

D. Nakamura · T. Hirajima

## Experimental evaluation of garnet–clinopyroxene geothermometry as applied to eclogites

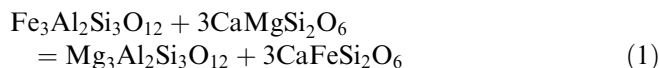
Received: 19 October 2004 / Accepted: 16 June 2005 / Published online: 19 November 2005  
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**Abstract** This study performed equilibrium experiments in order to evaluate previously proposed formulations of the garnet (Grt)–clinopyroxene (Cpx) thermometer as applied to eclogites. The starting material is fine-grained powder of natural eclogite ( $<10\ \mu\text{m}$ ), whose main constituents are Grt (Fe:Mg:Ca $\sim$ 44:28:28), Cpx (Na pfu $\sim$ 0.55–0.60), phengite, quartz and rutile. Experimental conditions are 1,100–1,250°C at 2.5 GPa, and the run duration is 193–334 h. The experimental run products mainly consist of Grt, Cpx, and glass. In a preliminary experiment at 1,000°C for 144 h, Cpx grains are clearly zoned and most Grt grains maintain primary compositions. In the higher  $T$  ( $\geq 1,100^\circ\text{C}$ ) and longer run ( $\geq 193$  h) experiments, Cpx in the run products becomes poorer in Na and higher in Fe/Mg compared with the starting material, and each grain does not show clear chemical zoning. Garnet compositions become poorer in Ca [ $\text{Ca}/(\text{Fe} + \text{Mn} + \text{Mg} + \text{Ca}) \sim 0.2\text{--}0.25$ ] and lower in Fe/Mg compared with the starting material. The average composition of Cpx and the average of Ca-poor Grt compositions in each run product were used to evaluate previously proposed formulations of the Grt–Cpx thermometer. Temperatures calculated with formulations by Pattison and Newton (1989) and Berman et al. (1995) are much lower than the experimental temperatures, even though these formulations are based on the compositional bracketing-type experiment. One of the reasons for this discrepancy might be uncertainty of solid-solution properties of Al in Cpx, because the value of the excess interaction parameter for Al in the generally low-Al Cpx modeled by Berman et al. (1995) is much higher than those proposed by independent experiments,

resulting in the estimated temperatures being significantly lower than the experimental temperatures.

### Introduction

The garnet (Grt)–clinopyroxene (Cpx) Fe–Mg distribution coefficient [ $K_D = (\text{Fe}/\text{Mg})^{\text{Grt}}/(\text{Fe}/\text{Mg})^{\text{Cpx}}$ ] is sensitive to temperature conditions. The Grt–Cpx thermometer is created using the following Fe–Mg exchange reaction.



After the first experimental calibration by Råheim and Green (1974), many experimental and theoretical calibrations have been performed (e.g. Ellis and Green 1979; Pattison and Newton 1989; Ai 1994). Among them, formulations by Ellis and Green (1979), Powell (1985), and Krogh (1988) have been favored and frequently used especially for eclogites and eclogitic rocks. However, these formulations are mainly based on synthetic experimental data using glass as starting material, which is highly metastable, and the direction of approach to equilibrium in those experiments cannot be known (e.g. Pattison and Newton 1989; Berman et al. 1995). Therefore, Pattison and Newton (1989) carried out compositional bracketing-type experiments (details of this experimental method are described in Pattison 1994) using starting material of garnet + small amount of clinopyroxene, and they proposed an empirical formulation for the Grt–Cpx thermometer applicable to amphibolites and granulites. The data of Pattison and Newton (1989), however, yield rather low temperatures at higher pressure conditions: 850–930°C for 1,150–1,200°C experiments at 3.0 GPa (Green and Adam 1991), and are also inconsistent with other compositional bracketing-type experiments by Perkins and Vielzeuf (1992) and Hackler and Wood (1989).

Communicated by W. Schreyer

D. Nakamura (✉) · T. Hirajima  
Department of Geology and Mineralogy,  
Graduate School of Science,  
Kyoto University, Kyoto 606-8502, Japan  
E-mail: daisuke@kueps.kyoto-u.ac.jp

Aranovich and Pattison (1995) and Berman et al. (1995), therefore, re-evaluated the experimental data of Pattison and Newton (1989) by considering compositional heterogeneity of the run products and found the data to be consistent with other experimental data when reasonable uncertainties are included. In combination with other compositional bracketing-type experimental data, Berman et al. (1995) proposed a new formulation for the Grt–Cpx thermometer with non-ideal terms for Grt and Cpx. The formulation by Berman et al. (1995) was satisfactory when applied to amphibolites and granulites, but gave significantly lower temperatures (440–560°C) for eclogite from the Dora Maira Massif, western Alps, compared with the values estimated by other methods (Nakamura and Hirajima 2000). Krogh-Ravna (2000) constructed yet another formulation of Grt–Cpx thermometer using many of the previous experimental data, without using the compositional bracketing-type experimental data by Pattison and Newton (1989) and Aranovich and Pattison (1995). The experiments used for calibration by Krogh-Ravna (2000) are basically synthetic type using glass as starting material. In summary, it is difficult to determine which formulation is the most reliable, at least for eclogitic rocks. In this paper, we carried out Grt–Cpx equilibrium experiments by using fine-grained eclogite powder for starting material in order to evaluate previous Grt–Cpx thermometers as applied to eclogites.

