

## Refinement of geothermobarometry for cordierite granulites

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MS received 26 March 1993; revised 13 July 1993

**Abstract.** Refined geothermobarometers are presented for cordierite granulites. The refinement was achieved by using internally consistent thermodynamic datasets.

Improved calibrations have been demonstrated for a number of granulite areas. Also, the usefulness of the improved geobarometer in identifying decompression paths has been discussed.

**Keywords.** Cordierite-granulite; internally consistent thermodynamic dataset; hydration; decompression.

### 1. Introduction

Cordierite-bearing granulite assemblages, such as cordierite garnet-sillimanite-quartz, are specially useful in evaluating P–T–t paths of granulites. It is known from experimental studies that cordierite is stable at lower pressures as compared to the assemblage garnet-sillimanite-plagioclase-quartz (Newton 1972), although the presence of H<sub>2</sub>O in cordierite extends its stability field to higher pressures (Newton 1989). In many areas cordierite-garnet-sillimanite-quartz assemblage occurs in close association with higher pressure assemblages of metapelites and calcgranulites (garnet-sillimanite-plagioclase-wollastonite). Initiation of cordierite forming reaction, namely, garnet + sillimanite + quartz → cordierite, as read from reaction textures, would imply drop in pressures.

A precise P–T estimate from cordierite-granulites is therefore needed to identify isothermal decompression paths, the drop in pressure (rapid uplift or slow exhumation) and the regional implication of the cordierite-granulites vis-a-vis other and more extensive granulite assemblages. Conversely, where the P–T estimates from the cordierite-granulites are similar to the regional P–T values, cordierite-granulites can be utilized to evaluate the fluid activity,  $f_{\text{H}_2\text{O}}$ .

The problem of geothermobarometry and hygrometry for cordierite-bearing granulites has been the paucity of experimental data and analytical data for water content of cordierite. The most recent attempts to overcome these difficulties are that of Bhattacharya and Sen (1985) and Bhattacharya *et al* (1988). However, their attempts at regression analysis from natural data entail large approximations and hence leave scope for refinement from the thermodynamic point of view.

Presently, two compilations of internally consistent thermodynamic data sets are available, namely of Berman (1988) and Holland and Powell (1990). A close scrutiny shows that the two data sets are closely comparable for the same mineral phases in both data sets. The difference appears to be the larger number of mineral phases

Table 1. Analytical data used for computations.

Area	Sample	Cordierite		Garnet			$X_{Mn}$	Assumed T°C	P (Kb)	Reference
		$X_{Fe}$	$X_{Mg}$	$X_{Fe}$	$X_{Mg}$	$X_{Ca}$				
Nain Complex	2-1729	0.605	0.395	0.813	0.069	0.032	0.067			
	KI-3557	0.555	0.445	0.810	0.140	0.040	0.010			
	74-980	0.492	0.508	0.835	0.147	0.011	0.008			
	2-893	0.436	0.564	0.765	0.188	0.027	0.019			
	2-1637	0.406	0.594	0.736	0.207	0.034	0.024			
	2-1726	0.404	0.595	0.775	0.172	0.027	0.026			
	2-1578	0.386	0.614	0.721	0.244	0.025	0.009			
	2-1572	0.362	0.638	0.672	0.292	0.025	0.011			
	2-1480	0.360	0.640	0.678	0.285	0.024	0.012			
	NK-420B	0.330	0.670	0.712	0.224	0.042	0.021		760	Berg 1977
	2-275	0.315	0.685	0.718	0.231	0.033	0.016			
	2-1455	0.311	0.689	0.625	0.335	0.030	0.013			
	NU-69	0.296	0.704	0.710	0.213	0.041	0.035			
	LKD-72-01	0.241	0.759	0.618	0.347	0.030	0.004			
	KI-3909	0.506	0.494	0.795	0.163	0.027	0.015			
	2-625	0.425	0.575	0.793	0.165	0.024	0.017			
South India	732	0.183	0.817	0.492	0.404	0.046	0.058			
	601	0.221	0.779	0.586	0.326	0.030	0.059	710	6	Harris and Jayram (1982)
	731	0.189	0.811	0.576	0.347	0.041	0.036			
	P-3	0.237	0.763	0.643	0.301	0.030	0.026			
	104	0.242	0.758	0.638	0.326	0.023	0.013			
	107	0.298	0.702	0.664	0.259	0.053	0.023			
	110	0.363	0.637	0.747	0.196	0.037	0.020			Harris <i>et al</i> (1982)
	112	0.264	0.736	0.661	0.288	0.031	0.020			
114	0.284	0.716	0.673	0.296	0.020	0.010				

