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Clinopyroxene Thermometry of Mantle Peridotites: Implication for the Evaluation of Their Diamond Potential

S. K. Simakov

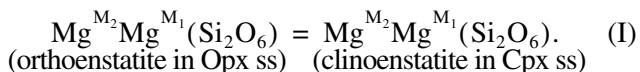
Presented by Academician I.D. Ryabchikov February 7, 2000

Received March 15, 2000

The elaboration of monomineral thermobarometers based on the composition of one phase is a challenging task in modern petrology. This is because xenoliths are lacking or rare, and only xenocrysts are available in many mantle-derived rocks. For example, prospecting and exploration for diamonds are commonly conducted with separate grains of mantle-derived associated minerals. The estimation of their formation temperature is important both for theoretical petrology and applied purposes.

The problem of the creation of such a thermometer may be solved by (1) the development of a basic model of a two-pyroxene (clino- and orthopyroxene) thermometer and (2) further elaboration of a monomineral clinopyroxene thermometer.

Solvus two-pyroxene thermometry is based on the following reaction:



The equilibrium constant for the reaction may be written as

$$K_d = \frac{X_{\text{CEn}}^{\text{Cpx}} \gamma_{\text{CEn}}}{X_{\text{OEn}}^{\text{Opx}} \gamma_{\text{OEn}}} = \frac{X_{M_2Mg}^{\text{Cpx}} X_{M_1Mg}^{\text{Cpx}} (X_{\text{Si}}^{\text{Cpx}})^2 \gamma_{\text{CEn}}}{X_{M_2Mg}^{\text{Opx}} X_{M_1Mg}^{\text{Opx}} (X_{\text{Si}}^{\text{Opx}})^2 \gamma_{\text{OEn}}}. \quad (\text{I})$$

To date, most two-pyroxene and clinopyroxene [8, 10] thermometers are still based on very primitive thermodynamic models. Therefore, their application for extrapolations far beyond the parameters of the experimental data bank remains questionable. Attempts to create thermodynamically substantiated versions have been made by Ryabchikov [4], who took into account the parameters of the interaction of elements at M_1 and M_2 sites for clino- and orthopyroxenes. The free energy of a two-pyroxene reaction (I) was determined as

$$\Delta G = 7000 - 4.34T(\text{K}) + 62.72P (\text{kbar}), \text{ J/mol}. \quad (\text{2})$$

In order to construct a new version of the thermometer, the activity of enstatite mineral in Cpx was calculated at the M_2 site, according to the model of nonsymmetric solutions using the data on Fe–Ca and Ca–Fe interactions from [7], Mg–Ca and Ca–Mg from [8], and Mg–Fe, Fe–Mg, Ca–Na, and Na–Ca from [11]. The value for Mg–Na and Na–Mg interactions were accepted as 18 000 J/mol. Symmetric parameters were admitted for the calculation of excess energies at the M_1 site for peridotitic compositions:

$$\text{Mg–Al} = \text{Al–Mg} = 44\,270 - 8.63T(\text{K}) \text{ J/mol}, \quad (\text{3})$$

$$\text{Mg–Fe} = \text{Fe–Mg} = -1000 \text{ J/mol}. \quad (\text{4})$$

Interaction between the sites [11] was also taken into account. The redistribution of Fe and Mg between M_1 and M_2 sites was determined using the scheme proposed by Wood and Banno [15]. The activity of the enstatite mineral in Opx was considered equal to unity.

The accuracy of the thermometer assessed by peridotitic mineral assemblages obtained from experiments in the range of 1050–1755°C and 20–60 kbar [1, 12–14] (46 analyses, in total) was as follows: $1\sigma = 54^\circ$ and Δ (mean) = 46°C. The Taylor thermometer (1998), which is based on the same data, has similar characteristics ($1\sigma = 54^\circ$ and $\Delta = 41^\circ$). However, it should be noted that the author achieved such an accuracy by introducing empirical corrections for the Fe, Ti, and tschermakite mineral contents in clinopyroxene.

