

## Lecture 9

### Trace Element Abundance Variations in Simple Melt-Solid Systems

- 1) We first focus on simple models that are not realistic but a thorough understanding of simple models provides insight into trace element behavior in more complex systems. Subsequent to defining and understanding controls on abundance variations of trace elements in simple systems, we will consider which assumptions are unrealistic and add complexities to the model.
- 2) **Mass Balance:** Consider a block of rock with the concentration of trace element,  $i$ ,  $C_i^0 = 1$  (superscript zero indicates the initial concentration) and  $D_i^{\text{solid/liquid}} = 0$  (i.e., “ $i$ ” is a perfectly incompatible element) (Figure 28).

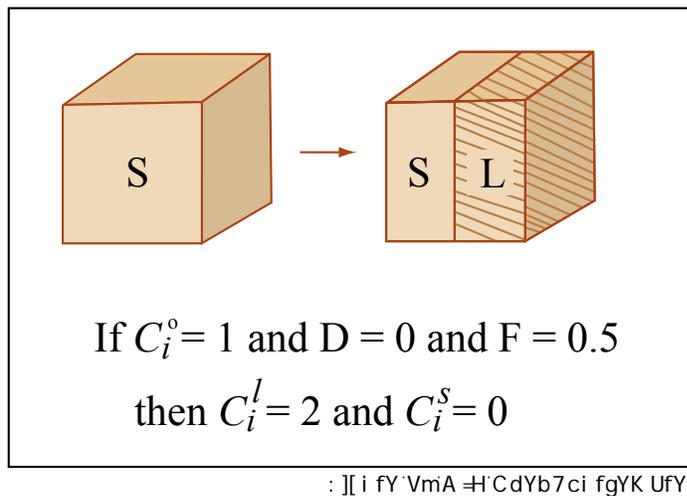


Figure 28. Mass balance for an element “ $i$ ” in a solid melt system, where

S = solid

L = melt

$F = L/S$  (wt. ratio)

$C_i^0$  is the concentration of element “ $i$ ” in initial solid  $C_i^0$  (left box),  $C_i^s$  and  $C_i^l$  are concentrations of “ $i$ ” in the residual solid and derived melt, respectively, in a partially melted or crystallized system (right box).

Now we ask if this solid mass of rock is melted to 50%, what is the concentration of “i” in the melt, i.e.,  $C_i^\ell = ?$  Since we are forcing all of the element “i” out of the solid into the melt, the ratio  $C_i^\ell / C_i^o = 2$ . Similarly, if the solid is melted only 10%,  $C_i^\ell / C_i^o = 10$ .

The important result that is characteristic of simple and complex models for partitioning of trace elements in solid-melt systems is that the abundance of a highly incompatible element in the melt is an inverse function of the melt fraction (F in wt.%).

The mass balance equation showing that the whole system is a sum of its parts, i.e., initial solid = partial melt + residual solid, is

$$C_i^o = C_i^\ell F + C_i^s (1 - F)$$

where  $C_i^o$  concentration of i in initial solid

$C_i^\ell$  = concentration of i in liquid

$C_i^s$  = concentration of i in the residual solid

F = L/S, i.e. the wt. function of liquid (melt)

Now we use the definition of partition coefficient, i.e.,  $D_i^{s/\ell} = C_i^s / C_i^\ell$  and the mass balance equation to derive

$$C_i^\ell / C_i^o = \frac{1}{F + D_i^{s/\ell} - D_i^{s/\ell} F} = \frac{1}{F + D_i^{s/\ell} (1 - F)}$$

This equation has some very important limits:

(a) As  $F \rightarrow 0$

$$C_i^\ell / C_i^o = 1/D$$

Consequently, if  $D < 1$ , there is a maximum limit to the concentration of “i” in the melt and if  $D > 1$ , there is a limit to the depletion of “i” in the melt (Figure 29a).

(b) As  $D \rightarrow 0$

$$C_i^\ell / C_i^o = 1/F$$

Consequently, for an incompatible element the enrichment of “i” in the melt is inverse to the melt fraction (Figure 29a).