Inari	194 III	0.270	0.730	0.632	0.323	0.032	0.013			
Complex	161 I	0.260	0.740	0.649	0.319	0.024	0.008	760	5	
	158 II	0.270	0.730	0.701	0.263	0.030	0.006			
	89 V	0.226	0.774	0.531	0.427	0.032	0.010			Ackermund cited in Newton (1983)
	93 VI	0.271	0.729	0.642	0.298	0.038	0.020			
	177 I	0.228	0.772	0.576	0.374	0.036	0.014			
	110 III	0.206	0.794	0.540	0.426	0.028	0.006			
	119 I	0.244	0.756	0.592	0.374	0.028	0.006			
Scottish	105765	0.363	0.637	0.760	0.210	0.030	0.000	710	5.5	
Caledonides	105557	0.285	0.715	0.664	0.274	0.038	0.025			Ashworth and Chinner (1978)
	105570	0.269	0.731	0.649	0.254	0.054	0.043			
	189	0.379	0.621	0.707	0.236	0.040	0.017			
Snyder	SN-211	0.498	0.501	0.822	0.155	0.000	0.024	710	4	
Group	SN-263	0.617	0.383	0.899	0.077	-----	0.024			
	SN-287	0.548	0.452	0.851	0.137	-----	0.012			Speer (1982)
	SN-288	0.456	0.544	0.831	0.155	-----	0.014			
	SN-309	0.533	0.467	0.835	0.155	-----	0.010			
	SN-374	0.531	0.469	0.831	0.143	-----	0.026			
Namaqualand	46	0.274	0.726	0.610	0.368	0.006	0.016	800	7.7	
	47A	0.182	0.818	0.585	0.383	0.018	0.015			Clifford <i>et al</i> (1981).
	47B	0.194	0.806	0.637	0.344	0.018	0.000			
	47	0.184	0.816	0.631	0.349	0.014	0.006			

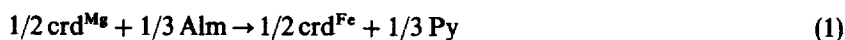
**Table 2.** Thermodynamic parameters of mineral phases at 1073°(K), 7 (Kbar). (From Holland and Powell 1990).

Mineral phases	$\Delta H_{P,T}(\text{kJ})$	$\Delta S_{P,T}(\text{J})$	$\Delta V_{P,T}(\text{J/b})$
Fe-Cordierite	- 7900.87	979.52	23.44
Mg-Cordierite	- 8617.78	918.89	23.13
Almandine	- 4874.12	708.94	12.89
Pyrope	- 5903.37	620.40	12.78
Sillimanite	- 2433.94	238.34	5.32
Quartz	- 896.45	92.15	2.38
Reaction (1)	15.371	7.97	0.11
From Berman (1988)			
Mg-Cordierite	- 8597.42	941.09	23.20
Pyrope	- 5900.62	626.03	11.49
Sillimanite	- 2433.62	238.03	5.01
Quartz	- 856.49	91.98	2.27
Reaction (10)			
From Berman	4.31	26.53	2.54
From Holland and Powell	- 4.76	16.97	1.78

[123] in Holland and Powell, as compared to Berman's [67]. Among the extra phases in Holland and Powell (1990), some are expected to improve marginally (reliability level 2) while some others are only preliminary determinations (reliability level 3). In the present study, Holland and Powell's (1990) data set is used for the Fe/Mg exchange reaction, because the Fe-cordierite is included in this data set (not in Berman's data set), although reliability levels for Fe-cordierite and Mg-cordierite are different. For such exchange reactions the differences (errors) in thermodynamic parameters are expected to cancel out. However, for the continuous reaction, involving Mg-cordierite, Mg-garnet, sillimanite and quartz, Berman's data set is used instead. Here, Holland and Powell's data set gives appreciably different changes in enthalpy, entropy and molar volume of reaction, probably as a consequence of the thermodynamic data of different reliability levels (table 2) and errors are propagated in geobarometric formulations.

