cordierite-garnet-sillimanite-quartz (Hutcheon et al. 1974; Thompson 1976; Holdaway and Lee 1977; Newton and Wood 1979; Martignole and Sisi 1981; Lonker 1981; Bhattacharya and Sen 1985), cordierite-spinel-quartz (Vielzeuf 1980), cordierite-garnet-spinel-sillimanite (Harris 1981) and cordierite-garnet-orthopyroxene-quartz (Hensen and Green 1973). In terranes where several of these geobarometers can be applied, computed pressures are found to be in serious disagreement. Also, the pressure values are at variance with the pressures estimated by applying experimentally calibrated and well en-

dorsed pressure sensors on spatially associated quartzofeldspathic and basic rocks.

In view of these disparities, it is desirable to examine the inherent shortcomings of the barometric formulations and to reformulate them by removing the inaccuracies as far as possible. Towards this end, five geobarometers, based on Fe-end member reactions in the  $\text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 (\pm \text{H}_2\text{O})$  system have been reformulated. The reactions are



The present communication addresses the calibration, applicability and reliability of these barometers with reference to granulite facies metapelites.

## Previous formulations

The disagreement in the estimated pressures from existing cordierite-bearing geobarometers can be traced to assumptions and approximations employed in the barometric formulations. These are discussed below.

### *Uncertainty in the $dP/dT$ slope of end-member reactions*

Experimentalists have encountered serious problems in controlling the reversibility of cordierite equilibria due to variability of partial pressure of  $\text{H}_2\text{O}$  and metastability of Mg-cordierite in wet and dry systems (Currie 1971; Hensen and Green 1971, 1972, 1973). For example, the Mg-end member cordierite-garnet- $\text{Al}_2\text{SiO}_5$ -quartz equilibrium, experimentally determined by Newton (1972) has been argued to be topologically inconsistent with some established phase relations and hence are thought to represent metastable equilibria (Longer 1981). Similar problems afflict the  $P - T$  location of the cordierite-garnet-orthopyroxene-quartz reaction (Hensen and Green 1973). In contrast, the Fe end-member

reaction for the cordierite-garnet-sillimanite-quartz assemblage, experimentally calibrated by several workers, has been located with reasonable accuracy (Weisbrod 1973a, b; Richardson 1968; Holdaway and Lee 1977). The generally good agreement between the reversed rackets determined by them suggests that equilibrium was attained during experimental runs, hence this equilibrium should serve as a model reaction for geobarometric purposes.

#### *Incompatibility in the input thermodynamic data*

In the absence of accurate high pressure phase experiments on most of the end-member reactions, cordierite-bearing geobarometers have been formulated from published thermochemical data e.g. the cordierite-garnet-sillimanite-quartz geobarometer (Hutcheon et al. 1974; Newton and Wood 1979; Martignole and Sisi 1981), cordierite-spinel-quartz geobarometer (Vielzeuf 1980) and the cordierite-garnet-spinel-sillimanite geobarometer (Harris 1981). In most cases, however, the input thermochemical data are not mutually compatible, resulting in conflicting pressure estimates from these barometers when applied to natural phase assemblages.

#### *Hydration of cordierite*

Experimental and phase equilibrium studies show that the stability of cordierite with respect to its breakdown products is dependent on the degree of hydration of cordierite. However, the effect of the variability of  $X_{\text{H}_2\text{O}}^{\text{crd}}$  on the computed pressures has been ignored by many workers (Hutcheon et al. 1974; Thompson 1976; Vielzeuf 1980; Harris 1981). Recently, Bhattacharya and Sen (1985) refined the activity-composition relationship of hydrated cordierites, using a one-site mixing model in the  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18} - \text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18} \cdot \text{H}_2\text{O}$  system, from experimental data at  $P(\text{H}_2\text{O}) = P(\text{total})$  conditions. Also, their findings at  $a_{\text{H}_2\text{O}} < 1$  are in good agreement with the experimental determinations of Johannes and Schreyer (1977, 1981) in the  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18} - \text{H}_2\text{O} - \text{CO}_2$  system, and hence best suited for barometric purposes.

#### *Activity-composition of Fe-Mg phases*

All geobarometric formulations involving cordierite-bearing equilibria proposed till date assume that Fe-Mg mixing in cordierites as well as other phases is ideal. Although this serves as a first approximation, natural and experimental studies indicate strong non-ideality, especially in multi-component garnet solid solutions (Dahl 1980; Ganguly 1979; Ganguly and Saxena 1984) and to some extent in binary Fe-Mg spinel and orthopyroxene solid solutions. Mixing in binary Fe-Mg cordierites is assumed to be ideal. It is desirable therefore that the barometric formulations should be corrected for non-ideality of the phases.