**Table 1** Chemical compositions of the starting material

	Bulk	Garnet	Omphacite	Phengite
SiO <sub>2</sub>	50.88	39.67	56.62	51.80
TiO <sub>2</sub>	1.57	0.06	0.07	0.60
Al <sub>2</sub> O <sub>3</sub>	16.49	22.16	12.49	24.59
FeO	10.35	20.89	3.27	1.65
MnO	0.16	0.46	n.d.	n.d.
MgO	6.35	7.13	7.85	4.71
CaO	8.72	9.95	11.38	n.d.
Na <sub>2</sub> O	3.29	n.d.	8.56	0.66
K <sub>2</sub> O	1.34	n.d.	n.d.	10.34
P <sub>2</sub> O <sub>5</sub>	0.30	n.d.	n.d.	n.d.
Total	99.45	100.31	100.24	100.31
O =		12	6	11
Si		3.017	1.994	3.483
Ti		0.003	0.002	0.030
Al		1.987	0.519	1.948
Fe		1.329	0.096	0.093
Mn		0.030	n.d.	n.d.
Mg		0.808	0.412	0.472
Ca		0.811	0.430	n.d.
Na		n.d.	0.584	0.086
K		n.d.	n.d.	0.887
Total		7.986	4.037	6.999
X <sub>Mg</sub>	0.522	0.378	0.811	0.835
X <sub>grs</sub>		0.272		
X <sub>sps</sub>		0.010		
X <sub>jd</sub>			0.507	
X <sub>cats</sub>			0.006	
X <sub>cel</sub>				0.483

Total iron is assumed to be Fe<sup>2+</sup>. n.d., not determined; X<sub>Mg</sub>, Mg/(Fe + Mg); X<sub>grs</sub>, Ca/(Fe + Mn + Mg + Ca); X<sub>sps</sub>, Mn/(Fe + Mn + Mg + Ca); X<sub>jd</sub>, Al–2(2–Si); X<sub>cats</sub>, 2–Si; X<sub>cel</sub>, Si–3

## Previous formulations

As described above, many formulations for the Grt–Cpx thermometer have been proposed. In this section, we briefly summarize those works for the Grt–Cpx thermometer. To clarify the difference among the formulations, we classify them into three groups:

Group 1 is formulations by Ellis and Green (1979), Powell (1985), Krogh (1988), Saxena (1979), Ai (1994), and Krogh-Ravna (2000), which are mainly based on experiments using glass as starting material (e.g. Råheim and Green 1974; Mori and Green 1978; Ellis and Green 1979). Ellis and Green (1979) and Powell (1985) formulations incorporated linear non-ideal correction term for Ca content of garnet. On the other hand, Krogh (1988) identified non-linear relation between  $\ln K_D$  and  $X_{Ca}^{Grt}$ , and incorporated empirical correction term for Ca content of garnet. Saxena (1979) theoretically calibrated the Grt–Cpx thermometer, in which both Grt and Cpx were treated as non-ideal solid solution; data set used by Saxena (1979) is Råheim and Green (1974), Irving (1973), Akella (1976), Wood (1976), and Saxena (1968). Ai (1994) constructed the Grt–Cpx thermometer using many original and previous experimental data, which include data of Pattison and Newton (1989); a total of 380 pairs were used for the regression in which 47 pairs were his own experiments in ultramafic system. Krogh-Ravna (2000) also constructed an empirical formulation using many previous experimental data, but the dataset did not include the Pattison and Newton (1989) data; a total of 311 experimental pairs and 49 natural pairs were used for the regression.

Group 2 is based on compositional bracketing-type experiments carried out by Pattison and Newton (1989) using synthesized garnet (90–95%) + small amount of clinopyroxene (5–10%), such as performed in Ferry and Spear (1978) for garnet–biotite thermometer. Even in these experiments, metastable compositions might be created owing to equilibration by a solution-precipitation process (Pattison 1994). Pattison and Newton (1989) proposed a formulation for the Grt–Cpx thermometer including empirical correction term of non-ideal effect; they showed non-ideality between Fe and Mg of garnet as well as the non-ideal effect of Ca content of garnet. Such rigorous compositional bracketing-type experiments were the first attempt in the history of the

