**Lecture 14**

**Ion Exchange Chromatography**

**(pertinent reference is Navon and Stolper, Geochemical Consequences of Melt Percolation: The Upper Mantle as a Chromatographic Column, Jour. Geol., 95, 285-307, 1987)**

In the simple case basaltic melt ascends through an overlying peridotite via porous flow and equilibrium is attained; for trace elements this process is analogous to batch melting. However, prior to attaining equilibrium there is a transient approach to equilibrium. Today we are interested in understanding this transient case.

Consider a porous solid that is in equilibrium with respect to major elements but not for trace elements. Note this is an <u>unrealistic</u> special case but it leads to a first order understanding of the effects of a chromatographic process on abundances of trace elements. We can subsequently consider the mineralogical changes within the peridotite matrix caused by major element disequilibrium.

We begin by evaluating what happens as an exotic melt ascends through a porous solid matrix with trace element concentration $C_s^o$ in the matrix and $C_m$ in the fluid occupying the pores that is $C_s^0/C_m = DC$. We assume that the concentration of the trace element $C_m^o$ in the exotic introduced fluid is not equal to $C_m$ (see Figure 49). Consequently this melt interacts with the matrix and converts the solid matrix to be in equilibrium with the introduced melt.

That is $C_s = DC_m^o$.

Therefore as the melt passes through the column and equilibrates the trace element composition of the solid and melt change.

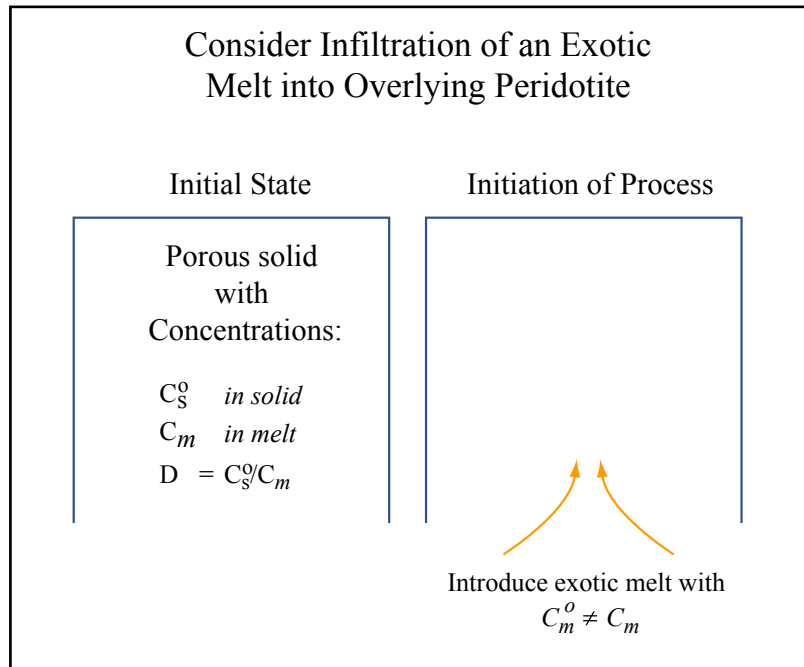Solid from $C_s^o$ to $C_s$.

Melt from $C_m$ to $C_m^o$



Consider Infiltration of an Exotic
Melt into Overlying Peridotite

Initial State                     Initiation of Process

Porous solid
with
Concentrations:

$C_s^o$   *in solid*
$C_m$   *in melt*
D   $= C_s^o/C_m$

Introduce exotic melt with
$C_m^o \neq C_m$

Figure 49. Infiltration of an exotic melt into an overlying porous peridotite; the infiltrating melt and initial solid matrix are not in equilibrium.

Initially as melt with $C_m^o$ enters at the bottom of the column, melt with $C_m$ leaves at the top, but at some critical time ($t_c$) the main mass of introduced melt reaches the top of the column. This melt will be made up of all elements that did not interact with the matrix, i.e. major elements (assumed) and $D = 0$ (i.e., perfectly incompatible) elements.

