

## ESS 312 Geochemistry – Practice midterm exam questions

### 1. Short-answer questions

Provide short definitions or explanations (either in words or formulae) to show you understand the meaning of the following concepts:

- Why are the heavy rare earth elements (e.g., Yb, Lu) compatible with garnet in the mantle, but incompatible with other mantle minerals such as olivine and orthopyroxene?

Large cation site in garnet accommodates heavy REE<sup>3+</sup> cations (in Grossular-type garnets this is the Ca<sup>2+</sup> site). No large cation site in olivine, opx.

- Why are the heat of formation (H) and free energy of formation (G) for nitrogen (N<sub>2</sub>) gas at room temperature and pressure equal to zero, while they are not zero for ozone (O<sub>3</sub>) gas at room temperature and pressure?

No absolute scale for G or H, so we define these quantities to be zero for the pure elements in their standard states – N<sub>2</sub> as gas, C as graphite etc. Std state for O is O<sub>2</sub> gas, not O<sub>3</sub>

- How do you calculate the free energy of a reaction ( $\Delta G_{\text{rxn}}$ ) at standard temperature but at any pressure?

$$\Delta G_{\text{rxn}, T_{\text{ref}}, P} = \int_{T_{\text{ref}}}^{T_{\text{ref}}, P} \int_1^P \Delta G_{\text{rxn}, T, P} dT dP = \Delta G_{T_{\text{ref}}, 1 \text{ bar}} + \int_1^P V dP$$

NOT PART OF THE REQUIRED ANSWER

if incompressible, this simplifies to  $\Delta G_{T_{\text{ref}}, 1 \text{ bar}} + V(P-1)$   
 $\rightarrow$  (otherwise =  $\Delta G_{T_{\text{ref}}, 1 \text{ bar}} + V_{T_{\text{ref}}, 1 \text{ bar}} e^{-\beta(P-1)}$ )

- Explain mathematically why, for any substance its free energy (G) increases with increasing pressure (P). If, in a G (y axis) vs. P (x axis) diagram, phase A has a greater slope than phase B, which will be the stable phase at high pressure? Explain.

i)  $dG_T = \left(\frac{\partial G}{\partial P}\right)_T dP = V_T dP$ . Volume is positive by convention.

ii) if  $\left(\frac{\partial G}{\partial P}\right)_A > \left(\frac{\partial G}{\partial P}\right)_B$  then  $V_A > V_B$ , so B will be stable at high P

- Do you expect the bonds in potassium bromide (KBr) to be primarily ionic or covalent in nature? Why?

STRONGLY IONIC – due to large difference in electronegativity between K, Br

6. Explain the difference between equilibrium (batch) crystallization, and fractional (Rayleigh) crystallization of a melt.

BATCH CRYSTALLIZATION: Equilibrium between crystals and melt as a whole.

FRACTIONAL CRYSTALLIZATION: instantaneous equilibrium between melt and crystals. Then

7. Given the following thermodynamic data for andalusite and sillimanite, does the equilibrium boundary between these minerals in P-T space have a positive or negative slope? Why?

Mineral	Volume (cm <sup>3</sup> )	Entropy (J/K)	Enthalpy (kJ)
Andalusite	52.29	245.1	-2,515.2
Sillimanite	50.23	246.9	-2,512.8

are removed from system.

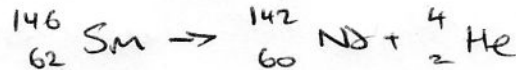
CLAUSIUS-CLAPÉRON equation  $\Rightarrow \frac{dP}{dT} = \frac{\Delta S}{\Delta V}$  along the phase boundary.  
 In this case, for reaction And  $\rightarrow$  Sil  $\Delta S$  is positive,  $\Delta V$  is negative, so slope is negative.

8. List three trace elements that are concentrated in the Earth's crust relative to the mantle, and explain why.

Rb, Cs, Sr, Ba, La, Ce, Pr, Nd, Sm, ..... Lu } all are incompatible in mantle minerals.  
 Zr, Nb, Ta, W, U, Th, Pb ...

9. <sup>146</sup>Sm is radioactive and decays by alpha decay with a decay constant  $\lambda = 6.73 \times 10^{-9} \text{ yr}^{-1}$ . [Note - this is not a typo for <sup>147</sup>Sm. The isotope <sup>146</sup>Sm is also radioactive].

- (a) Write a reaction for the decay of <sup>146</sup>Sm, indicating the daughter isotope.



