GY303 Igneous & Metamorphic Petrology

Lecture 9: Metamorphic Phase Equilibria
Phase Rule in Metamorphic Rocks

- $dF = C - P + 2$
- $dF$: degrees of freedom in the system
- $C$: number of chemical components
- $P$: number of phases
- The “2” in the equation is related to $T$ & $P$ that are the X and Y axes of a phase diagram
Application of the Phase Rule

- Aluminosilicate (Al$_2$SiO$_5$) Phase stability
Eskola’s Mineralogical Phase Rule

- Most metamorphic rocks are well represented by 7 chemical components (SiO₂, Al₂O₃, FeO, CaO, MgO, K₂O and Na₂O)
- A particular rock will most likely undergo metamorphism in a divariant field
- Therefore 2 = 7 – P + 2, so P = 7 (i.e. metamorphic rocks will contain at most 7 or fewer mineral phases)
A more complex Phase Diagram

- 2 components with 2 possible chemical reactions:
  - $A = B$
  - $C = D$
Thermodynamics and Metamorphism

• $\Delta G$: Gibb’s Free Energy quantifies the total chemical energy in the defined system. At chemical equilibrium $\Delta G = 0$

• $\Delta H$: Enthalpy, the amount of heat energy in the chemical reaction system

• $\Delta S$: Entropy, the amount of randomness in the chemical system.
Gibb’s Free Energy Equation

\[ \Delta G = \Delta H - T \Delta S + P \Delta V \]

- \( T \): temperature in degrees K
- \( P \): pressure in bar
- \( \Delta V \): change in volume for the reaction

• If \( \Delta G \) is negative the forward reaction will proceed
• Negative \( \Delta H \) reactions are **exothermic** and release heat
• Positive \( \Delta H \) reactions are **endothermic** and absorb heat from the universe
Gibb’s Free Energy cont.

- The free energy is equal to 0 at chemical equilibrium (a good assumption for metamorphic rocks)

\[ \Delta G = 0 = \Delta H - T\Delta S + P\Delta V \]

\[ P = T \frac{\Delta S}{\Delta V} + \frac{-\Delta H}{\Delta V} \]

- $\Delta S/ \Delta V = m = \text{slope}$
- $-\Delta H/ \Delta V = b = \text{y intercept}$
**ΔG and P-T Phase Diagrams**

- On a P-T graph a reaction can be graphed using Gibb’s Free Energy equation.

For reaction \( A = B \)

Slope = \( \frac{\Delta S}{\Delta V} \)

Y intercept = \( -\frac{\Delta H}{\Delta V} \)
Clapeyron Equation

• The Clapeyron equation is simply the $\Delta S / \Delta V$ slope of the Free Energy equation for a reaction:
  - If the slope is $> 0$ the reaction has a positive slope on a P-T phase diagram graph
  - If the slope is $< 0$ the reaction has a negative slope on a P-T phase diagram
Clapeyron Aluminosilicate Example

- Goal is to use tabulated values of $\Delta S$ and $\Delta V$ to plot the reaction Kyanite = Sillimanite on a P-T graph given the position of the invariant point.

<table>
<thead>
<tr>
<th></th>
<th>Molar Volume</th>
<th>Entropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kyanite</td>
<td>44.09 cm$^3$ mole$^{-1}$</td>
<td>83.76 J mole$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Sillimanite</td>
<td>49.90 cm$^3$ mole$^{-1}$</td>
<td>96.11 J mole$^{-1}$ K$^{-1}$</td>
</tr>
</tbody>
</table>

$\Delta S = S(\text{products}) - S(\text{reactants})$

$\Delta S = 96.11 - 83.76 = 12.35 \text{ J mole}^{-1} \text{ K}^{-1}$

$\Delta V = V(\text{products}) - V(\text{reactants})$

$\Delta V = 49.9 - 44.09 = 5.81 \text{ cm}^3 \text{ mole}^{-1} = 0.581 \text{ J bar}^{-1} \text{ mole}^{-1}$

Slope = $12.35/0.581 = 21.2 \text{ bar/K} = 0.0212 \text{ Kb/K}$
Ky=Sill Univariant Curve

- Assuming that the aluminosilicate invariant point is $T=350 \, ^\circ C$ and $P = 3.0 \, \text{Kb}$
Univariant Curves for Solid Solution Phases

• Solid solution in minerals such as garnet allows them to persist over a range in T & P
• As a solid solution phase such as garnet experiences different T & P the composition will adjust
• In many cases more than one solid solution phase is required to produce a geothermometer or geobarometer
Geothermometer Example: Ga+Bi

• Ga+Bi is an excellent geothermometer because these 2 phases are common in medium grade metamorphic rocks.

