

GY343 PETROLOGY METAMORPHIC PHASE EQUILIBRIA EXERCISE

Problem #1: Solve for the Pressure (Kilobar) and Temperature (°C) of the Al₂SiO₅ Triple Point. Remember that no matter which thermodynamic property you are manipulating, the change in that parameter during a reaction is always given by Products - Reactants.

Given the following thermodynamic data (data from Robie et al., 1979) for formation of the three aluminosilicate polymorphs from the elements:

Phase	Enthalpy(H)(J·mole ⁻¹)	Entropy(S)(J·mole ⁻¹ ·°K ⁻¹)	Molar Volume(V) (J·bar ⁻¹ ·mole ⁻¹)
Andalusite	-2587525	93.220	5.153
Sillimanite	-2585760	96.110	4.990
Kyanite	-2591730	83.760	4.409

where Enthalpy is in units J·mole⁻¹, Entropy is in J·mole⁻¹·°K⁻¹, and molar volume J·bar⁻¹·mole⁻¹.

The thermodynamic relationships at equilibrium follow the below equation:

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

You should recognize that the $-\Delta H/\Delta V$ term is the y intercept term, and $\Delta S/\Delta V$ is the slope term in the equation of a line in P-T space, T being the x axis, and P the y axis.

Solve:

(1) Using the above thermodynamic data fill in the below table (remember to use the [products - reactants] rule):

	And⇌Ky	And⇌Sill	Sill⇌Ky
$\Delta H(\text{J}\cdot\text{mole}^{-1})$			
$\Delta S(\text{J}\cdot\text{mole}^{-1}\cdot\text{°K}^{-1})$			
$\Delta V(\text{J}\cdot\text{bar}^{-1}\cdot\text{mole}^{-1})$			

(2) Using the above thermodynamic equation, fill in the below table. Remember that the thermodynamic equation is the equation of a line in PT space:

	And⇌Ky	And⇌Sill	Sill⇌Ky
Y-intercept (Bar)			
Slope (Bar·°K ⁻¹)			

(3) Using the linear equations for all three aluminosilicate reactions, fill in the below table for the pressure (bar) at 200 and 500 degree temperature(don't forget the conversion of °C to °K):

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Temp(°C)	P bar (And \rightleftharpoons Ky)	P bar (And \rightleftharpoons Sill)	P bar (Sill \rightleftharpoons Ky)
200			
500			

(4) Plot all three univariant curves on a T versus P graph with the following constraints:

X-axis: minimum T: 200 °C maximum T: 500 °C

Y-axis: minimum P: 0 bar maximum P: 8,000 bar

Plot the metastable extensions as dashed lines, the stable extensions as solid lines. Label the P and T of the triple point prominently on the diagram. Label the stable portions of the univariant curves with products and reactants (on the correct side!).

You may use a spreadsheet to solve the equations and plot the graph (see the spreadsheet template on the GY343 web site). If you do so, print out the calculations and the graph on separate sheets of paper.

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Problem #2: Solve for the PT of Coexisting Ga+Bi+Mu+Pl

Part 1

Given the following mineral compositions as calculated from microprobe analyses of coexisting mineral phases in a thin section from the southern Appalachian Blue Ridge belt:

Sample: RA-118 Probe Circle #1
 Mineral Assemblage: PL2+Bi4+Mu3+Ga6

Plagioclase Analysis

SAMPLE, SiO2, TiO2, Al2O3, Fe2O3, FeO, MnO, MgO, CaO, Na2O, K2O, TOTAL
 PLAG, 62.58, 0.04, 23.85, 0.00, 0.00, 0.00, 0.00, 5.10, 8.77, 0.20, 100.54

Biotite Analysis

SAMPLE, SiO2, TiO2, Al2O3, Fe2O3, FeO, MnO, MgO, CaO, Na2O, K2O, TOTAL
 BIOT, 33.77, 2.47, 18.28, 0.00, 23.91, 0.17, 8.32, 0.05, 0.68, 8.67, 96.32

Muscovite Analysis

SAMPLE, SiO2, TiO2, Al2O3, Fe2O3, FeO, MnO, MgO, CaO, Na2O, K2O, TOTAL
 MICA, 49.67, 0.89, 35.10, 0.00, 2.08, 0.00, 1.42, 0.00, 0.12, 10.66, 99.94