What about trace elements with $D > 0$? Concentration fronts, the change from $C_m$ to $C_m^o$ will travel through the solid at rates that are proportional to D. The equations describing this process are in Navon and Stolper (1987) who describe the process as follows (see Figure 50):
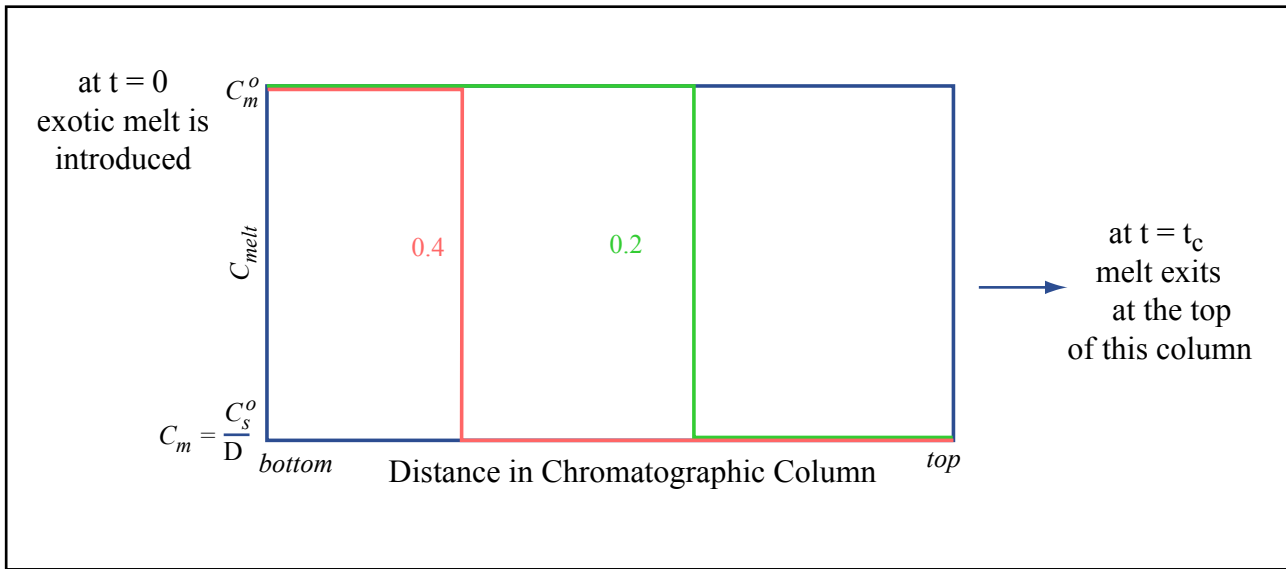
At t = 0
exotic melt is
introduced

$C_m^o$

$C_{melt}$

0.4    0.2

$C_m = \dfrac{C_s^o}{D}$

bottom    Distance in Chromatographic Column    top

at t = $t_c$
melt exits
at the top
of this column

Figure 50. Development of concentration fronts in a chromatographic column. At the beginning of the process, i.e. at time (t) = o, melt with trace element concentration, $C_m^o$ is introduced at the bottom of the column (left end). At t = $t_{critical}$ all elements that do not interact with the solid matrix, i.e. perfectly incompatible elements with D=0, exit the column (right end). However trace elements with D>0 react with the matrix and develop concentration fronts as shown for elements with D = 0.4 (red line) and D = 0.2 (green line). Ahead of the front, which is moving from left to right, the matrix has its initial concentration, $C_s^o$ and the fluid has a concentration given by $C_m = C_s^o/D$ but behind the front the introduced fluid has its concentration of $C_m^o$ and it has converted the matrix to have a concentration $C_s = D\,C_m^o$. Figure is adapted from Figure 1a of Navon and Stolper (1987).

Also Navon and Stolper state:

"The essence of the kind of process that we envision is: Melt is continuously introduced at the base of a column of rock and moves upward through it by permeable flow. The melt is initially out of equilibrium with the rock matrix and the two interact chemically. A snapshot of the column at any time would show for each element a concentration front, above which the melt is in equilibrium with the initial matrix of the column and below which the melt is unchanged from when it was introduced into the base of the column. Above the concentration front, the matrix retains the initial column composition; below it, the matrix has changed to be in equilibrium with the melt flowing into the column. The width of the front depends on the effectiveness of dispersive processes, such as diffusion, in the column."

"If we looked at a movie of the column, we would see the concentration front for each element sweeping upwards, with the fronts of the more incompatible elements moving faster than those of the more compatible ones. If we sat on the top of the column and sampled the liquids that emerged, we would first collect melt identical to that of an infinitesimal degree of partial melting of the initial matrix material. As the concentration front of each element reached the top of the column (the fronts would arrive in order of increasing compatibility), we would observe the melts changing from the concentration of that element in the incipient melt of the matrix to that of the melt flowing into the column's base. Eventually, the concentration fronts of even the most compatible elements will have reached our position, and thereafter, the melts that emerge will be identical to those injected into the base of the column."

