Rayleigh Fractional Crystallization

This treatment is modified from:

Albarède, F. (2003) Geochemistry: An Introduction, Cambridge Press, 262 pp.

Definitions:

M_l = mass of liquid
M_s = mass of solid
m_l = mass of element *i* in liquid
m_s = mass of element *i* in solid

Mass balance tells you that if a small amount of solid forms, then:

$$dM_l + dM_s = 0$$
$$dm_l + dm_s = 0$$

Instantaneous **equilibrium between liquid and solid** is embodied in the equation:

$$\frac{dm_s}{dM_s} = C_s = DC_l = D\frac{m_l}{M_l}$$

where C_s and C_l are concentrations of element *i* in the solid and the liquid phase, respectively.

Substitution of the mass balance equations into the equilibrium expression gives:

$$\frac{dm_l}{dM_l} = D\frac{m_l}{M_l} \qquad \text{or} \qquad \frac{dm_l}{m_l} = D\frac{dM_l}{M_l}$$

Since $C_l = \frac{m_l}{M_l}$, then $\ln C_l = \ln m_l - \ln M_l$, and differentiation gives $\frac{dC_l}{C_l} = \frac{dm_l}{m_l} - \frac{dM_l}{M_l}$

or, rearranging this expression: $\frac{dm_l}{m_l} = \frac{dC_l}{C_l} + \frac{dM_l}{M_l}$

Substitute back into $\frac{dm_l}{m_l} = D\frac{dM_l}{M_l}$ the new definition for $\frac{dm_l}{m_l}$, which gives

$$\frac{dC_l}{C_l} = (D-1)\frac{dM_l}{M_l}$$

The melt fraction, *F*, is defined as $F = \frac{M_l}{M_o}$, where M_o is the initial mass of the system.

Differentiating this expression gives $dF = \frac{dM_l}{M_o}$ and dividing both sides by *F* gives

$$\frac{dF}{F} = \frac{1}{F}\frac{dM_l}{M_o} = \frac{M_o}{M_l}\frac{dM_l}{M_o} = \frac{dM_l}{M_l}$$

Substitution of this result into $\frac{dC_l}{C_l} = (D-1)\frac{dM_l}{M_l}$ gives

$$\frac{dC_l}{C_l} = (D-1)\frac{dF}{F}$$

Now, we integrate both sides from the initial state to the final state:

$$\int_{C_o}^{C_l} \frac{dC_l}{C_l} = (D-1)\int_1^F \frac{dF}{F}$$

which gives

$$\ln\frac{C_l}{C_o} = (D-1)\ln F$$

Take the exponential of both sides and we have the Rayleigh equation:

$$\boxed{\frac{C_l}{C_o} = F^{D-1}}$$