- (b) What is the half-life of <sup>146</sup>Sm?

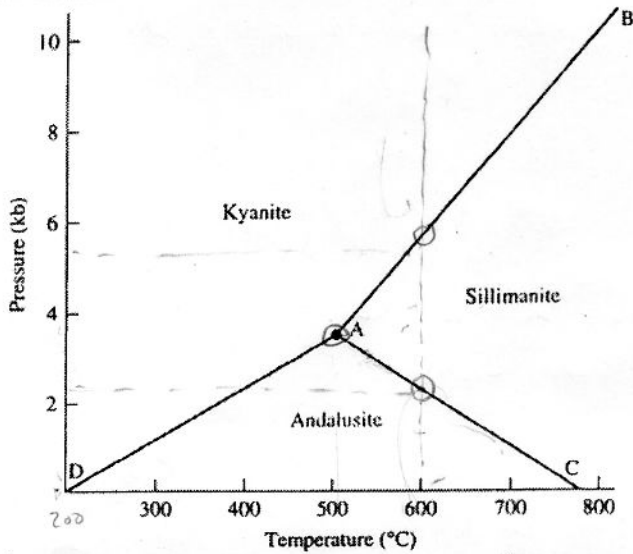
( $\alpha$  particle)

$$t_{1/2} = \frac{\ln(2)}{\lambda} = \frac{0.693}{6.73 \times 10^{-9}} = 103 \text{ Myr}$$

**Longer (multi-part) questions**

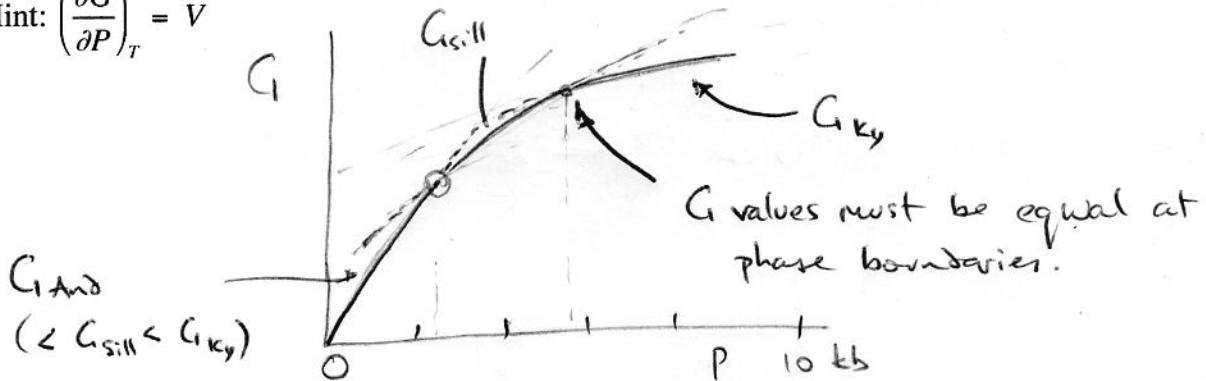
**Thermodynamics and mineral equilibria**

Shown below is the phase diagram for the  $\text{Al}_2\text{SiO}_5$  system:

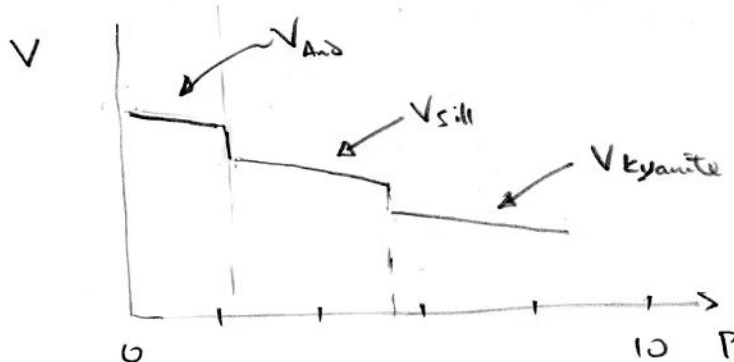


Sketch a **G vs P** diagram for a constant temperature of  $600^\circ\text{C}$ . Make **P** the x-axis, with pressures running from 0 – 10 kilobars. Make **G** the y-axis, but do not use a numerical scale.

