Lecture 37

Igneous geochemistry

Reading White Chapter 7

Today:

Using trace elements to study

1. crystallization

2. melting

Crystallization

Let's look at how we use differences in element distribution to understand **crystallization** process.

These would apply to the formation of crystals from a molten magma in a crustal magma body, or within a lava flow as it progresses across the landscape.

Crystallization

There are two "simple" end-member models for crystallization:

1. **Equilibrium crystallization:**

crystals form from a cooling melt in a closed system (i.e., no eruptions of magma out of the system or injections of fresh melt into the system). *Chemical equilibrium is maintained until the melt has completely crystallized.*

2. **Fractional or Rayleigh crystallization:**

crystals are in *instantaneous* chemical equilibrium with the melt as they form, but are immediately removed from contact with the melt (e.g., by settling to the bottom or floating to the top of a magma chamber). *Overall, the system as a whole is not at chemical equilibrium.*

Equilibrium aka "Batch" Crystallization

Consider a crystallizing melt in a closed reservoir, where the entire volume of melt and crystals are at chemical equilibrium:

Some Definitions

F= fraction of liquid (melt) remaining

C_l = concentration of some element in the liquid

$C°_l$ = initial concentration of that element in the liquid

$C°_s$ = concentration of some element in the solid

K_d *or* D = distribution coefficient for that element

Equilibrium aka "Batch" Crystallization

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for closed system equilibrium crystallization, **simple mass balance** between the phases yields:

$F\ C_l + (1-F)C_s = C°_l$ …. And since $K_d = C_s / C_l$
$F\ C_l + (1-F)K_d C_l = C°_l$
the ratio of $C_l/C°_l$ at any point during crystallization is:

$\boxed{C_l / C°_l = [F(1-K_d) + K_d]^{-1}}$ *also:* $\boxed{C_s / C°_l = K_d\,[F(1-K_d) + K_d]^{-1}}$

Fractional Crystallization

Now consider a system in which some crystals settle out of the melt or float to the top, so that they do not remain in chemical equilibrium with the melt.

The most extreme case would be the continual removal of infinitesimally small increments of crystals as they form.

This is termed *fractional or Rayleigh crystallization*.

We can derive the equation for this process as follows.

If *W* is the initial weight or mass of the melt, and crystallization removes a melt increment of mass *dW*, then the mass of an element put into crystals in each increment is *$C_s dW$*.

In order to maintain *mass balance*, this amount going into crystals has to equal the amount of the element removed from the liquid…

Fractional (a.k.a. Rayleigh) crystallization

amount removed from the liquid $\quad C_s\,dW = d(C_l W)$

or $\qquad\qquad\qquad\qquad\qquad C_s\,dW = C_l\,dW + W\,dC_l.$ $\quad$ (chain rule)

Rearrangement $\qquad\qquad\qquad\qquad \dfrac{dW}{W} = \dfrac{dC_l}{(C_s - C_l)}$

and so $\qquad\qquad \displaystyle\int_{W^\circ}^{W} \dfrac{dW}{W} = \int_{C_l^\circ}^{C_l} \dfrac{dC_l}{(C_s - C_l)}. \quad = \int dC_l/(DC_l - C_l)$

$$\ln\dfrac{W}{W^\circ} = \dfrac{1}{(\bar{k}-1)} \ln\dfrac{C_l}{C_l^\circ}. \qquad (\,\bar{k} = D\,)$$

Since $W/W^\circ = F =$ the proportion of residual liquid,

$$\boxed{F^{(\bar{k}-1)} = \dfrac{C_l}{C_l^\circ}. \qquad Or \quad F^{(D-1)} = C_l/C_l^\circ}$$

For the changes in concentration, C_s, in the solid phase:

$$kF^{(\bar{k}-1)} = \dfrac{C_s}{C_l^\circ}. \qquad Or \quad DF^{(D-1)} = C_s/C_l^\circ$$