## 2. Cordierite-garnet geothermometry

The equilibrium conditions at P and T for the reaction



can be written as

$$\begin{aligned} \Delta G_{P,T} = 0 = & \Delta H_{P,T} - T\Delta S_{P,T} + P\Delta V_{P,T} + RT \ln K_D + RT \ln \gamma_{\text{gt}} \left( \frac{\text{Mg}}{\text{Fe}} \right) \\ & + RT \ln \gamma_{\text{crd}} \left( \frac{\text{Fe}}{\text{Mg}} \right) \end{aligned}$$

where

$$K_D = (X_{Fe}/X_{Mg})^{crd}/(X_{Fe}/X_{Mg})^{gt} \quad (2)$$

$\Delta G_{P,T}$  denotes the free energy change of the reaction (1) at equilibrium P and T and  $\Delta H_{P,T}$ ,  $\Delta S_{P,T}$ ,  $\Delta V_{P,T}$  are respectively the changes in enthalpy, entropy (third law entropy) and molar volume of the reaction at P, T.

Bhattacharya *et al* (1988) used the relation  $\Delta G = 15079 - 8.55T$  (J) retrieved from analytical data, but the points used for regression cause large uncertainties. From Holland and Powell's internally consistent data set, the enthalpy and entropy change for the reaction are found to be 15371 (J) and 7.97 (J) respectively. The enthalpy, entropy and molar volume of the mineral phases at 1073° (K) and 7000 bar are calculated from Holland and Powell (1990), using the relations—

$$C_p = a + b \times T + c \times T^{-2} + d \times T^{-5} \quad (3)$$

and

$$V_{P,T} = V_{1,298} + \alpha V(T - 298) - \beta V/2(P)^2 \quad (4)$$

The results of these calculations are given in table 2.

Activity-composition relations in the almandine-pyrope binary join in quarternary garnet solid solutions used in this study is that proposed by Ganguly and Saxena (1984)—

$$RT \ln(\gamma_{Mg}/\gamma_{Fe})^{gt} = 2500(X_{Fe} - X_{Mg}) + 3000(X_{Ca} + X_{Mn}) \cdot \text{cal} \quad (5)$$

For cordierite, a regular solution model is used as in Bhattacharya *et al* (1988), where

$$\ln \gamma_i = W/RT(1 - X_i). \quad (6)$$

Thus

$$RT \ln(\gamma_{Fe}/\gamma_{Mg})^{crd} = W_{Fe-Mg}^{crd}(X_{Mg} - X_{Fe})^{crd} \quad (7)$$

The adjustable energy parameter  $W_{Fe-Mg}^{crd}$  varies with temperature and pressure. Bhattacharya *et al* (1988) used the average value of  $9.34 \pm 4.54$  kJ/mol (from regression of analytical data available), the present calculations from Holland and Powell (1990) shows much less deviation from the average, which is  $7.896 \pm 1.9$  kJ/mol (between 973°K and 1173°K).

Combining equations 2, 5, 7 and 8 and using the calculated values of

$$\Delta H_{P,T}, \Delta S_{P,T} \text{ and } \Delta V_{P,T} \quad (\text{table 2})$$

the thermometric expression is obtained as

$$T(K) = \frac{[1928.61 + 0.0152P + 1311(X_{Fe} - X_{Mg})_{gt} + 1573(X_{Ca} + X_{Mn})_{gt} + 991(X_{Mg} - X_{Fe})_{crd}]}{1 - 1.014 \ln K_D} \quad (9)$$

*Application.* The thermometer can be assessed by a comparative study of precision and accuracy as applied to some granulite areas (table 3). In terms of scatter the present formulation is distinctly more precise (less standard deviation) than the

**Table 3.** Comparative geothermometry for selected areas T°C).

Area	P.S	H + L	T	B-M-S	Recommended
Nain Complex n = 16	766(52)	768(74)	809(92)	762(48)	760
South India n = 19	715(22)	727(27)	758(31)	755(9)	710
Finnish Lapland n = 8	748(20)	779(75)	804(84)	779(36)	760
Scottish Caledonides n = 4	750(26)	731(26)	764(31)	782(9)	710
Snyder Group n = 6	746(53)	741(66)	777(80)	734(58)	710
Namaqualand n = 4	680(54)	721(91)	754(111)	743(61)	800

Note: Figures in parentheses denote standard deviation.

