

AN EQUATION FOR TRACE ELEMENT DISTRIBUTION DURING MAGMATIC CRYSTALLIZATION¹

L. PAUL GREENLAND, *U. S. Geological Survey, Washington, D.C. 20242*

ABSTRACT

Unlike previous models for the equilibrium distribution of elements between liquid and solid during crystallization, the general equation developed here can take account of variations in mineral proportions and in distribution coefficients. Several examples demonstrate the use of the equation and illustrate the magnitude of the errors involved in the assumptions of constant distribution coefficients and constant mineral proportions. The equation is expected to be of particular use to the petrologist wishing to relate individual samples of a suite to the degree of crystallization of the magma.

INTRODUCTION

Several discussions of the distribution of elements between crystals and liquid during crystallization differentiation of a magma have appeared in the literature, (Neumann, 1948; Holland and Kulp, 1949; Neumann *et al.*, 1954). These have been reviewed and discussed by McIntire (1963). More recently, Anderson and Greenland (1970) have shown that the variation of phosphorus in some rock suites may be directly related to the fraction of liquid remaining at any point, and Gast (1968) has used partition coefficients in a consideration of partial melting processes.

Previous models for the distribution of trace elements during crystallization are limited in their usefulness by two assumptions required in the mathematical derivation: (1) the various minerals occur in constant proportions throughout crystallization, (2) the distribution coefficient of an element between liquid and crystals is a constant. Neither of these assumptions can be regarded as geologically realistic. The purpose of the present paper is to derive a general equation giving the composition of liquid or solid as a function of the fraction of liquid crystallized (i.e., degree of crystallization) which does not require these assumptions.

The model described here is the "homogeneous crystallization" case of McIntire (1963); that is, as the liquid crystallizes the solids are effectively removed from the liquid and no reaction with subsequent liquids occurs. For this case, only Henry's law and the equations for conservation of mass need be considered. Thermodynamics and kinetics are excluded, since this is not a theoretical attempt to predict element distributions; it is a general analysis of mass balance as required to deduce crystallization histories from the chemistry of rocks.

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THEORETICAL

The symbols used in the following derivation are defined in table 1. We start with the mass balance equation.

$$dX_s + dX_L = 0 \quad (1)$$

which, with the definitions of table 1, may be written

$$dX_s + C_L M_o dF + M_L dC_L = 0 \quad (2)$$

Consider a small increment ΔM_L of crystallization: the concentration of an element in the liquid is

$$\frac{X_L - \Delta X_L}{M_L - \Delta M_L}$$

and its concentration in the new solid is $\Delta X_s / \Delta M_s$. We have $\Delta X_s = -\Delta X_L$ and $\Delta M_s = -\Delta M_L$ and, if the solid consists of several phases, $\Delta X_s = \sum \Delta x_i$ and $\Delta M_s = \sum \Delta m_i$. The Nernst distribution law, valid for trace elements, states that the concentration of an element in the liquid is proportional to that in the solid;¹ the proportionality constant is the weighted mean of the individual distribution coefficients

$$\frac{\sum \alpha_i \Delta m_i}{\sum \Delta m_i}$$

Thus

$$\frac{\sum \Delta x_i}{\sum \Delta m_i} = \left(\frac{\sum \alpha_i \Delta m_i}{\sum \Delta m_i} \right) \left(\frac{X_L + \sum \Delta x_i}{M_L + \sum \Delta m_i} \right) \quad (3)$$

Taking limits and simplifying, this becomes

$$\sum dx_i = C_L \sum \alpha_i dm_i \quad (4)$$

after substituting equation (4) into (2), simplification yields

$$\frac{1}{M_L} \sum \alpha_i dm_i + \frac{1}{F} dF + \frac{1}{C_L} dC_L = 0 \quad (5)$$

We shall assume that both the mass of any solid phase and the distribution coefficient of any element varies during crystallization as a smooth function of the fraction of liquid remaining: thus

¹ Strictly, one should consider the exchange equilibrium existing between the trace and major element in the two phases. In practical terms ignoring the stoichiometric limitation on lattice sites available to the trace element has no effect. Inclusion of this limitation complicates the formalism without altering any of the results or conclusions obtained here.