#### *Order-disorder in cordierites*

Recent experiments on the kinetics of polymorphism in anhydrous cordierites have revealed a continuous order-moderated change from a well ordered phase to a disordered phase above 1,450°C (Putnis and Bish 1983). This implies that the synthetic cordierites employed in phase equilibrium experiments were probably disordered high cordierites. Schreyer (1966) examined a set of 128 natural cordierites from different geological environments having distortion in-

degrees between 0-0.25. He suggested that the cordierites evolved from an initially high cordierite structure, possibly similar to those used in experimental runs (cf. Putnis 1980). Although no conclusive or comprehensive work has been done, it is possible that the synthetic cordierites (disordered) are different from natural cordierites (ordered?) and underscores the complexity of extending the data derived from phase equilibrium experiments to natural assemblages. However, the effect of variable degree of order in cordierites cannot be assessed. Also, since geobarometers involving cordierites are best suited to bracket equilibrium pressures rather than obtaining unique values, the errors in pressure estimation due to ordering may not be serious.

#### **Theoretical considerations**

The equilibrium condition for a reaction involving cordierite, such as



at anhydrous conditions ( $P_{\text{H}_2\text{O}} = 0$ ), can be explicitly written as

$$\Delta G_r^{P,T} = \Delta H - T \cdot \Delta S + P \cdot \Delta V + RT \ln \frac{(a_{\text{alm}}^{\text{Gt}})^{1/3} (a_{\text{AlSi}}^{\text{Sil}})^{2/3} (a_{\text{SiO}_2}^{\text{Qtz}})^{5/6}}{(a_{\text{Fe-crd}}^{\text{Crd}})^{1/2}} \quad (1)$$

where the change in free energy of the reaction at  $P$  and  $T$  is  $\Delta G_r^{P,T}$ ;  $\Delta H$ ,  $\Delta S$  and  $\Delta V$  are the changes in enthalpy, entropy and volume of the anhydrous phases,  $R$  is the universal gas constant and  $a_i^j$  is the activity of a component  $i$  in phase  $j$ . Under hydrous conditions ( $P_{\text{H}_2\text{O}} \neq 0$ ),  $a_{\text{Fe-crd}}^{\text{Crd}} = (X_{\text{Fe}})^2 (1 - X_{\text{H}_2\text{O}}^{\text{crd}})$  and Eq. 1 can be modified as

$$\Delta H - T \cdot \Delta S + P \cdot \Delta V + RT \ln \frac{(a_{\text{alm}}^{\text{Gt}})^{1/3} (a_{\text{AlSi}}^{\text{Sil}})^{2/3} (a_{\text{SiO}_2}^{\text{Qtz}})^{5/6}}{(X_{\text{Fe-crd}}^{\text{Crd}})(1 - X_{\text{H}_2\text{O}}^{\text{crd}})^{1/2}} = 0 \quad (2)$$

where  $(1 - X_{\text{H}_2\text{O}}^{\text{crd}})$ , the mole fraction of anhydrous cordierite, is expressed as a function of  $P$ ,  $T$  and  $f_{\text{H}_2\text{O}}$  in the vapour phase by the relation (Bhattacharya and Sen 1985)

$$X_{\text{H}_2\text{O}}^{\text{crd}} = \frac{f_{\text{H}_2\text{O}}^{P,T}}{\exp \left\{ -\frac{1}{RT} [64,775 - 32.26T + G_{\text{H}_2\text{O}}^{\text{H}_2\text{O}} T - P(9 \times 10^{-4}T - 0.5142)] \right\} + f_{\text{H}_2\text{O}}^P f_{\text{H}_2\text{O}}^T} \quad (3)$$

Equation (2) is a polynomial in  $P$ ,  $T$  and  $X_{\text{H}_2\text{O}}^{\text{crd}}$ , and can be uniquely solved for  $P$  at a fixed temperature if independent estimates of  $X_{\text{H}_2\text{O}}^{\text{crd}}$  are available. However, as the water contents of cordierites are seldom reported in the literature, Eqs. (2) and (3) have to be solved by iteration for determining  $P$  at a known  $T$  and  $P_{\text{H}_2\text{O}}/P_{\text{total}}$  ratio. It is important to note that actual equilibration pressures obtained from geobarometers involving cordierites will have values intermediate between those computed at  $P_{\text{H}_2\text{O}} = 0$  and  $P_{\text{H}_2\text{O}} = P_{\text{total}}$ .

