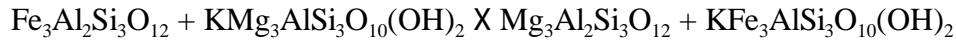


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I) Example: Mg-Fe exchange geothermometer in Garnet+Biotite

Almandine + Phlogopite \rightleftharpoons Pyrope + Annite



Given that a microprobe analysis of coexisting biotite and garnet yields:

$$X_{\text{Annite}} = 0.305 \qquad X_{\text{Almandine}} = 0.650$$

$$X_{\text{Phlogopite}} = 0.416 \qquad X_{\text{Pyrope}} = 0.176$$

For the above reaction:

$$R \text{ (gas constant)} = 1.987 \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$$

$$\Delta H = 12,454 \text{ cal} \cdot \text{mole}^{-1}$$

$$\Delta S = 4.662 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

$$\Delta V = 0.057 \text{ cm}^3 \cdot \text{mole}^{-1}$$

Molar volume must be converted to appropriate units:

$$\Delta V = 0.057 \text{ cm}^3 \cdot \text{mole}^{-1} \cdot [0.0242173 \text{ cal} \cdot (\text{cm}^3)^{-1} \cdot \text{bar}^{-1}] = 0.00138 \text{ cal} \cdot \text{bar}^{-1} \cdot \text{mole}^{-1}$$

$$K = \frac{a_{\text{pyrope}} \cdot a_{\text{annite}}}{a_{\text{almandine}} \cdot a_{\text{phlogopite}}} \quad (\text{K} = \text{Chemical Activity of Products} \div \text{Reactants})$$

Where “a” represents the chemical activity of the subscripted component. The activity of the components above are equal to the site occupancy mole fraction raised to the power of the number of sites, in this case 3 for all Fe and Mg components:

$$K = \frac{[X_{\text{pyr}}^{ga}]^3 [X_{\text{ann}}^{bi}]^3}{[X_{\text{alm}}^{ga}]^3 [X_{\text{phl}}^{bi}]^3} \quad (\text{X} = \text{site occupancy calculated from microprobe analysis})$$

Rearrangement of the thermodynamic equation above to solve for T yields:

$$T = \frac{P\Delta V + \Delta H}{\Delta S - (R)(\ln K)} \quad (\text{Rearrangement of Gibb's Free Energy Equation to solve for T}^\circ\text{K})$$

Note how units cancel:

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$$T = \frac{P\Delta V + \Delta H}{\Delta S - (R)(\ln K)} = \frac{\text{bar} \times \frac{\text{cal}}{\text{bar} \times \text{mole}} + \frac{\text{cal}}{\text{mole}}}{\frac{\text{cal}}{\text{mole} \times ^\circ K} - \left(\frac{\text{cal}}{^\circ K \times \text{mole}} \right) (\text{unitless})} = ^\circ K$$

$$\ln K = \ln \left[\frac{a_{py}^{ga} \cdot a_{ann}^{bi}}{a_{alm}^{ga} \cdot a_{phl}^{bi}} \right] = 3 \ln \left[\frac{X_{py}^{ga} \cdot X_{ann}^{bi}}{X_{alm}^{ga} \cdot X_{phl}^{bi}} \right] = 3 \ln \left[\frac{(0.176)(0.305)}{(0.650)(0.416)} \right] = -4.851$$

$$T = \frac{P(0.00138) + 12454}{(4.662) - (1.987)(-4.851)} = \frac{P(0.00138) + 12454}{14.26}$$

Assuming almost any reasonable pressure, for example, 6000 bar allows calculation of T:

$$T = \frac{(6000)(0.00138) + 12454}{14.26} = \frac{12462.3}{14.26} = 873.9^\circ K = 600.9^\circ C$$

As a check on our assumption, lets assume that the pressure of crystallization had been 1000 bar rather than 6000. What difference would that change make?

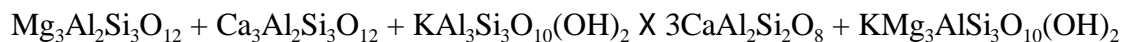
$$T = \frac{(1000)(0.00138) + 12454}{14.26} = 873.4^\circ K = 600.4^\circ C$$

The difference between the two pressure assumptions, 0.5°C, is much less than the expected accuracy of the geothermometer $\pm 20^\circ C$.

Example 2: Ga+Bi+Pl+Mu Geothermobarometer

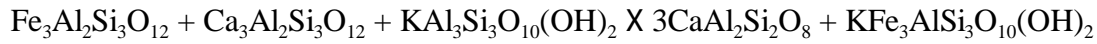
In this example the Ga+Bi geothermometer is combined with two reactions that have a moderate slope in P-T space to yield a solution for T and P. In effect the graphical plot of all three univariant curves intersect at the T and P of the mineral assemblage.

