# A revision of the garnet-clinopyroxene Fe<sup>2+</sup>-Mg exchange geothermometer

# Yang Ai

Geology Department, University of Tasmania, Hobart, Tasmania, 7001 Australia

Received January 7, 1992/Accepted June 11, 1993

Abstract. A comprehensive experimental dataset was used to analyse the compositional dependence of the garnet-clinopyroxene  $Fe^{2+}/Mg$  partition coefficient  $(K_d)$ . The Mg no. of garnet was found to have a significant effect on the  $K_d$ , in addition to calcium content of garnet. An empirical model was developed to relate these effects with equilibrium temperature and pressure in the form of a conventional geothermometer,

 $T(K) = \{-1629[X_{Ca}^{Gt}]^2 + 3648.55[X_{Ca}^{Gt}] - 6.59[Mg \text{ no. (Gt)}]\}$ 

 $+ 1987.98 + 17.66P(kbar) \} / (ln K_d + 1.076).$ 

Application of this thermometer produced reasonable temperature estimates for rocks from the lower crust (garnet amphibolites, granulites and eclogites) and the upper mantle (eclogite and lherzolite xenoliths in kimberlites, mineral inclusions in diamonds).

### Introduction

Several experimental studies have demonstrated that Fe<sup>2+</sup>/Mg partitioning between garnet and clinopyroxene is sensitive to external physical conditions and is strongly affected by internal compositional variations (e.g. Råheim and Green 1974a; Ellis and Green 1979; Pattison and Newton 1989). Råheim and Green (1974a) first calibrated the relationship between  $K_d [= (Fe^{2+}/Mg)^{Gt}/$  $(Fe^{2+}/Mg)^{Cpx}$  and equilibrium temperature (T) and pressure (P) to form a geothermometer. Ellis and Green (1979) recognised a significant effect of Ca-content on  $K_d$  and quantified this effect to produce an improved version of the thermometer, which found a broad application in the field of petrology. Krogh (1988) further improved the thermometer by replacing the simple rectilinear relationship of  $\ln K_d$  with  $X_{Ca}^{Gt} [ = Ca/(Ca + Mg + Fe^{2+} + Mn) ]$ established by Ellis and Green (1979) with a curvilinear relationship. This latter improvement is confirmed by Brey and Köhler (1990), but the improvement is limited by the amount of experimental data used and by the exact mathematical model chosen to formulate the thermometer.

A recent experimental study by Pattison and Newton (1989) showed that the Mg no. [ =  $100Mg/(Mg + Fe^{2+})$ ] of garnet also had an important effect on  $K_d$ . They fitted their experimental data to a third order polynomial equation to account for this effect, and derived a new version of the thermometer that is applicable to rocks with Mg no. (Gt) ranging from 12.5 to 60. However, when applied to same mineral assemblages, this and other forms of the garnet-clinopyroxene Fe<sup>2+</sup>/Mg exchange thermometer (e.g. Ellis and Green 1979; Ganguly 1979; Powell 1985) gave different temperature estimates.

Green and Adam (1991) specifically designed a new set of experiments to test various versions of this thermometer and found that none of the existing formulations could be safely applied to rocks of wide origin in terms of P, T and composition. In particular, Green and Adam (1991) found that the popular Ellis-Green thermometer reproduced their run temperatures for experiments at 30 kbar and 1150–1200 °C but increasingly overestimated equilibrium temperatures at lower pressures and lower temperatures. They also found that the Pattison-Newton graphic thermometer consistently underestimated their experimental temperatures but the Pattison-Newton mathematical formulation overestimated their experimental temperatures with two exceptions.

It is clear that additional experimental data are needed for further evaluation and improvement of this useful geothermometer. In this paper, I present new experimental results and use these in conjunction with published data to develop a refined empirical model to describe the partitioning behaviour of  $Fe^{2+}/Mg$  between garnet and clinopyroxene.

