A COMPARISON OF CLINOPYROXENE THERMOBAROMETRIC TECHNIQUES: APPLIED TO JWANENG, ORAPA AND MARKT KIMBERLITES

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INTRODUCTION

A single-mineral thermobarometer for kimberlitederived chrome diopside (clinopyroxene) is invaluable in acquiring information on the thermal state of the upper mantle and the extent of deep mantle sampling by the kimberlite magma (Nimis and Taylor, 2000). In this regard, clinopyroxene mineral chemical data from three southern African kimberlites (Jwaneng, Orapa and Markt) has been used to test the precision of the Nimis and Taylor (2000) thermobarometric formulation for calculating mantle equilibration conditions for individual clinopyroxene grains entrained during kimberlite emplacement.

THERMOBAROMETRY

Nimis and Taylor used experimentally synthesized clinopyroxenes to calibrate their thermobarometer at temperatures between 850 and 1500°C and pressures between 0 and 60kbar. They suggested that the formulation could be applied to a wide spectrum of depleted and fertile mantle compositions, given a number of fundamental assumptions:

- 1) All clinopyroxene grains were mantle-derived and hosted in high-pressure, garnet-bearing peridotites and;
- 2) A mineral equilibrium assemblage of clinopyroxene + garnet + orthopyroxene.

A combination of various filtering methods was used (Ramsay, 1995, Nimis, 1998) to confidently isolate garnet peridotite xenolith-borne clinopyroxenes from other mantle populations.

The barometer (equation 2) relies on the exchange of chrome between clinopyroxene and garnet in which diopside and CaCr-Tschermak's components in clinopyroxene react, producing uvarovite, grossular and knorringite components in garnet.

 $P(\text{kbar}) = -T(K)/126.9 \times \ln[a\text{CaCrTs}_{(\text{cpx})}] + 15.483 \times [\ln(\text{Cr#}_{(\text{cpx})})/T(K)] + T(K)/71.38 + 107.8$ (1)

where $aCaCrTs_{(cpx)} = Cr - 0.81 \times Cr\# \times (Na + K)$ (2)

The thermometer is based solely on the activity of the enstatite component in clinopyroxene. The thermometer is described in equation 3 as follows:

 $T(K) = [23166 + 39.28 \times P(kbar)]/[13.25 + 15.35 \times Ti + 4.50 \times Fe - 1.55 \times (Al + Cr - Na - K) + ln(a En_{(in cox)})$ (3)

where $a \operatorname{En}_{(\operatorname{in} \operatorname{cpx})} = (1 - \operatorname{Ca} - \operatorname{Na}) \times [1 - \frac{1}{2}(\operatorname{Al} + \operatorname{Cr} + \operatorname{Na})]$ (4)

Using P-T equilibration conditions for peridotitic clinopyroxene inclusions in diamonds, Nimis and Taylor were able to outline a number of fundamental criteria when assessing the reliability of their thermobarometer:

- All clinopyroxene grains used in the *P-T* calculation must be mantle-derived and of garnet peridotite affinity, therefore assuming equilibrium of the clinopyroxene population with orthopyroxene and garnet;
- 2) Evaluation of the crystal chemical criteria of clinopyroxene, where the cation sums on both the T and $M_1 + M_2$ sites is greater than 1.99 on a six-oxygen basis;
- A restricted compositional range for clinopyroxene Cr₂0₃ content of less than 5.0wt%; and
- A lower limit of 0.003 for the activity of the CaCr-Tschermak's (*a*CaCrTs_(cpx)) component (see equation 2).

PRESSURE AND TEMPERATURE ERRORS

Nimis and Taylor have shown that equation 4 reproduces experimental temperatures with an uncertainty of $\pm 30^{\circ}$ C at the 1 σ level. No systematic variations in the calculated and observed temperatures were reported. Errors in the experimental pressure determination are ± 2 kbar (1 σ) at pressures less than 40kbar and ± 3 kbar (1 σ) at pressures greater than 40kbar. The temperature dependence of the barometer is in the range of 1.2 to 2.4kbar/50°C (Nimis and Taylor, 2000).

An independent assessment of the error associated with the barometer was carried out using data from the Jwaneng and Markt kimberlites (Table 1). These data exhibit tightly constrained conductive thermal regimes.