Figure 51 shows the concentrations of elements in melts exiting the column exiting a chromatographic column for elements with various D at various times, $t = \infty$, $t = t_c$ and $t = 2_c$. At $t=\infty$ the concentration profile (red line) is that of the introduced melt; its concentration reaches a maximum of $C_m/C_s^o = 10$ for $D < 0.1$ because this melt is assumed to be a 10% batch melt of the initial matrix. At $t = t_c$ the porous melt initially in the column (blue line) ranges from $C_m/C_s^o = 1000$ for $D = 0.001$ and 1 for $D = 1$; i.e. the 1/D limit it. However, at $t = t_c$ (green line) there is an abrupt change in abundance ratio of elements with D values slightly greater or lesser than 0.03. This process is analogous to the ion exchange columns used by analytical geochemists to separate Sm from Nd, Rb from Sr, and Pb from U and Th.
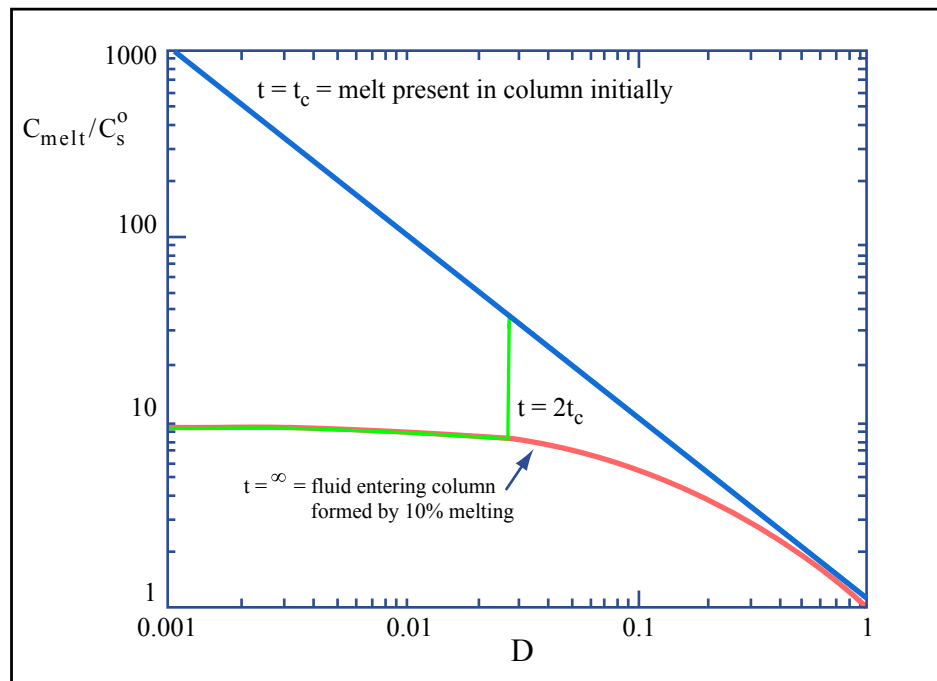


Figure by MIT OpenCourseWare.

Figure 51. Enrichment of melt relative to initial solid, i.e. $C_{melt}/C_s^o$, versus D showing the concentration fronts of incompatible elements with various D at $t = \infty$, $t = t_c$ and $t = 2t_c$. At $t = \infty$ the concentration profiles (red line) is that of the introduced melt. This melt is assumed to be a 10% melt of the initial matrix ($C_s^o$) so its $C_m/C_s^o$ reaches a maximum of 10 when $D < F$.
At $t = t_c$ the porous melt in the initial column (blue line) has concentration given by the 1/D limit.
At $t = 2t_c$ the melt (green line) shows an abrupt concentration front with elements with $D > 0.3$ having the initial porous melt contents whereas elements with $D < 0.3$ have contents equal to the introduced melt. Figure is adapted from Figure 1b of Navon and Stolper (1987).

Hence a distinctive characteristic of melts that reflect a chromatographic process are large differences in ratios of incompatible elements with very similar solid/melt partition coefficients. However, we have never found a temporal sequence of lavas showing abrupt changes in abundance ratios of trace elements with similar D. Very likely the explanation is that magmas easily mix; in fact, mixing is inherent in melting models such as accumulated fractional and continuous melts as well as in dynamic melting (Figure 40).

