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REVISION 2

Trace element thermometry of garnet-clinopyroxene pairs, revisited

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ABSTRACT. Two errors are identified in the implementation of a recently published thermometer based on the partitioning of trace elements between garnet and clinopyroxene. The errors compromise comparisons with other thermometers and experimental results. Using the same methodology, a new, simplified procedure is presented in order to rectify the errors, and test the consequences. In general, the corrected thermometer gives temperatures that are 30-50 °C higher than uncorrected values.

Keywords: geothermometer, garnet, clinopyroxene, REE

Garnet-clinopyroxene trace-element thermometry (Pickles et al. 2016) and thermobarometry (Sun and Liang 2015) are of great interest, despite issues related to sensitivity and disequilibrium. Given the issues, comparisons between different methodologies (see Pickles et al. 2016) suffer in response to errors in implementation. This article addresses two errors in the garnet-clinopyroxene trace-element thermometer published by Pickles et al. (2016). The theory and the strategy are well-conceived, clever and innovative. The two errors appear in the implementation in their EXCEL spreadsheet, as follows:

1. An extra element pair. The Pickles et al. (2016) thermometer is based on the partitioning of eight trace elements {Y, Nd, Sm, Eu, Gd, Er, Yb, Lu} between garnet and clinopyroxene. The procedure produces an average of the calculated temperatures for each pair of elements in the set {Y, 7 REE}, with outliers excluded from the average. There are of course 28 combinations of 2 of 8 elements. The

spreadsheet developed by Pickles et al. (2016) actually calculates the average temperature for 29 combinations, inadvertently counting one element-pair twice (Yb,Nd).

2. Incorrect formulation of components of garnet. Pickles et al. (2016) use incorrect formulations for the mole fractions X_m of the garnet components, where m = grs, prp, alm, sps, adr, uv. The abbreviations are consistent with recommendations by Kretz (1983) and Whitney and Evans (2011):

grs = $Ca_3Al_2Si_3O_{12}$ (grossular)
prp = $Mg_3Al_2Si_3O_{12}$ (pyrope)
alm = $Fe_3Al_2Si_3O_{12}$ (almandine)
sps = $Mn_3Al_2Si_3O_{12}$ (spessartine)
adr = $Ca_3Fe^{3+}{}_2Si_3O_{12}$ (andradite)
uv = $Ca_3Cr_2Si_3O_{12}$ (uvarovite)

The Pickles et al. (2016) formulations are as follows:

$$X_{grs} = (1 - X_{adr} - X_{uv})\ Ca/(Mg+Fe^{2+}+Mn+Ca)$$
$$X_{prp} = (1 - X_{adr} - X_{uv})\ Mg/(Mg+Fe^{2+}+Mn+Ca)$$
$$X_{alm} = (1 - X_{adr} - X_{uv})\ Fe^{2+}/(Mg+Fe^{2+}+Mn+Ca)$$
$$X_{sps} = (1 - X_{adr} - X_{uv})\ Mn/(Mg+Fe^{2+}+Mn+Ca)$$
$$X_{adr} = Fe^{3+}/(Fe^{3+}+Cr+Al)$$
$$X_{uv} = Cr/(Fe^{3+}+Cr+Al)$$

These formulations are only correct when $X_{adr} = X_{uv} = 0$. Otherwise, except in special instances, X_{grs} is overvalued and X_{prp}, X_{alm} and X_{sps} are undervalued. This can be shown by algebraic proof, but it is much easier to demonstrate by simple tests (pfu = per formula unit):

$$Ca_{pfu} = 3X_{grs} + 3X_{adr} + 3X_{uv}$$
$$Mg_{pfu} = 3X_{prp}$$
$$Fe^{2+}{}_{pfu} = 3X_{alm}$$
$$Mn_{pfu} = 3X_{sps}$$

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$Fe^{3+}_{pfu} = 2X_{adr}$

$Cr_{pfu} = 2X_{uv}$

None of the examples in Pickles et al. (2016) satisfies these tests. Of course the question arises, just what is a correct formulation for the garnet components? A simple approach is to transform atoms pfu to amounts of components. First, define in matrix form (**A**) each garnet component in terms of a unique set of elements. The following matrix will work for typical garnet:

"new" components	matrix						"old" components
x'	**A**						**x**
grs	**3**	0	0	0	0	0	Ca
prp	0	**3**	0	0	0	0	Mg
alm	0	0	**3**	0	0	0	Fe^{2+}
sps	0	0	0	**3**	0	0	Mn
adr	**3**	0	0	0	**2**	0	Fe^{3+}
uv	**3**	0	0	0	0	**2**	Cr

The amounts of the new components $n_{x'}$ are expressed in terms of the amounts of the old components n_x by the inverse of the transform of matrix **A**, that is $\mathbf{A^{-1}}$:

amount				$\mathbf{A^{-1}}$			amount atoms pfu
$\mathbf{n_{x'}, x'=}$							$\mathbf{n_x, x=}$
grs	**1/3**	0	0	0	**-1/2**	**-1/2**	Ca
prp	0	**1/3**	0	0	0	0	Mg
alm	0	0	**1/3**	0	0	0	Fe^{2+}
sps	0	0	0	**1/3**	0	0	Mn
adr	0	0	0	0	**1/2**	0	Fe^{3+}
uv	0	0	0	0	0	**1/2**	Cr

or:

$n_{grs} = n_{Ca}/3 - n_{Cr}/2 - n_{Fe3+}/2$

$n_{prp} = n_{Mg}/3$

$n_{alm} = n_{Fe2+}/3$

$n_{sps} = n_{Mn}/3$

$n_{adr} = n_{Fe3+}/2$

$n_{uv} = n_{Cr}/2$

These formulations are suitable where $n_{Ca} > 3/2\ (n_{Fe3+} + n_{Cr})$. In garnet with very low Ca, one or more of adr, uv and grs may not be possible, requiring a different strategy. One example (Table 1) should suffice to illustrate the magnitude of the problem.

The algorithm used by Pickles et al. (2016) to calculate temperature is sensitive to the amounts of the garnet components through the lattice strain factor r_0^{Grt}. For the purpose of making the necessary corrections, I designed a new spreadsheet using the algorithm of Pickles et al. (2016). This is available in a supplement. The spreadsheet is simplified, albeit somewhat awkward in the implementation of Pickles' et al. (2016) strategy. Nevertheless, the spreadsheet replicates Pickles' et al. (2016) results, but without weighting according to uncertainties in measured amounts of the trace elements and major elements.

A "quick and dirty" procedure

In the strategy used by Pickles et al. (2016) temperatures are calculated for each atom pair i-j, where i and j are trace elements. A solution for each $T_{i,j}$ can be determined by trial and error, for instance expedited by a simple binary search. The average of the individual $T_{i,j}$s is then computed, rejecting outliers. Criteria for rejection are $T_{i,j} < 600$ °C and $T_{i,j} > 2100$ °C (Pickles et al. 2016). The spreadsheet used here (supplement) was designed from a different perspective, but can also be used to implement the strategy of Pickles et al. (2016).

If the garnet and pyroxene are in perfect equilibrium, and assuming accurate chemical analyses, each pair of trace elements would give the same temperature. The equilibrium temperature would satisfy exactly the algorithm for each i-j pair of trace elements. This suggests a "quick and dirty" procedure,

wherein an initial, trial temperature is tested, without regard to an exact solution for each, individual $T_{i,j}$. Except by coincidence, the trial T, call it T_{trial}, is a solution to none of the individual $T_{i,j}$s. The average, call this Ave($T_{i,j}$), is then computed for the resulting set of *incorrect* values for $T_{i,j}$. Except under conditions of perfect equilibrium or pure coincidence, $T_{trial} \lesseqgtr Ave(T_{i,j})$. The "quick and dirty" strategy involves a search for the value of the T_{trial} for which $T_{trial} = Ave(T_{i,j})$. The procedure is expedited by a simple binary search.

