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## SHORT COMMUNICATIONS

# Quantitative Relations in the Fractionation of Trace Elements during the Crystallization Differentiation of Magmatic Melts

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As follows from experience in the simulation of the geochemical structures of differentiated complexes of mafic and ultramafic rocks [1–3], intrusive magma always contains intratelluric solid phases (there are no natural magmas overheated above their liquidus temperatures), and the solidification and development of differentiated intrusions is associated with the onset of sedimentation convection of the melt containing suspended crystals, which are formed near the roof of the magmatic chamber. The percentage of suspended crystals can be fairly significant (from a few to a few dozen percent), and this imposes certain constraints onto the action of fractionation laws. The point is that crystals suspended in melt can be regarded as occurring in equilibrium with it, which results in the violation of one of the conditions of Rayleigh fractionation, namely, the postulate about the infinitely small mass of the fractionated solid phase in equilibrium with the melt at any given moment of time. Because of this, a more realistic model for this natural process should involve the assumption of the finite mass of the solid phase in equilibrium with the melt. This should modify relations between the degree of solidification and the degree of fractionation of the crystallizing system.

In this situation, the differential equation describing mass balance in the system of melt and solid phases must be written in the form

$$\mathrm{dm}_i^1 = -\mathrm{dm}_i^{\text{s-fr}} - \mathrm{dm}_i^{\text{s-eq}}, \tag{1}$$

where $\mathrm{dm}_i^1$ l is the change in the mass of trace element $i$ in the melt, $\mathrm{dm}_i^{\text{s-fr}}$ is the change in the mass of the trace element in the fractionated solid phase, and $\mathrm{dm}_i^{\text{s-eq}}$ is the change in the mass of the trace element in the solid phase suspended in the melt and occurring in equilibrium with it.

Using the classic postulates of the fractionation law, namely,

* that the concentration of a trace element in a solid phase $c_i^{\mathrm{s}}$ in equilibrium with melt

$$c_i^{\mathrm{s}} = k_i c_i^1, \tag{2}$$

where $k_i$ is the distribution coefficient (which is assumed to be constant), and $c_i^1$ l is the concentration of the trace element in the melt;

* the fractionated solid phase is excluded from further interaction with the melt;

* the melt and the solid phase suspended in it are homogeneous throughout the whole melt volume;

and using the relations between the change in the trace-element mass in the phases and the changes in the masses of these phases themselves ($\mathrm{m}^1$, $\mathrm{m}^{\text{s-fr}}$, and $\mathrm{m}^{\text{s-eq}}$), terms of Eq. (1) can be written in the form

$$\mathrm{dm}_i^1 = \mathrm{d}(c_i^1\mathrm{m}^1) = c_i^1\mathrm{dm}^1 + \mathrm{m}^1\mathrm{d}c_i^1,$$

$$\mathrm{dm}_i^{\text{s-fr}} = \mathrm{d}(c_i^{\mathrm{s}}\mathrm{m}_i^{\text{s-fr}}) = c_i^{\mathrm{s}}\mathrm{dm}_i^{\text{s-fr}} = k_i c_i^1\mathrm{dm}_i^{\text{s-fr}},$$

$$\begin{aligned}\mathrm{dm}_i^{\text{s-eq}} &= \mathrm{d}(c_i^{\mathrm{s}}\mathrm{m}_i^{\text{s-eq}}) = c_i^{\mathrm{s}}\mathrm{dm}_i^{\text{s-eq}} + \mathrm{m}^{\text{s-eq}}\mathrm{d}c_i^{\mathrm{s}}\\ &= k_i c_i^1\mathrm{dm}_i^{\text{s-eq}} + k_i\mathrm{m}_i^{\text{s-eq}}\mathrm{d}c_i^1.\end{aligned}$$

Then, instead of Eq. (1), we can write

$$\begin{aligned}&c_i^1\mathrm{dm}^1 + \mathrm{m}^1\mathrm{d}c_i^1\\ &= -k_i c_i^1\mathrm{dm}^{\text{s-fr}} - k_i c_i^1\mathrm{dm}^{\text{s-eq}} - k_i\mathrm{m}^{\text{s-eq}}\mathrm{d}c_i^1.\end{aligned} \tag{3}$$

With regard for mass balance in the closed system,

$$\mathrm{m}_0 = \mathrm{m}^1 + \mathrm{m}^{\text{s-fr}} + \mathrm{m}^{\text{s-eq}}, \tag{4}$$

where $\mathrm{m}_0$ is the total mass of the system, $\mathrm{dm}^{\mathrm{s}} = -\,\mathrm{dm}^1$, and, upon excluding $\mathrm{dm}^1$ from the equation according to Eq. (4), we obtain the final equation for mass balance of the trace element in the form

$$\begin{aligned} c_i^1(\mathrm{dm}^{\text{s-fr}} + \mathrm{dm}^{\text{s-eq}}) - (\mathrm{m}_0 - \mathrm{m}^{\text{s-fr}} - \mathrm{m}^{\text{s-eq}})\mathrm{d}c_i^1 \\ = k_i c_i^1 \mathrm{dm}^{\text{s-fr}} + k_i c_i^1 \mathrm{dm}^{\text{s-eq}} + k_i \mathrm{m}^{\text{s-eq}} \mathrm{d}c_i^1. \end{aligned} \quad (5)$$