TABLE 1. DEFINITIONS OF SYMBOLS

Symbol	Definition
X_S	mass of trace element in solid phase
X_L	mass of trace element in liquid phase
M_S	mass of solid phase
M_L	mass of liquid phase
X_0	original mass of trace element
M_0	original mass of liquid
C_L	X_L/M_L = concentration of element in liquid
C_S	X_S/M_S = concentration of element in solid
C_0	original concentration of element in liquid
F	mass fraction of liquid remaining = M_L/M_0
m_i	mass of crystal i in solid
x_i	mass of element in crystal i
α_i	crystal-liquid distribution coefficient = concentration of element in crystal divided by concentration of element in liquid in equilibrium with it
α_{ij}	distribution coefficient between coexisting minerals, $\alpha_{ij} = \alpha_j/\alpha_i$.
m_{it}	total mass of crystal i after complete crystallization
k_i	proportionality constant; for the models given, $k_i = m_{iT}/M_0$
$f_j(F), g_j(F)$	arbitrary functions of the fraction of liquid remaining.

$$\frac{m_i}{M_0} = k_i \epsilon_i(F) \quad \text{and} \quad \alpha_i = g_i(F)$$

Note that only $(n-1)$ of the m_i are independent:

$$dm_i = -dM_L - \sum_{i=2}^n dm_i = -M_0 dF - M_0 \sum_{i=2}^n k_i d\epsilon_i(F)$$

Substitution of these relationships into equation (5) gives rise to a completely general equation for the concentration of a trace element in the liquid as a function of the extent of crystallization:

$$\int \frac{dC_L}{C_L} = \int \frac{[g_1(F) - 1]}{E} dF + \sum_{i=2}^n \int k_i [g_1(F) - g_i(F)] \frac{d\epsilon_i(F)}{F} \quad (6)$$

If all phases crystallize throughout, the integration limits are from $F=1$ to F and $C_L=C_0$ to C_L ; otherwise integration limits corresponding to the appearance and/or disappearance of phases must be specified.

To solve equation (6) it is necessary to choose a specific model making the $g_i(F)$ and $f_i(F)$ explicit functions. The construction of mathematically amenable crystallization models of an observed rock suite is not difficult. As examples, three arbitrary models are given below. Note that the

$f_i(F)$ must be chosen with the constraints

$$F = F_1 \Rightarrow \frac{m_i}{M_o} = 0; \quad F = F_2 \Rightarrow \frac{m_i}{M_o} = \frac{m_{it}}{M_o}$$

where F_1 and F_2 are the crystallization limits of a given phase; letting $q = (F - F_1)/(F_1 - F_2)$, a constant proportion of the i th mineral between the crystallization limits F_1 and F_2 is given by

$$\frac{m_i}{M_o} = k_i(1 - q) \quad (7a)$$

an increasing proportion is given by

$$\frac{m_i}{M_o} = k_i \frac{1 - q}{1 + q} \quad (7b)$$

and a decreasing proportion is given by

$$\frac{m_i}{M_o} = k_i(1 - q^2) \quad (7c)$$

These three models are plotted in Figure 1. For comparison, modal data from the Great Lake dolerite sheet of Tasmania (McDougall, 1964) have been plotted with these curves by assuming that depth in the drill hole is inversely proportional to the fraction of liquid remaining. It may be noted that the arbitrary models do not fit the Great Lake data very well; more realistic models could be devised at the cost of some additional mathematical complexity. Nevertheless, the arbitrary models are more realistic than the assumption of constant proportions and serve well enough for present purposes.

