

## Non-ideal Mg-Fe binary mixing in cordierite: Constraints from experimental data on Mg-Fe partitioning in garnet and cordierite and a reformulation of garnet-cordierite geothermometer

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**Abstract.** The non-ideal regular Mg-Fe binary in cordierite has been derived through multivariate linear regression of the expression  $RT \ln K_D + (P - 1) \Delta V_{1,298}^0$  along with updated subregular mixing parameter of almandine-pyrope solution (Hackler and Wood 1989; Berman 1990). The data base used for multivariate analyses consists of published experimental data ( $n = 177$ ) on Mg-Fe partitioning between garnet and cordierite in the  $P$ - $T$  range 650–1050°C and 4–12 K bar. The non-ideality can be approximated by temperature-dependent Margules parameters. The retrieved values of  $\Delta H_{(T)}^0$  and  $\Delta S_{(T)}^0$  of exchange reaction between garnet and cordierite and enthalpy and entropy of mixing of Mg-Fe cordierite were combined with recent quaternary (Fe-Mg-Ca-Mn) mixing data in garnet to obtain the geothermometric expressions to determine temperature ( $T$  Kelvin):

$$T(HW) = 6832 + 0.031(P - 1) - \{166(X_{Mg}^{Gt})^2 - 506(X_{Fe}^{Gt})^2 + 680 X_{Fe}^{Gt} X_{Mg}^{Gt} + 336(X_{Ca} + X_{Mn}) (X_{Mg} - X_{Fe})^{Gt} - 3300 X_{Ca}^{Gt} - 358 X_{Mn}^{Gt}\} + 954(X_{Fe} - X_{Mg})^{Crd} / 1.987 \ln K_D + 3.41 + 1.5 X_{Ca}^{Gt} + 1.23(X_{Fe} - X_{Mg})^{Crd}$$

$$T(Br) = 6920 + 0.031(P - 1) - \{18(X_{Mg}^{Gt})^2 - 296(X_{Fe}^{Gt})^2 + 556 X_{Fe}^{Gt} X_{Mg}^{Gt} - 6339 X_{Ca}^{Gt} X_{Mg}^{Gt} - 99(X_{Ca}^{Gt})^2 + 4687 X_{Ca}^{Gt} (X_{Mg} - X_{Fe})^{Gt} - 4269 X_{Ca}^{Gt} X_{Fe}^{Gt} - 358 X_{Mn}^{Gt}\} + 640(X_{Fe} - X_{Mg})^{Crd} / 1.987 \ln K_D + 3.40 + 1.095(X_{Ca}^{Gt})^2 + 1.1 X_{Ca}^{Gt} X_{Mg}^{Gt} + 1.09 X_{Ca}^{Gt} X_{Fe}^{Gt} + 0.78(X_{Fe} - X_{Mg})^{Crd} + 1.90 X_{Ca}^{Gt} (X_{Mg} - X_{Ca})^{Gt}$$

**Keywords.** Geothermometer; equilibrium; regression; mixing parameters.

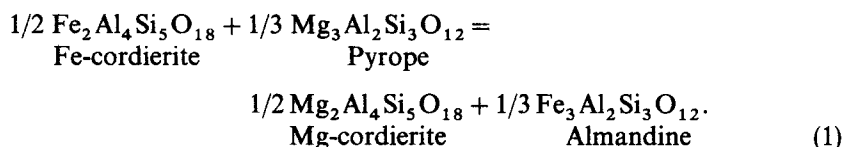
### 1. Introduction

Mg-Fe exchange between coexisting garnet and cordierite is known to be significantly dependent on temperature of equilibration. Due to the common occurrence of this mineral pair in medium to high-grade metamorphic rocks, the garnet-cordierite geothermometer has wide application. The calibrations based on  $K_{DFe-Mg}^{Gt-Crd}$  from metamorphic rocks of varying metamorphic grades have been proposed by Thompson (1976), Bhattacharya *et al* (1988) and others. Besides this the Mg-Fe exchange equilibrium between garnet and cordierite has been experimentally studied and calibrated for geothermometry (Hensen and Green 1971; Hensen 1977; Perchuk and Lavrent'eva 1983; Perchuk *et al* 1985; Aranovich and Podlesskii 1989; and Nichols *et al* 1992). Bhattacharya (1993) calibrated this equilibrium using the internally consistent data set of Berman (1988) and Holland and Powell (1990). The estimates of temperature through these geothermometers differ because of ideal or non-ideal mixing of Fe-Mg-Ca-Mn in garnet and different  $\ln K_D$  versus  $1/T$  slope. For the Mg-Fe mixing properties of cordierite, many authors except, Bhattacharya *et al* (1988), have assumed ideal Mg-Fe mixing in cordierite.

The main objectives of this paper are: (a) to derive new thermodynamic data on Mg-Fe exchange equilibria between garnet and cordierite from experimental data ( $n = 177$ ) in the FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system; (b) to determine the Margules parameters related to non-ideal Mg-Fe mixing in cordierite on the basis of recent data on Mg, Fe partitioning in almandine-pyrope system, and (c) to finally propose a garnet-cordierite geothermometer for application to metamorphic rocks of different grade.