#### *Source of thermodynamic data*

The enthalpy and entropy of  $\text{FeFeSi}_2\text{O}_6$ ,  $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ,  $\text{FeAl}_2\text{O}_4$ ,  $\text{Al}_2\text{SiO}_5$  and  $\text{SiO}_2$  at 1,000 K were calculated from the thermodynamic data base derived by Helgeson

**Table 1A.** Thermodynamic data of the relevant phases<sup>a</sup>

	$H_f^{0,298}$ (cal)	$S_{298}^0$ (cal·K <sup>-1</sup> )	$V_{298}^0$ (cal·bar <sup>-1</sup> )	$H_{oxide}^{1,000}$ (kcal)	$S_T^{1,000}$ (cal·K <sup>-1</sup> )
FeFeSi <sub>2</sub> O <sub>6</sub>	-570,990	45.20	1.5752	- 6.30	110.28
FeAl <sub>2/3</sub> SiO <sub>4</sub>	-423,009	22.82	0.9163	- 7.60	65.10
Al <sub>2</sub> SiO <sub>5</sub>	-615,099	23.13	1.1926	- 0.83	70.78
FeAl <sub>2</sub> O <sub>4</sub>	-464,436	25.40	0.9739	- 2.17	72.80
SiO <sub>2</sub>	-217,650	9.88	0.5423	0	27.46
FeAl <sub>2</sub> Si <sub>5/2</sub> O <sub>9</sub>			2.7734	-11.61	132.94

<sup>a</sup> Sources described in the text**Table 1B.** Heat capacity data<sup>b</sup>

	$a$	$b \times 10^3$	$c \times 10^{-5}$	
FeFeSi <sub>2</sub> O <sub>6</sub>	63.5756	—	23.1692	
FeAl <sub>2/3</sub> SiO <sub>4</sub>	32.5167	11.2333	6.2476	848
	35.6979	7.4092	3.5445	848
Al <sub>2</sub> SiO <sub>5</sub>	40.0240	7.3905	11.6741	
FeAl <sub>2</sub> O <sub>4</sub>	33.1405	10.3728	—	
SiO <sub>2</sub>	11.2200	8.2000	2.7000	848
	14.4100	1.9400	—	848

<sup>b</sup> Sources described in the text;  $C_p = a + bT + cT^{-2}$  (cal)**Table 2.** Thermodynamic constants for equilibrium (A) to (E) at 1,000 K

	$H^{1,000}$ (cal)	$S^{1,000}$ (cal·K <sup>-1</sup> )	$V^{298}$ (cal·bar <sup>-1</sup> )
Crd-Gt-Sil-Qtz (A)	3,460	2.23	-0.6101
Crd-Sp-Qtz (B)	9,440	8.51	-0.4438
Crd-Gt-Sp-Sil (C)	930	-1.82	-1.3866
Crd-Gt-Opx-Qtz (D)	-4,890	-6.73	-0.7863
Crd-Opx-Sil-Qtz (E)	7,630	6.71	-0.5221

et al. (1978) and Saxena and Erikson (1983) from experimentally determined phase relations. The enthalpy and entropy of Fe-cordierite at 1,000 K were computed from the thermodynamic constants of the Fe-crd-alm-sil-qtz equilibrium (Bhattacharya and Sen 1985) using their data base. These values are mutually compatible with the rest of the data in Table 1 and have been used to calculate the enthalpy and entropy change of equilibria (B) to (E) (Table 2). Due to lack of isothermal compressibility and thermal expansion data on Fe-cordierite, the volume change of the reactions are taken to correspond to 298 K and 1 bar.

#### Activity-composition relationships

The activity of the almandine component in multicomponent garnet solid solutions is computed from the relation

$$\ln v_{alm}^{Gt} = X_{Ca}^2(1.52 - 5.17X_{Fe}) + X_{Mg}^2(0.10 + 2.26X_{Fe}) + X_{Ca} \cdot X_{Mg}(3.01 - 6.67X_{Fe} + 1.50X_{Ca} - 1.50X_{Mg}) \quad (4)$$

suggested by Perkins and Chipera (1984), where  $a_{alm}^{Gt} = (X_{Fe} \cdot v_{alm})^3$ . Since the spessartine component in garnets from high grade metapelites are generally low (<2%), the last two terms in Eq. (A1) of Perkins and Chipera have been neglected. Trial calculations indicate that errors resulting from this approximation are of the order of 200 bar in the computed pressure values.