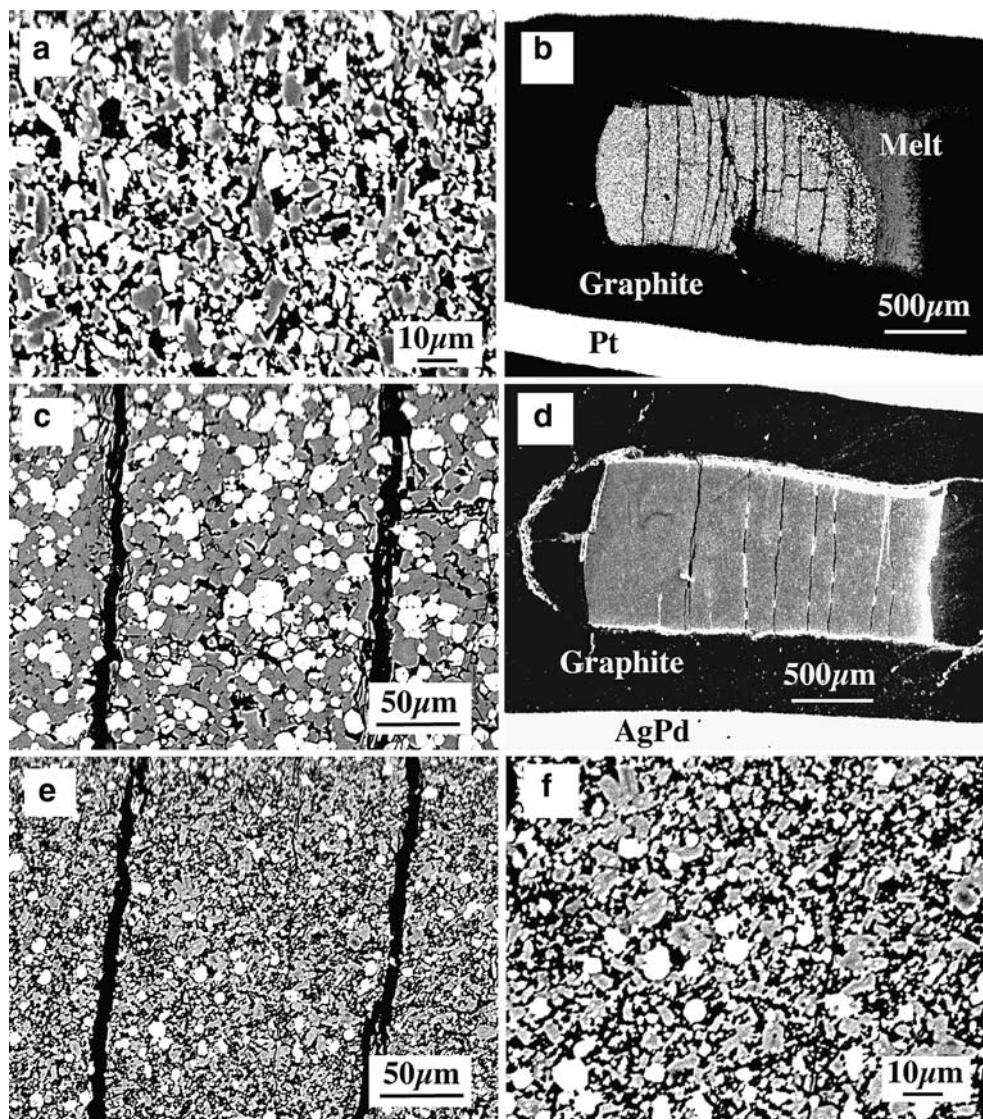
**Table 2** Experimental conditions

	Pressure (GPa)	Temperature (°C)	Duration (h)	Capsule
KP142	2.5	1,000	144	Au
KP148	2.5	1,100	334	Gr + AgPd
KP147	2.5	1,150	244	Gr + AgPd
KP149	2.5	1,175	244	Gr + AgPd
KP145	2.5	1,200	193	Gr + AgPd
KP150	2.5	1,250	193	Gr + Pt

Gr, graphite inner capsule



**Fig. 1** Back-scattered electron images of the run products. **a** Texture of the run product after the preliminary experiment at 1,000°C for 144 h (KP142). Omphacite grains (*gray part*) are clearly zoned. **b** Overall texture of the run product after the experiment at 1,250°C (KP150). Melt (*dark-gray part*) was highly created and distributed along the edge of the graphite capsule. Texture of the run product (KP149) is mostly the same as this one. **c** Texture of the run product after the experiment at 1,250°C (KP150). Grain sizes of garnet (*white part*) and omphacite (*gray part*) are significantly large ( $> 20 \mu\text{m}$  in many grains) in this run product. Grain growth apparently occurs. **d** Overall texture of the run product after the experiment at 1,100°C (KP148). **e** Texture of the run product at 1,100°C (KP148). **f** Detailed texture of the run product at 1,100°C (KP148). Garnet and omphacite grains are small ( $< 10 \mu\text{m}$  in many grains), and melt (*black part*) was created along grain boundaries. Similar textures are observed also in the other run products (KP147, KP145)