## 2. Thermodynamic background

The Mg and Fe exchange between garnet and cordierite (abbreviated Gt and Crd respectively) can be expressed as:



At equilibrium the equation is:

$$\begin{aligned} \Delta G_{PT}(1) = & \Delta H_{1,298}^0 + \int_{298}^T \Delta C_p^0(T) dT - T[\Delta S_{1,298}^0 \\ & + \int_{298}^T \Delta C_p^0(T) dT/T] + \int_1^P \Delta V^0(P) dP + RT \ln K_D \\ & + RT \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Gt}} + RT \ln(\gamma_{\text{Mg}}/\gamma_{\text{Fe}})^{\text{Crd}}, \end{aligned} \quad (2)$$

where,  $\Delta G_{PT}(1)$  is the molar Gibbs free energy change related to reaction (1) at specified  $P - T$ .  $\Delta H_{1,298}^0$ ,  $\Delta S_{1,298}^0$  and  $\Delta V_{1,298}^0$  are the standard state changes in enthalpy, entropy and volume respectively between pure phases at 1 bar and 298 (K) of the reaction (1);  $T$  is temperature (K);  $P$  is pressure (bar);  $\Delta C_p^0$  is change in heat capacity of the reaction (1);  $\gamma_i^j$  is the activity coefficient of the component  $i$  in phases  $J$  and  $R$  is the universal gas constant ( $1.987 \text{ cal K}^{-1}$ ).

A linear relation of  $\ln K + (P - 1)\Delta V_{1,298}^0/RT$  versus  $1/T(\text{K})$  (figure 1) suggests that  $\Delta C_p^0$  is negligible or cannot be resolved in the temperature range of the present study,  $\Delta H^0$  and  $\Delta S^0$  in equation (2) are therefore the average standard enthalpy and entropy differences respectively of the reaction for the experimental range of temperature (i.e.  $\Delta H_{\langle T \rangle}^0$  and  $\Delta S_{\langle T \rangle}^0$  proposed by Chatterjee 1991, p. 124). As the  $\Delta V^0$  of the reaction is small, the integral term of  $\Delta V^0$  can be ignored, and thus equation (2) can be written as:

$$\Delta G_{PT}(1) = 0 = \Delta H^0 - T\Delta S^0 + (P - 1)\Delta V_{1,298}^0 + RT \ln K, \quad (3)$$

where  $K$  is the equilibrium constant of reaction (1),  $K = RT \ln K_D + RT \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Gt}} + RT \ln(\gamma_{\text{Mg}}/\gamma_{\text{Fe}})^{\text{Crd}}$ ,  $K_D = (X_{\text{Fe}}/X_{\text{Mg}})^{\text{Gt}} \cdot (X_{\text{Mg}}/X_{\text{Fe}})^{\text{Crd}}$ ,  $X_{\text{Mg}}^{\text{Gt/Crd}} = \text{Mg}/(\text{Mg} + \text{Fe})$ ;  $X_{\text{Fe}}^{\text{Gt/Crd}} = \text{Fe}/(\text{Mg} + \text{Fe})$ .

## 3. Activity coefficient in garnet and cordierite

The activity coefficients in garnet  $\gamma_{\text{Fe}}^{\text{Gt}}$  and  $\gamma_{\text{Mg}}^{\text{Gt}}$ , were derived by using the subregular solution of Mg-Fe mixing expressions in garnet of Ganguly and Saxena (1984)

(equation 4) and Berman (1990) (equation 5).

$$RT \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Gt}} = W_{\text{Fe-Mg}} X_{\text{Mg}}^2 - W_{\text{Mg-Fe}} X_{\text{Fe}}^2 + 2(W_{\text{Mg-Fe}} - W_{\text{Fe-Mg}}) X_{\text{Fe}} X_{\text{Mg}}. \quad (4)$$

$$RT \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Gt}} = W_{223} X_{\text{Mg}}^2 - W_{233} X_{\text{Fe}}^2 + 2(W_{233} - W_{223}) X_{\text{Fe}} X_{\text{Mg}}. \quad (5)$$

The Fe-Mg mixing parameter ( $W$ ) is generally expressed by the following equation:

$$W = W_H - T W_S + P W_V, \quad (6)$$

where,  $W_H$ ,  $W_S$  and  $W_V$  are the non-ideal mixing parameters for enthalpy, entropy and volume respectively (Thompson 1976; Ganguly and Saxena 1984). By ignoring  $W_V$  and subtracting  $\gamma_{\text{Fe}}^{\text{Crd}}$  from  $\gamma_{\text{Mg}}^{\text{Crd}}$ , equation (7) is obtained using the regular solution of Fe-Mg mixing.

$$RT \ln(\gamma_{\text{Mg}}/\gamma_{\text{Fe}}) = W_{H,\text{Fe-Mg}} (X_{\text{Fe}} - X_{\text{Mg}})^{\text{Crd}} - T W_{S,\text{Fe-Mg}} (X_{\text{Fe}} - X_{\text{Mg}})^{\text{Crd}}. \quad (7)$$

Substituting equation (7) and (4) in equation (3) with  $W_{\text{Fe-Mg}}^{\text{Gt}} = 166$  cal and  $W_{\text{Mg-Fe}}^{\text{Gt}} = 506$  cal per cation (Hackler and Wood 1989) and rearranging gives:

$$\begin{aligned} RT \ln K_D - 0.031(P - 1) + 166 X_{\text{Mg}}^2 - 506 X_{\text{Fe}}^2 + 2(506 - 166) X_{\text{Fe}} X_{\text{Mg}} \\ = [Z] = -\Delta H + T \Delta S - W_{H,\text{Fe-Mg}} (X_{\text{Fe}} - X_{\text{Mg}})^{\text{Crd}} \\ + T W_{S,\text{Fe-Mg}} (X_{\text{Fe}} - X_{\text{Mg}})^{\text{Crd}}. \end{aligned} \quad (8)$$