P.S—Present Study; H + L—Holdaway & Lee (1977); T—Thompson (1976);

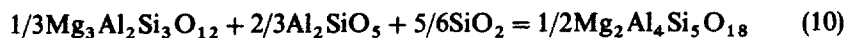
B-M-S—Bhattacharya *et al* (1988).

formulations of Holdaway and Lee (1977) and Thompson (1976) for all the areas. However, Bhattacharya *et al*'s formulation appears to be more accurate for four out of the six areas studied here (with less standard deviation). But considering the recommended temperatures for these areas (original authors' and the petrographic descriptions therein) the present formulation gives better temperature estimates (within  $\pm 12^\circ\text{C}$  of the recommended value). Bhattacharya *et al*'s (1988) formulation overestimates temperature by about  $20^\circ\text{C}$  to  $45^\circ\text{C}$  for the four areas. For the Namaqualand area the petrographic description reveals that 3 of the analytical data are related to retrograde alterations and the recommended temperature is from prograde garnet-orthopyroxene pair (according to Clifford *et al* 1981). The only analytical data related to prograde texture gives  $771^\circ\text{C}$  and  $834^\circ\text{C}$  in the present formulation and that of Bhattacharya *et al* respectively. For the Snyder group, the scatter is relatively large in all the thermometers (the lowest in the present formulation) and the recommended temperature appears to be an underestimate; the peak metamorphic temperature recorded from the area is about  $760^\circ\text{C}$  from garnet-orthopyroxene, garnet-clinopyroxene pairs and mafic rocks.

The recommended temperatures for Scottish Caledonides are also lower estimates, the peak temperature being recorded from garnet-orthopyroxene pairs.

### 3. Cordierite-garnet geobarometry

The equilibrium condition of the reaction



can be expressed as

$$\Delta G_{P,T} = 0 = \Delta H - T\Delta S + P\Delta V + RT\ln K_D + 0.5RT\ln(1 - X_{H_2O}) \quad (11)$$

where

$$K_D = X_{Mg}^{crd} / X_{Mg}^{gt}$$

For hydrous natural cordierites, the reduced activity is accounted for by the last term in equation (11), as given in Berman (1988), assuming that water mixes on two independent sites in cordierites.

Transposing equation (11), the barometric expression becomes,

$$P(\text{bar}) = (\Delta S/\Delta V)T - (\Delta H/\Delta V) - (R/\Delta V)T\ln K - 0.5(R/\Delta V)T\ln(1 - X_{H_2O})^{crd} \quad (12)$$

From Berman's (1988) data set,  $\Delta H$ ,  $\Delta S$  and  $\Delta V$  of reaction (10) were calculated at 1073°K and 7 Kb, using the relations-

$$C_P = k_0 + k_1 T^{-.5} + k_2 T^{-2} + k_3 T^{-3} \quad (13)$$

and

$$V_{P,T}/V_{1,298} = 1 + V_1(P - 1) + V_2(P - 1)^2 + V_3(T - 298) + V_4(T - 298)^2 \quad (14)$$

The results of these calculations are given in table 4. Using these values the barometric expression (12) becomes-

$$P(\text{bar}) = 10.46T - 1699.53 - 3.28 T\ln K_D - 1.639 T\ln(1 - X_{H_2O})^{crd} \quad (15)$$

This barometer gives the pressure estimates for garnet-cordierite-sillimanite-quartz assemblage for  $P_{H_2O} = P_{total}$  and  $P_{H_2O} = 0$  conditions including and excluding the last term respectively.

Table 4. Comparative geobarometry and fluid activity for selected areas.

Area	P(Kbar)	T°C	$P_{H_2O} = P_{total}$		$P_{H_2O} = 0$		$a_{H_2O}$	
	Assumed	Assumed	P.S	B.S	P.S	B.S	P.S	B.S
Nain Complex	3.5	760	5.97	6.02	3.78	3.81	0.006	0.018
South India	6.0	710	5.96	6.02	3.60	4.61	0.030	0.014
Inari Complex	5.0	760	5.70	5.03	4.80	4.50	0.287	0.293
Scottish Caledonides	5.5	710	6.53	5.50	3.26	4.17	0.174	0.039
Snyder Group	4.0	710	5.93	4.00	2.96	3.27	0.230	0.010
Namaqualand	7.7	800	9.65	7.80	4.83	5.10	0.157	0.106