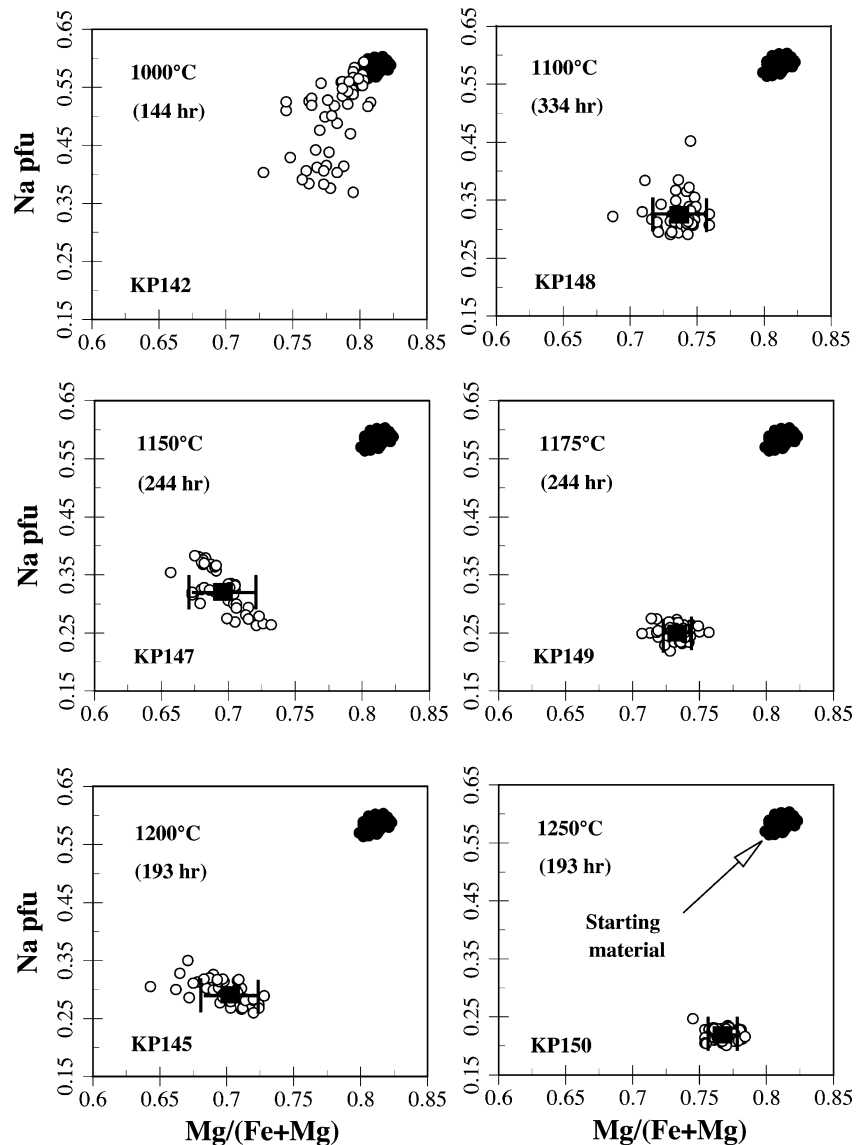


Grt–Cpx thermometer, but the data of Pattison and Newton (1989) appeared to be inconsistent with other compositional bracketing-type experimental data (Perkins and Vielzeuf 1992) as well as other synthetic experimental data (Green and Adam 1991). Aranovich and Pattison (1995) and Berman et al. (1995), therefore, re-evaluated the experimental data of Pattison and Newton (1989) and proposed a new formulation with non-ideal terms using subregular and regular solution models for Grt and Cpx, respectively. This formulation by Berman et al. (1995), based on low-Al clinopyroxene such as found in amphibolites and granulites, resulted in significantly low temperatures, at least for eclogite (Nakamura and Hirajima 2000). Possible reasons for this discrepancy will be shown in the later section.

Group 3 is formulations that are not mainly based on compositional bracketing-type experiments but are based on experiments without using glass as starting material. Ganguly (1979) proposed a theoretical formulation using experimental data by Wood (1976) in

conjunction with calorimetric data. Wood (1976) performed equilibrium experiments at 1,100–1,400°C, 2.0–4.5 GPa using starting material of crystal mixtures of Grt and Cpx, separated from ultramafic rock. Ganguly (1979) calibrated those experimental data and proposed a formulation of the Grt–Cpx thermometer with non-ideal regular solution term for garnet. Ganguly et al. (1996) proposed a new subregular type solution model of garnet using compositional bracketing-type experiments; displacement of the equilibrium grossular + 2 kyanite + quartz = 3 anorthite has been experimentally determined as a function of composition of garnet in the systems Mg–Mn–Ca, Fe–Mg–Ca, and Fe–Mg–Ca–Mn at 1,000°C. The calibration by Ganguly (1979) does not include synthetic experimental data using glass as starting material but lacks data in low- $T$  conditions ( $< 1,000^\circ\text{C}$ ). Dahl (1980) also proposed a formulation of the Grt–Cpx thermometer by using data of natural garnet- and pyroxene-bearing rocks.

**Fig. 2** Omphacite compositions of the run products. *Horizontal bars* are Mg/(Fe + Mg), and *vertical bars* are Na pfu based on O=6. *Open circles* are data of the run products, and *solid circles* are data of the starting material (natural eclogite). *Solid squares* are the average compositions of omphacite in each run product, and the standard deviations ( $1\sigma$ ) of Mg/(Fe + Mg) are also shown. These compositions are used for the examination of the garnet–clinopyroxene thermometry. *hr* hour