However, there are strong indicators of the chromatographic process in the trace element contents of peridotites; apparently many are the solid matrix that reacted with an exotic melt. It is very likely that evidence for the chromatographic process is retained in solids because diffusion is slow in solids and mixing of solids is difficult. The Horoman peridotite in Japan is an excellent example (Fig. 53).

Figure 52 illustrates the process; the paper and Fig. 53 from Takazawa et al. (1992) is an example.



Ion Exchange Reaction
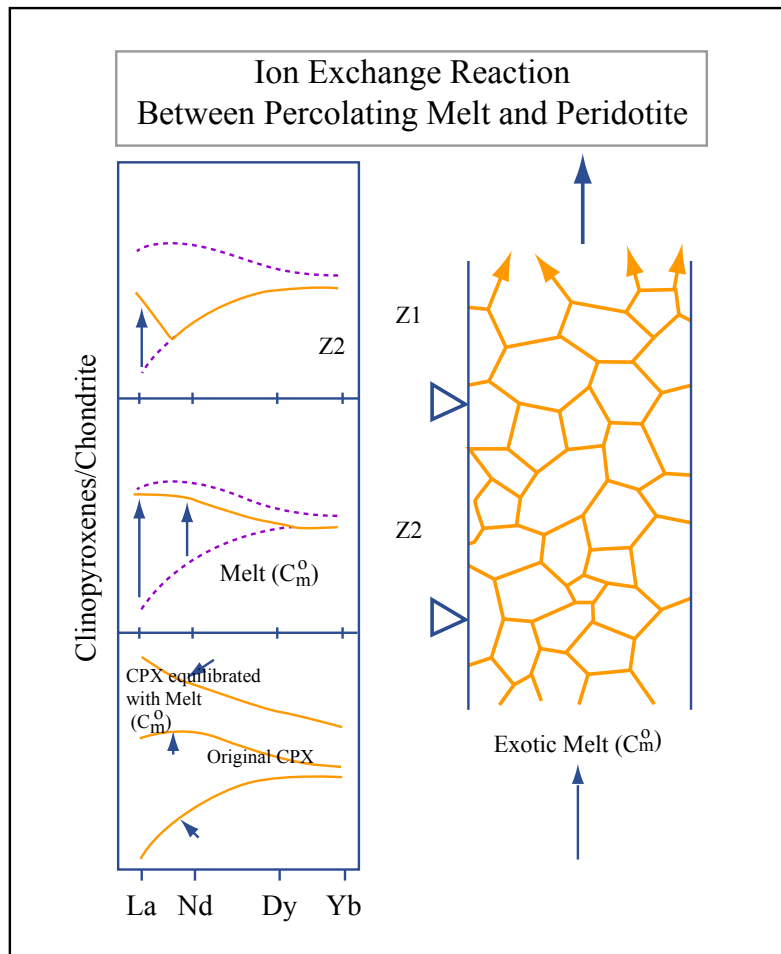Between Percolating Melt and Peridotite

Figure by MIT OpenCourseWare.

Figure 52. Right: A peridotite matrix in the upper mantle is infiltrated by an exotic melt whose rare-earth element concentrations (La, Nd, Dy, Yb) are not in equilibrium with the matrix.

Left: Approach of matrix to equilibrium with the exotic melt for time $<t_{critical}$ with solid state diffusion explicitly included in the calculation (see Takazawa et al., 2002).

Lower panel shows the REE pattern (chondrite-normalized) for the original clinopyroxene (cpx) in the matrix peridotite, the REE pattern for the introduced melt and cpx in equilibrium with this melt.

Middle panel shows the cpx at position Z2 (right panel) in the peridotite column. Here the cpx is nearly fully equilibrated with the introduced melt as indicated by the vertical arrows showing that La and Nd concentrations in the matrix (solid line in middle panel) have nearly reached the La and Nd contents of cpx in equilibrium with the introduced melt (upper dashed line).

Upper panel shows the cpx at position Z1 (right panel) in the peridotite column.

Here the concentration fronts of Nd, Dy and Yb have not yet reached this location in the column; only La concentrations have been increased from the level in the original cpx. The distinctive geochemical feature imparted by the chromatographic process is the abrupt inflection at Nd showing a marked increase in La/Nd ratio.

Such inflections are common in peridotites (see Fig. 53, Johnson et al., 1990; Takazawa et al., 1992).

12.479 Trace-Element Geochemistry

Spring 2013