Garnet Analysis

SAMPLE, SiO2, TiO2, Al2O3, Fe2O3, FeO, MnO, MgO, CaO, Na2O, K2O, TOTAL
 GARN, 36.29, 0.00, 20.68, 0.00, 30.68, 6.00, 1.62, 4.38, 0.00, 0.07, 99.72

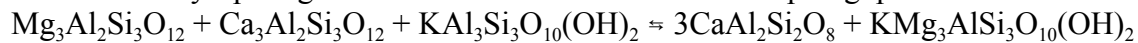
Also given are the below thermodynamic data:

Gas constant (R) in joules: R=8.314 J/(K mol)

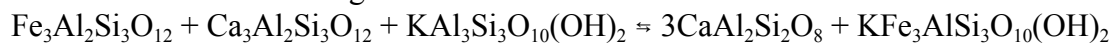
Phase	Enthalpy (H) J/mole	Entropy (S) J/(deg. mole)	Molar Volume (V) J/bar	Source
Anorthite	-4228730	200.1861	10.075	Berman 1992
Annite	-5142000	421.01	15.483	Berman 1992
Phlogopite	-6210391	334.346	14.977	Berman 1992
Muscovite	-5976740.12	293.1567	14.087	Berman 1992
Almandine	-5267216	340.007	11.511	Berman 1992
Pyrope	-6286547.62	266.3591	11.316	Berman 1992
Grossular	-6632859.38	255.15	12.538	Berman 1992

The geothermometer is based on the intersection in P-T space of the following three univariant reactions:

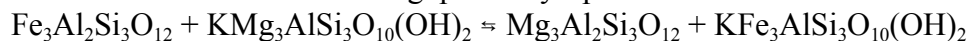
Reaction 1: Pyrope + grossular + muscovite \rightleftharpoons 3 anorthite + phlogopite



Reaction 2: Almandine + grossular + muscovite \rightleftharpoons 3 anorthite + annite



Reaction 3: Almandine + Phlogopite \rightleftharpoons Pyrope + Annite



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Use the above microprobe weight percent oxide analyses to calculate the mole fractions of components in mineral phases (e.g. mole fraction almandine in garnet). Below are the required mole fraction compositions of the mineral phases from sample RA-118 for calculating equilibrium constants. Use the "CMP2.EXE" utility program in "C:\TWQ" to calculate in the below values. Print out a copy of the "Sample.oxi" file in this directory to determine the data file format. Type the above oxide weight percent values into a text file using the same format as "Sample.oxi" to create an input file for "CMP2.EXE". You can use any text editor (i.e. Notepad) to create the data file.

Garnet

$X_{gr}^{ga} = \underline{\hspace{2cm}}$ (labeled as [-Gr-] in CMP2 output) Grossular component

$X_{pyr}^{ga} = \underline{\hspace{2cm}}$ (labeled as [-Py-] in CMP2 output) Pyrope component

$X_{alm}^{ga} = \underline{\hspace{2cm}}$ (labeled as [-Alm-] in CMP2 output) Almandine component

$X_{sp}^{ga} = \underline{\hspace{2cm}}$ (labeled as [-Sp-] in CMP2 output) Spessartine component

Muscovite (Mica)

$X_K^{mu} = \underline{\hspace{2cm}}$ (labeled as [-xK-] in CMP2 output) 12-coordinated K

$X_{Na}^{mu} = \underline{\hspace{2cm}}$ (labeled as [-xNa-] in CMP2 output) 12-coordinated Na

$X_{Al6}^{mu} = \underline{\hspace{2cm}}$ (labeled as [-xAl-] in CMP2 output) Octohedral site

$X_{OH}^{mu} = \underline{\hspace{2cm}}$ (labeled as [-xOH-] in CMP2 output) Hydroxyl site

Biotite

$X_K^{bi} = \underline{\hspace{2cm}}$ (labeled as [-xK-] in CMP2 output) 12-coordinated K

$X_{phl}^{bi} = \underline{\hspace{2cm}}$ (labeled as [-xMg-] in CMP2 output) Octohedral Mg