The activity of FeAl<sub>2</sub>O<sub>4</sub> were computed from the relation (Fuji 1977; Fuji and Scarfe, 1982)

$$a_{hc}^{Sp} = X_{Fe} \cdot \exp\left[\frac{-5129 + 3.99T}{1.98717T}\right] (1 - X_{Fe})^2 \quad (5)$$

for binary Mg-Fe spinels. However, natural spinels in metapelites are not binary principally due to the presence of substantial amounts of Fe<sup>3+</sup>, Cr<sup>3+</sup> and Zn<sup>2+</sup>. Also, there are potential difficulties in calculating Fe<sub>3</sub>O<sub>4</sub> from electron microprobe analyses. In this study, spinels have been assumed to be stoichiometric in the R<sup>3+</sup> site. First, all Al

and Cr were assigned to the Al site and the deficiency (2-Al-Cr) was calculated as Fe<sup>3+</sup>. The rest of the Fe<sup>2+</sup> was coupled with Mg to obtain X<sub>Fe</sub>.

Fe<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> and Mg<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> substitution in orthopyroxene are virtually ideal above 700° C (Saxena 1973; Sack 1980). Also, at low concentration of Al<sub>2</sub>O<sub>3</sub> in aluminous orthopyroxene, MgAl<sub>2</sub>SiO<sub>6</sub> is an ideal substituent in enstatite (Wood and Banno 1973). To this extent, the activity of FeFeSi<sub>2</sub>O<sub>6</sub> in orthopyroxene can be adequately expressed as (Wood and Banno 1973)

$$a_{fs}^{Opx} = (X_{Fe}^{M1})(X_{Fe}^{M2}) \quad (6)$$

where the larger M2 site incorporates Ca, Mn and Na while the smaller M1 site contains Al<sup>VI</sup>, Ti, Cr and Fe<sup>3+</sup>. The Mg and Fe<sup>2+</sup> are taken to be equipartitioned between M1 and M2.

There are no thermochemical data for the Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>-Fe<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub> solid solution. Also, the results of phase equilibrium experiments pertaining to Mg-Fe partitioning in cordierite-garnet and cordierite-biotite systems are not conclusive due to difficulties in obtaining homogeneous phases from experimental runs (Currie 1971; Hensen and Green 1971, 1972; Perchuk and Lavrenteva 1983). However, in the absence of quantitative data, most workers contend that the binary Mg-Fe cordierites can be approximated to an "ideal two-site" mixing,  $a_{Fe-crd}^{anhyd,Crd} = (X_{Fe})^2$  (Thompson 1976; Holdaway and Lee 1977; Lonker 1981).

#### Geobarometric expressions

The geobarometric equations for equilibrium (A) to (E) can be explicitly written from the data presented in Table 2 as

$$3,460 - 2.23T - 0.6101P + RT \ln \frac{(a_{alm}^{Gt})^{1/3}}{(a_{Fe-crd}^{Crd})^{1/2}} - 0.994T \ln(1 - X_{H_2O}^{Crd}) = 0. \quad (7)$$

$$9,440 - 8.51T - 0.4438P + RT \ln \frac{(a_{hc}^{Sp})}{(a_{Fe-crd}^{Crd})^{1/2}} - 0.994T \ln(1 - X_{H_2O}^{Crd}) = 0. \quad (8)$$

$$930 + 1.82T - 1.3866P + RT \ln \frac{(a_{alm}^{Gt})}{(a_{hc}^{Sp})(a_{Fe-crd})} - 1.9872T \ln(1 - X_{H_2O}^{Crd}) = 0. \quad (9)$$

$$-4,890 + 6.73T - 0.7863P + RT \ln \frac{(a_{alm}^{Gt})}{(a_{fs}^{Opx})(a_{Fe-crd}^{Crd})^{1/2}} - 0.994T \ln(1 - X_{H_2O}^{Crd}) = 0. \quad (10)$$

and

$$7,630 - 6.71T - 0.5221P + RT \ln \frac{(a_{\text{fs}}^{\text{Opx}})^{1/2}}{(a_{\text{Fe-crd}}^{\text{Crd}})^{1/2}} - 0.994T \ln(1 - X_{\text{H}_2\text{O}}^{\text{Crd}}) = 0. \quad (11)$$

It is important to note that under anhydrous conditions the last term in Eqs. (7) to (11) drops out.