#### The dataset

The dataset used to analyse the  $Fe^{2+}/Mg$  partition between garnet and clinopyroxene consists of mineral equilibrium data in fifteen publications (Table 1) and new experimental data in ultramafic systems from Ai (1992, Table 2). The majority of these studies in the dataset are made on ultramafic compositions. Five series of experiments specifically address garnet-clinopyroxene equilibria. Two series of experiments are in mafic systems. They cover a wide range of "bulk rock" compositions. The experimental conditions range

Reference no.	Source	Type of experiment	P (kbar)	T°C	No. of gt-cpx pairs	
1	Råheim and Green (1974a)	Gt-cpx equilibria	20-40	600-1500		
2	Råheim and Green (1974b)	Gt-cpx equilibria	12-30	1100-1300	6	
3	Wood (1976)	Gt-cpx equilibria	20-45	1100-1400	8	
4	Ellis and Green (1979)	Gt-cpx equilibria	15-30	750-1300	45	
5	Pattison and Newton (1989)	Gt-cpx equilibria	15-29	700-1200	123	
6	Johnston (1986)	Mafic system	23-30	1275-1455	7	
7	Green and Adam (1991)	Mafic system	10-30	950-1200	17	
8	Hensen (1973)	Ultramafic system	22.5-40.5	1110-1410	3	
9	Akella and Boyd (1973)	Ultramafic system	30-45	1100	5	
10	Akella (1976)	Ultramafic system	31-44	1100-1300	3	
11	Mori and Green (1978)	Ultramafic system	3040	950-1300	20	
12	Nickel (1983)	Ultramafic system	35	1000-1400	10	
13	Mengel and Green (1989)	Ultramafic system	25-28	975-1250	11	
14	Brey et al. (1990)	Ultramafic system	2860	900-1400	21	
15	Wallace and Green (1991)	Ultramafic system	2030	950-1100	15	
16	Table 2	Ultramafic system	25-38	1200-1500	47	

Gt, garnet; cpx, clinopyroxene

from 10 to 60 kbar in pressure and from 600 to 1500 °C in temperature, encompassing almost the entire lower crust-upper mantle region where garnet and clinopyroxene-bearing rocks originated. The dataset is therefore reasonably comprehensive and is meaningful for statistical analysis. However, the amount of data at low temperatures (below 900  $^{\circ}\mathrm{C}$ ) and high temperatures (above 1300  $^{\circ}\mathrm{C}$ ) is much less than in the middle temperature range (1000-1200 °C). The quality of these data is also not as good as that in the middle temperature range due to kinetic problems. At low temperatures, equilibrium is very difficult to achieve under laboratory conditions, especially in anhydrous systems. At high temperatures, the nucleation rate is so fast that metastable mineral compositions can often be preserved. Selection criteria such as cation totals to within  $\pm 0.02$ and weight percent of oxides to within  $\pm 2.0$  are employed to discriminate all experimental data available. The number of data is reduced to total 380 pairs.

#### Data analysis

Krogh (1988) proposed a general mathematical equation that governed the partitioning behaviour of  $Fe^{2+}/Mg$  between garnet and clinopyroxene:

$$\ln K_{d} = \frac{\{a[X_{Ca}^{Gt}]^{2} + b[X_{Ca}^{Gt}] + c + dP(kbar)\}}{T(K)} + e$$
(1)

where a, b, c, d and e are constants. This agrees in principle with the forms of all previous derivations (Råheim and Green 1974a; Ellis and Green 1979; Ganguly 1979; Saxena 1979; Wells 1979; Dahl 1980; Powell 1985), except that of Pattison and Newton (1989) where the ln  $K_d$ -pressure relationship is a kind of reciprocal relationship and is in apparent contradiction with the experimental observation that  $K_d$  increases with increasing pressure (Råheim and Green 1974a; Green and Adam 1991). Nonetheless, the experimental results of Pattison and Newton (1989) are important because they showed a clear dependence of  $K_d$ on Mg no. (Gt), particularly in the low Mg no. (Gt) region.

Figure 1 further demonstrates the negative correlation between  $\ln K_d$  and Mg no. (Gt) (only experimental data at 30 kbar are shown for clarity). Although the restricted Mg no. range and scatter of data points obscured any correla-



**Fig. 1.** The effect of Mg no. garnet, on  $\ln K_d$ . The correlation trends for most data at constant pressure and temperature are negative. For reasons of clarity, only data at 30 kbar are shown in this diagram (and Figs. 2, 3)