After substitution of equations (7) and (5) in equation (3) and using subregular Fe-Mg interaction parameter of Berman (1990),  $W_{223} = 18$  and  $W_{233} = 296$ , equation (9) can be obtained after rearrangement:

$$\begin{aligned} RT \ln K_D - 0.031(P - 1) + 18 X_{\text{Mg}}^2 - 196 X_{\text{Fe}}^2 + 2(196 - 18) X_{\text{Fe}} X_{\text{Mg}} \\ = [Z1] = -\Delta H + T \Delta S - W_{H,\text{Fe-Mg}} (X_{\text{Fe}} - X_{\text{Mg}})^{\text{Crd}} \\ + T W_{S,\text{Fe-Mg}} (X_{\text{Fe}} - X_{\text{Mg}})^{\text{Crd}}. \end{aligned} \quad (9)$$

If the terms on the left hand side of equations (8) and (9) are known, then four unknown parameters on the right hand side can be estimated by multivariate regression. The  $V_{1,298}^0$  of reaction (1) is  $(-0.031 \text{ cal bar}^{-1})$  calculated from the data of Holland and Powell (1990).  $K_D$  has been calculated from the experimental data related to Fe-Mg exchange reaction between garnet and cordierite (Hensen and Green 1971; Hensen 1977; Perchuk and Lavrent'eva 1983; Aranovich and Podlesskii 1983 and Bertrand *et al* 1991) for  $P - T$  range 650–1050°C and 4–12 Kbar.  $[Z]$  and  $[Z1]$  of the left hand side of equations (8) and (9) are computed at experimental  $P$  and  $T$  of equilibration (table 1).  $[Z]$  and  $[Z1]$  were chosen as the dependent variables and three terms ( $\Delta S$ ,  $W_{H,\text{Fe-Mg}}^{\text{Crd}}$  and  $W_{S,\text{Fe-Mg}}^{\text{Crd}}$ ) of the right hand side of equations (8) and (9) as the independent variables and  $\Delta H$  as the regression constant. The retrieved values of temperature dependent Margules parameters in cordierite, with 97% confidence level, derived from equations (8) and (9) respectively, are:

$$W_{G,\text{Fe-Mg}}^{\text{Crd}} = 954(\pm 329) - 1.23 T(\pm 0.48). \quad (8a)$$

$$W_{G,\text{Fe-Mg}}^{\text{Crd}} = 640(\pm 312) - 0.78 T(\pm 0.26). \quad (9a)$$

**Table 1.** [Z] and [Z1] values. Equations (8) and (9) computed from the two sub-regular mixing models for Fe-Mg garnets on the basis of experimental  $P$ ,  $T$ ,  $X_{Fe}^{Gt}$  and  $X_{Fe}^{Crd}$  data.

S. No	$P$ (bar)	$T$ (K)	$(X_{Fe} - X_{Mg})^{Crd}$	$T(X_{Fe} - X_{Mg})^{Crd}$	Z	Z1
<b>(a) Hensen and Green (1971)</b>						
1.	9000	1173	-0.62	-727.6	3176.1	3038.0
2.	7200	1223	-0.04	-48.9	2603.0	2523.7
3.	8100	1273	-0.60	-763.8	3432.2	3207.3
4.	9300	1273	-0.78	-992.9	4033.6	3759.8
<b>(b) Hensen (1977)</b>						
5.	9000	1273	-0.64	-814.7	2645.7	2557.4
<b>(c) Perchuk and Lavrenteva (1983)</b>						
6.	6000	923	-0.852	-786.3	4010.0	3969.4
7.	6000	923	-0.640	-590.7	3801.8	3852.5
8.	6000	923	-0.874	-806.7	4019.6	3965.1
9.	6000	923	-0.620	-512.3	3914.4	3894.1
10.	6000	923	-0.300	-276.9	3582.2	3705.1
11.	6000	923	-0.320	-295.4	3607.2	3697.7
12.	6000	973	-0.540	-525.4	3752.6	3820.5
13.	6000	973	-0.510	-496.2	3594.1	3661.9
14.	6000	973	-0.540	-525.4	3590.5	3649.8
15.	6000	973	-0.360	-350.2	3410.3	3505.1
16.	6000	973	-0.420	-408.6	3588.7	3678.9
17.	6000	973	-0.480	-467.0	3610.3	3687.0
18.	6000	973	-0.460	-447.6	3598.8	3679.9
19.	6000	973	-0.520	-505.9	3482.2	3541.5
20.	6000	973	-0.140	-136.2	3410.3	3542.9
21.	6000	973	-0.640	-622.7	3583.7	3609.8
22.	6000	973	-0.780	-758.9	3844.8	3825.7
23.	6000	973	-0.580	-564.3	3507.5	3549.9
24.	6000	973	-0.134	-130.4	3843.4	3990.9
25.	6000	973	-0.070	-68.1	3577.7	3586.6
26.	6000	973	-0.040	-38.9	3688.2	3835.6
27.	6000	973	-0.600	-538.8	3777.6	3828.3
28.	6000	973	-0.680	-661.6	3713.3	3731.6
29.	6000	973	-0.060	-58.3	3412.3	3544.9
30.	6000	973	-0.586	-570.2	3687.7	3738.1
31.	6000	973	-0.480	-467.1	3652.9	3731.8
32.	6000	973	-0.560	-544.8	3702.7	3761.9
33.	6000	973	-0.700	-681.1	3649.2	3656.1
34.	6000	973	-0.880	-856.2	3831.1	3757.4
35.	6000	973	-0.544	-529.3	3692.0	3755.5
36.	6000	973	-0.780	-758.9	3809.3	3788.5
37.	6000	973	-0.600	-583.8	3663.1	3707.5
38.	6000	973	-0.338	-328.8	3525.3	3629.8
39.	6000	973	-0.544	-529.3	3607.0	3661.1
40.	6000	973	-0.464	-451.5	3529.1	3605.8
41.	6000	973	-0.464	-451.5	3679.5	3763.8
42.	6000	973	-0.814	-792.0	3809.9	3771.8
43.	6000	973	-0.342	-332.7	3445.0	3544.9
44.	6000	973	-0.442	-430.1	3509.9	3591.0
45.	6000	973	-0.820	-797.8	3917.3	3881.1