The pressures obtained using the Nimis and Taylor barometer $(P_{observed})$ were compared with pressures obtained by projecting each clinopyroxene onto the 37mW/m^2 geotherm (P_{expected}) . The standard deviation (1σ) for the difference between the two pressure determinations is shown in Table 1. Secondly, the error in the pressure using the Nimis and Taylor formulation as a result of the uncertainty in temperature $(\pm 30^{\circ}C)$ was determined (Table 1). 30°C was added to or subtracted from each temperature value calculated using the Nimis and Taylor formulation. These new values were projected back onto the geotherm and the error was calculated as the difference between the new pressure and $P(_{\text{observed}}).$

Therefore, the total error in the Nimis and Taylor pressure calculation therefore incorporates the difference between $P(_{observed})$ and $P(_{expected})$ inclusive of the error calculated for the uncertainty in temperature determination (±9.99kbar and ±7.60kbar for the Jwaneng and Markt kimberlites respectively - Table 1). These calculations show that the calculated errors are significantly higher than those stated by Nimis and Taylor for experimentally synthesized clinopyroxene populations.

PRESSURE-TEMPERATURE ARRAYS

The thermobarometric formulation was applied to three clinopyroxene datasets obtained from the Jwaneng, Orapa and Market kimberlites. All data were filtered using an integrated approach so as to confidently isolate garnet peridotite, xenolith-borne clinopyroxene grains. The mantle equilibration conditions for each kimberlite are given in Figure 2 and discussed below.



Figure 1: Schematic diagram illustrating how the independent pressure errors were calculated.

JWANENG

Data (n = 681) for Jwaneng straddle the 37 and 40mW/nf^2 reference geotherms (Figure 1(a)) and are tightly constrained when data with $a \text{CaCrTs}_{(\text{cpx})} < 0.003$ are discarded.

ORAPA

Data (n = 883) for Orapa Mine show considerable scatter about the 37 and 40mW/m^2 reference geotherms (Figure 1(b)). Examination of the data used for the *P-T* calculations reveals a number of diversions from the criteria outlined by Nimis and Taylor. The majority of the *a*CaCrTs (cpx) values fall below 0.003 – Nimis and Taylor discarded all values below this in their evaluation of the reliability of the barometer. In addition, the average sum of the T and M₁ + M₂ site cations (1.966) falls below the minimum value stated by Nimis and Taylor (1.990).

MARKT

Data (n = 312) for the Markt kimberlite falls on, or close to the 40 mW/m² reference geotherm (as stated).



Figure 2 : Mantle equilibration conditions for the clinopyroxene data for the Jwaneng (a), Orapa (b) and Markt (c) kimberlites. 37 (green) and 40mW/m^2 (red) geotherms are also shown for reference.

Occurrence	P _{obs} - P _{expt} (1σ, kbar)	Error in T (±30°C, 1 σ , kbar)	95% confidence (2σ, kbar)
Jwaneng (n = 657)	±9.64	±9.99	±19.85
Markt (n = 311)	±7.60	±7.61	±8.87

Table 1: Independent calculated errors associated with the Nimis and Taylor (2000) barometer.

CONCLUSIONS

Results from this study have shown that the Nimis and Taylor (2000) thermobarometric formulation can be successfully used to determine mantle equilibration conditions for clinopyroxene grains recovered from a number of different southern African kimberlite bodies. A number of chemical criteria must be met in order to obtain reliable results. Isolation of a viable, mantle-derived garnet peridotite xenolith-borne clinopyroxene population was obtained using a combination of different discrimination criteria.

Data from the Jwaneng and Markt kimberlites show that agreement between the calculated equilibration conditions (pressures and temperatures) and the known geotherm for the respective occurrences is good. However, data collected from the Orapa kimberlite exhibits strong deviations from the criteria for reliable P-T calculations highlighted by Nimis and Taylor and subsequently, mantle equilibration conditions are considered spurious.

An independent analysis of the error associated with the chrome-in-clinopyroxene barometer shows that the maximum errors (\pm 3kbar at pressures greater than 40kbar) stated by Nimis and Taylor (2000) for experimentally synthesized clinopyroxenes are not reproducible using data obtained from the Jwaneng and Markt kimberlites, assuming that all chemical criteria have been met.

In addition, comparison of the current formulation with the thermometer provided by Finnerty and Boyd (1987) has shown that the relationship between the two temperature determinations is markedly non-linear at temperatures below approximately 900°C (Figure 3). This indicates that the error in the temperature determination may be higher than predicted by Nimis and Taylor at lower temperatures.



Figure 3: The relationship between the equilibration temperatures determined using the Finnerty and Boyd (1987) and Nimis and Taylor (2000) thermometers.

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