

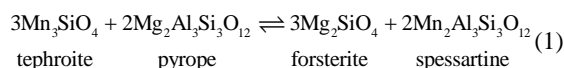
A semi-empirical manganese-in-garnet single crystal thermometer

Steven Creighton

Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada

An accurate understanding of the thermal conditions and the thickness of the subcratonic lithospheric mantle is essential for predicting the diamond potential of an area of interest. Mineral exchange thermobarometry of peridotite xenoliths gives the most accurate information regarding the local geothermal gradient and the thickness of the diamond window. During the early stages of diamond exploration programs mantle xenoliths are, however, not routinely identified but mantle derived xenocrystic garnet is common in heavy mineral concentrates. The composition of these garnet xenocrysts can be employed to determine both host rock paragenesis (harzburgitic/lherzolitic or eclogitic sources) and, for peridotitic sources, equilibration temperatures. The commonly applied geothermometer of Griffin et al. (1998) uses the Ni concentration of peridotitic garnets in equilibrium with olivine with an assumed constant composition. Because the Ni concentration in peridotitic garnets is typically below the detection limit of electron microprobes (EPMA), LA-ICPMS is commonly used for accurate measurements. The high cost of LA-ICPMS, however, strongly limits the numbers of grains analyzed to identify high priority targets during diamond exploration. To overcome this impediment, Smith et al. (1991) and Grütter et al. (1999) proposed empirical calibrations based on the concentration of the minor element (within the range of EPMA analyses) manganese in garnet in equilibrium with olivine. Here I present a re-calibration of the Mn-in garnet thermometer based on thermodynamic data and established relative to the garnet-olivine exchange thermometer of O'Neill and Wood (1979).

The temperature dependent exchange of Mn between olivine and garnet can be expressed by the following reaction:



for which an equilibrium constant K can be defined as:

$$K = \frac{(a_{\text{spess}}^{\text{gar}})^2 (a_{\text{for}}^{\text{olv}})^3}{(a_{\text{pyr}}^{\text{gar}})^2 (a_{\text{teph}}^{\text{olv}})^3} \quad (2)$$

Activities of spessartine and pyrope in garnet were calculated using a reciprocal solid solution model assuming ideal mixing on the dodecahedral

and octahedral sites (Wood and Nicholls 1978) using garnet thermochemical data from Ontonello et al. (1996). Forsterite and tephroite activities in olivine were derived assuming a symmetric solution model with site interaction energy values from Wood et al. (1994).

Calculation of the activities is simplified using co-variations observed between composition and activity. The activities of all the components relevant to equation (1) can be described by simple relationships between the mole fraction of either Mg or Mn and the activity of the corresponding component. The following linear equations were used to calculate the pyrope and spessartine activities in garnet and the tephroite activity in olivine:

$$a_{\text{py}}^{\text{gar}} = \frac{\text{Mg}}{\text{Mg} + \text{Fe} + \text{Ca} + \text{Mn}} - 0.374 \quad (3)$$

$$\ln(a_{\text{spss}}^{\text{gar}}) = 460 \times \left(\frac{\text{Mn}}{\text{Mg} + \text{Fe} + \text{Ca} + \text{Mn}} \right) - 18.7 \quad (4)$$

$$\ln(a_{\text{teph}}^{\text{olv}}) = 2153 \times \left(\frac{\text{Mn}}{\text{Mg} + \text{Fe} + \text{Mn}} \right) - 14.75 \quad (5)$$

The forsterite activity in olivine is best fit with the second degree polynomial equation:

$$a_{\text{for}}^{\text{olv}} = 4.17 \times \left(\frac{\text{Mg}}{\text{Mg} + \text{Fe} + \text{Mn}} \right)^2 - 6.44 \times \left(\frac{\text{Mg}}{\text{Mg} + \text{Fe} + \text{Mn}} \right) + 3.27 \quad (6)$$

Using the above simplifications, I have formulated a thermometer based on equilibrium (1) using published and unpublished mineral chemical data from 70 garnet peridotite xenoliths primarily from South African kimberlites. Temperatures were estimated using the garnet-olivine Fe-Mg exchange thermometer of O'Neill and Wood (1979 also O'Neill 1980; $T_{\text{O'Neill}}$) calculated iteratively with pressures determined using the orthopyroxene-garnet barometer of Brey and Köhler (1990, P_{BKN}). Multiple linear regression of the xenolith P-T- $\ln K$ data (Figure 1) provides a reasonable fit to the natural data and yields the following thermometer equation:

$$T(^{\circ}\text{C}) = 970 + 92 \times P - 62 \times \ln(K) \quad (P \text{ in GPa}) \quad (7)$$

This formulation reproduces $T_{\text{O'Neill}}$ of the xenoliths to better than $\pm 100^{\circ}\text{C}$ calculated at P_{BKN} for a dataset of

311 garnet-bearing xenoliths from worldwide locations and hence has a precision comparable to T_{Ni} .