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$$X_{ann}^{bi} = \underline{\hspace{2cm}} \quad (\text{labeled as [-xFe-] in CMP2 output) Octohedral Fe}$$

$$X_{Ti}^{bi} = \underline{\hspace{2cm}} \quad (\text{labeled as [-xTi-] in CMP2 output) Octohedral Ti}$$

$$X_{Al}^{bi} = \underline{\hspace{2cm}} \quad (\text{labeled as [-xAl-] in CMP2 output) Octohedral Al}$$

$$X_{OH}^{bi} = \underline{\hspace{2cm}} \quad (\text{labeled as [-xOX-] in CMP2 output) Hydroxyl site}$$

Plagioclase

$$X_{an}^{pl} = \underline{\hspace{2cm}} \quad (\text{labeled as [-xAn-] in CMP2 output)}$$

$$X_{ab}^{pl} = \underline{\hspace{2cm}} \quad (\text{labeled as [-xAb-] in CMP2 output)}$$

$$X_{ab}^{pl} = \underline{\hspace{2cm}} \quad (\text{labeled as [-xOr-] in CMP2 output)}$$

The chemical activities (X) are defined within the CMP2 program as:

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

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

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

These can be calculated by hand by converting weight percent oxides from the microprobe analysis to cation proportions, however, it is faster and more accurate to use the CMP2 program.

Now calculate the T and P of metamorphic recrystallization using the provided thermodynamic data and mineral compositions.

Follow the below calculation steps:

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1. Calculate the ΔH , ΔS , and ΔV for all three reactions used in the Ga+Bi+Mu+Pl geothermobarometer (refer to your class notes). Show all steps in the calculations and attach a copy of the calculations to the back of this exercise. Do this for the following steps also. If you wish you may organize the calculations in a spreadsheet and attach that document to the back of this exercise. Remember the $\Delta = (\text{Products} - \text{Reactants})$ rule.

	ΔH	ΔS	ΔV
Reaction 1			
Reaction 2			
Reaction 3			

2. Calculate the equilibrium constant (K) for all three reactions.

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

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

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

	Equilibrium Constant (K)
Reaction 1	
Reaction 2	
Reaction 3	

3. Solve for the slope and Y intercept terms for all three reactions. Use the below equation to calculate slope and Y intercept terms. Remember that the slope term must take into account the equilibrium constant when the mineral phases involved in the reactions are solid solution systems:

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

	Slope (bar/°C)	Y-intercept (bar)
Reaction 1		
Reaction 2		
Reaction 3		

4. Plot graphically all three univariant curves on a sheet of graph paper with a T range of 200-800°C, and a P range of 0 to 12,000 bar. Remember that the thermodynamic equations use T in °K but you are plotting in °C. Attach graph to the back of this exercise. You may plot the graph with a spreadsheet application.

5. Graphically solve for the T and P of recrystallization and label the intersection point on the graph with your solution. Also label each curve on the graph with products and reactants on the correct side of each univariant reaction curve.

T= _____ °C

P= _____ bar

Part 2

Answer/plot the following using the results of the above calculations and the PT graph:

1. On the P-T graph you will see three univariant curves intersecting at the PT conditions of the sample. With a pen or spreadsheet drawing tool label reaction lines as (1), (2), or (3).

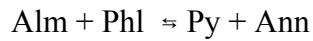
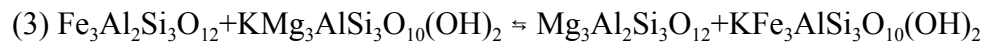
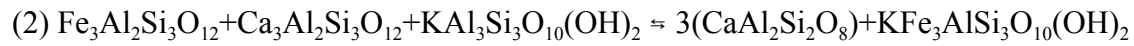
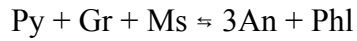
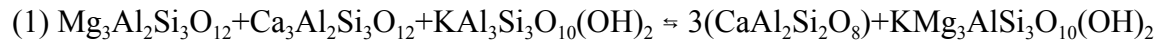
2. Which of the three reactions would be the best geothermometer (1,2, or 3)? _____

3. Which of the three reactions would be the best geobarometer (1,2, or 3)? _____

4. Label the univariant lines with the abbreviated mineral names placing the reactants and products on the correct side of the univariant line. The full balanced equation and its abbreviated

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equivalent are listed below:



5. Using a pen or spreadsheet drawing tool make the metastable extensions of the univariant lines “dashed” on the P-T graph.