Equation (6) is written in terms of the liquid composition; however, a similar expression in terms of the composition of the solid phase would be more generally useful. From (3) we have

$$\frac{C_s}{C_o} = \frac{\sum \alpha_i \Delta m_i}{\sum \Delta m_i} \left(\frac{C_L}{C_o} \right) \quad (8)$$

Distribution coefficients between coexisting minerals are better known than crystal-liquid coefficients. Equation (8) may be re-written

$$\frac{C_L}{C_o} = \frac{\frac{1}{\alpha_j} \sum_k \Delta m_k}{\Delta m_j + \sum_i \Delta m_i \alpha_{ij}} \quad (9)$$

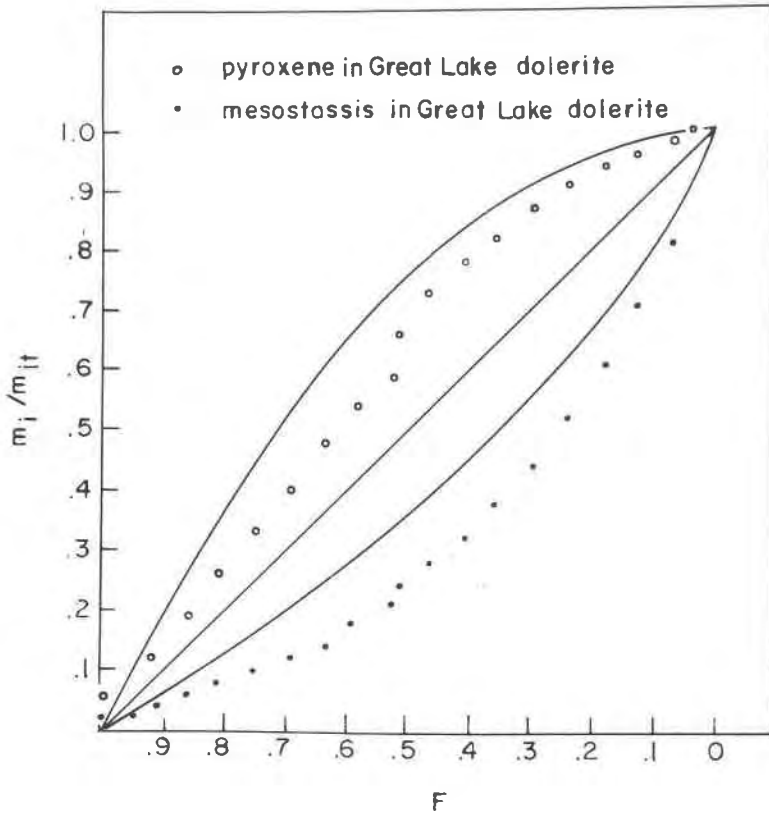


FIG. 1. Cumulative mass fraction of a mineral crystallized as a function of the fraction of liquid remaining where the mineral constitutes a decreasing fraction of the total solids (upper curve, equation 7c), a constant fraction (straight line, equation 7a), and an increasing fraction (lower curve, equation 7b). Modal data of McDougall (1964) from the Great Lake sheet plotted for comparison—see text.

where $\gamma^i \neq 0$ and $i \neq j$. The Δm terms may be regarded as the modal proportions of the minerals in the hand specimen; application of equation (9) to equation (6) is then straightforward. For computational purposes, however, the Δm must be written explicitly for increments of crystallization. As an example, consider the crystallization of two phases in the increment $F_1 \rightarrow F_2$: we have

$$\Delta m_2 = k_2 M_o [\epsilon_2(F_2) - \epsilon_2(F_1)] \equiv k_2 M_o \Delta F$$

and

$$\Delta m_1 + \Delta m_2 = M_o (F_1 - F_2)$$

Substitution and simplification of (9) gives

$$\frac{C_L}{C_o} = \frac{F_1 - F_2}{\alpha_2 k_2 \Delta F (1 - \alpha_{12}) + \alpha_2 \alpha_{12} (F_1 - F_2)} \left(\frac{C_s}{C_o} \right) \quad (10)$$

Equation (10) (or similar equations for more components) may be used after integration of equation (6) to determine the composition of the solid phase at the point $F = \frac{1}{2} (F_1 + F_2)$.

DISCUSSION

The effects of changing mineral proportions and changing distribution coefficients with crystallization will be considered through several examples. These examples also should clarify the application of equation (6) to real geological problems.