tion trend for data at 900 °C and 1500 °C, the trend is very obvious for data 1000-1400 °C. The effect of aluminium cations in clinopyroxene on  $K_d$  is insignificant, and is perhaps more dependent on bulk rock composition than temperature and pressure. A correlation between  $\ln K_d$ and  $X_{Ca}^{Cpx}$  [ = Ca/(1 - Na)] (Ca and Na are cations in clinopyroxene for a 6-oxygen formulation) seems to be evident from Fig. 2, but this simply reflects close correlations of temperature with both  $\ln K_d$  and  $X_{Ca}^{Cpx}$  (Bertrand and Mercier 1985; Brey and Köhler 1990). Although Ellis and Green (1979) implied that correction of the  $X_{Ca}^{Cpx}$  effect on  $K_d$  was accomplished by an  $X_{Ca}^{Gt}$  term, there does not seem to be a simple relationship between  $X_{Ca}^{Gt}$  and  $X_{Ca}^{Cpx}$  (Fig. 3). Therefore the dependence of  $K_d$  on  $X_{Ca}^{Cpx}$  is effectively taken into account by the temperature term and it follows that the composition terms which should be included in modelling the  $\ln K_d - T$  relation are  $X_{Ca}^{Gt}$  and Mg no. (Gt). Presence of Fe<sup>3+</sup> in both garnet and clinopyroxene poses an additional problem for interpreting natural mineral assemblages (Luth et al. 1990), but at present this could not be evaluated with experimental data obtained from microprobe analysis.



**Fig. 2.** The  $\ln K_d - X_{Ca}^{Cpx}$  relationship. The parameter  $X_{Ca}^{Cpx}$  essentially reflects temperature. The three parameters,  $\ln K_d$ ,  $X_{Ca}^{Cpx}$  and the reciprocal of temperature, are positively correlated. Only 30 kbar data are shown



**Fig. 3.** The  $X_{Ca}^{Ca} - X_{Ca}^{Cpx}$  correlation diagram. There is no clear, straight-forward relationship between  $X_{Ca}^{Gt}$  and  $X_{Ca}^{Cpx}$ . Only 30 kbar data are shown

Following Krogh (1988) and adding a Mg no. (Gt) term in addition to  $X_{Ca}^{Gt}$ , I derived a modified model to describe the partitioning behaviour of Fe<sup>2+</sup>/Mg between garnet and clinopyroxene:

 $\ln K_d =$ 

$$\frac{\left\{a[X_{Ca}^{Gt}]^2 + b[X_{Ca}^{Gt}] + c[Mg \text{ no. } (Gt)] + d + eP(kbar)\right\}}{T(K)} + f$$
(2)

where a, b, c, d, e and f are constants. A statistical analysis of the 380 pairs of data in Tables 1 and 2 suggests that in a normal probability plot, data points which are inconsistent with the general trend may be in error. A total of 109 pairs of such erroneous data points are detected and excluded. The final dataset is left with 271 pairs of data points. Multiple linear regression analysis of the 271 pairs of coexisting garnet and clinopyroxene to fit the above gave: a = -1629( ± 636), model b = 3648.55 $(\pm 391.72), c = -6.59 (\pm 0.35), d = 1987.98 (\pm 79.81),$  $e = 17.66 \ (\pm 0.68), \ f = -1.076 \ (\pm 0.036) \ (R^2 = 0.981).$ Regression with a [Mg no. (Gt)]<sup>2</sup> term included did not produce a better fit, so that this term was excluded. Consequently the revised garnet-clinopyroxene geothermometer becomes:

$$T(K) = \{ -1629 [X_{Ca}^{Gt}]^2 + 3648.55 [X_{Ca}^{Gt}] - 6.59 [Mg no. (Gt)] + 1987.98 + 17.66P(kbar) \} / (ln K_d + 1.076).$$
(3)

In Fig. 4, the new thermometer [Eq. (3)] is compared with previous formulations by Ellis and Green (1979) [Fig. 4a] and Krogh (1988) [Fig. 4b] by plotting the difference between computed temperatures by each method for synthetic garnet-clinopyroxene pairs and the experimental temperatures against the relevant experimental run temperatures. Equation (3) reproduces all experimental run temperatures within  $\pm 100$  °C, and gives more accurate temperature estimates, with less scatter for temperatures below 1200 °C. Both the Ellis-Green and Krogh expressions tend to overestimate temperatures below 1200 °C. Whereas estimates above 1200 °C for all three methods are similar, the Krogh expression is most discrepant and the Ellis-Green expression shows a trend of underestimation with increasing experimental temperature (Fig. 4a, b).

## Applications

Equation (3) is constructed on the basis of a large amount of experimental data over a wide range of P, T, and composition, therefore it should be applicable to rocks of wide origins and may be successfully extrapolated to natural environments below the experimental temperature range. This is tested in Table 3 by calculation of equilibrium temperatures for rocks from the lower crust (amphibolites, granulites, crustal eclogites) and the upper mantle (eclogite and lherzolite xenoliths in kimberlites, mineral inclusions in diamonds). The new thermometer generally gives more realistic temperature estimates than previously published garnet-clinopyroxene thermometers. For instance, when applied to the metamorphic suites listed by Pattison and Newton (1989), the new thermometer not only produces reasonable temperatures, but also gives narrower ranges of the estimated temperatures for each suite than the Pattison-Newton formulation. Other thermometers (e.g. Krogh 1988; Powell 1985; Ellis and Green 1979) tend to yield temperatures outside the range expected for the corresponding metamorphic grade.