Hint:  $\left(\frac{\partial G}{\partial P}\right)_T = V$



Draw a **V versus P** diagram, assuming a constant temperature of  $600^\circ\text{C}$ . Make **P** the x-axis, with pressure running from 0 – 10 kilobars. Put **V** on the y-axis.



Given that the entropy of andalusite is  $251.31 \text{ J mol}^{-1} \text{ K}^{-1}$  and that of kyanite is  $242.42 \text{ J mol}^{-1} \text{ K}^{-1}$ , determine the **difference** in molar volume between kyanite and andalusite.

Hints: Determine the slope of the andalusite-kyanite univariant line. The triple point (A) is located at  $500^\circ\text{C}$  and  $3.76 \text{ kbar}$ . Use the Clapeyron equation. Keep careful track of units – and remember that  $1 \text{ cm}^3 = 0.1 \text{ J bar}^{-1}$ .

Andalusite  $\rightarrow$  Kyanite  $\Delta S = S_{\text{ky}} - S_{\text{And}} = -8.89 \frac{\text{J}}{\text{mol K}}$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

$$\Delta V = \frac{\Delta S}{\text{slope}} = \frac{-8.89 \text{ J/mol K}}{12.53 \text{ bar/K}} = -0.7093 \frac{\text{J}}{\text{mol bar}}$$

convert via  $1 \text{ J/bar} = 10 \text{ cm}^3$

$$\Delta V = -7.09 \text{ cm}^3/\text{mol}$$

$$\text{slope} = \frac{3760 \text{ bar}}{300 \text{ K}} = 12.53 \text{ bar/K}$$

Arrange the minerals in order of *increasing* molar volume and explain briefly why you put them in that order.

$V_{\text{ky}} < V_{\text{sill}} < V_{\text{And}}$  As  $P \uparrow$  Andalusite transforms to sillimanite and then kyanite.

### Trace element partitioning

For the following problem, we will model the melting and crystallization processes that control trace element abundances in magmas formed over an ocean island hot spot in the Pacific.

Assume that the mantle in the magma source region has a mineralogy of:

Olivine:	65%	Determine bulk D values from mineral D values e.g. $D_{\text{Ni}} = f_{\text{olivine}} D_{\text{Ni, olivine}} + f_{\text{opx}} D_{\text{Ni, opx}} + f_{\text{cpx}} D_{\text{Ni, cpx}} + f_{\text{gar}} D_{\text{Ni, gar}}$ $= 0.65 \times 10 + 0.2 \times 4 + 0.1 \times 2 + 0.05 \times 0.04$ $= 7.50$
Orthopyroxene:	20%	
Clinopyroxene:	10%	
Garnet:	5%	

Use the following values for the distribution coefficients:

	% mineral	Ni	Cr	Rb	Th	Ce	Yb
Olivine	65	10	20	0.001	0.001	0.001	0.002
Orthopyroxene	20	4	9	0.001	0.001	0.003	0.05
Clinopyroxene	10	2	6	0.001	0.001	0.1	0.3
Garnet	5	0.04	2	0.001	0.001	0.02	4

from above:  $D_{\text{Bulk}}$       7.50      15.5      0.001      0.001      0.0123      0.2413

a) For a 10% batch partial melt, what is the Ce/Yb ratio of the resulting magma?

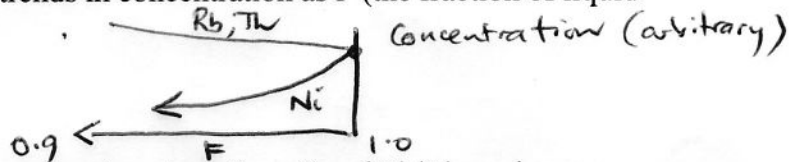
For BATCH MELTING  $C_L = C_0 / (F + D - FD)$

So  $\frac{C_{L,Ce}}{C_{L,Yb}} = \left(\frac{C_e}{Y_b}\right)_L = \left(\frac{C_e}{Y_b}\right)_0 \times \frac{(F + D_{Yb} - FD_{Yb})}{(F + D_{Ce} - FD_{Ce})}$ . For  $F = 0.1$ ,  $= \left(\frac{C_e}{Y_b}\right)_0 \times 2.86$