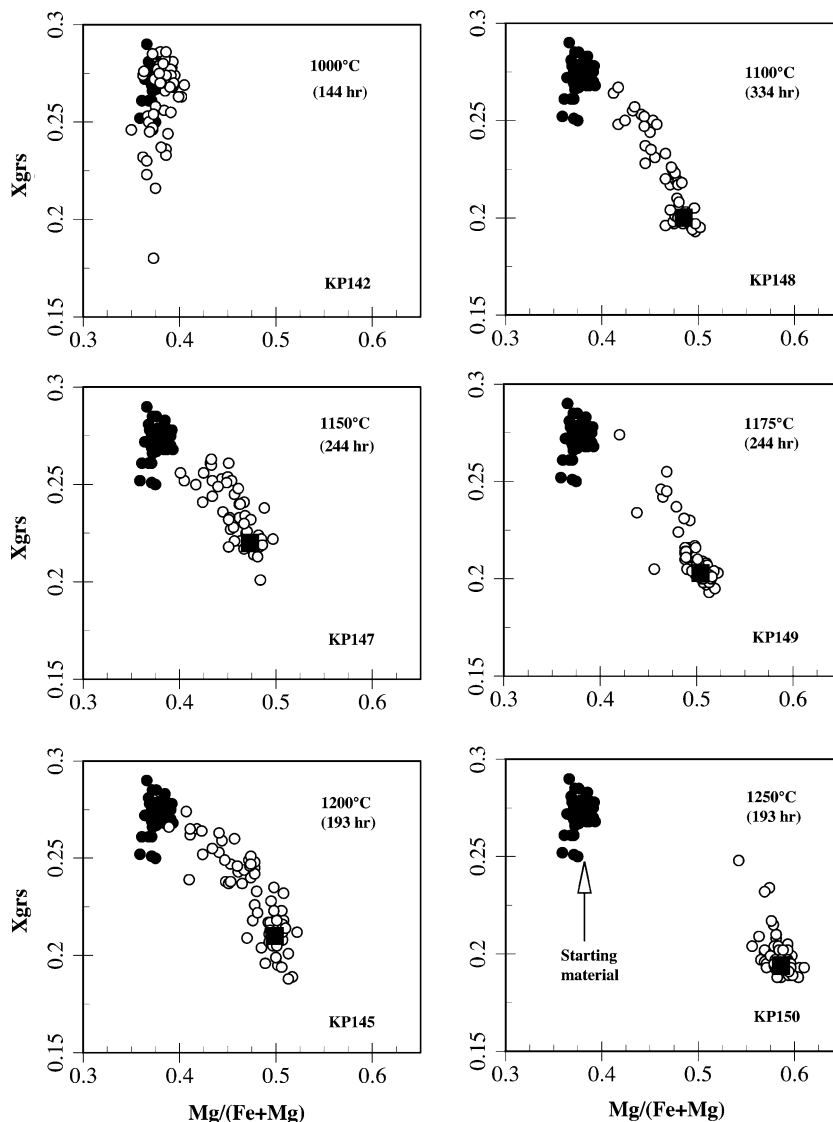


## Experimental methods

Experiments were performed with Kennedy-type piston-cylinder apparatus at Magma Factory of Tokyo Institute of Technology. The 0.5-in. diameter talc–pyrex assembly was used with a graphite heater and MgO pressure medium. Temperatures were measured with W–Re thermocouples. Pressure correction was made with quartz–coesite transition at 1,000°C, and about 17% friction loss was identified. A sample of phengite-bearing eclogite from Yangkou of the Sulu region, eastern China (YK34a), was finely ground ( $<10\ \mu\text{m}$ ) and used as starting material. Bulk composition of the starting material is similar to the average bulk composition of eclogites from the Dabie–Sulu region, China (Nakamura 2003). Mineral assemblage of the eclogite is garnet + omphacite + phengite + quartz + rutile with small amount of secondary minerals (e.g. amphibole,

plagioclase). Metamorphic  $P$ – $T$  conditions of the Yangkou eclogite were estimated to be 700–800°C, 3.1–4.1 GPa by using Powell (1985) and Krogh (1988) formulations of Grt–Cpx thermometer with garnet + clinopyroxene + kyanite +  $\text{SiO}_2$  barometer (Hirajima and Nakamura 2003). The bulk and average composition of garnet, omphacite, and phengite of the eclogite are listed in Table 1. Considering the bulk composition and mineral assemblage, about 1 wt%  $\text{H}_2\text{O}$  would be present in this eclogite, which will enhance diffusivities of elements during the experiments. A preliminary experiment at 1,000°C, 2.5 GPa during 144 h was performed in order to observe degree of attainment of the equilibrium state. Run conditions of the main experiments are 1,100–1,250°C at 2.5 GPa, and heating durations are 193–334 h (Table 2). The fine-grained powder of the eclogite was encased in graphite capsule (1.9 mm OD) to attain conditions of  $\text{Fe}^{\text{total}} = \text{Fe}^{2+}$ , and the graphite capsule was sealed in  $\text{Ag}_{50}\text{Pd}_{50}$  or Pt

**Fig. 3** Garnet compositions of the run products. *Horizontal bars* are  $Mg/(Fe+Mg)$ , and *vertical bars* are mole fractions of grossular component [ $=Ca/(Fe+Mn+Mg+Ca)$ ]. *Open circles* are data of the run products, and *solid circles* are data of the starting material (natural eclogite). *Solid squares* are the average compositions of selected low-Ca garnet compositions. These compositions are used for the examination of the garnet–clinopyroxene thermometer. *hr* hour



capsule. The most important character of this experiment is that the heating durations are longer enough than many of the other previous studies, favoring (but not proving) the attainment of an equilibrium state.