• Almandine + Phlogopite = Pyrope + Annite

• $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{K}\text{Mg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 = \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$
Ga+Bi Geothermometer Example

• Given that a microprobe analysis of coexisting biotite and garnet in a thin section yields (X represents mole fraction):
  – (X)Annite = 0.305
  – (X)Almandine = 0.650
  – (X)Phlogopite = 0.416
  – (X)Pyrope = 0.176
Ga+Bi Geothermometer cont.

• Given the following values:
  – $R$ (gas constant) = 1.987 cal mole$^{-1}$ K$^{-1}$
  – $\Delta H = 12,454$ cal mole$^{-1}$
  – $\Delta S = 4.662$ cal K$^{-1}$ mole$^{-1}$
  – $\Delta V = 0.057$ cm$^3$ mole$^{-1}$

• Note that all of the above values were calculated using the (Products – Reactants) equation

• Molar volume must be converted to appropriate units:
  – $\Delta V = 0.057$ cm$^3$ mole$^{-1}$ x [0.0242173 cal (cm$^3$)$^{-1}$ bar$^{-1}$]
  – $\Delta V = 0.00138$ cal bar$^{-1}$ mole$^{-1}$
Ga+Bi Equilibrium Constant (K)

• For solid solution the Gibb’s Free Energy equation includes a term for the equilibrium constant (K)
• $K = \frac{a_{\text{pyrope}} \cdot a_{\text{annite}}}{a_{\text{almandine}} \cdot a_{\text{phlogopite}}}$
Activity (a) vs. Concentration (X)

- Chemical activity (a) for ideal solid solution can be assumed to equal mole fraction (X)
- If an element is present in the formula more than once its mole fraction is raised to the occupancy power

\[ K = \frac{[X_{pyr}^{ga}]^3[X_{ann}^{bi}]^3}{[X_{alm}^{ga}]^3[X_{phl}^{bi}]^3} \]
Gibb’s Free Energy Equation

• For solid solution the equilibrium constant occurs in an additional term:
  – At equilibrium $\Delta G = 0 = \Delta H - T \Delta S + P \Delta S + RT \ln(K)$
• Re-arranging the equation to solve for $T$ yields:

$$T = \frac{P \Delta V + \Delta H}{\Delta S - (R)(\ln K)}$$
Units of T Estimate

• The below equation will result in degrees K

\[
T = \frac{P \Delta V + \Delta H}{\Delta S - (R)(\ln K)} = \frac{\text{bar} \times \frac{\text{cal}}{\text{bar} \times \text{mole}} + \frac{\text{cal}}{\text{mole}}}{\frac{\text{cal}}{\text{mole} \times ^\circ \text{K}}} - \left(\frac{\text{cal}}{^\circ \text{K} \times \text{mole}}\right) \text{(unitless)} = ^\circ \text{K}
\]
The equilibrium constant $K$ is the ratio of the chemical activities of the Products/Reactants.

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

- The substitution of all known values into the re-arranged Gibb’s Free Energy equation yields $T$ as a function of $P$.
- If this reaction is a good geothermometer it should have a large slope therefore the value of $P$ will have little effect on the result.

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

- Assuming a P=6,000 bar, $T = 873.9 \, \text{K} \,(600.9 \, \text{C})$
- Other P values yield:
  - P = 12,000 bar, $T = 874.5 \, \text{K} \,(601.5 \, \text{C})$
  - P = 1,000 bar, $T = 873.4 \, \text{K} \,(600.4 \, \text{C})$
- Choice of P makes no significant difference therefore Ga+Bi is an excellent geothermometer

\[
T = \frac{(6000)(0.00138) + 12454}{14.26} = \frac{12462.3}{14.26} = 873.9^\circ \text{K} = 600.9^\circ \text{C}
\]
Graphical Ga+Bi Geothermometer

- T estimate ultimately depends on K since $\Delta H$, $\Delta S$ and $\Delta V$ do not change
Ga+Bi+Ms+Pl
Geothermobarometer

• Fe and Mg exchange in Ga+Bi act as thermometer
• 2 other reactions have an intermediate Clapeyron slope so the intersection with the Ga+Bi thermometer defines a single invariant point for P-T
Ga+Bi+Ms+Pl Reactions

• (1) Pyrope + grossular + muscovite = 3 anorthite + phlogopite
  \[ \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 = 3\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 \]

• (2) Almandine + grossular + muscovite = 3 anorthite + annite
  \[ \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 = 3\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 \]

• (3) Almandine + Phlogopite = Pyrope + Annite
  \[ -\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{K}\text{Mg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 = \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 \]
Calculation of X (mole fraction)

- Compositional mole fraction is calculated from microprobe data

\[
X_{an}^{pl} = \frac{Ca}{Ca + Na + K}
\]

\[
X_{phl}^{bi} = \frac{Mg}{\text{Octohedral}}
\]

\[
X_{ann}^{bi} = \frac{Fe}{\text{Octohedral}}
\]

\[
X_{K}^{mu} = \frac{K}{K + Na + Ca + Ba}
\]

\[
X_{Al6}^{Mu} = \frac{Al}{\text{Octohedral}}
\]

\[
X_{pyr}^{ga} = \frac{Mg}{Mg + Fe + Ca + Mn}
\]
Equilibrium Constants (K)