(c) Also for two elements A and B the change in abundance ratio from the initial solid to that of the melt is given by:

$$\frac{(C_A/C_B)^\ell}{(C_A/C_B)^o} = \frac{F + D_B^{s/\ell}(1-F)}{F + D_A^{s/\ell}(1-F)} \quad \text{so that for } F = 0 \text{ the maximum change in}$$

$$\frac{(C_A/C_B)^\ell}{(C_A/C_B)^o} \text{ is given by } \frac{D_B^{s/\ell}}{D_A^{s/\ell}}, \text{ e.g., if } D_B = 0.5 \text{ and } D_A = 0.1, \text{ then } \frac{(C_A/C_B)^\ell}{(C_A/C_B)^o}$$

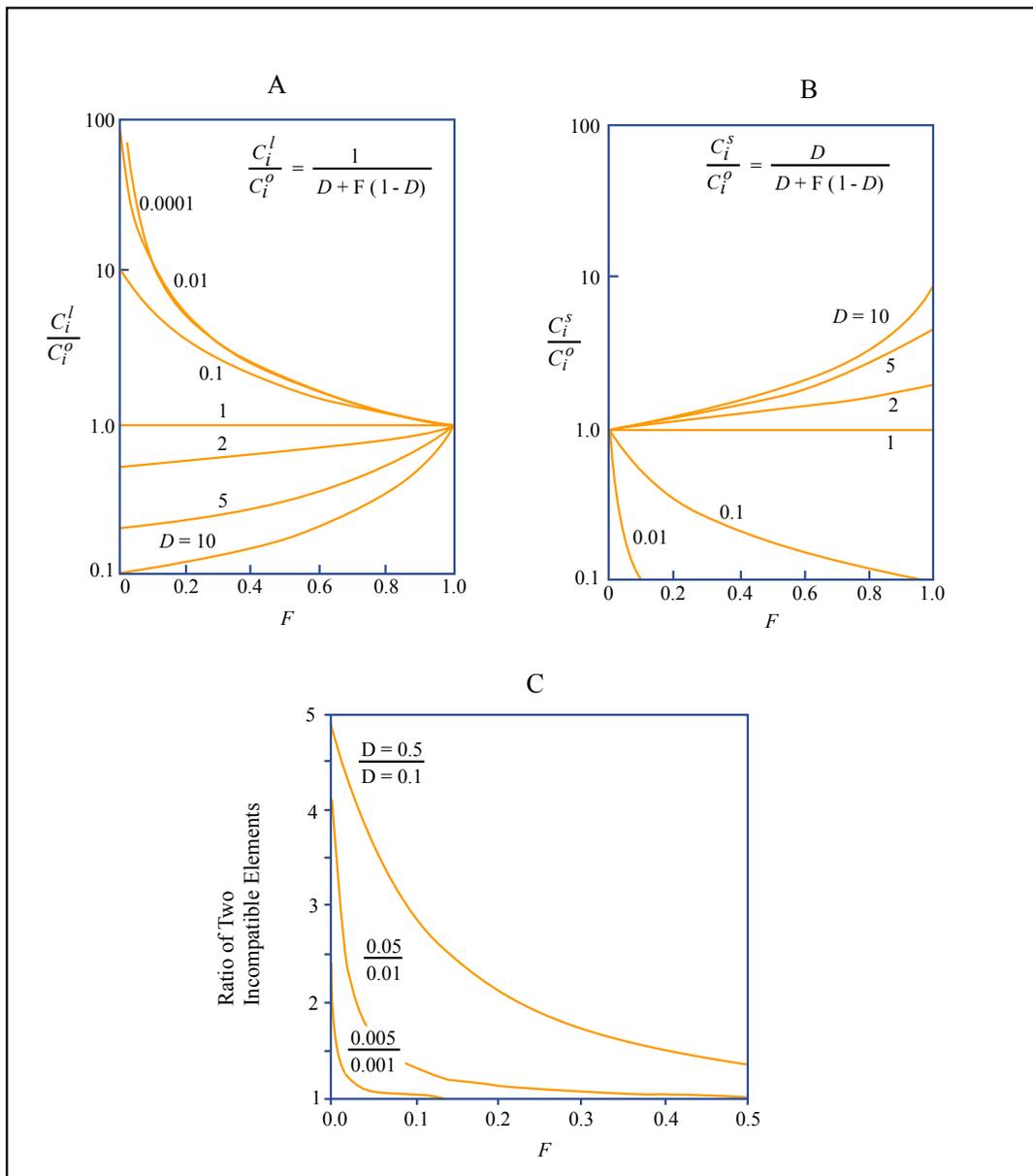
= 5; this is the maximum change that is possible (Figure 29c).

