Lecture 10

Fractional Crystallization

1) Model

In Lecture 9 we considered solid-melt equilibrium using a mass balance equation and assumed that both the solid and melt are homogeneous in composition. The resulting equations and trace element behavior as a function of melt composition and partition coefficient are equally valid for partial melting and partial crystallization. However, minerals precipitated from melts, e.g., plagioclase phenocrysts, are commonly heterogeneous in composition; i.e. they are zoned. This zoning can result from the relatively slow diffusion rates characteristic of solid-state diffusion.

A simple model that explains compositional zoning of a mineral is fractional crystallization. Consider precipitation of crystals as a melt cools and in particular the situation where crystal growth is rapid relative to the rate at which solid-state diffusion can maintain the entire crystal in equilibrium with the residual melt which is assumed to be homogeneous. If this system is quenched to low temperature we expect to see a compositionally zoned crystal.

Fractional crystallization is a process that leads to compositionally zoned minerals forming from a homogeneous residual melt. This process is commonly described as

- surface equilibrium or

- Rayleigh equilibrium or

- Logarithmic equilibrium

The appropriate equations are derived from the basic assumption that

$C_{crystal\ surface} = D\ C_l$

D = solid/melt partition coefficient

where

C_l, C_s, C_o are concentration of trace element in melt, solid and initial system

X_l, X_s, X_o are masses of trace element in melt, solid and initial system

M_l, M_s, M_o are total masses of melt, solid, initial system

So $C_l = X_l/M_l = (X_o-X_s)/(M_o-M_s)$

Then the basic assumption for Fractional Crystallization is

dX_s/dM_s = the concentration on crystal surface = $DC_l = D[(X_o-X_s)/(M_o-M_s)]$

So $dX_s/(X_o-X_s) = D\ dM_s/(M_o-M_s)$

integrate to get

$$ln\ (X_o-X_s) = D\ ln\ (M_s-M_o) + C$$

evaluate C since at t = 0

   $X_s = 0$

   $M_s = 0$

So $C = ln\ X_o - D\ ln\ M_o$

Leads to

$$ln\ [(X_o-X_s)/X_o] = D\ ln\ [(M_o-M_s)/M_o]$$

and

$$X_s = X_o[1-(1-M_s/M_o)^D]$$

Now we want an expression

For $C_{\text{surface crystal}} = d\, X_s / d\, M_s$

From above, by differentiation, we find

$$C_{\text{crystal surface}} = \frac{DX_o}{M_o}(1 - M_s/M_o)^{D-1} \quad \text{where} \quad C_o = \frac{X_o}{M_o} \text{ and } F = (1 - M_s/M_o)$$

or

$$C_{\text{crystal surface}}/C_o = D\, F^{D-1}$$

Since

$$C_{\text{crystal surface}} = D\, C_l$$

$$C_l/C_o = F^{D-1}$$

Note as D->0

$$C_l/C_o -> 1/F$$

As F->0

$$C_l/C_o -> \text{infinity}$$

For the average concentration in the zoned crystal $(\overline{C}_s)$, one can show that

$$\overline{C}_s/C_o = \frac{1 - (F)^D}{1 - F}$$

2) Effects of Fractional Crystallization On Residual Melts

Comparison of surface equilibrium and total equilibrium equations

a) For incompatible elements, e.g. D=0, in order to increase C_l/C_o by a factor of 10 requires 90% crystallization (Figure 30a) or 10% melting (i.e. F = 0.1) (Figure 29a).

b) For compatible elements, e.g. D=10, during fractional crystallization, C_l/C_o decreases quickly as F decreases from 1 to 0.8 whereas for partial melting compatible element concentration varies by less than a factor of 2 from 0 to 20% melting (F = 0 to 0.2) (cf. Figures 30a and 29a).

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c) An especially important result for the ratios of two incompatible elements in the melt during fractional crystallization is:

$$C_\ell^A / C_o^A = F^{D_A - 1}$$
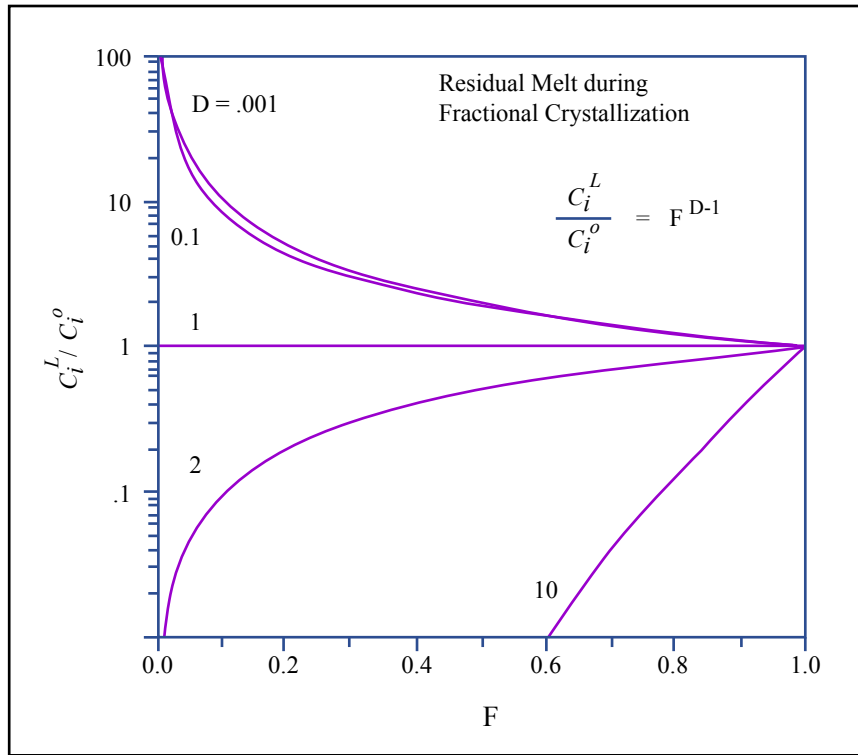
$$C_\ell^B / C_o^B = F^{D_B - 1}$$

So that

$$\frac{(C^A / C^B)_\ell}{(C^A / C^B)_o} = F^{D_A - D_B}$$

What is important is the difference between $D_A - D_B$ and for incompatible elements $D_A - D_B$ will always be small, so that the ratio change in the residual melt during fractional crystallization cannot be large (see Figure 30b). Contrast this result with the large change in ratio at low F for the equilibrium model (Figure 29c). Note, however, that the abundance ratio for two compatible elements (e.g., D=4 and 8) in a residual melt is very sensitive to the extent of fractionation (Figure 30b).

3) **Complications Arising From Kinetic Effects, i.e. Diffusion Coefficients**

Albarède and Bottinga (1992) considered the importance of diffusion in both the residual melt and derived solids during crystallization. They considered 5 cases (see Figure 31). They are:

A-1 Equilibrium between solid and a melt that forms an infinite reservoir; hence C_i^ℓ is constant. We have already considered this case (see Figure 29 and relevant text).