### Application to granulites

The geobarometers were applied to mineral assemblages from high grade terranes distributed worldwide. The temperatures of equilibration varied from 650° C (Central Massachusetts) to 900° C (Antarctica); the compositional spreads of cordierites and garnets in terms of Fe/Fe + Mg were between 0.082 and 0.605 and 0.444 to 0.891 respectively. Temperatures for most of the areas have been calculated either from biotite-garnet pairs (Ferry and Spear 1978; Perchuk and Lavrent'eva 1983) or from garnet-cordierite pairs (Thompson 1976; Holdaway and Lee 1977; Perchuk and Lavrent'eva 1983); where analytical data on both the pairs were available, temperatures were estimated from the "combined" data. In case of the Finnish Lapland, the Scottish Caledonides and the Antarctica granulites, "consensus"

temperature values suggested by the original authors were adopted (Newton 1983). For most of the areas uncertainties in equilibrium  $T$  values are believed not to exceed  $\pm 60^\circ \text{C}$ . Errors in temperature estimation of the order of  $\pm 50^\circ \text{C}$  introduce discrepancies of about 100 bar in equilibrium (A) and 300–500 bar in equilibrium (B) to (E). Where minerals are reported to be zoned, all barometric computations were based on core compositions. No attempt was made to estimate  $X_{\text{H}_2\text{O}}$  in the vapour phase from independent equilibria for the sake of deriving unique pressure values; instead the minimum and maximum (in parenthesis) pressures are reported for each sample (Table 3).

Since all five geobarometers were calibrated using an internally consistent data base and activity-composition relations constrained from natural and experimental data, all equations should, ideally, register comparable pressure estimates. However, lack of analytical data on the concerned mineral phases restricts the comparability to four areas only e.g. South India (Harris and Jayaram 1982; Harris et al. 1982), the Scottish Caledonides (Ashworth and Chinner 1978), the Nain Complex (Berg 1977a and b) and the Enderby Land, Antarctica (Grew 1982). Pressure estimates of the associated quartzofeldspathic, intermediate and basic granulites for these areas are between 6.5–9.5 kbar, 2.6–4.1 kbar, 1.4–4.6 kbar and 7.0–8.1 kbar respectively (New-

**Table 3.** Pressures estimated from the five barometers for metapelites of different granulite terrains garnet

$T$ (° C)	Sample no.	$X_{\text{Fe}}^{\text{crd}}$	$X_{\text{Fe}}$	$X_{\text{Mg}}$	$X_{\text{Ca}}$	$a_{\text{Fe}}^{\text{gt}}$	$a_{\text{Fe}}^{\text{opx}}$	$a_{\text{Fe}}^{\text{sp}}$	Estimated pressures				
									(A)	(B)	(C)	(D)	(E)
South India <sup>a, b, c</sup>													
740		0.167	0.567	0.399	0.034	0.693		0.576	6.7 (8.5)	7.5 (10.1)	6.4 (8.0)		
740		0.167	0.562	0.404	0.034	0.689		0.553	6.6 (8.4)	7.3 (9.9)	6.4 (8.0)		
720	732	0.183	0.522	0.429	0.049	0.649			6.1 (8.0)				
720	601	0.221	0.622	0.346	0.032	0.730			5.9 (7.8)				
720	731	0.189	0.598	0.360	0.043	0.704			6.3 (8.2)				
720	P3	0.237	0.660	0.309	0.031	0.754			5.8 (7.7)				
710	104	0.242	0.646	0.330	0.024	0.754			5.7 (7.5)				
710	107	0.298	0.680	0.265	0.054	0.739			5.0 (6.7)				
710	110	0.152	0.762	0.200	0.038	0.803			7.4 (9.4)				
710	112	0.264	0.675	0.294	0.031	0.762			5.5 (7.3)				
710	114	0.284	0.680	0.299	0.021	0.777			5.3 (7.1)				
Scottish Caledonides <sup>d</sup>													
720	105765	0.363	0.760	0.210	0.030	0.810			4.6 (6.4)				
720	105557	0.285	0.681	0.280	0.039	0.756			5.2 (7.0)				
720	105570	0.269	0.679	0.265	0.056	0.755	0.424		5.4 (7.2)		7.8 (9.3)	3.6 (5.5)	
720	193C	0.486	0.838	0.130	0.032	0.854			3.9 (5.6)				
720	196C	0.490	0.836	0.131	0.033	0.852			3.6 (5.5)				
800	187C	0.381	0.735	0.225	0.040	0.785			4.3 (6.0)				
800	189C	0.379	0.719	0.240	0.041	0.775			4.2 (5.9)				
Central Massachusetts <sup>e</sup>													
650	FW283	0.250	0.710	0.264	0.026	0.787			5.7 (7.3)				
650	FW154	0.280	0.709	0.266	0.026	0.787			5.4 (7.0)				
650	FW122	0.290	0.716	0.249	0.035	0.780			5.3 (6.9)				
650	FW407	0.286	0.713	0.253	0.035	0.779			5.3 (7.0)				