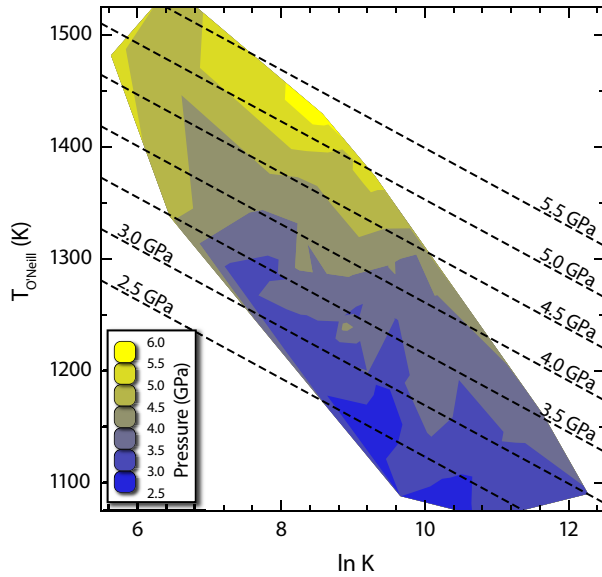


Figure 1: Olivine-garnet Fe-Mg exchange temperature ($T_{O'Neil}$) in Kelvin vs. $\ln K$ of mantle xenoliths from South African kimberlites. The data are contoured in pressure (P_{BKN}) showing the co-dependency of K on both P and T .

In order to apply this thermometer to peridotitic garnets for diamond exploration two additional input parameters are required that cannot be directly derived from garnet EPMA analyses. First, a correction for the unknown equilibration pressure of garnet xenocrysts must be used in place of P_{BKN} and second, reasonable activities of forsterite and tephroite in mantle-derived olivine must be assumed. The pressure dependency of K (Figure 1) may be used to derive a pressure correction for the thermometer. Regression of the P - T - $\ln K$ relationship of the same xenolith database leads to the following pressure correction:

$$P^* = 8.75 - 0.554 \times \ln(K) \quad (8)$$

Which may be substituted into equation 7 to give the pressure corrected T_{Mn} :

$$T_{Mn} (^{\circ}C) = 1775 - 86 \times \ln(K) \quad (9)$$

The pressure corrected T_{Mn} reproduces $T_{O'Neil}$ from ~700 to 1450°C within $\pm 150^{\circ}C$ for 289 of the 311 xenoliths (93%) in the database (Figure 2).

The choice of assumed forsterite and tephroite activities in olivine for the Mn-in-garnet thermometer depends on the application. The information most pertinent for diamond exploration is whether a garnet derives from within the diamond stability field. A large proportion of garnets from depleted harzburgitic sources within the diamond stability field would indicate a high priority target. Hence, a thermometer (using temperature as a proxy for depth) should be most accurate in the temperature range where

the diamond-graphite transition intersects the local geothermal gradient. The diamond-graphite transition (Kennedy and Kennedy 1976) occurs in cratonic mantle lithosphere within a temperature range from approximately 900°C to 1150°C assuming that P - T co-variation in subcratonic lithospheric mantle may be described by model conductive geotherms from ~38 to 44 mW/m² surface heat flow (Pollack and Chapman 1977). The average forsterite and *log* tephroite activities of 120 olivines from xenoliths with temperatures within the specified range are 0.879 and -5.44, respectively. Substituting these values into equation 2, for use as a single crystal thermometer, produces results with slightly larger error than temperatures calculated with known olivine compositions but 86% are within $\pm 150^{\circ}C$ of $T_{O'Neil}$ (Figure 3). Relative to $T_{O'Neil}$, my formulation underestimates the temperature of several sheared peridotites that have equilibration temperatures $>1350^{\circ}C$.

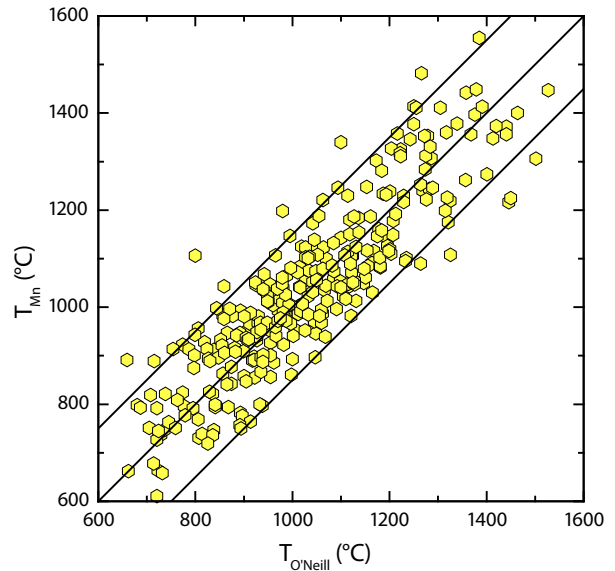


Figure 2: Comparison of $T_{O'Neil}$ and T_{Mn} for xenoliths with known olivine compositions. The T_{Mn} for most xenoliths is within $\pm 150^{\circ}C$ of $T_{O'Neil}$.