1. Pyrope + grossular + muscovite X 3 anorthite + phlogopite

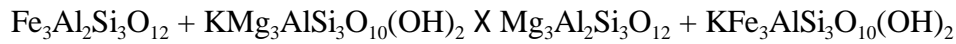


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2. Almandine + grossular + muscovite X 3 anorthite + annite



3. Almandine + Phlogopite X Pyrope + Annite



The equilibrium constants for the above reactions are:

$$K_1 = \frac{[X_{an}^{pl}]^3 [X_{phl}^{bi}]^3}{[X_K^{mu}] [X_{Al6}^{mu}]^2 [X_{pyr}^{ga}]^3 [X_{gr}^{ga}]^3}$$

$$K_2 = \frac{[X_{an}^{pl}]^3 [X_{ann}^{bi}]^3}{[X_K^{mu}] [X_{Al6}^{mu}]^2 [X_{alm}^{ga}]^3 [X_{gr}^{ga}]^3}$$

$$K_3 = \frac{[X_{pyr}^{ga}]^3 [X_{ann}^{bi}]^3}{[X_{alm}^{ga}]^3 [X_{phl}^{bi}]^3}$$

The chemical activities (X) can be calculated from microprobe analyses, which determine the chemical composition of individual 10 micron “spots” on the grain, using the following activity models:

$$X_{an}^{pl} = \frac{Ca}{Ca + Na + K} \quad X_{phl}^{bi} = \frac{Mg}{\text{Octohedral}} \quad X_{ann}^{bi} = \frac{Fe}{\text{Octohedral}}$$

$$X_K^{mu} = \frac{K}{K + Na + Ca + Ba} \quad X_{Al6}^{Mu} = \frac{Al}{\text{Octohedral}}$$

$$X_{pyr}^{ga} = \frac{Mg}{Mg + Fe + Ca + Mn} \quad (\text{Almandine and grossular are calculated in the same way}).$$

According to Ghent and Stout (1981), the best experimental data have estimated the thermodynamics properties to be:

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Phase	Enthalpy (H) J/mole	Entropy (S) J/(deg. mole)	Molar Volume (V) J/bar	Source
Anorthite	-4228730.0	200.186	10.075	Berman 1992
Annite	-5142000.0	421.010	15.483	Berman 1992
Phlogopite	-6210391.0	334.346	14.977	Berman 1992
Muscovite	-5976740.1	293.157	14.087	Berman 1992
Almandine	-5267216.0	340.007	11.511	Berman 1992
Pyrope	-6286547.6	266.359	11.316	Berman 1992
Grossular	-6632859.4	255.150	12.538	Berman 1992

The above values may be used to calculate the ΔH , ΔS , and ΔV for the above three reactions. Calculation for the equilibrium constants (K) from microprobe analyses would then allow for the solution of the slope and Y intercept terms for all three univariant curves in P-T space. Where the three curves intersect yields the P and T of metamorphic recrystallization.

Calculation of ΔH

For reaction #1 the calculation of ΔH proceeds from the H values of the products and reactants in the reaction:

$$\Delta H = (\text{H of Products}) - (\text{H of reactants}) = [3(H_{an}) + H_{phl}] - [H_{py} + H_{gr} + H_{mu}]$$

and so on for ΔS and ΔV . Note the coefficient of 3 for anorthite. The ΔH , ΔS , and ΔV for all three reactions should be calculated before proceeding to the next step. The below table contains the tabulation:

Reaction	ΔH J/mole	ΔS J/(mole deg. K)	ΔV J/bar
(1)	-433.9	120.238	7.261
(2)	48625.5	133.254	7.572
(3)	49059.4	13.016	0.311

The next step will always be the calculation of the equilibrium constant (K) for each of the three reactions. This step consists of solving the fraction containing the concentrations of products over that of the reactants. For example, reaction #1 would be calculated as:

$$K_1 = \frac{[X_{an}^{pl}]^3 [X_{phl}^{bi}]^3}{[X_K^{mu}] [X_{Al6}^{mu}]^2 [X_{pyr}^{ga}]^3 [X_{gr}^{ga}]^3}$$

The concentrations of components in each mineral have been calculated from microprobe data as:

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Component	Activity
Xan (plag)	0.3233
Xann (bi)	0.3246
Xphl (bi)	0.4425
XAl6 (mu)	0.8991
Xk (mu)	0.8710
Xalm (ga)	0.6494
Xpy (ga)	0.1836
Xgr (ga)	0.0788