Krogh (1988) calculated equilibrium temperatures in the range of 690–790 °C for a suite of eclogitic rocks from the Tromsø nappe complex within the northern Scandinavian Caledonides. Equation (3) suggests a relatively lower equilibrium temperature range of 636-740 °C, which may be more appropriate for these rocks because eclogites generally have lower equilibrium temperatures than granulites and temperatures higher than 700 °C are normally considered to belong to the granulite facies.

Application of Eq. (3) to four diamondiferous eclogites from southern Africa (Smith et al. 1989), one diamondiferous lherzolite from Sloan, USA (McCallum and Eggler 1976), and two diamondiferous lherzolites from Finsch, South Africa (Shee et al. 1982) generates equilibrium temperatures consistent with diamond stability (Table 3).

Unreliable estimate of  $Fe^{3+}$  content in garnet and clinopyroxene, and non-equilibrium between garnet and clinopyroxene are two major sources of errors in estimating equilibrium temperatures of natural rocks. For example, Koons (1984) applied the Ellis-Green thermometer to a suite of eclogites from the Sesia zone of the western Alps. Italy and calculated their temperatures

Table 2.	New	experimental	data	on	Fe <sup>2+</sup>	/Mg	exchange	between	garnet and	l clinopyroxene	a
----------	-----	--------------	------	----	------------------	-----	----------	---------	------------	-----------------	---

Run no.	P (kbar)	<i>T</i> °C	$X_{Ca}^{Cpx}$	Mg no. (cpx)	Mg no. (gt)	$X_{\mathrm{Ca}}^{\mathrm{Gt}}$	ln K <sub>d</sub>
T3239	20	1200	0.7708	89.68	82.79	0.1546	0.5908
T3101	25	1200	0.7883	89.05	82.71	0.1589	0.5312
T3168	25	1200	0.7242	89.95	83.91	0.1601	0.5409
T3126	27	1200	0.7331	88.86	83.08	0.1507	0.4856
T3454	28	1200	0.8144	90.41	83.32	0.1528	0.6351
T3151	30	1200	0.7700	89.36	82.01	0.1466	0.6106
T3306	35	1200	0.7972	90.38	82.51	0.1377	0.6883
T3355	26	1300	0.7576	89.69	84.16	0.1503	0.4926
T3136	27	1300	0.7250	89.01	83.72	0.1539	0.4543
T3247	27	1300	0.6423	88.88	84.17	0.1468	0.4071
T3364	28	1300	0.7492	89.63	83.20	0.1535	0.5571
T3160	30	1300	0.6432	90.26	86.16	0.1494	0.3981
T3345	35	1300	0.7156	89.56	83.65	0 1416	0 5174
T3167	27	1400	0.6377	88 29	84.28	0.1494	0.3406
T3453	28	1400	0.5393	88 64	85.94	0.1503	0 2444
T3576	20	1400	0.6431	89.03	85.22	0 1430	0.3418
T3163	30	1400	0.6120	88 72	85.05	01527	0.3239
T3342	35	1400	0.6224	89.02	83 59	0.1386	0.4648
T2200	35	1400	0.5080	80/0	85.86	0.1500	0 3383
T2279	22	1500	0.4486	80 17	86.05	0.1455	0.2885
T2240	20	1500	0.5251	80.77	87.07	0.1455	0.2594
T2420	30	1500	0.3231	89.72	86.53	0.1530	0.2521
13430	22	1500	0.4565	89.20	86.25	0.1350	0.2521
13327	33	1500	0.4061	00.26	86.02	0.1414	0.2732
13302	33 27 5	1300	0.4901	90.30	81.69	0.1725	0.5441
132/3	27.5	1200	0.7908	07.00	01.00 01.00	0.1723	0.0873
1 3201	30	1200	0.0001	90.02	82.02	0.1079	0.0203
1 3 3 4 8	32	1200	0.7040	90.01	92.02	0.1744	0.0000
13209	33 ·	1200	0.0115	90.05	03.30	0.1741	0.0380
1 3440	28	1200	0.7557	07.40 90.76	02.70 92 <b>7</b> 7	0.1727	0.5176
13423	30	1300	0.7225	89.20 00.22	03.27 93.00	0.1/09	0.5120
13556	32	1300	0.7519	90.23	82.90	0.1021	0.044.0
13402	33	1300	0.7307	89./1 80.27	02.13	0.1740	0.0408
13451	32	1400	0.6101	89.27	84.14	0.1001	0.4304
13417	35	1400	0.0531	89.90	04.Z0 95.72	0.1705	0.3060
13517	32	1500	0.5211	89.04	03.13	0.1703	0.3032
T3429	34	1500	0.5114	89.32	02.00	0.1022	0.3165
13268	35	1500	0.4802	89.79	84.02	0.1082	0.4093
T3573	32	1200	0.7982	89.76	81.40	0.1004	0.0933
T3528	35	1200	0.8094	90.01	81.34	0.1795	0.7203
T3583	32	1300	0.7431	89.16	81.96	0.1731	0.3935
T3562	35	1300	0.7260	89.37	81.67	0.1742	0.0357
T3593	38	1300	0.7157	89.73	81.66	0.1861	0.6737
T3568	32	1400	0.6331	88.84	83.20	0.1755	0.4751
T3604	33.5	1400	0.6212	88.82	85.50	0.1722	0.4654
T3536	35	1400	0.6058	88.77	83.40	0.1729	0.4529
T3534	35	1500	0.4643	88.63	84.69	0.1623	0.3428
T3598	38	1500	0.4635	89.31	84.50	0.1740	0.4264