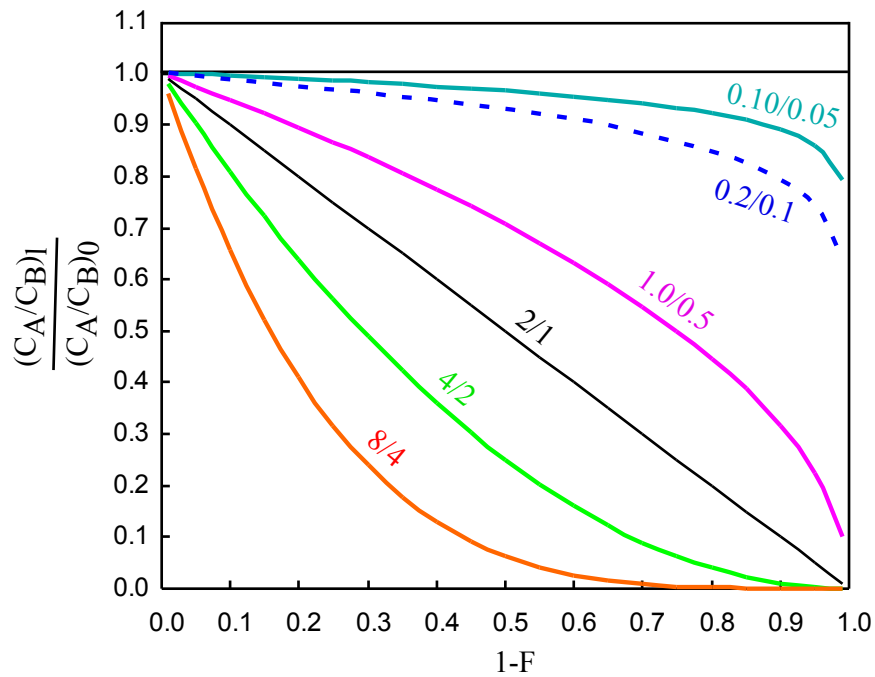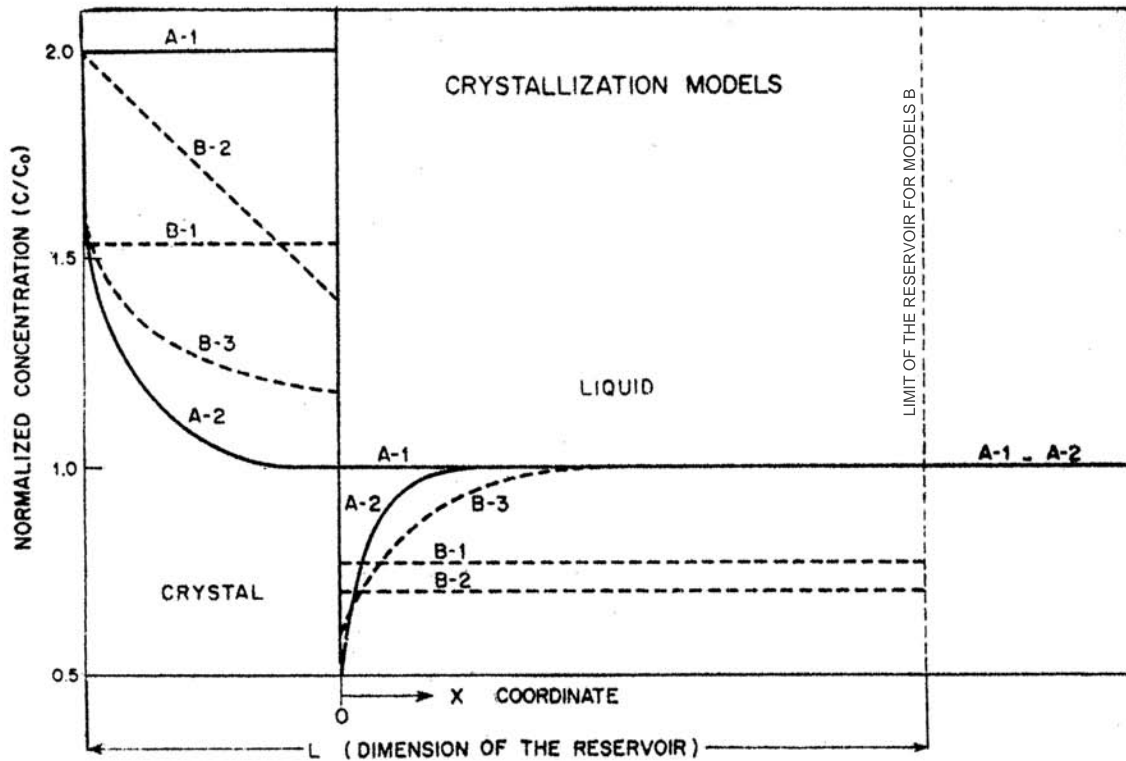:][i fY˙Vm˙A =H˙C dYb˙7ci fgY˙K UfY"

Figure 30. a) Plot of the equation for fractional crystallization: $C_i^L / C_i^O = F^{D-1}$ showing
how C_i^L / C_i^O varies as a function of D and F (wt% fraction of melt which is unity
when the process begins).

(b) Abundance ratio of two elements A and B showing that for the residual melt
during fractional crystallization;

$\dfrac{(C^A/C^B)_\ell}{(C^A/C^B)_o} = F^{D_A - D_B}$, i.e., the ratio change, is sensitive to the absolute values of D_A and D_B rather

than D_A/D_B (cf. with Figure 29c).

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A-2 Crystal growth from an infinite reservoir of melt but diffusion in melt and solids are slow relative to crystal growth rate; hence both the residual melt and derived solid are zoned. We have not yet considered this case. Note that as the process procedes to steady-state the concentration in the crystal approaches the concentration in the infinite reservoir so that the partition coefficient approaches unity as the crystal grows. Also for a compatible element the melt is depleted adjacent to the solid (Figure 31).

Figure 31.   Normalized concentration, i.e., C^{ℓ}/C^{O} and C^{S}/C^{O} for different assumptions regarding solid and liquid state diffusion coefficients relative to crystal growth rate. Trajectories are for a partition coefficient of 2. The 5 cases (A-1, A-2 B-1, B-2 and B-3) are discussed in the text and are considered in detail in Albarede and Bottinga (1972) (this is Figure 1 from their paper).

B-1 This case is similar to case A-1 except the initial melt is a finite reservoir; hence the concentration in the residual melt differs from the concentration in the initial melt. As with Case A1 both melt and solid are homogeneous; this case is considered in Figure 29. The only difference is that for case A-1, $C_i^o = C_i^{melt}$ and in Case B-2, $C_i^o = FC_i^l + (1-F)C_i^s$.