Note: P.S-Present study. B.S-Bhattacharya and Sen (1985)

Further, transposing equation (15), at known P, T the water content of Mg-cordierite is given by—

$$X_{\text{H}_2\text{O}}^{\text{crd}} = 1 - \exp\{1/T(1037.05 + 0.61P) + 21\ln K_D - 6.384\} \quad (16)$$

For the Fe-end members Bhattacharya and Sen (1985) considered the reaction



They calculated the free energy change of this reaction from the experimental P, T brackets of Holdaway and Lee (1977) and their formulation can be expressed as

$$P(\text{bar}) = 5183.47 - 3.346T + 2.976T\ln K_D - 1.49T\ln(1 - X_{\text{H}_2\text{O}}^{\text{crd}}) \quad (18)$$

where

$$K_D = (X_{\text{Fe}}^{\text{gt}})/(X_{\text{Fe}}^{\text{crd}})$$

and transposing equation (18) at known P, T

$$X_{\text{H}_2\text{O}}^{\text{crd}} = 1 - \exp\{1/T(3483 - 0.672P) + 2\ln K_D - 2.248\} \quad (19)$$

For fluid activity ( $a_{\text{H}_2\text{O}}$ ) at known (equilibrium) P, T, Bhattacharya and Sen (1985) used the high pressure experimental data on hydration of Mg-cordierite (Holdaway 1976; Mirwald and Schreyer 1977 at  $P_{\text{H}_2\text{O}} = P_{\text{total}}$  and Johannes and Schreyer 1981 for  $P_{\text{H}_2\text{O}} = 0$ ). Using  $G_{\text{H}_2\text{O}}^0$  values from Berman's data set, for internal consistency, their formulation is modified to give—

$$a_{\text{H}_2\text{O}}^{\text{P,T}} = \frac{\exp\{-1/RT[64582 - 32.26T - P(0.0009T - 0.5142)]\} X_{\text{H}_2\text{O}}^{\text{crd}}}{(1 - X_{\text{H}_2\text{O}}^{\text{crd}})} \quad (20)$$

Bhattacharya and Sen's (1985) barometric formulation is derived for the Fe-end members, whereas their data on hydration of cordierite are for Mg-cordierite. Obviously  $a_{\text{H}_2\text{O}}$  for Mg-cordierite (equation 20) should be more consistent with the present barometric formulation (15) derived for Mg-end members.

*Application:* The equilibrium recommended pressures from some granulite areas are closely comparable to the garnet-cordierite pressure estimates at  $P_{\text{H}_2\text{O}} = 0$ , as exemplified by the Nain complex and the  $a_{\text{H}_2\text{O}}$  values determined on the basis of equations (16) and (19) are low. On the other hand, equilibrium pressures are intermediate between the cordierite-garnet pressure estimates for  $P_{\text{H}_2\text{O}} = 0$  and  $P_{\text{H}_2\text{O}} = P_{\text{total}}$  conditions, as exemplified by four granulite areas (Inari complex, Scottish Caledonides, Snyder group and Namaqualand) and here the  $a_{\text{H}_2\text{O}}$  values are relatively high (0.2 to 0.3). However, Bhattacharya and Sen's (1985) model gives inconsistent results, e.g. in Scottish Caledonides and Snyder group the equilibrium pressure is closely comparable to P estimate for  $P_{\text{H}_2\text{O}} = P_{\text{total}}$  condition in Bhattacharya and Sen's barometer, while  $a_{\text{H}_2\text{O}}$  value in their model is quite low (0.04 and 0.01 respectively). This inconsistency is probably the consequence of P estimate from Fe-end members and  $a_{\text{H}_2\text{O}}$  estimate from Mg-cordierite in their model.

An isothermal decompression path is implied where the equilibrium pressure is significantly higher than the cordierite-garnet P estimate for  $P_{\text{H}_2\text{O}} = 0$  condition, while the  $a_{\text{H}_2\text{O}}$  is quite low, as exemplified by the South Indian granulite area (table 4).



### Acknowledgements

The author thankfully acknowledges the advice and suggestions offered by Prof. S K Sen during the preparation of the manuscript. The comments of the anonymous reviewers were of great help in the preparation of the final manuscript.

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