Therefore, the calculation of equilibrium constant 1 (K₁) would be written as:

$$K_1 = \frac{[0.3233]^3 [0.4425]^3}{[0.8710][0.8991]^2 [0.1836]^3 [0.0788]^3} = 1373.2$$

Now the calculated values above can be used to solve for the slope and Y intercept of the univariant reactions. Using reaction #1 again as an example, we from prior arguments that:

$$\text{Slope} = \frac{\Delta S - R \ln K}{\Delta V} = \frac{120.2385 - (8.314)(7.225)}{7.261} = 8.287$$

$$Y_Intercept = \frac{-\Delta H}{\Delta V} = \frac{433.9}{7.261} = 59.75$$

The slope and Y intercept of reactions (2) and (3) should be calculated in the same manner as above. These values are summarized below:

	Slope (bar/deg. C)	Y intercept (bar)
Reaction (1)	8.287	59.75
Reaction (2)	14.85	-6421.75
Reaction (3)	168.02	-157747.20

The slope and Y intercepts are the equations of three univariant curves, which can now be plotted in P-T space. Where the three curves intersect solves for the T and P of recrystallization. The below chart is a graphical representation of the solution:

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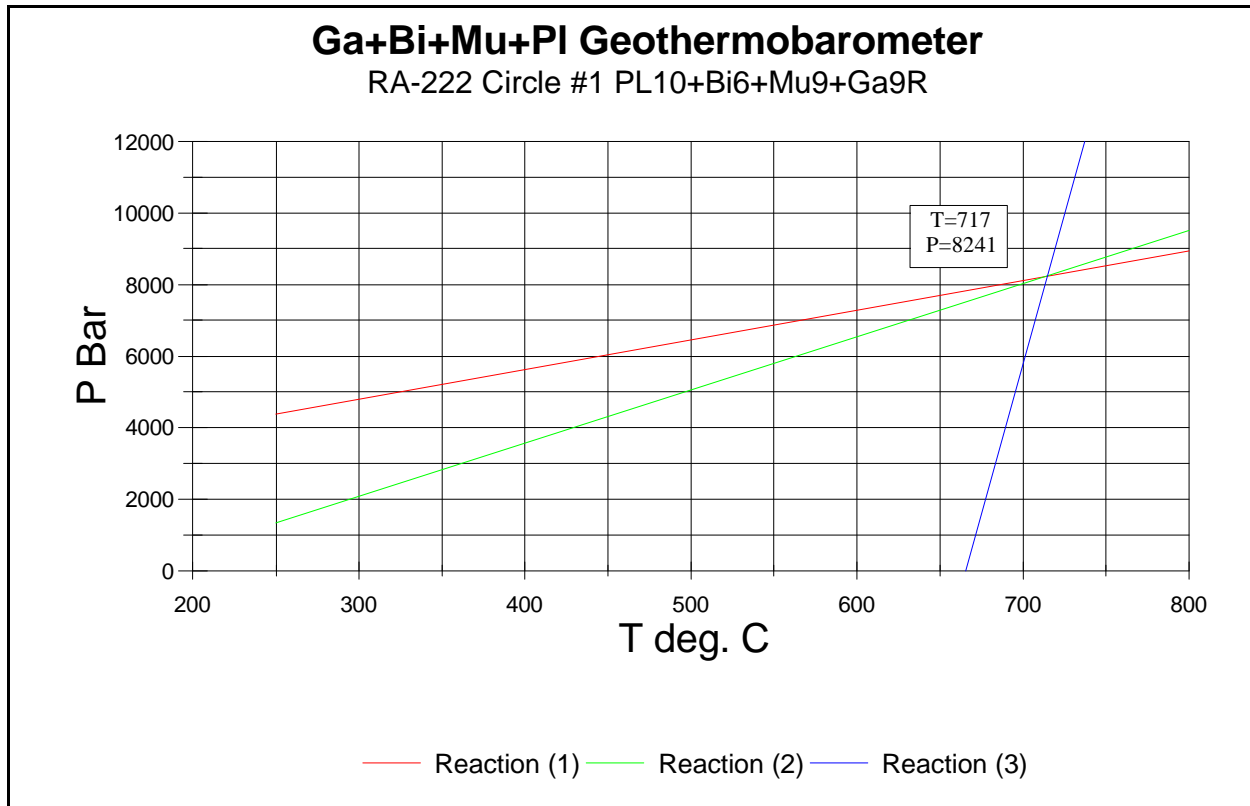


Figure 31: Graphical solution for the Ga+Bi+Mu+Pl geothermobarometer with sample RA-222 data.

Note the steep nature of the slope for reaction #3, which is why the Fe-Mg exchange in Ga+Bi is termed a geothermometer.