<sup>a</sup> Data from Ai (1992)

ranging from 400 to 1040 °C. He suggested that the spread was caused by the high-jadeite pyroxene solid solutions. Equation (3) gives an even larger temperature range (316–1065 °C) for these rocks. However, if all Fe is allocated to Fe<sup>2+</sup> in both garnets and clinopyroxenes, the calculated temperatures for half of the rocks reported by Koons (1984) fall in the range of 604–649 °C. Within the other half, two have relatively low calculated temperatures (475 and 384 °C) and two have relatively high calculated temperatures (1083 and 817 °C, Table 3). There is no clear relation between the calculated temperatures and the Na<sub>2</sub>O content of the clinopyroxenes. Koons (1984) mentioned that these garnets are usually zoned so the anomalously wide range of temperature estimates may also be a result of non-equilibrium between garnet and clinopyroxene. A suite of eclogite from Cima di Gagnone, Switzerland (Evans et al. 1979) provides another example. The garnets in this suite are zoned, but the clinopyroxenes are not, except in one metarodingite (163-M). If the unzoned clinopyroxene compositions and the garnet rim compositions in samples other than 163-M are used to calculate the equilibrium temperature, a range of 657-716 °C is obtained from Eq. (3) (Table 3). If the garnet core compositions are used, the calculated temperatures range from 582 to 864 °C. In the metarodingite (163-M) the garnet is not zoned but the clinopyroxene is. The clinopyroxene rim composition corresponds to a calculated temperature of 1343 °C; and the core composition,

Table 3. Results of calculated equilibrium temperatures for a range of natural rocks