(d) Note that by using the mass balance equation, we are assuming that the solid and melt are homogeneous and in equilibrium.

(e) Also, the mass balance equation and the equations derived from it are valid for partial melting and partial crystallization, i.e., the equations are equally valid for partial melting of an initial solid to various degrees or partial crystallization of a melt.

(f) Also, for the solid the pertinent equation is  $C_i^s / C_i^o = \frac{D_i^{s/\ell}}{F + D_i^{s/\ell}(1-F)}$

(Figure 29b).



: ] i fY `VmA =H C dYb7ci fgYK UFV"

Figure 29. a) Plot of the equation  $C_i^L/C_i^O = \frac{1}{D_i^{S/\ell} + F(1-D_i^{S/\ell})}$  showing how  $C_i^L/C_i^O$  varies as a function of  $F$  (wt. fraction of melt) and  $D_i^{S/\ell}$ .

Note that as  $C_i^L/C_i^O = 1$  as  $F \rightarrow 1$ , and that there is a maximum limit for  $C_i^L/C_i^O = 1/D_i^{S/\ell}$  as  $F \rightarrow 0$ .

b) Plot of the equation  $C_i^S/C_i^O = \frac{D_i^{S/\ell}}{D_i^S + F(1-D_i^{S/\ell})}$  showing how  $C_i^S/C_i^O$  varies as function of  $F$  and  $D_i^{S/\ell}$ .

c) Ratio of two incompatible elements in partial melts relative to initial ratio in unmelted solid, i.e.  $(C_A/C_B)^\ell / (C_A/C_B)^O$

as a function of  $F$ . Note that the maximum increase is given by the ratio of partition coefficients but that as  $F$  increases the ratio change is lower if the  $D$ 's are  $\ll 1$ .

### 3) Adding Realistic Complexities:

So far we have considered the solid to be a single phase with a specific  $D$ . In reality rocks consist of multiple solid phases with different  $D$ 's. Hence we must define a bulk solid/melt partition coefficient, i.e., for a solid composed of phases  $\alpha$ ,  $\beta$ , and  $\gamma$  the

$$D_i^{\text{bulk solid/melt}} = D_i^{\alpha/\ell} x_\alpha + D_i^{\beta/\ell} x_\beta + D_i^{\gamma/\ell} x_\gamma$$

where  $x$ 's indicate wt. fractions of each phase in the solid.

With this definition, the equation  $C_i^\ell / C_i^o = \frac{1}{F + D^{\text{bulk solid/melt}}(1-F)}$  is valid.

However, if one wants a realistic description of how  $C_i^\ell / C_i^o$  varies with  $F$  there are two additional complexities:

- (a) The mineral/melt partition coefficient (i.e.,  $D^{\alpha/\ell}, D^{\beta/\ell}, D^{\gamma/\ell}$  must be known as a function of melt and phase composition and variations in pressure and temperature.
- (b)  $D^{\text{bulk solid/melt}}$  will vary as mineral proportions in the solid change.

As an example consider melting of a solid initially composed of weight fractions  $x_0^\alpha, x_0^\beta, x_0^\gamma$  with  $\sum x_0^i = 1$ . After partial melting the weight fractions of each phase contributing to the melt is  $Y^\alpha + Y^\beta + Y^\gamma = \Delta Y$ , the total amount of melt.

Therefore the initial bulk solid/melt partition coefficient

$$D_0^{\text{bulk solid/melt}} = D^{\alpha/\ell} x_0^\alpha + D^{\beta/\ell} x_0^\beta + D^{\gamma/\ell} x_0^\gamma$$

becomes during the melting process

$$D^{\text{bulk solid/melt}} = \frac{D^{\alpha/\ell}(x_o^\alpha - Y^\alpha) + D^{\beta/\ell}(x_o^\beta - Y^\beta) + D^{\gamma/\ell}(x_o^\gamma - Y^\gamma)}{1 - \Delta Y}$$

It is instructive to consider the effects on  $D^{\text{bulk solid/melt}}$  by substituting numerical values for  $x_o^i$  and  $D_i^{\text{mineral/melt}}$ .