In order to elaborate the clinopyroxene monoverversion of the thermometer, it is necessary to consider the distribution of Mg, Ca, and Fe between M_1 and M_2 sites in coexisting Cpx and Opx and to elaborate a way to calculate Mg at M_1 and M_2 sites in Opx based on the Cpx composition [3, 10]. Discriminant schemes for the calculation of the Opx composition are presently available [3, 10]. They were most fully developed by Ul'yanov [3] on the basis of experimental and natural data.

By using the above discriminant schemes as a basis, the relationships between Fe and Mg in Cpx and Opx at M_1 and M_2 sites were considered following the Wood–Banno method of calculation [15]. The available experimental data indicate that the Fe contents at the M_1 site are approximately equal both in Cpx and Opx. The

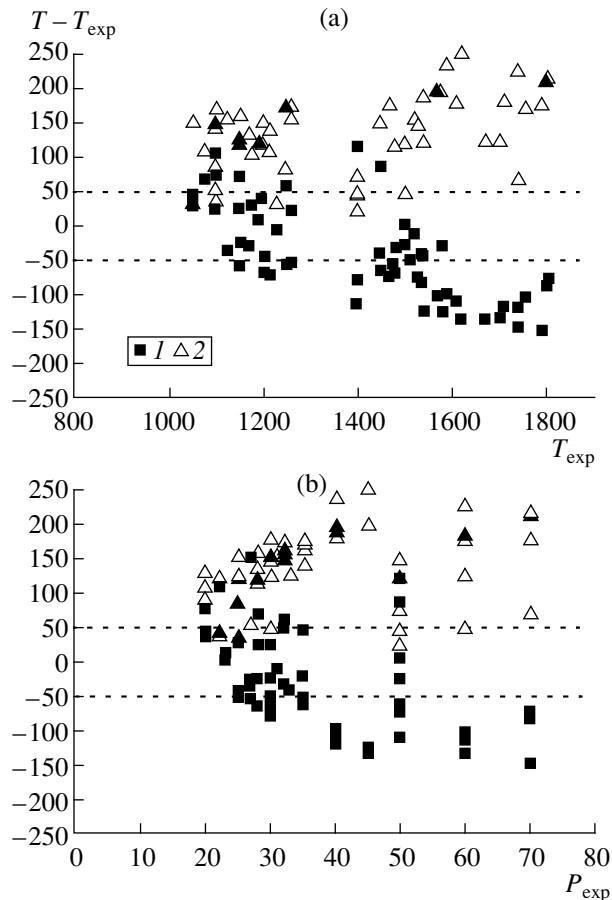


Fig. 1. The difference in temperature calculated (1) by the Mercier method and (2) the proposed thermometer depending on experimental (a) temperature and (b) pressure. Analyses for calculation were taken from [1, 12–14].

Fe contents are also nearly equal to those at M_1 and M_2 sites in Opx. The Mg content at M_1 and M_2 sites in Opx may be expressed as follows [3]:

$$X_{MgM_2}^{Opx} = 0.95 - X_{FeM_1}^{Cpx},$$

$$X_{MgM_1}^{Opx} = (X_{MgM_1}^{Cpx} + X_{FeM_1}^{Cpx}) / (1 - 0.85X_{Na}^{Cpx}) - X_{FeM_1}^{Cpx}.$$

These expressions were substituted into the equation of reaction constant (I). The accuracy of the clinopyroxene version of the thermometer for the same experimental data in the range of 1050–1820°C and 20–70 kbar (61 analyses, in total) was $1\sigma = 73^\circ$ and $\Delta = 62^\circ$ (Fig. 1). The temperature of garnet–clinopyroxene assemblages without orthopyroxene was also estimated (this is important for its application to natural minerals). The accuracy of this method is higher than that of all other empirical versions. For example, the clinopyroxene thermometers proposed by Mercier [10] and Lindsley [9] provide accuracies of $1\sigma = 145^\circ$ ($\Delta = 135^\circ$) and $1\sigma = 107^\circ$ ($\Delta = 100^\circ$), respectively. The clinopyroxene modification of the Taylor