Sample	ln K <sub>d</sub>	$X_{ m Ca}^{ m Gt}$	Mg. no. (gt)	No. of samples	P (kbar)	T3(°C)	TK(°C)	TP(°C)	T(EG) °C	T(PN) °C T(BM) °C
Amphibolite and gra	nulite (Patti	son and Ne	wton 1989)							
Mica Creek Eastern Dalradian Kapuskasing Central Gneiss Belt Adirondack	2.13–2.30 1.63–2.26 1.25–2.13 1.50–1.73 1.12–2.00	0.29-0.37 0.24-0.32 0.18-0.30 0.17-0.22 0.19-0.21	12.07–18.97 15.38–18.84 13.64–42.86 16.22–32.05 13.51–36.99	5 6 11 8 11	6 8 6.5 10 8	596–693 631–756 554–808 707–971 595–894	645744 680799 590894 727986 638951	663–765 697–806 635–904 752–1027 670–957	682–779 714–821 657–917 771–1031 691–967	521-654 583-752 517-758 625-777 568-916
Eclogite (Tromsø, N	orth Norwa	y; Krogh 19	38)							
	1.50-2.26	0.15-0.44	17–55	17	15	631–740	688–790	705-832	725844	428-783
Eclogite (Sesia Zone	of the West	ern Alps, Ita	ly; Koons 198	(4)						
(With Fe <sup>3+</sup> ) (Without Fe <sup>3+</sup> )	0.87–3.51 0.85–3.04	0.13-0.30 0.13-0.30	12.12–28.15 12.06–28.13	8 8	15 15	316–1065 384–1083	324 <i>–</i> 987 387–1002	3811024 4451037	406–1035 471–1047	220-1330 287-1362
Eclogite (Cima di G	agnone, Tici	no, Switzerla	and; Evans et	al. 1979)						
(Gt. core) (Gt. rim) 163-M. Cpx rim 163-M. Cpx core	1.88–2.90 1.82–2.49 1.34 2.02	0.25–0.43 0.17–0.42 0.77 0.77	25.25-46.68 37.56-53.61 56.02 56.02	4 4 1 1	25 25 25 25	582–864 657–716 1343 987	608-899 693-766 1066 798	636–929 734–779 1501 1178	655–941 757–796 1481 1176	
All Fe in garnet allo	cated to Fe <sup>2</sup>	2 +								
163-M. Cpx rim 163-M. Cpx core	2.62 1.95	0.71 0.71	40.98 40.98	1 1	25 25	789 1028	670 862	937 1161	944 1159	
Diamondiferous eclo	gite (souther	rn Africa; Sn	nith et al. 1989	))						
EX2 EX10 JJG144 XM23	1.09 1.14 1.25 1.19	0.24 0.27 0.19 0.23	59.08 55.45 51.67 52.74	1 1 1 1	50 50 50 50	1237 1247 1088 1180	1196 1204 1027 1129	1161 1165 1030 1105	1172 1175 1048 1119	
Diamondiferous lher	zolite (Sloan	ı, Wyoming,	USA; McCall	um and E	ggler 1976)	)				
S1L102	0.96	0.13	83.67	1	51ª	1091	1063	1097	1113	1056
Diamondiferous lher	zolite (Finsc	h, South Afi	rica; Shee et al	. 1982)						
XM46 XM48	1.02 1.06	0.15 0.16	83.94 82.83	1 1	63ª 57ª	1185 1126	1125 1103	1138 1110	1153 1126	1173 1089
Diamond inclusions	(Sloan, Wyo	oming, USA;	Otter and Gu	rney 1989	)					
A37 A73 1-10 1-15(1) 1-15(2)	1.28 1.16 1.03 0.61 1.15	0.26 0.19 0.16 0.09 0.09	44.33 65.02 55.84 66.23 78.34	1 1 1 1 1	50 50 50 50 50 50	1176 1106 1171 1357 929	1113 1077 1085 1192 884	1087 1072 1097 1250 967	1101 1088 1113 1259 990	
Diamond inclusions	(Koffiefonte	in, South Af	rica; Rickard e	et al. 1989)						
K2a K8a K16a K41a K42a K43a K56a	0.79 1.39 1.72 0.67 0.74 0.65 0.97	0.10 0.22 0.21 0.09 0.12 0.09 0.17	87.41 62.56 36.41 49.09 45.87 63.21 68.14	1 1 1 1 1 1	50 50 50 50 50 50 50 50	1141 1013 922 1361 1370 1325 1199	1093 1000 864 1142 1177 1153 1152	1152 997 875 1209 1208 1220 1147	1167 1015 897 1221 1219 1231 1160	
Diamond inclusions	(Western Au	ıstralia; Jaqı	ies et al. 1989)							
Argyle E4/17	0.69–1.30 1.17	0.28–0.36 0.22	34.86–66.11 52.40	6 1	50 50	1281–169′ 1174	71213–1621 1116	1184–1520 1097	1192–1508 1112	

T3, equation (3) of this study; TK, Krogh (1988); TP, Powell (1985); T(EG), Ellis and Green (1979); T(PN), Pattison and Newton (1989); T(BM), the two-pyroxene thermometer of Bertrand and Mercier (1985)

<sup>a</sup> Pressures are calculated from the barometer of Nickel and Green (1985). Others are assumed



Fig. 4. Comparison of temperatures calculated from Eq. (3) of this study, *solid squares*, the Ellis-Green thermometer, *empty triangles* in (a), and the Krogh formulation, *empty diamonds*, in (b) with the experimental run temperatures. This is shown by the difference between calculated temperatures from each thermometer and the experimental run temperatures. Equation (3) reproduces experimental run temperatures within 100 °C. Both Ellis-Green and Krogh formulations tend to overestimate the experimental run temperature range of 900 and 1300 °C)

987 °C. Both are significantly higher than the estimates for other samples, which is a direct consequence of the high  $Fe^{3+}$  given to the garnet by Evans et al. (1979). Assuming no  $Fe^{3+}$  in the garnet, the calculated temperatures for the corresponding clinopyroxene rim and core compositions are 789 and 1028 °C (Table 3). It is noted that the garnet in 163-M contains exceptionally high  $Fe^{3+}$  compared with other samples from the same locality and that the given cation total per 12 oxygens for this garnet in 8.053.

