

GEOCHEMICAL MODELING OF IGNEOUS FRACTIONAL CRYSTALLIZATION.
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Chemical variation among igneous rocks that are plausibly related is often modeled by assuming simple fractional crystallization (Rayleigh fractionation) [e.g., 1,2,3]. This methodology is typically at variance with the results of laboratory experiments, which indicate that trace element partition coefficients (D) are not constant (as the Rayleigh equation assumes), but are complex functions of temperature (T), pressure (P) and composition (X) [4,5,6]. Still, the results of many geochemical models yield results that produce reasonable fits to the analytical data and that at least appear to be reasonable in terms of the fraction of the original system that is crystallized.

Method. Here I examine three different formulations of the fractional crystallization equation: (i) simple Rayleigh fractionation with constant partition coefficients; (ii) fractional crystallization, with a linear relation between temperature and fraction crystallized (F), but allowing D to change with temperature; (iii) fractional crystallization, using a freezing point depression (FDP) model for T-X relationships, and again allowing D to vary with temperature. The third model in particular is thought to be fairly realistic. The models in which D is allowed to vary assume that crystallization begins at 1200°C, with D= 0.3 and afterwards changing as

$$\ln D = -\Delta H/RT, \quad (1)$$

where R is the gas constant and ΔH is the change in enthalpy of the trace element between the solid and liquid state. The D was chosen to be large enough that complications might arise from choosing the wrong partition coefficient, and ΔH is taken to be -50 kcal/mole -- such that D changes by a factor of two every 50°C. In model (i) there may always be a finite amount of liquid remaining, regardless of temperature. In model (ii), where the fraction crystallized is modeled as varying linearly with T, the solidus is taken to be 1050°C. In other words,

$$T = T_0 - kF. \quad (2)$$

In model (iii) crystallization occurs according the freezing point depression law

$$\ln(1-F) = -\Delta H/R * (1/T_0 - 1/T) \quad (3)$$

where T_0 is 1200°C and ΔH is -50 kcal/mole. Thus, as in model (i), complete solidification is not defined.

In both models (ii) and (iii), numerical integration of the fractional crystallization equation is necessary. In general the equation has the form

$$C/C_0 = \int_0^F (1-D(F')) * (1-F')^{(D(F')-2)} dF' \quad (4)$$

normalized such that the value of the integral evaluated at F=0 is unity.

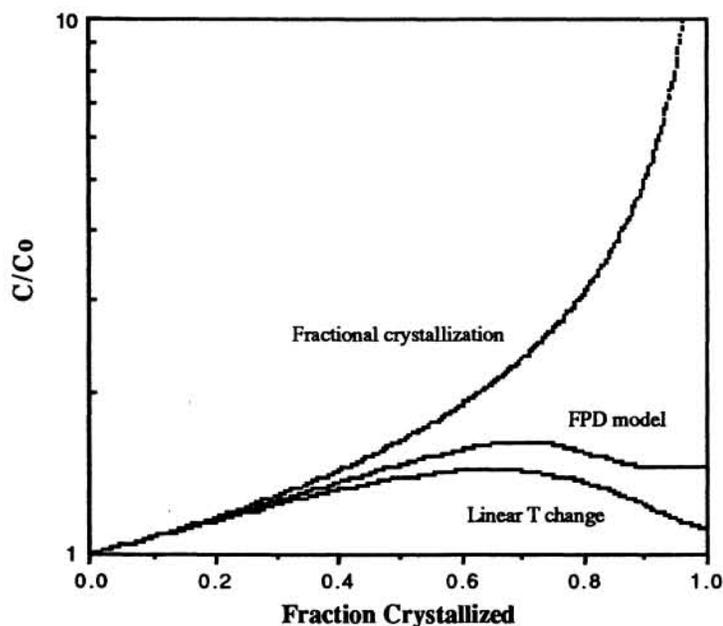
Results. A summary of changes in composition (C/C_0) as a function of degree of solidification is shown in Figure 1. Somewhat surprisingly, very little difference between the three models is observed until ~40% solidification. By this point, D values in models (ii) and (iii) have increased to 0.62 and 0.50, respectively. Thus, for substantial amounts of fractionation, the three models are virtually indistinguishable. In both models (ii) and (iii) the curves of C/C_0 show maxima between 0.6 and 0.7 fraction crystallized. In model (iii) concentration of the tracer remains essentially constant from 0.85-1.0 fraction crystallized. This is because, in the late stages of the FDP model, D values increase as $1/(1-F)$ while increases in C due to concentration in the

liquid are also changing as $\sim 1/(1-F)$ -- maintaining a quasi-steady state.

These results indicate that, for many situations, modeling of analytical data from natural samples is not particularly sensitive to the exact D value that is chosen. Conversely, extraction of a unique D value from modeling of natural rocks seems difficult. At best, probably only a mean D value ($\langle D \rangle$) can be extracted from fits to data from natural samples.

These results also raise the question of why concentrations of incompatible elements are expected to monotonically increase during fractional crystallization. If partition coefficients do increase with decreasing temperature and/or changes in composition, then there is no *a priori* reason for elements to remain incompatible. Suggestions have been made that such large increases in D values have been observed in natural rocks [7], but these have not been confirmed [8]. The turnovers for models (ii) and (iii) shown in Figure 1 are because partition coefficients have become greater than unity. Very little lag [2] is observed between the time that $D=1$ and the time that the curves for models (ii) and (iii) turn over.

Conclusions. The results here indicate that, while traditional fractional crystallization models may often serve to reproduce natural processes, this success may in some cases be fortuitous. Clearly, in the models presented here, little serves to differentiate between the various models at $F < 0.4$. Additionally, if D values appropriate to natural processes do increase with decreasing temperature, it is surprising that high concentrations of incompatible elements, such as the REE, are ever achieved by fractional crystallization processes.



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