Values in parenthesis indicate pressures computed at  $P_{\text{H}_2\text{O}} = P_{\text{total}}$

<sup>a</sup> Harris (1981); <sup>b</sup> Harris et al. (1982); <sup>c</sup> Harris and Jayaram (1982); <sup>d</sup> Ashworth and Chinner (1978); <sup>e</sup> Tracy et al. (1976); <sup>f</sup> Berg (1977a); <sup>g</sup> Berg (1977b); <sup>h</sup> Ellis et al. (1980); <sup>i</sup> Grew (1982); <sup>j</sup> Ackermund (cited in Newton 1983); <sup>k</sup> Lonker (1980); <sup>l</sup> Clifford et al. (1980); <sup>m</sup> Kays and Medaris (1976)

Table 3 (continued)

T (° C)	Sample no.	$X_{Fe}^{rd}$	$X_{Fe}$	$X_{Mg}$	$X_{Ca}$	$a_{Fe}^{st}$	$a_{Fe}^{px}$	$a_{Fe}^{sp}$	Estimated pressures				
									(A)	(B)	(C)	(D)	(E)
Nain Complex, Labrador <sup>f, g</sup>													
750	2-275	0.315	0.732	0.235	0.033	0.791	0.516				7.1 (8.6)		
750	2-625	0.425	0.807	0.168	0.024	0.842	0.605				6.0 (7.5)		
750	2-893	0.436	0.781	0.191	0.027	0.824	0.603				5.8 (7.4)		
750	2-1455	0.311	0.631	0.339	0.030	0.738	0.508				6.7 (8.2)		
750	2-1572	0.362	0.679	0.295	0.026	0.770	0.530				6.4 (8.0)		
750	2-1637	0.406	0.754	0.212	0.034	0.802	0.594				5.9 (7.4)		
750	74-98a	0.492	0.841	0.148	0.011	0.874	0.649				5.6 (7.2)		
750	KI-3557	0.555	0.818	0.141	0.041	0.834	0.664				4.8 (6.3)		
750	KI-3909	0.506	0.807	0.166	0.027	0.840	0.654				4.8 (6.3)		
750	LRD72011	0.241	0.621	0.349	0.030	0.732	0.422				8.3 (9.8)		
750	NK420B	0.330	0.728	0.229	0.043	0.778	0.486				7.2 (8.7)		
750	NU69	0.296	0.736	0.221	0.043	0.783	0.485				7.5 (9.0)		
750	2-1729	0.605	0.891	0.074	0.034	0.891			3.2 (4.8)				
750	2-1729X	0.518	0.839	0.124	0.037	0.851		0.934		3.3 (4.9)			
Enderby Land, Antarctica <sup>h</sup>													
900	76283368	0.082	0.454	0.542	0.004	0.631	0.232				9.2 (10.8)		
900	76283350	0.105	0.455	0.541	0.004	0.632	0.224				8.2 (9.8)		
Gage Ridge, Antarctica <sup>i</sup>													
900	2083C	0.130	0.444	0.515	0.040						7.2 (8.8)		
900	2083D	0.132	0.444	0.515	0.040						7.1 (8.7)		
Inari Complex, Finland <sup>j</sup>													
760	194III	0.270	0.640	0.327	0.032	0.740					5.3 (6.9)		
760	160III	0.233	0.609	0.326	0.029	0.726					5.7 (7.3)		
760	169I	0.219	0.490	0.480	0.029	0.638					5.5 (7.2)		
760	161I	0.260	0.654	0.322	0.024	0.759					5.5 (7.1)		
760	158I	0.233	0.626	0.352	0.022	0.745					5.8 (7.4)		
760	158II	0.270	0.705	0.265	0.030	0.780					5.5 (7.1)		
760	89V	0.226	0.536	0.431	0.032	0.676					5.6 (7.2)		
760	93VI	0.271	0.657	0.305	0.038	0.748					5.3 (6.9)		
760	24II	0.289	0.750	0.223	0.027	0.807					5.4 (7.0)		
760	177I	0.228	0.584	0.379	0.037	0.701					5.7 (7.3)		
760	110III	0.206	0.543	0.429	0.028	0.683					5.1 (6.8)		
760	119I	0.244	0.596	0.376	0.028	0.719					5.5 (7.1)		
Frontenac Axis, Ontario <sup>k</sup>													
750	ON/ GN-18-76	0.350	0.740	0.223	0.037	0.791					4.6 (6.2)		
750	ON/ WP-112-77	0.173	0.548	0.427	0.024	0.690					6.5 (8.2)		
750	ON/ WP-136-77	0.148	0.635	0.318	0.047	0.721					7.2 (9.0)		
750	ON/ WP-221-78	0.235	0.537	0.420	0.043	0.662					5.4 (7.0)		
750	ON/ GN-22-76	0.269	0.652	0.309	0.039	0.743					5.3 (7.0)		
Namaqualand <sup>l</sup>													
800	46	0.274	0.620	0.374	0.006	0.762					5.3 (6.9)		
800	47a	0.182	0.593	0.388	0.018	0.729					6.6 (8.3)		
800	47b	0.194	0.637	0.344	0.018	0.756					6.5 (8.1)		
800	47	0.184	0.635	0.351	0.014	0.760					6.7 (8.3)		
Hara Lake, Manitoba <sup>m</sup>													
720	K93	0.283	0.731	0.240	0.029	0.795					5.4 (7.1)		
720	K291	0.404	0.784	0.187	0.028	0.825					4.4 (6.1)		
720	K359	0.436	0.799	0.173	0.028	0.834					4.1 (5.7)		
720	K376	0.368	0.778	0.191	0.032	0.819					4.6 (6.4)		

