LETTERS TO THE EDITORS

PHYSICAL SCIENCES

Deposition of Trace Elements in Basic Magma

Perhaps the most detailed investigation of the fractionation of trace elements during the deposition of a mineral is that carried out on the basic magma of the Skaergaard intrusion[1]. We will consider the formation from the melt of the solid silicate phase of this magma, examining the inclusion of trace elements. The time sequence of the solidification is fairly well established[1]. Thus the deposition of the trace elements can be followed as a function of the percentage, X, of the solid phase formed. This is done in Figs. 1 and 2, where R gives the ratio of the concentration of the element in the liquid after X per cent solidification to the concentration in the initial liquid. A downward curvature to a line represents preferential removal of the element or a partition coefficient of that element favouring the solid rather than the liquid. The orders of deposition are:

$$\mathrm{Ni^{II}} > \mathrm{Co^{II}} > \mathrm{Fe^{II}},\ \mathrm{Ni^{II}} > \mathrm{Cu^{II}},\ \text{and}$$
$$\mathrm{Cr^{III}} > \mathrm{V^{III}} > \mathrm{Sc^{III}} > \mathrm{Ga^{III}} > \mathrm{Fe^{III}}$$

I offer the following explanation of these orders.

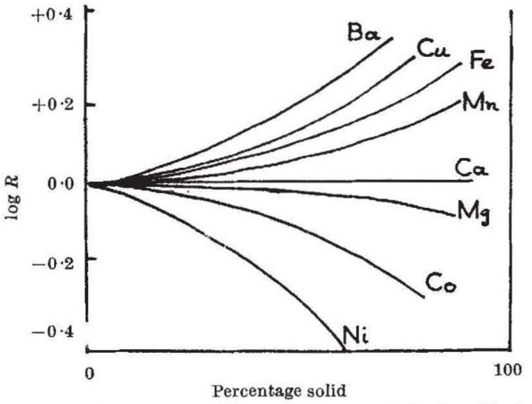

Fig. 1. The uptake of divalent cations into the silicate

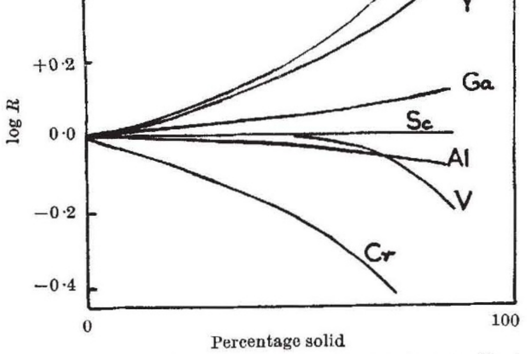

Fig. 2. The uptake of trivalent cations into the silicate

The process of the uptake of an ion into a crystal from a melt can be thought of as being characterized by (1) an increase in average co-ordination number to a fixed value for all the atoms, and (2) a decrease of the interatomic distances. The two terms are consistent with a greater bond energy, lower heat content, on formation of the solid phase. This is generally observed. The change in heat content can be further analysed. An element which is particularly stabilized in a given co-ordination site, say, in an octahedral hole, will be expected to gain greatly in stability on passing from a melt of irregular co-ordination number to a regular solid which provides such an octahedral hole. Again, ions which have large energies of polarization will gain in energy considerably on transfer from the liquid to the solid phase due to the shortening of interatomic distances. Polarization energies are very dependent upon these distances. Now it is well established that the polarization energies of d electrons are important in the stabilization of transition metal ions in certain symmetry positions, co-ordination spheres, rather than in others[2]. In an octahedral site these polarization energies are in the orders:

$$\mathrm{Ni^{II}} > \mathrm{Co^{II}} > \mathrm{Fe^{II}} > \mathrm{Mn^{II}} \gg \mathrm{Ca^{II}},\ \mathrm{Ni^{II}} > \mathrm{Cu^{II}} > \mathrm{Zn^{II}}$$
$$\text{and } \mathrm{Cr^{III}} > \mathrm{V^{III}} > \mathrm{Sc^{III}} = \mathrm{Ga^{III}} = \mathrm{Fe^{III}}$$

These orders are almost exactly those found for the selective uptake of the ions into the Skaergaard intrusion silicates. The above ions normally go into octahedral holes in such minerals as these silicates. We conclude that selective uptake is based upon polarization energies which are highly dependent upon hole symmetry and interatomic distances. We expect that the same trace elements will be accumulated preferentially in silicates generally. This might explain the absence of nickel and chromium in biological systems. In minerals such as sulphides, the polarization will be different in origin and copper will be preferentially absorbed. In minerals providing holes of quite other symmetry, the order of uptake will be different again.

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[1] Wager and Mitchell, *Geochim. Cosmochim. Acta*, **1**, 129 (1951).

[2] Orgel, *J. Chem. Soc.*, 4756 (1952).

Origin of the Worzel Deep-Sea Ash

In a recent paper[1], Worzel announced the discovery of an extensive ash deposit at the bottom of the Pacific Ocean. Ewing, Heezen and Ericson[2] have suggested in a companion paper that the deposit may well be of world-wide extent. If this should prove to be the case, the origin of the Worzel ash layer becomes a matter of extraordinary interest. The mass of a world-wide layer would be of the order of 1×10^{20} gm., which exceeds by a factor of ~ 300 the yield of the largest volcanic eruption recorded during historic times (Tambora, 1815).