Comparison with the two previous empirical formulations (Smith et al. 1991; Grütter et al. 1999) indicates improved precision of my re-calibration. The formulation of Smith et al. (1991) when used as a single crystal thermometer (using an average mantle olivine MnO concentration of 0.104 wt%) systematically underestimates $T_{O'Neil}$ by 150°C below 800°C and overestimates at $T_{O'Neil} > 1100^{\circ}C$ by 150-300°C. The garnet-olivine Mn thermometer of Grütter et al. (1999) overestimates temperatures with deviations being most pronounced at temperatures below ~1000°C, leading to an overestimation of the proportion of samples derived from the diamond stability field.

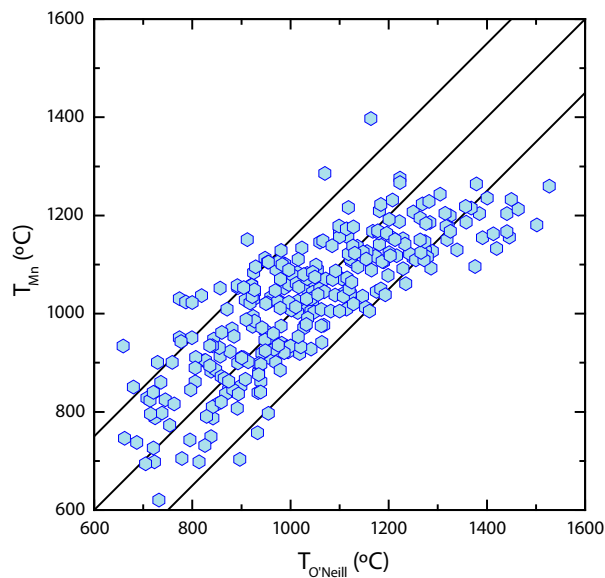


Figure 3: Comparison of $T_{O'Neill}$ for xenoliths with known olivine compositions and T_{Mn} calculated with assumed olivine compositions. The scatter is somewhat larger than Figure 2 but T_{Mn} for most xenoliths is still within $\pm 150^\circ\text{C}$ of $T_{O'Neill}$. The samples with underestimated T_{Mn} at $T_{O'Neill} > 1350^\circ\text{C}$ are sheared xenoliths mainly from Lesotho.

References

- Brey GP, Köhler T (1990) Geothermobarometry in four-phase lherzolites II. New thermometers, and practical assessment of existing thermobarometers. *J Petrol* 31:1353-1378
- Griffin WL, Cousens DR, Ryan CG, Sie SH, Suter GF (1998) Ni in chrome pyrope garnets: a new geothermometer. *Contrib Mineral Petrol* 103:199-202
- Grütter H, Apter DB, Kong J (1999) Crust-Mantle Coupling: Evidence from Mantle-Derived Xenocrystic Garnets. In: Gurney JJ, Gurney JL, Pascoe MD, Richardson SH (eds) *Proceedings of the VIIth International Kimberlite Conference*, vol 1. Red Roof Design, Cape Town, South Africa, pp 307-313
- Kennedy CS, Kennedy GC (1976) The equilibrium boundary between graphite and diamond. *J Geophys Res* 81:2467-2470
- O'Neill HSC (1980) An experimental study of Fe-Mg partitioning between garnet and olivine and its calibration as a geothermometer: Corrections. *Contrib Mineral Petrol* 72:337
- O'Neill HSC, Wood BJ (1979) An experimental study of Fe-Mg partitioning between garnet and olivine and its calibration as a geothermometer. *Contrib Mineral Petrol* 70:59-70
- Ottone G, Bokreta M, Sciuto P (1996) Parameterization of energy and interactions in garnets; end-member properties. *Am Min* 81:429-447

Pollack HN, Chapman DS (1977) On the regional variation of heat flow, geotherms, and lithospheric thickness. *Tectonophysics* 38:279-296

Smith D, Griffin W, Ryan C, Sie S (1991) Trace-element zonation in garnets from The Thumb: heating and melt infiltration below the Colorado Plateau. *Contrib Mineral Petrol* 107:60-79

Wood B, Hackler R, Dobson D (1994) Experimental determination of Mn-Mg mixing properties in garnet, olivine and oxide. *Contrib Mineral Petrol* 115:438-448

Wood BJ, Nicholls J (1978) The thermodynamic properties of reciprocal solid solutions. *Contrib Mineral Petrol* 66:389-400