Batch and Fractional Crystallization compared

Elements with different D values will be "fractionated" from each other in predictable ways as crystallization proceeds.
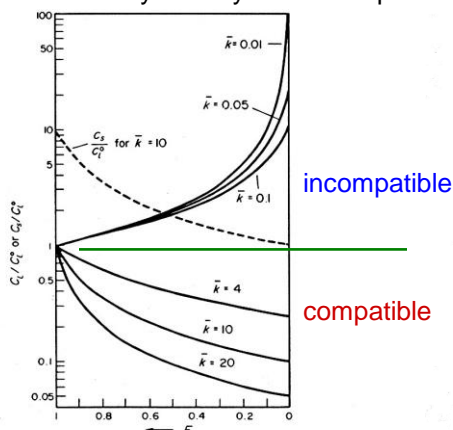

FIG. 8.18. Relative changes in the concentration of an element in a magma as a function of the proportion of remaining liquid (F) during conditions of equilibrium crystallization (as defined by equation 8.21) for various values of the bulk partition coefficient, $\bar{k}$, and for the coexisting solid when $\bar{k} = 10$ (equation (8.22)). *Henderson, Inorganic Chemistry", 1984*
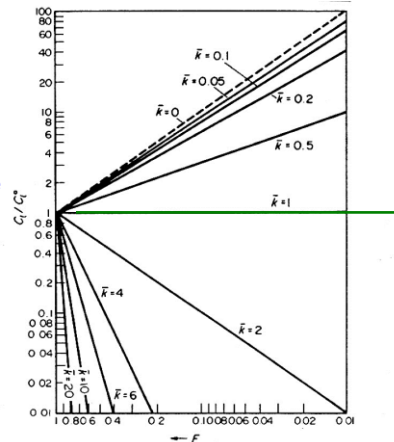
FIG. 8.19. Relative concentration changes in a magma as a function of proportion of remaining liquid (F) during fractional crystallization (equation 8.28), plotted on log-log scales for different values of the bulk partition coefficient ($\bar{k}$). *Henderson, Inorganic Chemistry", 1984*

$$C_l / C_l^\circ = [F(1-K_d) + K_d]^{-1} \qquad\qquad C_l / C_l^\circ = F^{(K_d-1)}$$

Crystallization example 1

Let's look at a couple of classic examples. The **Skaergaard** magmatic system is one in which crystallization was a major control on trace element composition. It is a large mafic intrusion that crystallized slowly.

These diagrams are smoothed plots of compositional variations of 2+ and 3+ ions as a function of the percent of solid formed (= 100 x [1 – F]). The percentage of solid (crystals) was determined from thin sections.

Notice that Ba (D <<1) increases more rapidly toward the end, whereas Ni (D >1) decreases pretty rapidly to low levels.

Does this look more like batch or fractional crystallization to you?

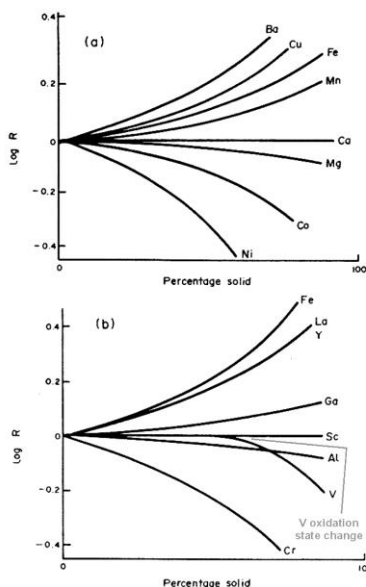FIG. 5.3. Relative changes in element concentration in the magma during crystal fractionation of the Skaergaard intrusion. *R* is the ratio of concentrations of the element in the magma at successive amounts of solidification to the element's initial concentration: (a) divalent cations; (b) trivalent cations. (After Williams, 1959)
Henderson, Inorganic Chemistry", 1984

Crystallization example 2

The lower part of the **Muskox** intrusion consists of a thick sequence of dunite layers (nearly all olivine) with rhythmic variations in Fo and Ni caused by olivine settling out as the magma crystallized. Fractional crystallization applies here.

Assuming D_{Ni} = 15 in the dunite, we can use the change in Ni content from bottom to top of a given horizon to calculate F for that horizon.

