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89.304 - IGNEOUS & METAMORPHIC PETROLOGY
TRACE ELEMENT MELTING AND CRYSTALLIZATION MODELS

Trace elements are now widely used in petrology to further our understanding of petrogenetic processes. The term trace element cannot be rigidly defined but is usually taken to mean those elements present in rocks in concentrations of less than a few thousand parts per million (ppm), and generally in the 1 - 100 ppm range. Trace elements of particular interest in igneous petrology include Rb, V, Ba, Sr, Zr, Y, Nb, Th, the rare earth elements (La to Lu), Ni, and Cr.

Minerals may incorporate or exclude trace elements with even greater selectivity than they do major elements. These preferences have a significant influence on trace element distributions during igneous processes. Hence, an analysis of trace element distributions can lead to constraints on the nature and composition of the mineral assemblages that crystallized from a magma.

When a mineral is in chemical equilibrium with a liquid elements are partitioned between the two phases according to their chemical activity in each phase. For an element whose concentration is low in both phases application of Henry's Law leads to the relationship

$$K_D = \frac{\text{Concentration in mineral}}{\text{Concentration in liquid}}$$

where K_D is a constant known as the *distribution* or *partition coefficient* for the given crystal-liquid equilibrium. The distribution coefficient varies as a function of changes in the composition of either phase, temperature, and, in some cases, pressure. In practice an average value for a particular partition coefficient is used for a range of compositions.

In order to consider the evolution of a magmatic liquid we need to quantify its equilibrium with more than a single mineral phase. In this case, partitioning is described by the bulk distribution coefficient *D* which is calculated from the weight proportion *w* of each mineral in the assemblage

$$D = \sum_{i=1}^{n} w_i K_{D_i}$$

For example, for a hypothetical garnet peridotite consisting of 60% olivine, 25% orthopyroxene, 10% clinopyroxene, and 5% garnet (see Table 1 for K_D's) the bulk distribution for Ce is

$$D_{ce} = (0.6)(0.001) + (0.25)(0.003) + (0.1)(0.1) + (0.05)(0.02) = 0.012$$

Elements with D<<1 are termed *incompatible* - they will be preferentially concentrated in the liquid phase (excluded from the solid phases) during melting and crystallization. In contrast, those with D>1 are called *compatible* and these will be preferentially retained in the solid phase (or excluded from the liquid phase).

A number of relationships have been developed which predict the distribution of trace elements during various melting and crystallization processes. We shall consider two cases, batch melting and fractional crystallization. Models for other possible cases can be found in PetMin (both the program and the accompanying documentation).

Batch melting. This is the simplest model for partial melting of a complex mineral assemblage. The liquid remains at the site of melting and is in chemical equilibrium with the solid residue until mechanical conditions allow it to escape as a single batch of primary magma. Since the minerals are usually entering the magma in different proportions than they occur in the rock (this is referred to as *nonmodal melting*) we must consider the impact this has on the bulk partition coefficient of the solid.

$$C_L = \frac{C_o}{D + F(1 - P)}$$

where C_L = concentration of element in liquid, C_O = concentration of element in rock, D = bulk partition coefficient, F = fraction of melt formed (i.e., 1% melt = 0.01), and P = bulk partition coefficient for the phases entering the melt.

Fractional crystallization. Consider a closed system in which a body of magma is isolated in a magma chamber and undergoes continuous crystal fractionation. The crystals are effectively isolated from the magma as soon as they form. For this process the appropriate relationship is

$$C_L = C_o F^{(D-1)}$$

where C_L = concentration of the element in the residual melt, C_O = initial concentration of the element in the melt, F = fraction of the melt that remains, and D = bulk partition coefficient for the crystallizing solids.

Use the partition coefficient values in Table 1 for the following problems.

Table 1. Partition coefficients for various minerals

	Partition coefficients		
Mineral	Ce	Yb	Ni
Olivine	0.001	0.002	10
Orthopyroxene	0.003	0.05	4
Clinopyroxene	0.10	0.28	2
Garnet	0.02	4.0	0.4
Plagioclase	0.10	0.03	0.01
Tridymite	0.001	0.001	0.001

1. Let us assume that we have a rock whose composition can be represented by the system forsterite-anorthite-SiO_2. This is the ternary phase diagram you used in the phase diagram exercises. For a rock with composition B

   a. Determine the relative proportions of En, Plag, and Tr in the rock.

   b. Calculate the bulk partition coefficients D for the elements Ce, Yb, and Ni using the mineral proportions determined in (a).

   c. Determine the relative proportions of the phases entering the melt. The first melt will have the composition of the eutectic (point E).

   d. Calculate the bulk partition coefficients P for the elements Ce, Yb, and Ni, using the mineral proportions entering the melt determined in part (c).

e. The rock contains 5 ppm Ce, 2 ppm Yb, and 100 ppm Ni. Calculate the abundances of these elements in the melt after 1% and 5% melting.

f. Determine the amount of melt when Tr disappears from the rock. Determine the abundances of Ce, Yb, and Ni in this melt.

2. Consider the partial melting of a garnet peridotite consisting of 60% olivine, 25% orthopyroxene, 10% clinopyroxene, and 5% garnet. During the early stages of melting the minerals enter the melt in the ratio 10 Ol : 20 Opx : 40 Cpx : 20 Gt. The rock contains 1.6 ppm Ce, 0.4 ppm Yb, and 2400 ppm Ni.

   a. Calculate the amount of Ce, Yb, and Ni in the melt after 1% partial melting.

b. Calculate the amount of Ce, Yb, and Ni in the melt after 10% melting.

c. Compare and contrast the concentrations of these elements in the two melts. What conclusions can you draw from these concentrations.

3. Assume that we have a liquid whose composition can be represented by the system forsterite-anorthite-SiO_2 (as previously). A liquid whose composition is represented by point A contains 20 ppm Ce, 2 ppm Yb, and 200 ppm Ni.

   a. From the phase diagram, determine how much of the liquid would have crystallized before the composition reached the reaction curve.

   b. Calculate the abundance of Ce, Yb, and Ni in this residual liquid. Remember that up to this point only forsterite will have crystallized.

4. We have a basaltic melt that contains 14.8 ppm Ce, 1.6 ppm Yb, and 330 ppm Ni.

   a. Olivine, pryoxene, and plagioclase crystallize from the melt in the ratio 10 Ol : 40 Cpx : 50 plag. After 50% crystallization, calculate the concentrations of Ce, Yb, and Ni in the melt.

   b. Starting with the residual liquid from (a), we now crystallize pyroxene and plagioclase in the ratio 20 Cpx : 80 plag. After 75% crystallization what are the concentrations of Ce, Yb, and Ni in the melt. NOTE: You are starting (b) with 100% liquid but the trace element abundances inherited from part (a).