In the limiting case of the crystallization of a single phase with a constant distribution coefficient, equation (6) reduces to

$$\int_{C_o}^{C_L} \frac{dC_L}{C_L} = \int_1^F \frac{(\alpha - 1)}{F} dF \quad (11)$$

which integrates to

$$C_L / C_o = F^{(\alpha-1)} \quad (12)$$

This is the well-known Rayleigh (1896) fractionation law; it is applicable to geological systems only if all minerals crystallize in constant proportions (or all have equal distribution coefficients) and have unchanging distribution coefficients.

Rayleigh's law can be generalized to admit a varying distribution coefficient through equation (6). For example, assume a linear variation of the distribution coefficient with crystallization such that $\alpha = a + bF$; thus α changes from $a + b$ to a . Equation (6) reduces to

$$\int_{C_o}^{C_L} \frac{dC_L}{C_L} = \int_1^F \frac{a + bF - 1}{F} dF \quad (13)$$

which integrates to

$$\ln \frac{C_L}{C_o} = (a - 1) \ln F + b(F - 1) \quad (14)$$

Nassau (1964), Saxena (1968), and Iiyama (1968) among others have demonstrated changes in trace element distribution coefficients with changing major element composition; thus equation (14) is at least somewhat more realistic than the original Rayleigh law.

The effect of changing mineral proportions on the composition of the

liquid during crystallization may be seen by assuming the crystallization of two solid phases, only one of which accepts the trace element. With a constant distribution coefficient, substitution of the three arbitrary models into equation (6) gives:

(constant proportion)

$$\int_{C_0}^{C_L} \frac{dC_L}{C_L} = (\alpha k_2 - 1) \int_1^F \frac{dF}{F} \quad (15a)$$

or:

$$\frac{C_L}{C_0} = F^{(\alpha k_2 - 1)}$$

(decreasing proportion)

$$\int_{C_0}^{C_L} \frac{dC_L}{C_L} = - \int_1^F \frac{dF}{F} + 2\alpha k_2 \int_1^F dF \quad (15b)$$

or:

$$\ln C_L/C_0 = - \ln F + 2\alpha k_2(F - 1)$$

(increasing proportion)

$$\int_{C_0}^{C_L} \frac{dC_L}{C_L} = - \int_1^F \frac{dF}{F} + 2\alpha k_2 \int_1^F \frac{dF}{F(1+F)^2} \quad (15c)$$

or:

$$\ln C_L/C_0 = - \ln F + 2\alpha k_2 \left[\frac{1}{1+F} - \ln \frac{1+F}{F} - \frac{1}{2} + \ln 2 \right]$$

These functions are plotted in figure 2 for the case $\alpha=6$, $k_2=0.5$. It is apparent that large differences in the inferred liquid composition are obtained from the different models. For example, after 20 percent crystallization, the concentration of an element in the liquid has decreased to 37 percent, 64 percent, or 86 percent of the original value for models (7c), (7a), or (7b) respectively. Thus the usual assumption of constant proportions of minerals (model 7a, here) is not even approximately valid for most natural situations; models (7b) and (7c) are more realistic but, given a specific suite, better models probably could be devised.

Equations (15) are relevant in the consideration of large ions (e.g. U, Cs, etc.) which are not accepted into the common rock forming minerals. For these elements, the bulk rock content reflects liquid trapped by the crystallizing mineral aggregate. If the trapped liquid is the same as that in equilibrium with the crystals and if no interaction with subsequent liquids occurs, the trapped liquid may be mathematically considered as another solid phase with $\alpha=1$. Equation (15a) can then be