Mineral inclusions in single diamonds may not necessarily be in mutual chemical equilibrium. If not, the calculated temperatures may be abnormal. This is best illustrated by Otter and Gurney (1989) and Rickard et al. (1989) and further elaborated by Gurney (1989). Equation (3) is employed to estimate equilibrium temperatures for eclogitic inclusions in diamonds from three localities (Sloan, USA, Otter and Gurney 1989; Koffiefontein, South Africa, Rickard et al. 1989; and Western Australia, Jaques et al. 1989). Most these calculated temperatures are within the range of 1013–1370 °C, with two exceptionally low values (one in the Sloan diamonds, one in the Koffiefontein diamonds) and one extremely high value (in the Western Australia diamonds). These exceptions are probably a result of disequilibrium between garnet and clinopyroxene.

Most calculated temperatures from Eq. (3) are in accordance with estimates from other constraints [e.g. (1) phase relations such as the metamorphic grade and the presence of kyanite; (2) other thermometers based on different reaction schemes such as the two-pyroxene thermometer]. The improvement of the new thermometer over previously published garnet-clinopyroxene thermometers lies in the low temperature range (below  $1200 \,^{\circ}$ C) and for rocks with low Mg no. of garnet (mostly high grade metamorphics). For high pressure mantle rocks with temperature above  $1200 \,^{\circ}$ C, the new thermometer produces similar temperature estimates to the Ellis and Green thermometer.

Acknowledgements. Prof. D.H. Green, Drs. G. Nicholls, and T.J. Falloon are thanked for valuable suggestions and beneficial discussions. Prof. D.H. Green is also acknowledged for his inspiration and encouragement. Comments and corrections made by Prof. T.H. Green, Drs. R.L. Rudnick, D.J. Ellis and R.A. Binns improved the presentation. This research was supported by a postgraduate research award from the University of Tasmania.

#### References

- Ai Y (1992) Major and minor element systematics in the lherzolite system: a petrological and experimental study (unpublished). PhD thesis, Univ Tasmania
- Akella J (1976) Garnet pyroxene equilibria in the system CaSiO<sub>3</sub>-MgSiO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> and in a natural mineral mixture. Am Mineral 61:589-598
- Akella J, Boyd FR (1973) Effect of pressure on the composition of coexisting pyroxene and garnet in the system CaSiO<sub>3</sub>-MgSiO<sub>3</sub>-FeSiO<sub>3</sub>-CaAlTi<sub>2</sub>O<sub>6</sub>. Carnegie Inst Washington Yearb 72:523-526
- Bertrand P, Mercier J-CC (1985) The mutual solubility of coexisting ortho- and clinopyroxene: toward an absolute geothermometer for the natural system? Earth Planet Sci Lett 76:109–122
- Brey GP, Köhler T (1990) Geothermobarometry in four-phase lherzolites. II. New thermometers, and practical assessment of existing thermometers. J Petrol 31: 1353–1378
- Brey GP, Köhler T, Nickel KG (1990) Geothermobarometry in four-phase lherzolites. I. Experimental results from 10 to 60 kbar. J Petrol 31:1313–1352
- Dahl PS (1980) The thermal-compositional dependence of Fe<sup>2+</sup>-Mg distributions between coexisting garnet and pyroxene: applications to geothermometry. Am Mineral 65: 852–866
- Ellis DJ, Green DH (1979) An experimental study of the effect of Ca upon garnet-clinopyroxene Fe-Mg exchange equilibria. Contrib Mineral Petrol 71:13-22
- Evans BW, Trommsdorff V, Richter W (1979) Petrology of an eclogite-metarodingite suite at Cima dia Gagnone, Ticino, Switzerland. Am Mineral 64:15-31
- Ganguly J (1979) Garnet and clinopyroxene solid solutions, and thermometry based on Fe-Mg distribution coefficient. Geochim Cosmochim Acta 43:1021-1029
- Green TH, Adam J (1991) Assessment of the garnet-clinopyroxene Fe-Mg exchange thermometer using new experimental data. J Metamorphic Geol 9:341-347
- Gurney JJ (1989) Diamonds. In: Ross J et al (eds) Kimberlites and related rocks, vol 2. Geol Soc Aust Spec Publ 14, pp. 936-965