(Continued)

Table 1. (Continued)

S. No	P(bar)	T(K)	$(X_{Fe} - X_{Mg})^{Crd}$	$T(X_{Fe} - X_{Mg})^{Crd}$	Z	Z1
46.	6000	973	-0.600	-583.8	3777.6	3828.3
47.	6000	973	-0.380	-369.7	3599.0	3698.4
48.	6000	973	-0.550	-535.1	3646.6	3705.8
49.	6000	973	-0.890	-865.9	3772.8	3691.5
50.	6000	973	-0.480	-467.8	3120.2	3171.0
51.	6000	973	0.040	038.9	3343.6	3496.1
52.	6000	973	-0.160	-155.7	3423.0	3553.2
53.	6000	1023	-0.380	-380.7	3405.2	3450.3
54.	6000	1023	-0.640	-654.7	3625.6	3643.8
55.	6000	1023	-0.320	-327.3	3251.7	3338.7
56.	6000	1023	-0.360	-368.3	3405.7	3491.3
57.	6000	1023	-0.416	-425.5	3485.8	3562.5
58.	6000	1023	-0.476	-486.9	3498.0	3560.3
59.	6000	1023	-0.320	-327.3	3320.6	3410.8
60.	6000	1023	-0.480	-491.0	3410.1	3466.8
61.	6000	1023	-0.648	-662.9	3554.5	3566.1
62.	6000	1023	-0.818	-836.8	3587.2	3530.2
63.	6000	1023	-0.372	-380.5	3442.6	3527.4
64.	6000	1023	-0.400	-409.2	3408.6	3485.3
65.	6000	1023	-0.464	-474.7	3393.5	3453.7
66.	6000	1023	-0.560	-572.8	3660.3	3706.8
67.	6000	1023	-0.340	-347.8	3356.7	3440.1
68.	6000	1023	-0.172	-175.9	3303.6	3420.3
69.	6000	1023	-0.232	-237.3	3301.6	3407.9
70.	6000	1023	-0.300	-306.9	3227.1	3317.3
71.	6000	1023	-0.480	-497.0	3375.7	3430.7
72.	6000	1023	-0.580	-593.3	3464.8	3495.0
73.	6000	1023	-0.620	-634.3	3566.1	3588.3
74.	6000	1023	-0.760	-777.5	3622.0	3592.5
75.	6000	1023	-0.749	-766.2	3692.0	3624.3
76.	6000	1023	-0.338	-345.8	3228.0	3420.8
77.	6000	1073	-0.220	-236.0	3233.8	3332.3
78.	6000	1073	-0.460	-493.6	3353.0	3293.7
79.	6000	1073	-0.320	-343.4	3296.5	3377.7
80.	6000	1073	-0.240	-257.5	3302.4	3399.9
81.	6000	1073	-0.080	-085.8	3126.7	3244.8
82.	6000	1073	-0.164	-175.9	3203.5	3310.8
83.	6000	1073	-0.660	-708.2	3486.9	3482.4
84.	6000	1073	-0.830	-890.6	3524.2	3453.6
85.	6000	1073	-0.520	-557.9	3397.7	3427.9
86.	6000	1073	-0.220	-236.0	3254.8	3354.2
87.	6000	1073	-0.100	-107.3	3161.8	3278.1
88.	6000	1123	-0.400	-449.2	3180.9	3230.8
89.	6000	1123	-0.160	-179.7	3033.9	3128.1
90.	6000	1123	-0.140	-157.2	3032.4	3130.8
91.	6000	1123	-0.096	-107.8	3100.6	3209.3
92.	6000	1123	-0.222	-249.3	3035.4	3118.4
93.	6000	1123	-0.240	-269.5	3080.3	3161.4
94.	6000	1123	-0.340	-381.8	3167.5	3231.1
95.	6000	1123	-0.310	-348.1	3056.0	3123.9
96.	6000	1123	-0.264	-296.5	3285.2	3369.1

(Continued)

Table 1. (Continued)