- Remember that element sites with a “3” subscript are raised to the “3” power in the K ratio

\[
K_1 = \frac{[X^\text{pl}_{an}]^3[X^\text{bi}_{phl}]^3}{[X^\text{mu}_K][X^\text{mu}_{Al6}]^2[X^\text{ga}_{pyr}]^3[X^\text{ga}_{gr}]^3}
\]

\[
K_2 = \frac{[X^\text{pl}_{an}]^3[X^\text{bi}_{ann}]^3}{[X^\text{mu}_K][X^\text{mu}_{Al6}]^2[X^\text{ga}_{alm}]^3[X^\text{ga}_{gr}]^3}
\]

\[
K_3 = \frac{[X^\text{ga}_{pyr}]^3[X^\text{bi}_{ann}]^3}{[X^\text{ga}_{alm}]^3[X^\text{bi}_{phl}]^3}
\]
Thermodynamic Data (H, S and V)

- Thermo data should be from an internally consistent database (Berman, 1992)

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

- Slope and Y-intercepts for all 3 reactions
- Note the steep slope on reaction 3 (geothermometer)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ J/mole</th>
<th>$\Delta S$ J/(mole deg. K)</th>
<th>$\Delta V$ J/bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>-433.9</td>
<td>120.238</td>
<td>7.261</td>
</tr>
<tr>
<td>(2)</td>
<td>48625.5</td>
<td>133.254</td>
<td>7.572</td>
</tr>
<tr>
<td>(3)</td>
<td>49059.4</td>
<td>13.016</td>
<td>0.311</td>
</tr>
</tbody>
</table>
Solving for K1

- Solving for equilibrium constant K1 requires substitution of mole fractions into K1 ration (products/reactants)

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

\[
K_1 = \frac{[0.3233]^3[0.4425]^3}{[0.871][0.8991]^2[0.1836]^3[0.0788]^3} = 1373.2
\]
Calculation of Reaction (1) Slope

- Remember that slope is derived from rearrangement of Gibb's Free Energy equation

\[
P = T \left( \frac{\Delta S - R \ln K}{\Delta V} \right) + \frac{- \Delta H}{\Delta V}
\]

\[
\text{Slope} = \frac{\Delta S - R \ln K}{\Delta V} = \frac{120.2385 - (8.314)(7.225)}{7.261} = 8.287
\]
Calculation of Reaction (1) Y-
intercept

• Derived from Free Energy Equation

\[ P = T \frac{\Delta S - R \ln K}{\Delta V} + \frac{-\Delta H}{\Delta V} \]

\[ Y_{\text{Intercept}} = \frac{-\Delta H}{\Delta V} = \frac{433.9}{7.261} = 59.75 \]
Summary of Univariant Curves

- The 3 univariant lines intersect at the P-T of recrystallization

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Slope (bar/deg. C)</th>
<th>Y intercept (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction (1)</td>
<td>8.287</td>
<td>59.75</td>
</tr>
<tr>
<td>Reaction (2)</td>
<td>14.85</td>
<td>-6421.75</td>
</tr>
<tr>
<td>Reaction (3)</td>
<td>168.02</td>
<td>-157747.20</td>
</tr>
</tbody>
</table>
Graphical Solution for P-T

• Internally consistent thermo database should always intersect at a point
• Ga+Bi thermometer is apparent from high positive slope (reaction 3)
Summary for Final Exam

- Ternary igneous phase diagram
- Origin of tholeiitic vs. alkaline mafic magma (Ne-OI-Opx-Q-Pl phase diagram)
- Tholeiitic vs. Calc-Alkaline magma
- Textural and compositional terms for igneous and metamorphic (corona, poikioblast, etc.)
- Trace element fractionation problem (equation given)
- Phase rule in metamorphic rocks (use aluminosilicates as example)
- Solve for T given the composition of coexisting Garnet and Biotite, Gibb’s Free Energy equation, and equation for K
- Norm calculation (quartz normative)
- Metamorphic facies and geotherms
- Note: Bring CIPW norm calculation rules, calculator and ruler
\[ \frac{C_L}{C_O} = F^{(D-1)} \]

\[ T = \frac{P \Delta V + \Delta H}{\Delta S - (R)(\ln K)} \]

\[ df = C - P + 2 \]

\[ K = \frac{\left[ X_{pyr}^{ga} \right]^3 \left[ X_{ann}^{bi} \right]^3}{\left[ X_{alm}^{ga} \right]^3 \left[ X_{phl}^{bi} \right]^3} \]