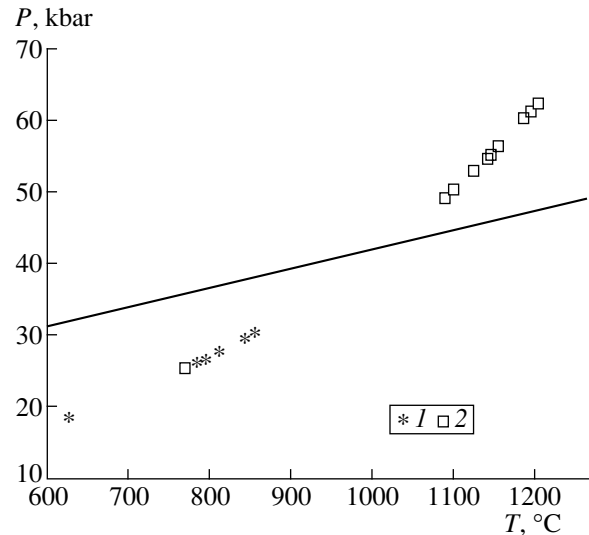


Fig. 2. Calculated temperature and pressure for peridotite xenoliths from (1) the Obnazhennaya and (2) Udachnaya pipes relative to the graphite–diamond equilibrium. Analyses were taken from [2, 4]; the initial temperature was calculated at $P = 30$ kbar and then plotted on the shield geotherm.

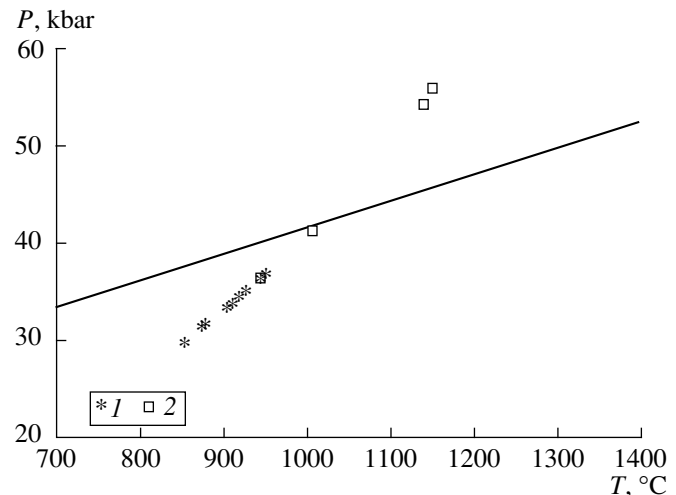


Fig. 3. Calculated temperature and pressure for peridotite xenoliths from (1) Pipe 200, northern Lesoto and (2) the Premier Pipe relative to the graphite–diamond equilibrium. Analyses were taken from [5, 6]; the initial temperature was calculated at $P = 30$ kbar and then plotted on the shield geotherm.

(1998) thermometer based on discriminant schemes yields $1\sigma = 103^\circ$ and $\Delta = 80^\circ$. As follows from Fig. 1, this version of the thermometer may overestimate the temperature and pressure at $T < 1000^\circ\text{C}$ and $P < 25$ kbar, and, on the contrary, underestimate these parameters at $T > 1500^\circ\text{C}$ and $P > 50$ kbar. Therefore, the optimum range of application of the thermometer is $T = 1100$ – 1500°C and $P = 25$ – 50 kbar.

The model was used for the estimation of the PT parameters related to the formation of diamond-bearing and barren peridotite xenoliths from Yakutian and South African kimberlites, and the estimated temperatures were plotted on the shield geotherm. For Yakutian xenoliths, the depth increases from the diamond-free Obnazhennaya Pipe to the diamond-bearing Udachnaya Pipe (Fig. 2). A similar tendency was revealed for the South African Pipes: the depth increases from depleted xenoliths from the Pipe 200 in Northern Lesotho (PT parameters were originally estimated as $T = 906\text{--}950^\circ\text{C}$ and $P = 25\text{--}31$ kbar) to lherzolite nodules from the diamond-bearing Premier Pipe (Fig. 3).

The results obtained indicate that the elaborated modification of the thermometer allows one to estimate the formation temperature of deep clinopyroxene xenocrysts. It fits the petrological criteria and may be applied to the estimation of the diamond potential of mantle-derived rocks.

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