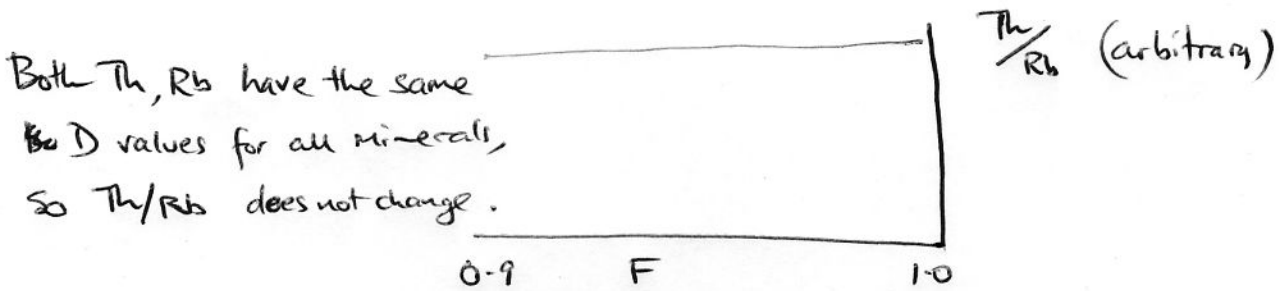
b) This magma sits in a magma chamber and undergoes 5% fractional crystallization of olivine only. Draw a diagram of element concentration (y axis) vs F (x axis) showing how the concentrations of Ni, Rb and Th change as crystallization proceeds. You don't need to show values for the concentrations, just the trends in concentration as F (the fraction of liquid remaining) runs from 1.0 to 0.9.

Rb, Th INCOMPATIBLE - INCREASE

Ni COMPATIBLE - DECREASES



c) On a similar diagram with F as the x axis, show how the ratio of Th/Rb evolves as crystallization proceeds.



d) Assume the magma starts with an initial Cr concentration of 400 ppm. What is the final Cr concentration after 5% fractional crystallization of olivine.

USE THE RAYLEIGH EQUATION  $C_L = C_0 \cdot F^{(D-1)}$

$C_{Cr} = 400 \text{ ppm} \times 0.95^{(20-1)}$   
 $= 151 \text{ ppm}$

↑  
 $D_{Cr}^{\text{olivine-melt}}$

## Radioactive isotopes and geologic dating methods

The isotope  $^{87}\text{Rb}$  decays to  $^{87}\text{Sr}$ , with a decay constant  $\lambda_{87\text{Rb}} = 1.42 \times 10^{-11} \text{ yr}^{-1}$ .

To a first approximation the solar system condensed to form the planets at about 4.55 billion years ago. But in detail, we can determine that different planetary bodies formed at slightly different times. For example, different types of meteorites (from different planetary bodies) appear to preserve different formation times. One way to determine this is by using the evolution of  $^{87}\text{Sr}/^{86}\text{Sr}$  (due to the decay of  $^{87}\text{Rb}$ ) in the early solar system.

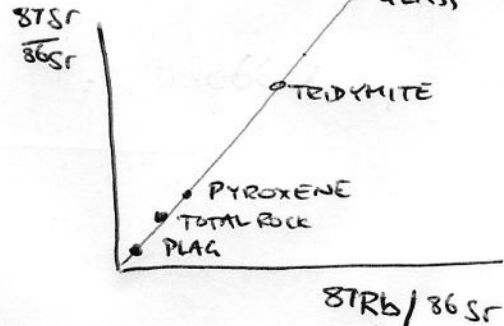
a) (? points) Below are Rb and Sr isotope data for several minerals from the meteorite Juvinas. Calculate the **crystallization age** of the meteorite, and the **initial**  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio at the time of its formation. Show your calculations

Sample	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
Glass	0.0876	0.70473
Tridymite	0.0231	0.70063
Plagioclase	0.00301	0.69914
Pyroxene	0.00714	0.69950
Total rock	0.00407	0.69927

USE THE ISOCHRON DIAGRAM

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_0 + \left( \frac{^{87}\text{Rb}}{^{86}\text{Sr}} \right) (e^{\lambda t} - 1)$$

$$Y = B + X \cdot M$$



$$\text{slope from Glass - Plagioclase} = \frac{0.70473 - 0.69914}{0.0876 - 0.00301} = 0.06608 = e^{\lambda t} - 1$$

$$\Rightarrow e^{\lambda t} = 1.06608 \quad \text{so } t = \frac{1}{\lambda} \ln(1.06608)$$

$$= 4.507 \text{ Gyr}$$

Initial ratio from point - slope:  $y_0 = y_i - Mx_i$ , eg. from plagioclase:

$$\left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_0 = 0.69914 - 0.06608 \times 0.00301$$

$$= 0.69894$$