Case 1: For example, assume that  $x_i^\alpha = x_o^\beta = 0.5$ ,  $\Delta Y = 0.06$  with  $Y^\alpha = Y^\beta = 0.03$ ,  $D^{\alpha/\ell} = 0.01$  and  $D^{\beta/\ell} = 0.1$ . Substitution of these values into the equation for variation of  $D^{\text{bulk solid/melt}}$  during the melting process leads to

$$D^{\text{bulk solid/melt}} = (0.5-0.03)(0.01) + (0.5-0.03)(0.1) = 0.0517.$$

Case 2: Now consider the effects on  $D^{\text{bulk solid/melt}}$  if only phase  $\beta$ , melts, i.e.,  $Y^\beta = 0.06$ . Then  $D^{\text{bulk solid/melt}} = (0.5)(0.01) + (0.5-0.06) 0.1 = 0.049$ .

These calculations illustrate an important point: The major element composition in Case 1 is determined by a 50:50 mixture of phases  $\alpha$  and  $\beta$  whereas in case 2 the major element composition of the melt is that of phase  $\beta$ . Thus the major element composition of the two melts are quite different, but since the  $D^{\text{bulk solid/melt}}$  for the generic trace element (i) is quite similar, the melts will have very similar contents of this trace element. Hence, this example illustrates how major and trace element compositions can be decoupled.

Case 3: Another point is the sensitivity of trace element abundance to small amounts of a residual phase that preferentially incorporates the trace element; i.e. the trace element is highly compatible in a residual phase. For example, consider a solid with  $x_o^\alpha = x_o^\beta = 0.495$ ,  $x_o^\gamma = 0.01$  and

$$D^{\alpha/\ell} = 0.01, D^{\beta/\ell} = 0.1, D^{\gamma/\ell} = 10, Y^\beta = 0.06 \text{ (only phase } \beta \text{ melts)}.$$

In this case:

$$D^{\text{bulk solid/melt}} = 0.495 (0.01) + (0.495 - 0.06)(0.1) + 0.01 \quad (10)$$

= 0.148, i.e., the  $D^{\text{bulk solid/melt}}$  value for Case 3 is ~3 times that for Cases 1 and 2!

#### 4) Several important Generalizations Can Be Made

- (a) Unless phases melt in their modal proportion, an unlikely situation, the  $D^{\text{bulk solid/melt}}$  will vary with extent of melting even if the  $D^{\text{mineral/melt}}$  values remain constant, which is also an unlikely situation.
- (b) If a phase that is initially present completely melts, it has no effect on  $D^{\text{bulk solid/melt}}$ , and it has no effect on the trace element content of the melt.
- (c) As long as the fraction of a phase entering the melt relative to the initial fraction of the phase in the unmelted solid is small, the trace element content of the melt is independent of the phases that melt. Since the major element content of the melt is sensitive to the phases contributing to the melt, a decoupling of trace element and major element abundance is likely.
- (d) The trace element content of the melt can be controlled by small amounts of a phase with a large  $D^{\text{mineral/melt}}$ . An example for melting of upper mantle is garnet controlling abundances of heavy rare-earth elements (Figure 18). For melting of crustal rocks, likely examples are accessory phases such as zircon and apatite. In island arc settings rutile is an accessory phase which controls Ti, Nb and Ta (e.g., Schmidt et al., 2004).
- (e) Shaw (1970) showed that this variation in bulk solid/melt partition coefficient

during the melting process can be expressed as  $D_1^{s/\ell} = \frac{D_1^o - PF}{1 - F}$  where  $D_1^{s/\ell}$  is

the bulk solid/melt partition coefficient as partial melting progresses and  $D_i^o$  is the bulk solid/melt at the beginning of partial melting and  $P = D^{\alpha/\ell} p^\alpha + D^{\beta/\ell} p^\beta$  etc. where  $p^j$  is the proportion of phase  $j$  in the melt, and  $\sum_j P_j = 1$  (or  $\frac{Y_j}{\Delta Y}$  in our earlier notation).

Shaw further showed that if a solid melts in non-modal proportions the

equation for modal melting  $C_i^\ell / C_i^o = \frac{1}{F + F(1 - D_i)}$  becomes for non-modal

$$\text{melting } C_i^\ell / C_i^o = \frac{1}{D_i^o + F(1 - P)}.$$

Correspondingly for the residual solid the equation for modal melting

$$C_i^s / C_i^o = \frac{D_i^{s/\ell}}{D_i^{s/\ell} + F(1 - D_i^{s/\ell})} \text{ becomes for non-modal melting:}$$

$$C_i^s / C_i^o = \frac{D_i^o - PF}{1 - F} \left( \frac{1}{D_i^o + F(1 - P)} \right).$$

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