S. No	P(bar)	T(K)	$(X_{Fe} - X_{Mg})^{Crd}$	$T(X_{Fe} - X_{Mg})^{Crd}$	Z	Zi
97.	6000	1123	-0.810	-909.6	3485.0	3416.5
98.	6000	1123	-0.660	-741.2	3285.6	3264.8
99.	6000	1123	-0.596	-669.3	3242.8	3238.8
100.	6000	1123	-0.544	-610.9	3263.7	3278.5
101.	6000	1123	-0.462	-518.8	3351.6	3393.6
102.	6000	1123	-0.334	-375.1	3242.5	3310.9
103.	6000	1123	-0.120	-134.8	3001.6	3102.4
104.	6000	1123	-0.440	-494.1	3397.4	3447.3
105.	6000	1123	-0.300	-336.9	3213.5	3287.9
106.	6000	1123	-0.460	-516.6	3201.8	3237.2
107.	6000	1123	-0.392	-440.2	3202.8	3255.7
108.	6000	1123	0.006	006.7	2950.0	3069.6
109.	6000	1123	-0.622	-698.5	3409.4	3406.7
110.	6000	1123	0.116	130.2	2960.8	3096.4
111.	6000	1123	-0.044	-049.4	2998.4	3111.8
112.	6000	1123	-0.168	-188.7	3037.0	3130.4
113.	6000	1123	-0.300	-336.9	3263.6	3340.3
114.	6000	1123	-0.386	-433.5	3314.5	3375.5
115.	6000	1123	-0.460	-516.6	3175.6	3209.8
116.	6000	1173	-0.224	-262.7	3174.4	3306.7
117.	6000	1173	-0.038	-044.6	2998.9	3106.6
118.	6000	1173	-0.122	-143.1	2898.0	2988.6
119.	6000	1173	-0.356	-417.6	3067.2	3115.8
120.	6000	1173	-0.656	-769.5	3463.6	3441.0
121.	6000	1173	-0.360	-422.3	3079.8	3128.1
122.	6000	1173	-0.344	-403.5	3183.4	3239.5
123.	6000	1173	-0.168	-197.1	2973.6	3037.6
124.	6000	1173	-0.500	-586.5	3085.4	3138.2
125.	6000	1173	-0.380	-445.2	3149.1	3195.7
126.	6000	1173	-0.160	-187.7	2962.4	3048.1
127.	6000	1173	-0.086	-100.9	2943.6	3042.5
128.	6000	1223	-0.062	-075.8	2630.2	2718.1
129.	6000	1223	0.140	171.2	2369.5	2482.9
130.	6000	1223	-0.240	-293.5	2704.1	2759.1
131.	6000	1223	0.200	244.6	2619.1	2749.2
132.	6000	1223	0.022	026.9	2589.9	2691.4
133.	6000	1223	-0.074	-090.5	2508.0	2588.7
134.	6000	1223	-0.154	-188.3	2540.3	2606.5
135.	6000	1223	-0.440	-538.1	2856.2	2871.0
136.	6000	1223	0.226	276.4	2756.2	2893.7
137.	6000	1223	0.254	310.6	2610.4	2747.9
138.	6000	1223	0.110	134.5	2665.0	2783.1
139.	6000	1223	0.002	002.4	2683.5	2784.2
140.	6000	1223	-0.120	-146.8	2908.4	2995.8
141.	6000	1223	-0.324	-396.3	2782.5	2822.0
142.	6000	1223	-0.306	-374.2	2725.1	2766.2
143.	6000	1223	-0.194	-237.2	2677.0	2740.9
144.	6000	1223	-0.088	-107.6	2587.1	2668.2
145.	6000	1223	-0.014	-017.1	2591.3	2689.3
146.	6000	1223	-0.860	-1051.8	2998.9	2895.0
147.	6000	1223	-0.634	-775.3	3033.8	3001.6

(Continued)

Table 1. (Continued)

S. No	P(bar)	T(K)	$(X_{Fe} - X_{Mg})^{Crd}$	$T(X_{Fe} - X_{Mg})^{Crd}$	Z	Z1
148.	6000	1223	-0.718	-878.1	3003.6	2944.7
149.	6000	1223	-0.800	-978.4	3026.2	2942.0
150.	6000	1223	-0.850	-1039.6	2903.6	2801.2
151.	6000	1223	-0.040	-048.9	2470.8	2556.5
152.	6000	1223	0.122	149.2	2653.7	2773.3
153.	6000	1273	-0.360	-458.3	2887.8	2919.5
154.	6000	1273	-0.132	-168.0	2724.8	2796.6
155.	6000	1273	-0.277	-346.3	2827.7	2874.3
<b>(d) Aranovich and Podleskii (1983)</b>						
156.	4000	973	-0.12	-116.7	3293.2	3450.7
157.	5000	973	0.10	097.3	3289.1	3421.7
158.	6000	973	0.38	369.7	3405.0	3498.2
159.	8000	973	0.78	758.9	3774.1	3755.0
160.	5000	1023	-0.12	-116.7	3064.8	3212.3
161.	8000	1023	0.66	642.2	3471.9	3478.6
<b>(e) Bertrand et al (1991)</b>						
162.	10000	1173	-0.82	-961.8	3176.1	3093.7
163.	10000	1173	-0.72	-844.6	1781.1	1701.2
164.	10000	1173	-0.72	-844.5	2015.4	1932.9
165.	10000	1173	-0.68	-797.6	2933.8	2890.8
166.	10000	1273	-0.58	-738.3	2365.2	2325.6
167.	10000	1273	-0.58	-738.3	2744.5	2715.0
168.	10000	1273	-0.60	-763.8	2806.0	2773.1
169.	10000	1273	-0.64	-814.7	2741.1	2694.9
170.	10000	1273	-0.67	-841.6	3112.9	3073.3
171.	11000	1273	-0.74	-942.0	2733.2	2659.3
172.	11000	1273	-0.68	-865.6	3069.3	3023.1
173.	11000	1273	-0.72	-916.5	2847.1	2782.1
174.	12000	1273	-0.78	-992.9	3100.4	3023.6
175.	10000	1298	-0.60	-778.8	3059.4	3033.4
176.	10000	1298	-0.72	-943.5	3639.3	3596.4
177.	10000	1323	-0.62	-820.3	2706.8	2727.9

#### 4. Formulation of garnet-cordierite geothermometer

##### 4.1 $\Delta H$ and $\Delta S$ of reaction (1):

Using the Margules parameter of Fe-Mg subregular solution of mixing in garnet (Hackler and Wood 1989 and Berman 1990), the regular solution of Fe-Mg mixing in cordierite derived in this study and the  $K_D$  calculated from the experimental data, the equation (2) is rearranged as:

$$\begin{aligned} \ln K_D + \ln(\gamma_{Fe}/\gamma_{Mg})^{Gt} + \ln(\gamma_{Mg}/\gamma_{Fe})^{Crd} + (P-1)V_{1,298}^0/RT \\ = -\Delta H^0/RT + \Delta S^0/R. \end{aligned} \quad (10)$$