Chemical compositions of the run products were analyzed using an electron-probe microanalyzer, Hitachi scanning electron microscope, S550, with an energy-dispersive X-ray analytical system (Kevex 8000 + Kevex Quantum detector) at Kyoto University. The analytical procedure follows that of Mori and Kanehira (1984) and Hirajima and Banno (1991). This routine paid special care to the low-energy tail correction, an inevitable feature for the EDX detection. A 20 kV accelerating potential and a 500 pA beam current were employed with 250 s live-time for counting. This analytical method gives concordant analyzed compositions to compositions obtained with WDS and wet chemistry (Hirajima and Banno 1991; Hiramatsu et al. 1995). For each run product, more than 100 points were randomly analyzed to observe compositional heterogeneity of garnet and clinopyroxene.

## Experimental results

The run product of the preliminary experiment at 1,000°C for 144 h was found out to be far from equilibrium. Omphacite grains are clearly zoned (Fig. 1a). Na contents decrease from about 0.60 to 0.40, and cores of the omphacite grains preserve the original Na-rich compositions (Fig. 2). In addition, chemical compositions of garnet mostly overlap those of the starting material garnet (Fig. 3), indicating that garnet compositions did not change even by the heating during 144 h at 1,000°C. To attain the equilibrium state, longer heating and higher temperatures should be necessary. Therefore, we carried out the experiments at higher temperatures (1,100–1,250°C) for longer time (heating duration is longer than 193 h). However, in the experiments at 1,175°C (KP149) and 1,250°C (KP150), significant partial melting occurred in those run products (Fig. 1b), and garnet and omphacite grains have become quite large ( $\approx 20 \mu\text{m}$ ; Fig. 1c),



**Table 3** Compositions of garnet and omphacite in the run products

	1,100°C, 2.5 GPa		1,150°C, 2.5 GPa		1,200°C, 2.5 GPa		1,175°C, 2.5 GPa		1,250°C, 2.5 GPa	
	Garnet	Omphacite	Garnet	Omphacite	Garnet	Omphacite	Garnet	Omphacite	Garnet	Omphacite
SiO <sub>2</sub>	40.23	52.86	39.92	52.22	40.09	51.58	40.06	52.03	40.48	51.80
TiO <sub>2</sub>	0.55	1.11	0.76	1.26	0.52	1.42	0.66	1.29	0.53	0.84
Al <sub>2</sub> O <sub>3</sub>	21.87	10.24	21.45	10.92	22.01	10.84	21.82	8.76	22.38	9.07
FeO	19.03	6.31	19.17	7.29	18.48	7.51	18.59	7.08	16.00	6.65
MnO	0.40	n.d.	0.45	n.d.	0.41	n.d.	0.46	n.d.	0.41	n.d.
MgO	10.07	9.92	9.65	9.35	10.34	9.92	10.62	10.92	12.70	12.28
CaO	7.27	14.49	8.09	14.03	7.74	14.35	7.56	16.33	7.35	16.42
Na <sub>2</sub> O	n.d.	4.65	n.d.	4.60	n.d.	4.14	n.d.	3.55	n.d.	3.12
Total	99.42	99.58	99.48	99.68	99.58	99.75	99.77	99.96	99.86	100.17
O =	12	6	12	6	12	6	12	6	12	6
Si	3.036	1.915	3.025	1.897	3.018	1.877	3.013	1.896	3.001	1.879
Ti	0.030	0.030	0.043	0.034	0.030	0.039	0.038	0.035	0.029	0.023
Al	1.946	0.437	1.916	0.468	1.953	0.465	1.934	0.376	1.956	0.388
Fe	1.201	0.191	1.215	0.221	1.163	0.228	1.169	0.216	0.992	0.202
Mn	0.026	n.d.	0.029	n.d.	0.026	n.d.	0.029	n.d.	0.026	n.d.
Mg	1.133	0.536	1.090	0.507	1.160	0.538	1.190	0.593	1.404	0.664
Ca	0.588	0.563	0.657	0.546	0.624	0.559	0.610	0.638	0.584	0.638
Na	n.d.	0.327	n.d.	0.324	n.d.	0.292	n.d.	0.251	n.d.	0.220
Total	7.960	3.999	7.974	3.997	7.975	3.998	7.983	4.006	7.992	4.014
$X_{Mg}$	0.485	0.737	0.473	0.696	0.499	0.702	0.504	0.733	0.586	0.767
$X_{grs}$	0.199		0.220		0.210		0.203		0.194	
$X_{sps}$	0.009		0.010		0.009		0.010		0.009	
$X_{jd}$		0.267		0.262		0.219		0.168		0.146
$X_{cats}$		0.085		0.103		0.123		0.104		0.121
$K_D$	2.973		2.550		2.362		2.700		2.325	