For the gray area $C_s \approx$ 1700 ppm at the top; $C^o_s \approx$ 3100 ppm. From the bottom of slide 5:

$C_s/C^o_l = DF^{(D-1)} = C_s/(C^o_s/D)$ as $D = C^o_s/C^o_l$

$C_s/C^o_s = F^{(15-1)} = F^{14}$ → $1700/3100 = F^{14}$

$\ln(1700/3100) = 14 \ln F$

$F = 0.958$

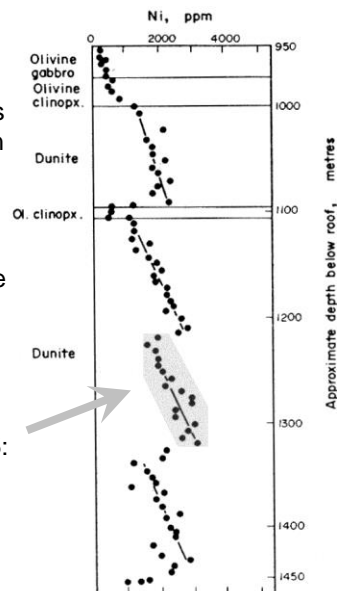**So about 4% of the liquid solidified in this episode.**

FIG. 8.21. Variation in the Ni content of rocks of part of the Muskox intrusion, Northwest Territories, Canada. (After Irvine and Smith, 1967)
Henderson, Inorganic Chemistry", 1984

Melting

Similar equations can be derived for the generation of *melt* from a mixture of minerals; i.e., a source rock.

As with crystallization, there are two "simple" end-member melting scenarios:

1. **Equilibrium or batch melting:** melt forms from crystals in a closed system, and chemical equilibrium is maintained between the phases.

2. **Fractional or Rayleigh melting:** increments of melt form from crystals at instantaneous chemical equilibrium with the melt, but the melt is continuously removed as it is formed (e.g., escapes by porous flow and its own buoyancy). Overall, the system is not at chemical equilibrium for all the original phases and materials involved.

Equilibrium or batch melting
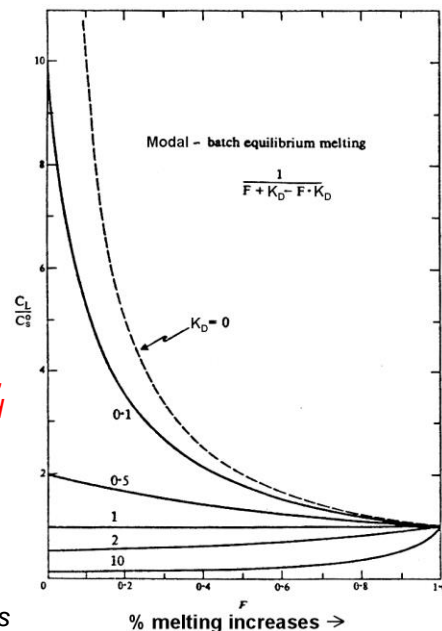
$C_l/C^{\circ}_s = 1/[D_0 + F(1-P)]$

where **F is now the fraction of solid melted**, and D_0 is D at the start of melting, when $F = 0$.

C°_s = initial concentration of a trace element in the source.

C_l = liquid concentration at any point.

Notice that this equation is rather similar to the equilibrium crystallization equation, except that C°_s has now been substituted for C°_l, and we have a new variable, P.

P = the bulk distribution coefficient for the melting assemblage of minerals *weighted by the proportion that each mineral contributes to the melt – not by its proportion in the original solid.*

Modal – batch equilibrium melting

$$\frac{1}{F + K_D - F \cdot K_D}$$

$K_D = 0$

% melting increases →

Equilibrium (aka "Batch") Melting

$P = k_d^a \cdot$(fraction of mineral a in melting assemblage) +

$+ k_d^b \cdot$(frac. min. b in in melting assemblage)

$+ k_d^c \cdot$(frac. min. c in melting assemblage)

$+ \ldots$ *ad infinitum*

vs. $D = k_d^a \cdot$(frac. min. a in unmelted source) $+ k_d^b \cdot$ (frac. min. b in unmelted source) $+ k_d^c \cdot$(frac. min. c in melting source) $+ \ldots$)