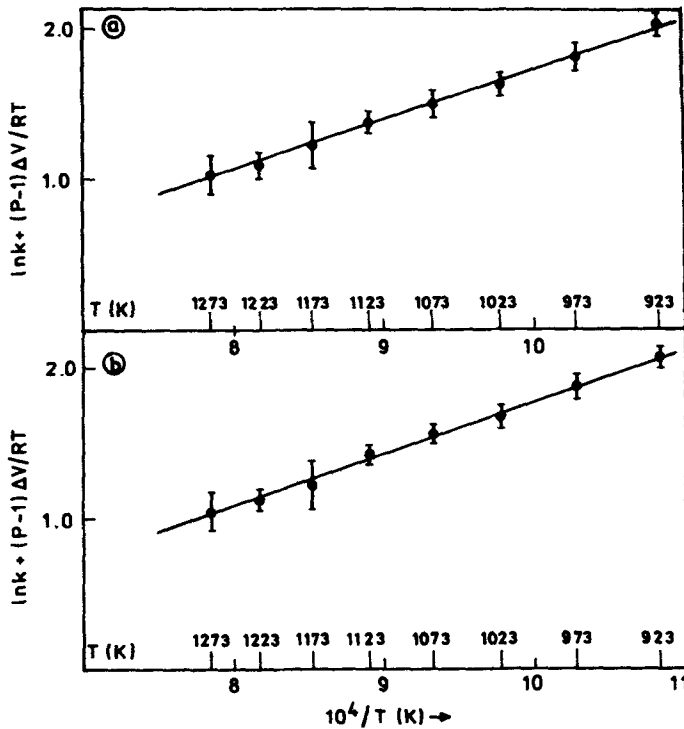


Figure 1(a and b). A plot of  $\ln K$  (at 1 bar) +  $(P-1)\Delta V^0/RT$  for reaction (1) versus  $10^4/T(K)$  of experimental data in the  $P-T$  range 650 to 1050°C and 4 to 12 Kbar pressure for subregular mixing model of Hackler and Wood (1989) and Berman (1990) respectively. Solid circles with bar represent the mean and standard deviation of  $\ln K$  at 1 bar.

Thus a plot of the left hand side of equation (10) versus  $1/T(K)$  yields a slope of  $-\Delta H^0/RT$  and an intercept of  $\Delta S^0/R$  from least square fit measurements (figures 1a and b). The derived values of  $\Delta H^0$  and  $\Delta S^0$  are  $-6832(\pm 160)$ ,  $-6920(\pm 169)$  cal and  $-3.41(\pm 0.047)$ ,  $-3.40(\pm 0.046)$  cal  $K^{-1}$ , respectively. The retrieved values of  $\Delta H^0$  and  $\Delta S^0$  of reaction (1) pass through the experimental bracket of all the above mentioned published experimental data (figures 1a and b).

The Fe-Mg relationship derived through equations (8) and (9) has been extended to include the effect of  $X_{Ca}$  and  $X_{Mn}$  in garnet on  $\ln K_D - T$  relations. Thus, by taking the Ca-Mg binary as symmetric  $W_{Mg-Ca}^{Gt} = W_{Ca-Mg}^{Gt} = 3300 - 1.5T$  (Newton and Haselton 1981); the Ca-Fe and Fe-Mn binary to be ideal, Mg-Mn binary symmetric i.e.,  $W_{Mg-Mn}^{Gt} = 358$  cal per cation (Wood *et al* 1994); Fe-Mg binary as asymmetric (Hackler and Wood 1989), equation (11) is obtained:

$$\begin{aligned}
 RT \ln(\gamma_{Fe}/\gamma_{Mg})^{Gt} = & W_{Fe-Mg} X_{Mg}^2 - W_{Mg-Fe} X_{Fe}^2 + 2(W_{Mg-Fe} - W_{Fe-Mg}) X_{Fe} X_{Mg} \\
 & + 1/2(W_{Mg-Fe} + W_{Fe-Mg})(X_{Ca} + X_{Mn})(X_{Mg} - X_{Fe}) \\
 & - W_{Mg-Ca} X_{Ca} - W_{Mg-Mn} X_{Mn}.
 \end{aligned} \quad (11)$$

Considering ternary (Fe-Mg-Ca) subregular mixing in garnet of Berman (1990)



with additional term  $W_{\text{Mg-Mn}}$ , the following equation is obtained:

$$\begin{aligned} RT \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Gt}} = & W_{223} X_{\text{Mg}}^2 - W_{233} X_{\text{Fe}}^2 + 2(W_{233} - W_{223}) X_{\text{Fe}} X_{\text{Mg}} \\ & + X_{\text{Ca}}^2 (W_{113} - W_{112}) + (W_{123} - 2W_{122}) X_{\text{Ca}} X_{\text{Mg}} \\ & + (2W_{133} - W_{123}) X_{\text{Ca}} X_{\text{Fe}} + W_{123} X_{\text{Ca}} (X_{\text{Mg}} - X_{\text{Fe}}) \\ & - W_{\text{Mg-Mn}} X_{\text{Mn}}, \end{aligned} \quad (12)$$

where  $W_{112} = 1718 - 1.5T$ ;  $W_{122} = 5513 - 1.5T$ ;  $W_{133} = 209 - 0.405T$ ;  $W_{113} = 1619 - 0.405T$ ;  $W_{123} = 4687 - 1.90T$ , calories on one cation basis.  $W_V$  term of Berman (1990) has been ignored.