ton 1983; Bohlen et al. 1983; Perkins and Chipera 1984). However, for the Scottish Caledonides, phase assemblages indicate that the pressure of formation should have been close to the  $\text{Al}_2\text{SiO}_5$  triple point and hence the pressure estimate of 1.4–4.6 kbar is on the lower side. According to Ashworth and Chinner (1978), the range of pressure values for the Glen Scaddle area were 5.6–5.9 kbar and those from the Strontian area less than 5 kbar. In all the four areas, the pressures estimated from the cordierite-garnet-sillimanite-quartz (A), cordierite-spinel-quartz (B) and cordierite-garnet-spinel-quartz (C) geobarometers at  $P_{\text{H}_2\text{O}} = 0$  and  $P_{\text{H}_2\text{O}} = P_{\text{total}}$ , brackets the equilibrium pressure values adequately (Table 3). In other areas, the computed pressures from (A) are in good agreement with the values quoted by the respective authors. The maximum dispersion in the pressure values (expressed as  $\pm 1$  standard deviation) does not exceed 1.2 kbar. It is important to note that varying  $P_{\text{H}_2\text{O}}/P_{\text{total}}$  ratios in different metapelitic units within a field area could also generate dispersion of  $P$  values.

The pressures obtained from the cordierite-garnet-orthopyroxene-quartz (D) and cordierite-orthopyroxene-sillimanite-quartz (E) geobarometers are in disagreement with the pressures computed from reactions (A), (B) and (C) (Table 3). The anomalous pressure values registered by the orthopyroxene-bearing geobarometers for the Scottish Caledonides, the Nain Complex and the Antarctica granulites could be attributed to disequilibrium and extensive zoning among the phases. If so, the estimated pressures from other geobarometers should have been similarly affected, which is evidently not the case. An examination of orthopyroxene analyses from these rocks show that they contain about 8 wt. %  $\text{Al}_2\text{O}_3$ . The orthopyroxene in terms of the Fe-component can be described by the formula  $(\text{Fe}_{1.8}\text{Al}_{0.4}\text{Si}_{1.8}\text{O}_6)$  – a solid solution intermediate between  $(\text{Fe}_2\text{Si}_2\text{O}_6)$  and  $(\text{FeAlAlSiO}_6)$ . Since neither the thermodynamic properties of aluminous Fe-rich orthopyroxenes nor the activity-composition relationships of such pyroxenes in the presence of an Al-saturated phase, e.g.  $\text{Al}_2\text{SiO}_5$  are known, it is not possible to refine the barometric expressions any further. Charlu et al.'s (1975) heat of solution measurements in the  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system indicate that the enthalpy of formation of  $\text{MgSiO}_3$  from its oxides at 970 K is 1.8 kbar more negative than aluminous pyroxenes  $(\text{MgSiO}_3)_{0.9}(\text{Al}_2\text{O}_3)_{0.1}$ . If the difference in the enthalpy of aluminous Fe-pyroxene and  $\text{FeSiO}_3$  is of the same order of magnitude, pressures computed from equilibrium (D) will be revised downward and equilibrium (E) will register higher pressures. Taking enthalpy of  $\text{FeSiO}_3$  to be  $-1.35$  kcal, trial calculations show that equilibrium (D) registers pressures in the range of 1.0–3.7 kbar and 10.7–11.2 kbar for the Nain Complex and the Enderby Land granulites. These values are in better agreement with those obtained from independent estimates (Newton 1983; Bohlen et al. 1983).