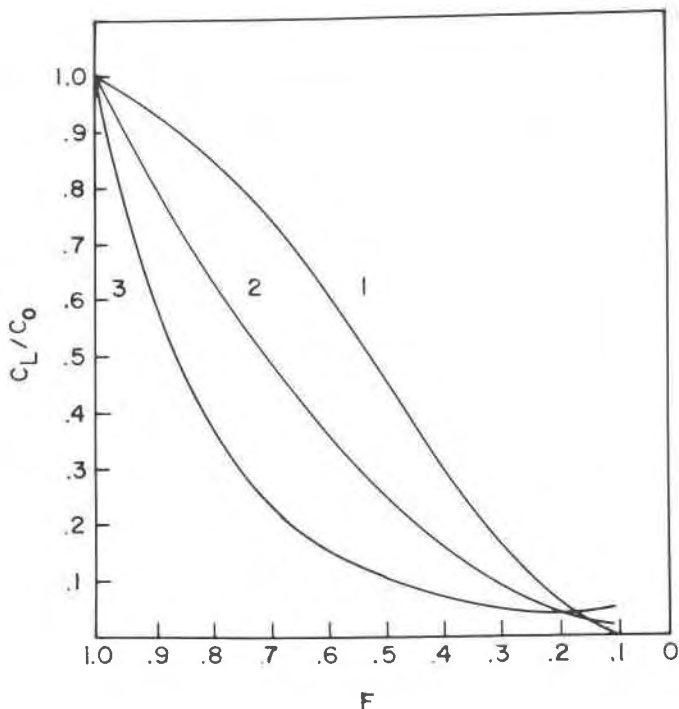


FIG. 2. Effect of differing mineral proportions on the composition of the residual liquid with $\alpha_2 = 6$ and $k_2 = 0.5$,

- (1) increasing proportion, equation 15c
- (2) constant proportion, equation 15a
- (3) decreasing proportion, equation 15b.

written in terms of the composition of the solid phase by application of equation (10).

$$\frac{C_s}{C_0} = k_2 F^{(k_2 - 1)} \quad (16)$$

This equation is plotted in Figure 3 for 3 percent and 20 percent trapped liquid. These curves show the greatly increased concentrations in the late crystallization products commonly observed for large ions in natural systems.

As a final example, let us consider the effect of varying both the distribution coefficient and the proportions of minerals on the abundance of a trace element in the bulk rock as a function of crystallization. Assume: the crystallization of two phases, the second phase decreases in relative abundance, $\alpha_1 = 0$, $\alpha_2 = a + bF$; thus α_2 changes continuously from $a + b$ to a . Equation (6) becomes

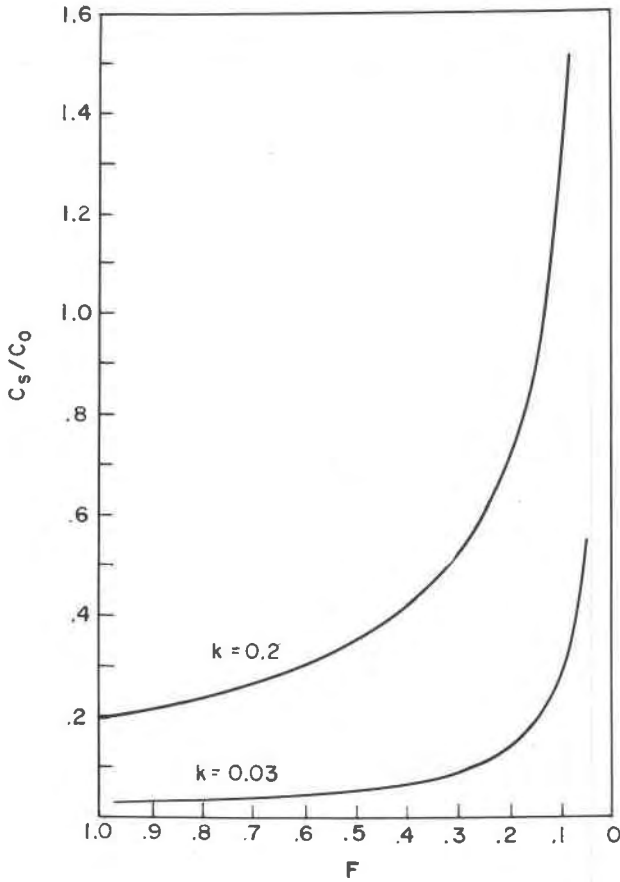


FIG. 3. Composition of solid phase where the sole contributor of a trace element is the trapped liquid. c.f. equation (16).