Combining equations (11), (12) and (7) with equation (3), the following geothermometric expression for the Mg-Fe exchange between garnet and cordierite is derived:

$$\begin{aligned} T(HW) = & 6832 + 0.031(P - 1) + 954(X_{\text{Fe}} - X_{\text{Mg}})^{\text{Crd}} - A/RT \ln K_D \\ & + 3.41 + 1.23(X_{\text{Fe}} - X_{\text{Mg}})^{\text{Crd}} + B, \\ A = & 166 X_{\text{Mg}}^2 - 506 X_{\text{Fe}}^2 + 680 X_{\text{Fe}} X_{\text{Mg}} + 336(X_{\text{Ca}} + X_{\text{Mn}})(X_{\text{Mg}} - X_{\text{Fe}}) \\ & - 3300 X_{\text{Ca}} - 358 X_{\text{Mn}} B = 1.5 X_{\text{Ca}}, \end{aligned} \quad (13)$$

$$\begin{aligned} T(\text{Br}) = & 6920 + 0.031(P - 1) + 640(X_{\text{Fe}} - X_{\text{Mg}})^{\text{Crd}} - C/RT \ln K_D \\ & + 3.40 + 0.78(X_{\text{Fe}} - X_{\text{Mg}})^{\text{Crd}} + D, \\ C = & 18 X_{\text{Mg}}^2 - 296 X_{\text{Fe}}^2 + 556 X_{\text{Fe}} X_{\text{Mg}} - 6339 X_{\text{Ca}} X_{\text{Mg}} - 99 X_{\text{Ca}}^2 \\ & - 4269 X_{\text{Ca}} X_{\text{Fe}} - 358 X_{\text{Mn}} + 4687 X_{\text{Ca}} (X_{\text{Mg}} - X_{\text{Fe}}). \\ D = & 1.095 X_{\text{Ca}}^2 + 1.1 X_{\text{Ca}} X_{\text{Mg}} + 1.09 X_{\text{Ca}} X_{\text{Fe}} + 1.90 X_{\text{Ca}} (X_{\text{Mg}} - X_{\text{Fe}}). \end{aligned} \quad (14)$$

where  $A$  and  $C = RT \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Gt}}$ ,  $W_H$  is related to Fe-Mg-Ca-Mn mixing in garnet;  $B$  and  $D = RT \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Gt}}$ ,  $-W_S$  refers to Fe-Mg-Ca-Mn mixing in garnet;  $K_D = (X_{\text{Fe}}/X_{\text{Mg}})^{\text{Gt}} \cdot (X_{\text{Mg}}/X_{\text{Fe}})^{\text{Crd}}$ ,  $l = (\text{Fe} + \text{Mg} + \text{Ca} + \text{Mn})$ ;  $X_{\text{Mg}}^{\text{Gt}} = \text{Mg}/l$ ;  $X_{\text{Fe}}^{\text{Gt}} = \text{Fe}/l$ ;  $X_{\text{Ca}}^{\text{Gt}} = \text{Ca}/l$ ;  $X_{\text{Mn}}^{\text{Gt}} = \text{Mn}/l$ ;  $X_{\text{Mg}}^{\text{Crd}} = \text{Mg}/\text{Fe} + \text{Mg}$ ;  $X_{\text{Fe}}^{\text{Crd}} = \text{Fe}/\text{Fe} + \text{Mg}$ . The value of  $R$  is  $1.987 \text{ cal K}^{-1}$ . The numerical values given in the expressions of the geothermometers in equations (13) and (14) can be obtained in joules if multiplied by 4.184.

## 5. Application and accuracy of the geothermometer

The reformulated geothermometers have been applied to high-grade metamorphic rocks across a wide compositional range from different localities (South Central Maine, Osberg 1971; North East Bavaria, Okrusch 1971; Nain Complex, Berg 1971; Sonapahar, Lal *et al* 1978; Scottish caledonides, Ashworth and Chinner 1978; South India, Harris 1981; Finnish Lapland, Hörmann *et al* 1980; Ajitpura, Sharma and MacRae 1981 and Limpopo belt, Harris and Holland 1984). It is an improvement over the existing garnet-cordierite geothermometers, because these are derived from

Table 2. Comparison of the result obtained from present formulation  $T(HW)$  and  $T(Br)$  with other garnet-cordierite geothermometers.