Modal melting:
If all the minerals in the source melt in the ***same proportions as those in which they occur in the source,*** then we have modal melting, and **P = D₀.** This is rare.
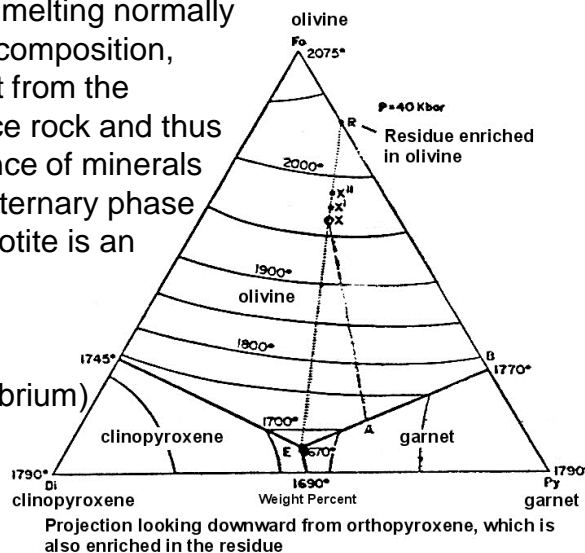
Non-modal melting:
Usually, the minerals melt in ***different proportions*** than those in which they occur in the source, and **P ≠ D₀.** This is called non-modal melting.

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Equilibrium aka "Batch" Melting

Non-modal melting is much more common. For example, melting normally starts at a eutectic melt composition, which is usually different from the composition of the source rock and thus from the modal abundance of minerals in the source rock. The ternary phase diagram for garnet peridotite is an example.

"E" is the eutectic (equilibrium) melt composition.

Projection looking downward from orthopyroxene, which is also enriched in the residue

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Equilibrium aka "Batch" Melting

What does batch melting imply physically?

That melt and solids stay intermingled as a closed system until melting ceases.

This figures depicts melting in a diapir of mantle rising adiabatically toward the surface.

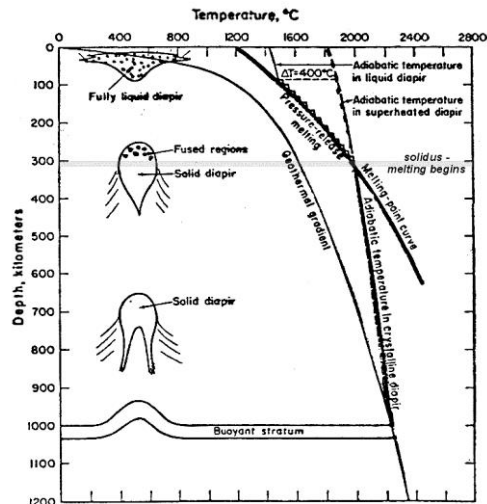The black dots are melt pockets that rise with the diapir

FIGURE 4-11 Magma generation model of Ramberg (1972, p. 58, Figure 10) based on perturbation in buoyant stratum, diapiric rise of a solid mass, and pressure-release melting. (With permission of the Elsevier Publishing Company.)

Fractional or Rayleigh melting

If buoyant melts segregate from the solid as soon as they form, this other "simple" end-member melting model pertains.

It's analogous to fractional crystallization.

Each fraction of melt is only momentarily in equilibrium with the solid, and then escapes.

Melt fractions may or may not combine (pool) later, say in a magma chamber.

Fractional or Rayleigh melting

The equations describing this process use the same variables as for batch melting, F, C_l, C_s, D, and P.