This equation can be rewritten with the separations of the variables and combination of homonymous terms

$$\begin{aligned} [\mathrm{m}_0 - \mathrm{m}^{\text{s-fr}} - (1-k_i)\mathrm{m}^{\text{s-eq}}]\mathrm{d}c_i^1 \\ = c_i^1(1-k_i)(\mathrm{dm}^{\text{s-fr}} - \mathrm{dm}^{\text{s-eq}}) \end{aligned}$$

or

$$\begin{aligned} \mathrm{d}c_i^1/c_i^1 \\ = (1-k_i)(\mathrm{dm}^{\text{s-fr}} - \mathrm{dm}^{\text{s-eq}})/[\mathrm{m}_0 - \mathrm{m}^{\text{s-fr}} - (1-k_i)\mathrm{m}^{\text{s-eq}}]. \end{aligned} \quad (6)$$

This equation contains three independent variables ($c_i^l$, $\mathrm{m}^{\text{s-fr}}$, and $\mathrm{m}^{\text{s-eq}}$) and cannot be integrated in the general form. However, some of its partial solutions can be interesting.

(1) The classic Rayleigh model in the complete absence of the solid phase. In this situation, $\mathrm{m}^{\text{s-eq}} = 0$, $\mathrm{dm}^{\text{s-eq}} = 0$, $\mathrm{dm}^{\text{s}} = \mathrm{dm}^{\text{s-fr}}$, and, at the initial conditions $\mathrm{m}^1 = \mathrm{m}_0$ and $c_i^1 = c_{i0}^1$, we obtain the known equation

$$\mathrm{c}_i^1 = c_{i0}^1(1-F)^{k_i-1} = c_{i0}^l(1-X)^{k_i-1}, \quad (7)$$

in which the designation $F = \mathrm{m}^{\text{s–fr}}/\mathrm{m}_0$ is used, which corresponds to the degree of fractionation, equal (in our situation) to the degree of solidification $X = \mathrm{m}^{\text{s}}/\mathrm{m}_0$.

(2) A model in which a constant mass of the suspended solid phase is assumed (intratelluric phase at the initial moment of time, this phase is preserved until complete solidification), i.e., assuming $\mathrm{m}^{\text{s–fr}} = \text{const} = a\mathrm{m}_0$ ($a < 1 = \text{const}$ is the fraction of the suspended solid phases in the melt relative to the total mass of the system), and, correspondingly, $\mathrm{dm}^{\text{s-eq}} = 0$, $\mathrm{dm}^{\text{s}} = \mathrm{dm}^{\text{s-fr}}$. Then, integration at the initial conditions $\mathrm{m}^1 = \mathrm{m}_0 - \mathrm{m}^{\text{s-eq}}$ and $c_i^1 = c_{i0}^1$ (as in the classic model, in this one, $c_{i0}^1$ is the initial concentrations of component $i$ in the liquid phase) results in the expression

$$c_i^1 = c_{i0}^1(1-F)^{k_i-1} = c_{i0}^1(1-X/p)^{k_i-1}, \quad (8)$$

in which $p = 1 + (k_i - 1)a$. This situation implies two possible solution variants. If $k_i < 1$, $p$ is always smaller than one (note that the absolute value of $k_i - 1$ is smaller than one, and $p$ cannot be negative), and the degree of fractionation $F$ is always greater than the degree of solidification $X$. If $k_i > 1$, $p$ is also greater than one, and the degree of fractionation is always smaller than the degree of solidification.

(3) A model in which the absence of an intratelluric solid phase is assumed, but the newly formed solid phase produced in the course of solidification is partly fractionated ($\mathrm{dm}^{\text{s-fr}} > 0$) and partly remains suspended in the melt ($\mathrm{dm}^{\text{s-eq}} > 0$), $\mathrm{dm}^{\text{s}} = \mathrm{dm}^{\text{s-fr}} + \mathrm{dm}^{\text{s-eq}}$. If a constant relation

$$\mathrm{dm}^{\text{s-eq}} = b\mathrm{dm}^{\text{s-fr}}, \quad b = \text{const}$$

is assumed between these variables, integration at the initial conditions $\mathrm{m}^1 = \mathrm{m}_0$, and $c_i^1 = c_{i0}^1$ leads to the expression