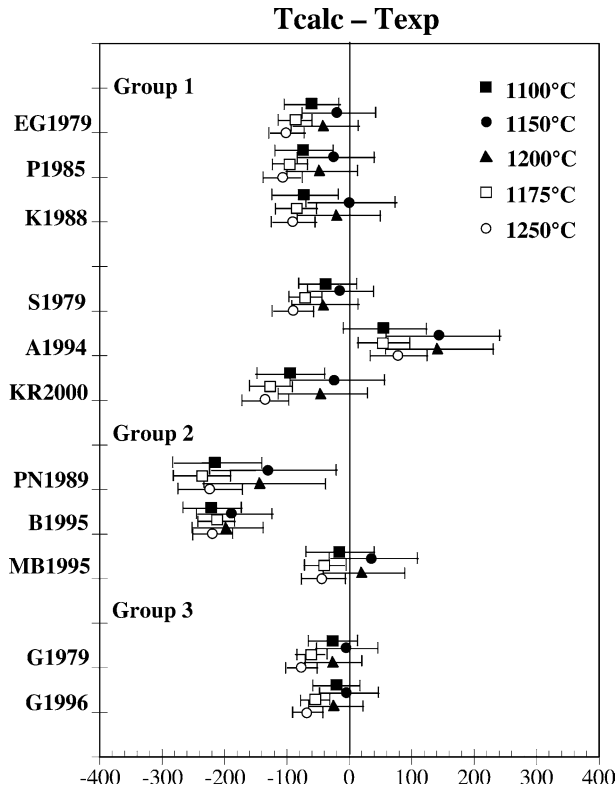
Note: n.d., not determined. Total iron is assumed to be Fe<sup>2+</sup>.  $X_{Mg}$ , Mg/(Fe+Mg);  $X_{grs}$ , Ca/(Fe+Mn+Mg+Ca);  $X_{sps}$ , Mn/(Fe+Mn+Mg+Ca);  $X_{jd}$ , Al-2(2-Si);  $X_{cats}$ , 2-Si;  $K_D$ , (Fe/Mg)<sup>Grt</sup>/(Fe/Mg)<sup>Cpx</sup>. For detail descriptions see the text

indicating that they have clearly grown during the heating. Clinopyroxene is rather compositionally homogeneous in those run products (Fig. 2), and garnet is also relatively homogenous compared with other experiments (Fig. 3), suggesting recrystallization. In the other three experiments at 1,100, 1,150, and 1,200°C, melt is distributed randomly along grain boundaries, and growth of garnet or omphacite was not identified; grain sizes of garnet and omphacite are still less than 10 µm (Fig. 1f). Omphacite composition in those run products is clearly different from original composition in the starting material (Fig. 2). On the other hand, garnet composition in the run products of 1,100, 1,150, and 1,200°C are significantly varied; garnet compositions are distributed from near-original to Ca-poor and Mg-rich compositions (Fig. 3). Thus, complete equilibrium states were not achieved even in these long experiments, but we assume that those Ca-poor and Mg-rich compositions of garnet are in equilibrium with clinopyroxene because those compositions are the most different from the original compositions. Thereby, the Ca-poorest compositions of garnet are applied for discussion. Considering analytical errors, several Ca-poor garnet compositions were averaged in each run product (filled square in Fig. 3) and those average compositions are used for discussion. For clinopyroxene, all analyzed data were averaged (filled square in Fig. 2) and those average values are used for discussion. Fe<sup>total</sup> = Fe<sup>2+</sup> is assumed for both Grt and Cpx. Those chemical compositions are listed in Table 3.

## Discussion

First, we applied previous formulations of the Grt-Cpx thermometer to our run products at 1,100–1,250°C. The applied formulations are as follows: Ellis and Green (1979), EG1979; Powell (1985), P1985; Krogh (1988), K1988; Saxena (1979), S1979; Ai (1994), A1994; Krogh-Ravna (2000), KR2000; Pattison and Newton (1989), PN1989; Berman et al. (1995), B1995; Berman et al. (1995) with modification of excess interaction parameter for Cpx, MB1995; Ganguly (1979), G1979; Ganguly et al. (1996), G1996; and the results are shown in Fig. 4, in which differences between the calculated temperature and the experimental temperature are shown. Error bars are due to compositional heterogeneity of clinopyroxene ( $1\sigma$ ). The formulation by Dahl (1980) gave extremely higher temperatures by >200°C, and hence the result is not plotted in Fig. 4. The formulations by Ellis and Green (1979), Powell (1985), and Krogh (1988) gave concordant temperatures for the experiments at 1,150 and 1,200°C, but they yielded slightly lower temperatures for the experiment at 1,100°C. Applications of the data at 1,175 and 1,250°C lead to lower temperatures by about 100°C than experimental temperatures (Fig. 4).

The formulation by Saxena (1979) led to rather concordant temperatures in our experiments, and all data at 1,100, 1,150, and 1,200°C fall within the range of error bars. However, the formulation by Ai (1994) gave clearly higher temperatures by about 50–150°C,