- Hensen BJ (1973) Pyroxenes and garnets and geothermometers and barometers. Carnegie Inst Washington Yearb 72:527-534
- Jaques AL, Hall AE, Sheraton JW, Smith CB, Sun SS, Drew RM, Foudoulis C, Ellingsen K (1989) Composition of crystalline inclusions and C-isotopic composition of Argyle and Ellendale diamonds. In: Ross J et al (eds) Kimberlites and related rocks, vol 2. Geol Soc Aust Spec Publ 14, pp 966–989
- Johnston AD (1986) Anhydrous *P-T* phase relations of near-primary high-alumina basalt from the South Sandwich Islands. Contrib Mineral Petrol 92:368-382
- Koons PO (1984) Implications to garnet-clinopyroxene geothermometry of non-ideal solid solution in jadeiitic pyroxenes. Contrib Mineral Petrol 88:340-347
- Krogh EJ (1988) The garnet-clinopyroxene Fe–Mg geothermometer - a reinterpretation of existing experimental data. Contrib Mineral Petrol 99:44–48
- Luth RW, Virgo D, Boyd FR, Wood BJ (1990) Ferric iron in mantle-derived garnets. Contrib Mineral Petrol 104:56-72
- McCallum ME, Eggler DH (1976) Diamonds in an upper mantle peridotite nodule from kimberlite in southern Wyoming. Science 192:253-256
- Mengel K, Green DH (1989) Stability of amphibole and phlogopite in metasomatized peridotite under water-saturated and waterundersaturated conditions. In: Ross J et al (eds) Kimberlites and related rocks, vol 1. Geol Soc Aust Spec Publ 14, 571–581
- Mori T, Green DH (1978) Laboratory duplication of phase equilibria observed in natural garnet lherzolites. J Geol 86:83–97
- Nickel KG (1983) Petrogenesis of garnet and spinel peridotites (unpublished). PhD thesis, Univ Tasmania
- Nickel KG, Green DH (1985) Empirical geothermobarometry for garnet peridotites and implications for the nature of the lithosphere, kimberlites and diamonds. Earth Planet Sci Lett 73:158-170
- Otter ML, Gurney JJ (1989) Mineral inclusions in diamonds from the Sloan diatremes, Colorado-Wyoming state line kimberlite district, North America. In: Ross J et al (eds) Kimberlites and related rocks, vol 2. Geol Soc Aust Spec Publ 14, pp 1042–1053

- Pattison DRM, Newton RC (1989) Reversed experimental calibration of the garnet-clinopyroxene Fe-Mg exchange thermometer. Contrib Mineral Petrol 101:87–103
- Powell R (1985) Regression diagnostics and robust regression in geothermometer/geobarometer calibration: the Fe-Mg exchange thermometer revisited. J Metamorphic Geol 3:231-243
- Råheim A, Green DH (1974a) Experimental determination of the temperature and pressure dependence of the Fe-Mg partition coefficient for coexisting garnet and clinopyroxene. Contrib Mineral Petrol 48:179-203
- Råheim A, Green DH (1974b) Experimental petrology of lunar highland basalt composition and application to models for the lunar interior. J Geol 82:607-622
- Rickard RS, Harris JW, Gurney JJ, Cardoso P (1989) Mineral inclusions in diamonds from Koffiefontein Mine. In: Ross J et al (eds) Kimberlites and related rocks, vol 2 Geol Soc Aust Spec Publ 14, pp 1054–1062
- Saxena SK (1979) Garnet-clinopyroxene geothermometer. Contrib Mineral Petrol 70:229–235
- Shee SR, Gurney JJ, Robinson DN (1982) Two diamond-bearing peridotite xenoliths from the Finsch kimberlite, South Africa. Contrib Mineral Petrol 81:79–87
- Smith CB, Gurney JJ, Harris JW, Robinson DN, Shee SR, Jaqoutz E (1989) Sr and Nd isotopic systematics of diamond-bearing eclogite xenoliths and eclogitic inclusion in diamond from southern Africa. In: Ross J et al (eds) Kimberlites and related rocks vol 2. Geol Soc Aust Spec Publ 14, pp 853–863
- Wallace ME, Green DH (1991) The effect of bulk rock composition on the stability of amphibole in the upper mantle: implications for solidus positions and mantle metasomatism. Mineral Petrol 44:1-19
- Wells PRA (1979) Chemical and thermal evolution of Archaean Sialic crust, southern West Greenland J Petrol 20:157-226
- Wood BJ (1976) The partitioning of iron and magnesium between garnet and clinopyroxene. Carnegie Inst Washington Yearb 75:571-574

Editorial responsibility: R. Binns