# Zr-almandine thermodynamics, and implications for zircon equilibria.

H.S. TOMKINS

School of Geosciences, Monash University, Victoria, 3800;
helen.tomkins@sci.monash.edu.au

Of all the minerals used for thermobarometry in metamorphic rocks, garnet is the most widely employed. It is also the mineral most commonly looked to for links between dateable accessory phases and metamorphic history. Therefore relating the Zr composition of a typical almandine garnet to pressure, temperature, zircon formation and zircon resorption would be extremely useful in the rapidly evolving field of thermochronology.

A compilation of natural and experimental data demonstrates that in garnets of dominantly almandine composition, the concentration of Zr is strongly dependent on temperature. The Zr concentration increases with increasing temperature, from ~1.0 ppm Zr at 730 ºC, to ~250 ppm at 1100 ºC, and 8-10 kbar. A less significant pressure effect is also evident (Zr decreases with increasing P). From this data set, expressions of $K_{eq}$ can be derived. Mixing on sites is assumed to be ideal, with Zr substituting for Al on the octahedral site through coupled substitution; $ZrAlAl_{-1}Si_{-1}$.

Thermodynamic properties for the following reaction have been derived; $Fe_3Zr_2Al_2SiO_{12} + 4SiO_2 \rightarrow Fe_3Al_2Si_3O_{12} + 2ZrSiO_4$.

Such that, $K = \frac{a_{alm}.a_{zcn}^2}{a_{Zr-alm}.a_{qtz}^4}$ where $X_{Zr-alm} = \frac{27}{4} X_{Fe}^3 X_{Zr}^2 X_{Al}^2 X_{Si}$

Whilst ΔS and ΔH of reaction can be determined by plotting lnK vs 1/T using the available compositional information, no data exist for $V_{Zr\text{-}alm}$. Therefore to determine ΔV of reaction we take advantage of the fact that the substitution mechanism of Zr into almandine is the same as that for Zr substitution into grossular for kimzeyite-grossular ($Ca_3Zr_2Al_2SiO_{12}$-$Ca_3Al_2Si_3O_{12}$) solid solution. The unit cell volumes for kimzeyite have been determined previously by [1]. Therefore combining this data with known grossular and almandine volumes from [2], the theoretical volume for Zr-almandine can be extrapolated:

$$V = 11.532 + 2.019 X_{Zr}^{alm}\ Jbar^{-1}mol^{-1}$$

The results obtained from this thermometer are highly dependent on the precision and accuracy of Zr in garnet analyses. Results derived from Zr-poor garnet (such as those formed in low T environments like eclogites) should therefore be treated with caution.

**References**

[1] Yamakawa J., Henmi C., and Kawahara A. (1993) *Min. J.* **16,** 371-377.

[2] Robie R. A., and Hemingway B. S. (1995) *USGS Bull.* **2131**.