$$\int_{C_0}^{C_L} \frac{dC_L}{C_L} = - \int_1^F \frac{dF}{F} + 2k_2 \int_1^F (a + bF) dF$$

which integrates to

$$\ln \frac{C_L}{C_0} = - \ln F + k_2 [b(F^2 - 1) + 2a(F - 1)] \quad (17)$$

For this case, equation (10) reduces to

$$\ln \frac{C_L}{C_0} = \ln \frac{C_s}{C_0} - \ln [k_2(a + bF)(F_1 + F_2)]$$

thus (17) becomes

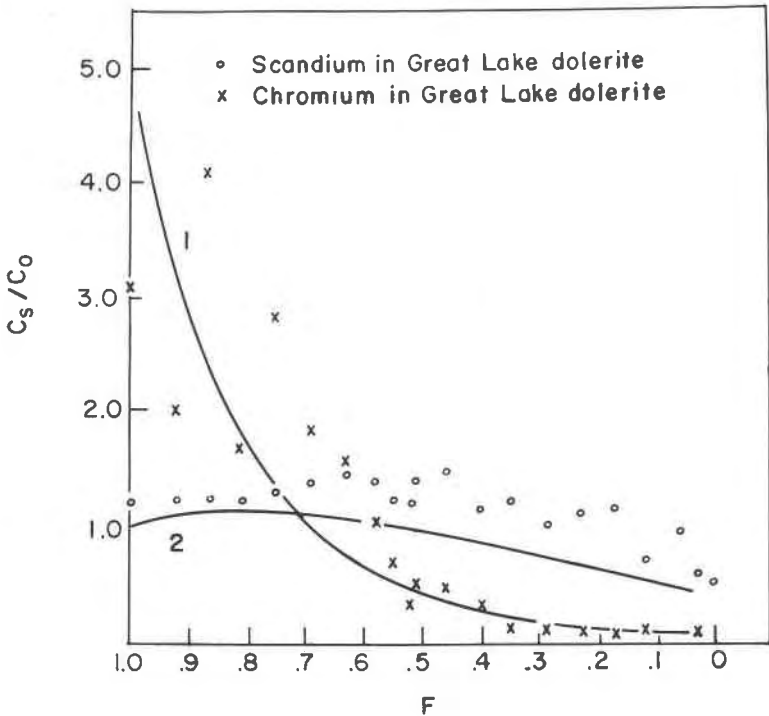


FIG. 4. Composition of solid phase when α decreases from 3 to 1 (curve 1) or increases from 1 to 3 (curve 2). cf. equation (18). Great Lake data from Greenland and Lovering (1966) plotted for comparison.

$$\ln \frac{C_s}{C_0} = \ln \left[\frac{k_2(a + bF)(F_1 + F_2)}{F} \right] + k_2[b(F^2 - 1) + 2a(F - 1)] \quad (18)$$

This function is plotted in Figure 4 for α changing from 1 to 3 (curve 2) and from 3 to 1 (curve 1).

Equation (18) may be relevant to the variation of many elements in differentiated dolerite suites in that pyroxene decreases in relative abundance with crystallization and is the primary contributor to the bulk rock content of many trace elements. Data for the distribution of Cr and Sc in the Great Lake dolerite (Greenland and Lovering, 1966) are compared with the distribution curves in Figure 4. The fit of these data to the theoretical curves must be considered remarkable since there was no *a priori* reason for choosing the distribution coefficient functions plotted in Figure 4. In spite of the element of fortuitousness, this comparison does demonstrate that equation (6) can be applied directly to natural systems.

Many examples of some theoretical interest can be derived from equation (6). Of more direct use is the determination of the fraction of liquid crystallized corresponding to a given hand specimen from a knowledge of the modal composition, bulk composition, and appropriate distribution coefficients.

Distribution coefficients are becoming known (Iiyama, 1968; Onuma *et al.*, 1968) and the other parameters can be determined readily by the petrologists; thus the general mass balance equation presented here may be of increasing practical use to the study of particular magmatic suites.

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