We have three possible scenarios:

Modal fractional melting	Non-modal fractional melting
For the liquid:	
$C_l/C°_s = (1/D_0)\cdot[1 – F]^{(1/D_o)-1}$	$C_l/C°_s = (1/D_0)\cdot[1- PF/D_0]^{(1/P)-1}$
For the solid:	
$C_s/C°_s = [1 – F]^{(1/D_o)-1}$	$C_s/C°_s = (1/[1- F])\cdot[1- PF/D_0]^{(1/P)-1}$
Accumulated fractional melting: If all the fractional melts accumulate and mix before eruption, the aggregrate liquid is described by:	
$C_l/C°_s = (1/F)\cdot[1– (1– F)^{1/D_o}]$	$C_l/C°_s = (1/F)\cdot[1 – (1 – PF/D_0)^{1/P}]$

Fractional Melting

for $D = K_d >1$ exponent is <1 so C_l increases as F increases.
for $D = K_d <1$ exponent is >1 so C_l decreases as F increases.
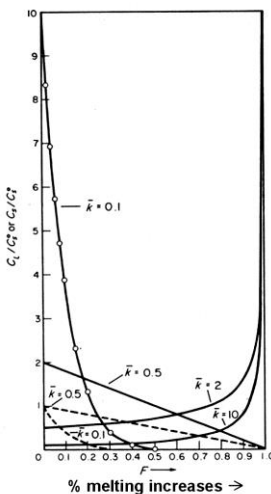
Fractional Melting- Liquid Evolution (instantaneous melt compositions)

non-modal

$$\frac{C_\ell}{C°_S} = \frac{1}{K_D}\left(1 - \frac{PF}{K_D}\right)^{\left(\frac{1}{P}-1\right)}$$

Solid evolution (not shown in figure)

$$\frac{C_s}{C°_S} = \left(1 - \frac{PF}{K_D}\right)^{\left(\frac{1}{P}-1\right)}$$

modal eqns for liquid and solid:

$$\frac{C_\ell}{C°_S} = \frac{1}{K_D}(1-F)^{\left(\frac{1}{K_D}-1\right)} \qquad \frac{C_s}{C°_S} = (1-F)^{\left(\frac{1}{K_D}-1\right)}$$

Note that **highly incompatible elements** are severely **depleted** rather quickly to values less than those in the original source (= 1). Also, note that ratios of moderately incompatible to highly incompatible elements can be **reversed** as F increases. This doesn't happen in batch melting.
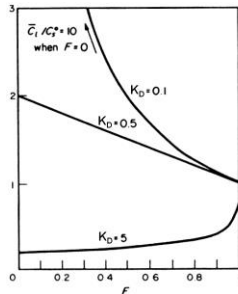
FIG. 8.23. Variation in relative concentration of an element in the liquid as a function of degree of fractional fusion (F), according to equation (8.37), for different bulk partition coefficients $\bar{k}$. The dashed lines are the variations shown by the coexisting solid when $\bar{k} = 0.5$ and 0.1 (equation (8.38)).

Accumulated Fractional Melts and Batch Melts Compared

Pooling all the fractional melts together dampens the extreme compositions seen in the previous slide, and broadly resembles the batch melting case.

But AFM can cause large incompatible trace element fractionation because in essence, each melt increment formed is like a very small degree batch melt.
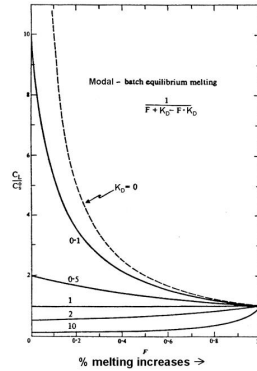
Accumulated Fractional Melts - Liquid Evolution

$\bar{C}_i/C_s^o = 10$ when $F = 0$

$K_D = 0.1$
$K_D = 0.5$
$K_D = 5$

non-modal

$$\frac{\bar{C}_l}{C_s^o} = \frac{1}{F}\left(1 - \frac{P \cdot F}{K_D}\right)^{1/P}$$

modal

$$\frac{\bar{C}_l}{C_s^o} = \frac{1}{F}\left(1 - F\right)^{1/k_D}$$

FIG. 8.24. Variation in relative concentration of an element in the aggregate liquid as a function of melt fraction (F) according to equation 8.39 for three values of the bulk partition coefficient, K_D.