B-2 Again the melt is a finite reservoir but diffusion in the solid is too slow to maintain equilibrium with the changing concentration in the residual melt. This is the model of fractional crystallization whereby only the crystal surface is able to equilibrate with the residual melt. We have already considered this case (see Figure 30 and relevant text).
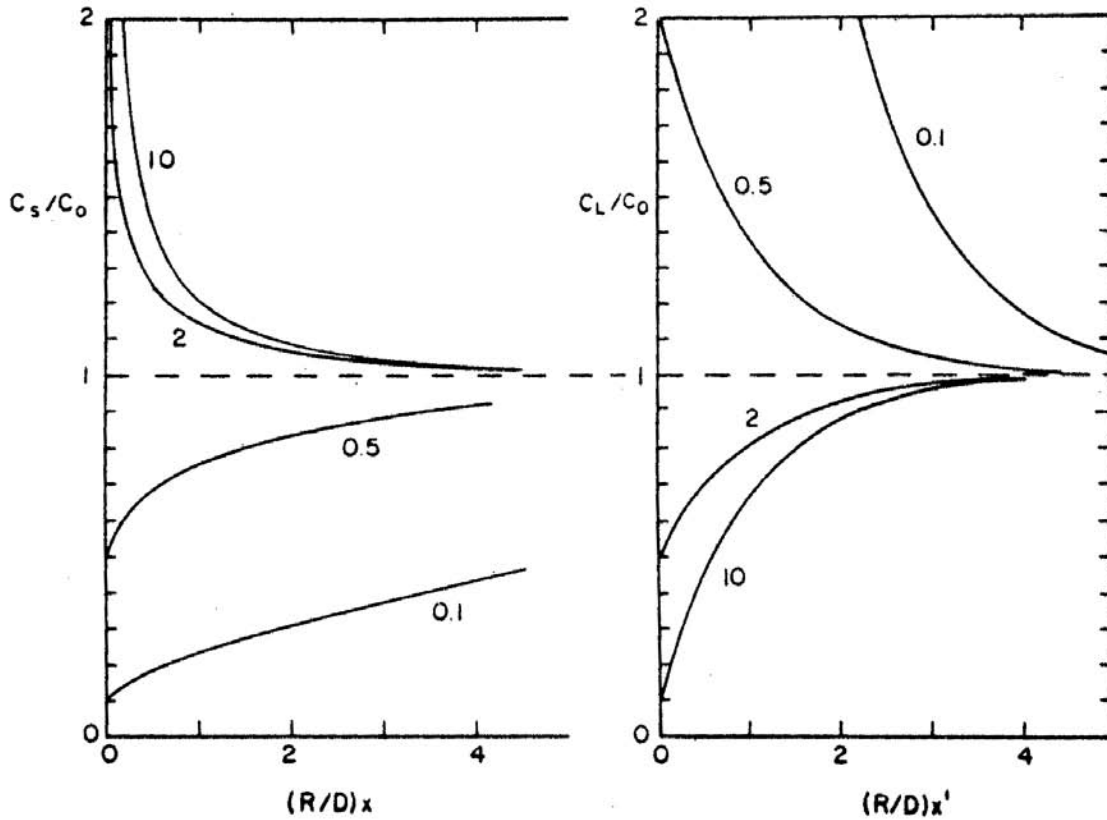
B-3 Again the melt is a finite reservoir but in this case diffusion in the melt is too slow to maintain a homogenous melt, hence both the melt and solid are zoned (Figure 31).

With information on crystal growth rates and diffusion coefficients in silicate melts it is possible to evaluate if compositional zonation of melts adjacent to newly formed crystals is likely.

We evaluate case A-2. Albarède and Bottinga (1992) showed that for this case

$C_i^l / C_i^o = 1 + \dfrac{1-k}{k} \exp(-\dfrac{R}{D}x)$ where k is the solid/melt partition coefficient because D is used for diffusion coefficient and R is the crystal growth rate in the x direction.

Consider Figure 32 which shows C^ℓ / C^o and C^S / C^o for various values of partition coefficient (0.1, 0.5, 2, and 10) as a function of (R/D)x. Using R = 10^{-7} cm/sec and D = 10^{-11} cm^2/sec, both typical of feldspar, we see that if x is on the order of 10^{-4} cm (i.e. one micron) zoning of trace elements is expected in both solids and melts; i.e. (R/D)x = 1 for $(10^{-7}\,cm/sec)(10^{11}\,sec/cm^2)(10^{-4}\,cm)$.

Figure 32. C_S/C_O and C_l/C_O as a function of (R/D)x for various values of partition coefficient (k) (0.1 to 10) for case A-2 discussed in the text.

Left: Concentration profiles in a solid (C_s), which grows in one dimension with a constant rate R form a non-convecting liquid of initial concentration C_o, D is the diffusion coefficient in the liquid, and x is the distance in the solid in the direction of growth. The numbers labeling the curves are the different values of the equilibrium partition coefficient, $k = C_s/C_L$.

Right: Concentration profiles in the liquid C_L after steady state has been reached. x^1 is the distance in the liquid from the crystal-liquid interface in the direction of growth. Figure from Margaritz and Hofmann, 1978.

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