S. No.	Rock type	Locality	Sample no.	aT	T <sub>Th</sub>	T <sub>P</sub>	T <sub>B</sub>	T <sub>A,P</sub>	T <sub>Ni</sub>	T <sub>BS</sub>	T(HW)	T(Br)
1.	Gt-crd-and-q	South	3a	550	541	544	642	543	480	670	587	586
2.		Central	4c	550	549	550	655	550	486	685	593	592
3.		Maine, n = 3	6a	550	542	544	649	544	480	677	587	586
			M.Std.	544 ± 4	546 ± 3	648 ± 5	677 ± 4	545 ± 5	482 ± 3	677 ± 4	589 ± 3	588 ± 3
4.	Gt-crd-and/sil-q	North East Bavaria, n = 3	Sm6G Op170G Op157C	640 640 640	621 641 572	614 631 571	648 673 602	634 640 588	582 587 531	686 720 641	658 668 620	663 674 622
			M.Std.	611 ± 29	605 ± 25	641 ± 30	682 ± 25	620 ± 23	566 ± 25	682 ± 25	648 ± 19	653 ± 20
7.	Crd-Hy-gt-sil	Limpopo Belt, n = 8	BB22a BB25C BB11d BB20a	670 670 670 670	653 704 734 725	642 685 712 703	650 667 724 709	649 687 722 724	572 615 663 660	656 675 698 719	655 700 730 723	662 705 737 737
			M.Std.	722 ± 38	701 ± 32	704 ± 35	706 ± 40	714 ± 37	651 ± 45	706 ± 40	719 ± 30	728 ± 31
11.	Gt-crd-sil-q	North East Bavaria, n = 8	Op124G Sm27G Op146G	680 680 680	682 625 662	667 618 650	688 614 644	685 639 673	641 593 631	732 660 693	704 663 691	711 667 697
			M.Std.	649 ± 31	638 ± 27	645 ± 30	659 ± 27	614 ± 30	660 ± 32	680 ± 20	685 ± 21	
14.	Ged-crd-gt-sil-q	Ajitpura Rajasthan n = 10	R 9 24	700 700 700	642 719 685	633 699 671	666 737 685	665 719 672	595 663 608	712 780 723	674 727 695	680 734 702
			M.Std.	662 ± 50	650 ± 43	702 ± 34	735 ± 38	668 ± 40	604 ± 45	735 ± 38	682 ± 20	687 ± 20
17.	Gt-crd-sil-q	Sonapahar Assam, n = 2	734b 81/684	700 700	619 676	613 662	686 704	628 673	571 623	717 733	676 702	683 705
			M.Std.	647 ± 29	637 ± 25	695 ± 9	725 ± 9	650 ± 23	597 ± 26	725 ± 9	690 ± 10	694 ± 10

(Continued)

Table 2. (Continued)

S. No.	Rock type	Locality	Sample no.	aT	T <sub>Th</sub>	T <sub>P</sub>	T <sub>B</sub>	T <sub>A,P</sub>	T <sub>Ni</sub>	T <sub>BS</sub>	T(HW)	T(Br)
19.	Gt-crd-sil-q	Scottish	105765c	700	754	728	756	750	711	794	758	764
20.		Caledonides	10557c	700	718	698	758	734	680	786	731	746
21.		n = 10	187c	700	823	786	794	815	790	838	795	798
22.			190c	700	725	703	720	723	686	774	736	744
				M.Std.	726 ± 61	704 ± 52	737 ± 41	731 ± 50	689 ± 62	746 ± 42	737 ± 34	746 ± 35
23.	Gt-sp-crd-	South	1	740	703	684	693	706	641	713	720	724
24.	sil-q	India n = 2	2	740	710	690	697	712	648	720	722	726
				M.Std.	706 ± 4	687 ± 3	695 ± 1	709 ± 3	644 ± 4	716 ± 4	721 ± 1	725 ± 1
25.	Gt-crd-hy-q	Finnish	891	760	809	774	766	797	750	788	790	803
26.		Lapland	158I	760	761	735	749	750	697	771	755	762
27.		n = 4	161I	760	790	759	711	776	731	723	779	787
				M.Std.	806 ± 40	772 ± 31	761 ± 24	791 ± 33	745 ± 40	756 ± 35	789 ± 21	799 ± 21
28.	Gt-crd-hy-q	Nain	KI-355	770	875	827	776	860	861	784	843	857
29.		Complex	74-989	770	774	744	725	753	734	750	773	774
30.		n = 16	2-893	770	820	782	777	803	784	762	806	813
31.			2-1726	770	728	706	732	726	688	742	740	745
32.			2-1572	770	797	763	778	789	758	760	790	790
33.			2-4203	770	740	716	747	756	703	765	748	760
				M.Std.	805 ± 76	769 ± 62	770 ± 47	762 ± 62	766 ± 78	775 ± 51	794 ± 40	790 ± 41

All temperature computed at pressure inferred by respective authors. Where a T = Authors estimate of temperature °C. Prefix T in Th, p, etc., means temperature in °C for geothermometer given as (Th = Thompson 1976; P = Perchuk *et al* 1985; B = Bhattacharya *et al* 1988; A, P = Aranovich and Podlesskii 1989; Ni = Nichols *et al* 1992 and BS = Bhattacharya 1993). M.Std. is the mean and standard deviation of temperature in °C. Crd = cordierite, Gt = Garnet, Ged = gedrite, Hy = hypersthene, sil = sillimanite, Sp = spinel, q = quartz, n = number of data taken for calculation of temperature.

experimental data and are based on recent data on activity-composition relationship in (Fe-Mg-Ca-Mn) garnet solid solution. The error estimate in temperature for equations (13) and (14) is calculated by using the method of Chatterjee (1991, equations 9-66, p. 296 and 9-69, p. 296). Assuming 10% uncertainty in  $\ln K$  values, uncertainty in the temperature estimates at 1000 K is  $\pm 40^\circ\text{C}$ . A comparison of the temperature estimates (table 2) from this study  $T(HW)$  (equation 13) and  $T(\text{Br})$  (equation 14) with those obtained from other calibrations ( $T_{\text{Th}}$ , Thompson 1976;  $T_{\text{P}}$ , Perchuk *et al* 1985;  $T_{\text{B}}$ , Bhattacharya *et al* 1988;  $T_{\text{A.P}}$ , Aranovich and Podlesskii 1989;  $T_{\text{Ni}}$ , Nichols *et al* 1992; and  $T_{\text{BS}}$ , Bhattacharya 1993) reveals that (1) there is no compositional dependence in the temperature estimates with respect to garnet and cordierite solid solutions of the present study, (2) the standard deviation in the temperature estimates is lowest for  $T(HW)$  and  $T(\text{Br})$  as compared to other calibrations and (3) the estimated temperature in the present study is consistent with temperature estimates of different authors using various geothermometers.

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