Modal – batch equilibrium melting

$$\frac{1}{F + K_D - F \cdot K_D}$$

$K_D = 0$
0·1
0·5
1
2
10

% melting increases →

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Melting and Crystallization Scenarios Compared

Here's a summary of the relative effects of different melting and crystallization models for two incompatible elements (D = 0.01 and D = 0.1).
For melting, the concentrations of each element are assumed to all be the 1 ppm in the unmelted source. Crystallization trajectories are plotted starting from a 10% partial equilibrium melt
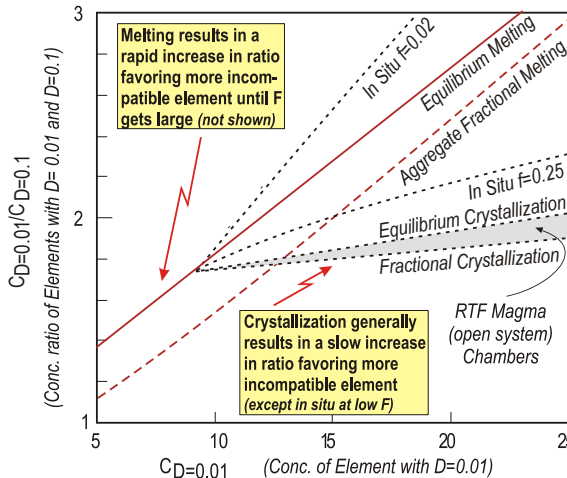
$C_{D=0.01}/C_{D=0.1}$
(Conc. ratio of Elements with D= 0.01 and D=0.1)

Melting results in a rapid increase in ratio favoring more incompatible element until F gets large *(not shown)*

In Situ F=0.02
Equilibrium Melting
Aggregate Fractional Melting
In Situ f=0.25
Equilibrium Crystallization
Fractional Crystallization

Crystallization generally results in a slow increase in ratio favoring more incompatible element *(except in situ at low F)*

RTF Magma (open system) Chambers

$C_{D=0.01}$ *(Conc. of Element with D=0.01)*

Figure 7.34. Plot of the ratio of two incompatible elements (one with D=0.01, the other with D=0.1) vs. the concentration of the more incompatible element. Plot shows calculated effects of equilibrium partial melting and aggregate partial melting assuming concentra-tions of 1 in the source for both elements. Other lines show the ef-fect of crystallization on the composition of a liquid produced by 10% equilibrium melting. Fractional crystallization, equilibrium crystallization, and open system crystallization (RTF magma chambers) produce less variation of the ratio than does partial melting. *In Situ* crystallization can mimic the effect of partial melting if the valueof f, the fraction of liquid returned to the magma, is sufficiently small.
modified from White, Geochemistry

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More Complicated Melting Scenarios

Igneous systems can be very complex, and relatively simple melting models don't always apply, at least not from beginning to end of melting.

Furthermore, it is often difficult to estimate precisely the abundances of trace elements in the unmelted source.

Also, there's usually some uncertainty in the range of P and T conditions during melting within a rising volume of mantle.

More Complicated Melting Scenarios

For these reasons, more complex models have been developed.

For melting, the next level of sophistication is a class of models of "**dynamic melting.**"   Dynamic melting can be "*incremental*" or "*continuous*" (analogous to fractional and accumulated fractional melting).

For dynamic melting, the source region is modeled as a long column of solid infused with melts that form and migrate upward within it, changing composition as they migrate.

Dynamic or Continuous Melting

This scenario is somewhere in between batch melting (where all solid and liquid are in equilibrium) and fractional melting (where melt is removed as soon as it forms).

Melt porosity

There is a finite incremental porosity that always stays with the solids and becomes modified as it migrates through the solid.

Added melt is extracted away to keep the *porosity constant*.

The equations are too complex to reproduce here (they are essentially integrated versions of the fractional or batch melting equations) but the figures on the next slide show some early applications to basalts from Skye (Scotland), Troodos (Greece) and the Reykjanes Peninsula (Iceland).

Melt models applied

Modeling Igneous Petrogenesis

Melting and crystallization usually operate in sequence to make and transform a magma.

Normally one will work backward from an observed composition to correct our crystallization effects, yielding a parent melt composition.

Then one will model melting in a forward sense using an assumed or estimated source composition.

We will look at this I more detail next time.