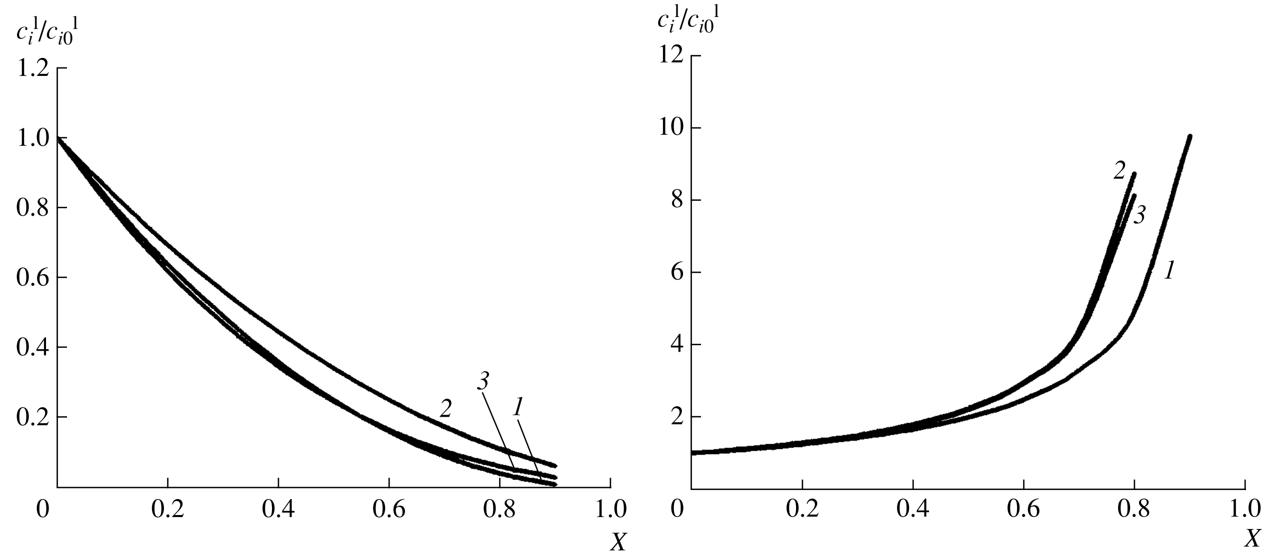
$$c_i^1 = c_{i0}^1(1-qX)^{(k_i-1)(1+b)/q}, \quad (9)$$

in which $q = 1 - (k_i - 1)b$. If it is assumed as a realistic situation that the fraction of the solid phase remaining suspended in the melt is always smaller than the fraction of the fractionated phase ($b < 1$) and is relatively insignificant, two solutions are possible in this case. If $k_i < 1$, $q$ is always greater than one, and the degree of fractionation $F$ is greater than the degree of solidification $X$. If $k_i > 1$, $q < 1$ and the degree of fractionation is smaller than the degree of solidification.

The physical meaning of these solutions is as follows: the solid phase suspended in melt incorporates the admixture and thus decreases the mass of the melt, in which its concentration systematically varies in the course of crystallization differentiation. The process does not disturb the correlation between the concentrations of trace element in the rocks following from the logarithmic form of the fractionation law, but, in contrast to the Rayleigh equations, the correlation parameters are not uniquely related to the distribution coefficients (these relations are sometimes used in interpreting geochemical data).

In the general case, the analytical solution is impossible, but numerical equations can be easily solved, for example, within the framework of the widely used COMAGMAT program complex [4, 5].

Although, as was demonstrated by calculations (see figure), the effects described above are quantitatively relatively insignificant. However, in the modeling of the geochemical structure of layered magmatic complexes, their consequences are as follows: the degree of fractionation of the interstitial melt captured in cumulate rocks does not occur to be rigorously correlated with the position of the rock in the layered series. This effect is interesting in the context of the possible loci where rocks enriched in incompatible (including ore) elements can appear in the vertical sections of layered magmatic series. In the numerical example of the behavior of an incompatible element ($k_i = 0.01$) shown



Evolution of the relative concentration of a trace element in melt ($c_i^1/c_{i0}^1$) depending on the degree of solidification (*X*). The left-hand diagram is for a minor element with a distribution coefficient $k_i = 3$, and the right-hand plot is for a minor element with a distribution coefficient $k_\mathrm{i} = 0.01$. Line *1* is the distribution according to the Rayleigh law, line *2* is the distribution according to the model with a constant fraction of the solid phase suspended in the melt ($a = 0.1$), and line *3* is the distribution according to the model with a constant ratio of the masses of the fractionated and equilibrated with the melt solid phases ($b = 0.1$).

in the figure for a degree of solidification equal to 0.6, the concentration of the element in the melt is roughly equal to the degree of fractionation (0.7).

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