#### *Effect of partial pressure of $\text{H}_2\text{O}$ on barometric results*

The partial pressure of  $\text{H}_2\text{O}$  advocated for the South Indian granulites and those of the Scottish Caledonides is 0.35 (Janardhan et al. 1981) and 0.60 (Ashworth and Chinner 1978) respectively. Berg (1977) provides evidence that “granulitisation” of rocks at peak metamorphic conditions was caused by emplacement of anorthosite pluton which was responsible for desiccating its environs. In Antarctica, Grew (1980) argues, on the basis of phase relations, that the granu-

lites were “dried” by a previous episode of metamorphism. In such cases it is possible that the  $X_{\text{H}_2\text{O}}$  in spatially associated rocks of varying bulk chemistry was similar. But in terranes where granulitisation has resulted as a consequence of prograde metamorphism, a unique  $P_{\text{H}_2\text{O}}/P_{\text{total}}$  value across lithologic differences is possible only if the lithological units communicated with an external fluid reservoir (cf. Newton et al. 1980). However, in recent literature there has been a growing awareness that the chemically distinct rock groups often behave as “closed” systems. As a result the ambient activity of  $\text{H}_2\text{O}$  in the fluid phase is largely controlled by the properties of the precursor rocks (Rice and Ferry 1982). Different  $X_{\text{H}_2\text{O}}$  in adjacent rock formations could also be generated by preferential extraction of  $\text{H}_2\text{O}$  by anatectic melting, as has been shown to be the case for Madras charnockites and metapelites (Bhattacharya and Sen, in press). Such variable behaviour of  $\text{H}_2\text{O}$  underscores the need for estimating the magnitude of  $P_{\text{H}_2\text{O}}$  before pressures are computed on the basis of cordierite-bearing equilibria.

In the absence of quantitative data on  $X_{\text{H}_2\text{O}}$  in rocks, rough estimates were obtained using the  $X_{\text{H}_2\text{O}}$  values recommended by the respective investigators: South India (5.7–7.9 kbar), the Scottish Caledonides (4.7–6.0 kbar), the Nain Complex (3.2 kbar) and the Enderby Land (8.2–9.2 kbar) – from the cordierite-garnet-sillimanite-quartz equilibrium. The corresponding values for South India estimated from the cordierite-spinel-quartz equilibrium and the cordierite-garnet-spinel-quartz equilibrium are 7.9–8.2 kbar and 7.2 kbar respectively. On the other hand, equilibrium (C) registers 3.3 kbar for the Nain Sample at  $P_{\text{H}_2\text{O}} = 0$ . Also, the pressures computed from equilibrium (A) at  $X_{\text{H}_2\text{O}} = 0.35$  (Hörman et al. 1980) for the samples from the Finnish Lapland are between 5.9–6.5 kbar. The range of pressure values is in excellent agreement with the “consensus”  $P$  estimates for this area e.g. 5.5–7.2 kbar obtained from orthopyroxene-garnet-plagioclase-quartz, clinopyroxene-garnet-plagioclase-quartz and garnet-plagioclase-sillimanite-quartz geobarometers in the associated rocks (Bohlen et al. 1983; Newton 1983).

#### **Concluding remarks**

In general the convergence of pressure values registered by the barometers, especially (A), (B) and (C) implies that the  $dP/dT$  slopes of the reactions in wet and dry systems are of the right magnitude. The close comparability of the estimated pressures is attributed to (i) the internally consistent thermodynamic data base of the pure phases employed in calibrating the geobarometers, (ii) the refined activity-composition relations that have been adopted to account for mixing in garnet, spinel and pyroxene and (iii) improved theoretical modelling of hydration of cordierite at variable  $P-T-a_{\text{H}_2\text{O}}$  conditions.

Nonetheless certain important factors need be evaluated more quantitatively before the potentiality of cordierite geobarometers are fully realised. These factors pertain to (i) the nature of ordering in natural and synthetic cordierites and its effect on the  $dP/dT$  slopes of the different equilibria, (ii) the energetics of mixing in binary Fe–Mg cordierites, (iii) the presence of different types of  $\text{H}_2\text{O}$  in cordierite channels (Aines and Rossman 1985) and (iv) changes in chemistry and  $\text{H}_2\text{O}$  contents of cordierites during depressurisation and uplift. Till specific answers to these problems are avail-

able, the present formulations offer improved pressure sensors which are capable of bracketing equilibrium pressure values with reasonable accuracy.

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