**Fig. 4** Comparisons between calculated temperatures ( $T_{\text{calc}}$ ) and experimental temperatures ( $T_{\text{exp}}$ ). Horizontal bar is the difference between  $T_{\text{calc}}$  and  $T_{\text{exp}}$  ( $^{\circ}\text{C}$ ). EG1979 Ellis and Green (1979), P1985 Powell (1985), K1988 Krogh (1988), S1979 Saxena (1979), A1994 Ai (1994), KR2000 Krogh-Ravna (2000), PN1989 Pattison and Newton (1989), B1995 Berman et al. (1995), MB1995 Berman et al. (1995) modified as  $W_{\text{MgAl}} - W_{\text{FeAl}} = 0$  for clinopyroxene, G1979 Ganguly (1979), G1996 Ganguly et al. (1996)

whereas Krogh-Ravna (2000) yielded relatively concordant temperatures for the experiments at 1,150 and 1,200 $^{\circ}\text{C}$ . Formulations by Ganguly (1979) and Ganguly et al. (1996), which are based on equilibrium experiments using garnet + clinopyroxene mixture as starting material (Wood 1976) and calorimetric data, gave very concordant temperatures to the experimental temperatures (Fig. 4), although these formulations lack direct experimental data at low- $T$  conditions ( $< 1,000^{\circ}\text{C}$ ). The important point is the difference in bulk composition of starting material between the experiments by Wood (1976) and this study. The formulation by Ganguly (1979) is mainly based on experiments using garnet and clinopyroxene from ultramafic rocks (Wood 1976), and hence garnet is rich in Mg ( $\text{Fe}/\text{Mg} = 0.25\text{--}0.35$ ) and clinopyroxene is poor in Na and Al ( $\text{Na}_2\text{O} < 0.4$  wt%,  $\text{Al}_2\text{O}_3 < 4.7$  wt%). On the other hand, our experiments used basaltic composition wherein it showed that garnet is not so rich in Mg ( $\text{Fe}/\text{Mg} = 1.0\text{--}1.2$ ) and clinopyroxene is rich in Na and Al ( $\text{Na}_2\text{O} = 4.1\text{--}4.7$  wt%,  $\text{Al}_2\text{O}_3 = 10.2\text{--}10.9$  wt%). Any non-ideal correction terms for Fe/Mg in garnet and Na and Al in clinopyroxene are not incorporated into the formulation of

Ganguly (1979). Nevertheless, the above clear differences in mineral compositions did not affect temperature estimations, meaning that such non-ideal effects should be trivial in the application of the Grt-Cpx thermometer.

The formulation by Pattison and Newton (1989) gave significantly lower temperatures by about 150–200 $^{\circ}\text{C}$ , which is similar to that found by Green and Adam (1991) and Perkins and Vielzeuf (1992). Therefore, Aranovich and Pattison (1995) and Berman et al. (1995) re-examined the experimental data by Pattison and Newton (1989), plus other compositional bracketing-type experimental data. The resulting formulation by Berman et al. (1995) also gave significantly lower temperatures (about  $-200^{\circ}\text{C}$ ) in this study (Fig. 4). We consider that the deviation of Berman et al. (1995) formulation might be due to their solid-solution model of clinopyroxene. They incorporated non-ideal term for Al content in clinopyroxene, but the adopted excess interaction energy ( $W_{ij}$ ) appears to be too high:  $W_{\text{MgAl}} - W_{\text{FeAl}} = 11.81$  kJ/mol. Holland (1990) deduced excess interaction energy for clinopyroxene from independent experiments and concluded that the excess interaction energy between Mg and Al is mostly the same as that between Fe and Al in clinopyroxene: that is,  $W_{\text{MgAl}} - W_{\text{FeAl}} \approx 0$  kJ/mol. Therefore, we tentatively recalculated temperatures by using the formulation by Berman et al. (1995) with  $W_{\text{MgAl}} - W_{\text{FeAl}} \approx 0$  kJ/mol (MB1995 in Fig. 4), and the obtained temperatures are well consistent with the experimental temperatures. Clinopyroxene in eclogite is rich in Al, and hence the formulation by Berman et al. (1995) has given significantly lower temperatures for eclogite.

## Conclusions

Applications of previously proposed formulations of the Grt-Cpx thermometer to long-heating equilibrium experiments in this study relevant to eclogites confirmed that the formulation based on compositional bracketing-type experiments by Pattison and Newton (1989) yielded significantly lower temperatures than the experimental temperatures. The formulation by Berman et al. (1995) also gives lower temperatures in our experiments, perhaps due to the overestimated excess interaction energy for clinopyroxene. Although the formulation by Berman et al. (1995) may be applicable to samples containing low-Al clinopyroxene, it is not suitable for eclogite. Among the many previous formulations, Saxena (1979), Ganguly (1979), and Ganguly et al. (1996) gave the most concordant temperatures to the present experimental temperatures, but formulations by Ellis and Green (1979), Powell (1985), Krogh (1988), and Krogh-Ravna (2000) also gave relatively concordant temperatures for experiments at 1,150 and 1,200 $^{\circ}\text{C}$ . We do not have experimental data at low- $T$  conditions for eclogite, so that potential uncertainties still remain for low- $T$  ( $< 1,000^{\circ}\text{C}$ ) eclogitic rocks.

**Acknowledgments** We deeply appreciate E. Takahashi for his guidance on the experimental work at Tokyo Institute of Technology and also his constructive comments on this study. We would like to thank T. Mori, M. Obata, and S. Banno for their fruitful advices and also H. Tsutumi for polishing the run products. Critical comments from D.R.M. Pattison and J.C. Schumacher and editorial work by W. Schreyer are gratefully acknowledged. This study is partially supported by a Grant-in-Aid for the 21st Century COE Program (Kyoto University, G3). D. Nakamura acknowledges the financial support of a JSPS Research Fellowship for Young Scientists during his post-doctoral position at Tokyo Institute of Technology.

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