Table 2 and Figure 1 give results for a selection of data from Pickles et al. (2016). All calculations were done using the EXCEL spreadsheet in the supplement. Unlike Pickles et al. (2016), the calculations do not involve any weighting of terms $T_{i,j}$ according to uncertainty in the measured chemical analyses for elements i and j. Line 3 gives temperatures without corrections for the problems in the Pickles et al. (2016) procedure. Line 4 gives temperatures without the extra $T_{Nd,Yb}$ term. The values on lines 3 and 4 for sample RD56 are the same because the $T_{Nd,Yb}$ term was rejected (no solution for $T_{Nd,Yb}$). Otherwise, of course, the influence of the extra $T_{Nd,Yb}$ term in Pickles et al. (2016) depends entirely on the discrepancy between $T_{Nd,Yb}$ and the average temperature. Line 5 gives temperatures calculated with a corrected formulation for the garnet components and no extra $T_{Nd,Yb}$ term. For the selection of data in Table 2 the temperatures calculated with the corrected garnet are 33-49 °C higher than temperatures calculated with Pickles' et al. (2016) faulty formulations for garnet components. The "quick and dirty" temperatures (line 6) are respectably close to the best solutions (line 5), despite significantly higher standard deviations in the former. In both the Pickles et al. (2016) strategy and the "quick and dirty" strategy, the standard deviation is for the set of calculated $T_{i,j}$s (excluding rejected values). In practice, for any garnet-clinopyroxene pair, the "quick and dirty" temperature is useful for considering the merit, and effort, of proceeding with the Pickles et al. (2016) strategy.

IMPLICATIONS

Trace-element garnet-clinopyroxene thermometry is important for calculating equilibrium conditions in eclogite and garnet-bearing ultramafic rock (e.g., Pickles et al. 2016; Sun and Liang 2015; and references therein). The corrections described herein call into question any results obtained from Pickles et al. (2016), or at the very least generously expand the uncertainty. The simplified Excel spreadsheet in the supplement makes the method easily adaptable to any sets of trace elements.

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Figure caption

FIGURE 1. Comparison of calculated temperatures and experiments temperatures (Table 2) for selected data sets in Pickles et al. (2016).

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Table 1. Garnet BL58 in Pickles et al. (2016)

Garnet BL58	apfu		
Si	2.96		
Ti	0.01		
Al	1.78		
total Fe	0.39		
Mn	0.02		
Mg	2.22		
Ca	0.49		
Na	0.00		
K	0.00		
Cr	0.13		
sum	8.00		
Fe^{3+}	0.16		
Fe^{2+}	0.23		
	Pickles et al.	Matrix method	
n(x'), x' =	(2016)		normalized
grs	0.144	0.018	0.019
prp	0.647	0.740	0.750
alm	0.067	0.077	0.078
sps	0.005	0.007	0.007
adr	0.077	0.080	0.081
uv	0.061	0.065	0.066
sum	1.000	0.987	1.000
Test by calculating, apfu			
n(x), x=			
total Fe = 3 alm +2 adr	0.355	0.390	0.395
Mn = 3 sps	0.017	0.020	0.020
Mg = 3 prp	1.935	2.220	2.250
Ca = 3 (grs+adr+uv)	0.847	0.490	0.497
Fe^{3+} = 2 adr	0.154	0.160	0.162
Fe^{2+} = 3 alm	0.200	0.230	0.233
etc.			

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Table 2. Calculated temperatures for selected samples in Pickles et al. (2016)

Notes	Sample	RD56	G25	BL88	V547	RD25	V546	BL58
1	P(experimental), GPa	3	5	3	6	3.4	8	3
2	T(experimental), °C	1200	1200	1100	1400	1200	1400	1200
Calculated T (°C)* using spreadsheet in supplement. No weighting of chemical analyses according to uncertainty.								
3	T, bad Grt, extra $T_{Nd,Yb}$	1137 (239)	1352 (215)	1140 (216)	1385 (189)	1157 (156)	1472 (105)	1229 (144)
4	T, bad Grt	1137 (239)	1338 (211)	1135 (221)	1384 (192)	1152 (157)	1471 (106)	1226 (146)
5	T, corrected Grt	1173 (244)	1375 (214)	1168 (223)	1426 (185)	1190 (151)	1512 (106)	1275 (148)
6	T, Q&D, corrected Grt	1246 (388)	1360 (328)	1185 (408)	1488 (263)	1237 (325)	1502 (229)	1299 (259)

1,2 Experimental conditions reported in Table 5 in Pickles et al. (2016).

* Values in parentheses express the standard deviation for the set of calculated $T_{i,j}$, i.e., in Excel stdev(array $T_{i,j}$).

3 No corrections.

4 Pickles et al. (2016) formulation for garnet components. No extra $T_{Nd,Yb}$.

5 Garnet components according to formulations introduced here. No extra $T_{Nd,Yb}$.

6 Quick and dirty strategy, supplement. Corrected Grt. No extra $T_{Nd,Yb}$.

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Figure 1 - Abbott