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Distribution of Trace Rare Earth Element Ions in the Crystallization Process of Alums

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Synopsis. The distribution coefficients of rare earth element ions between alums and aqueous solution were determined.

We have studied the effects of ionic size on the distribution of trace ions between crystal and aqueous solution. Rare earth element ions are suitable for this purpose, since they are all similar in chemical properties, differing only in ionic size.1) In addition, the large variety of alums and the existence of more than 200 different compounds with the structure $M(I)M(III)(RO_4)_2\cdot 12H_2O$, ($M(I) = Na^+$, K^+, NH_4^+, Rb^+, Cs^+, Tl^+ ⋯; $M(III) = Al^{3+}$, Ga^{3+}, In^{3+}, Cr^{3+}, ⋯; R=S, Se, ⋯)2) provide us a good chance to clarify the effects of ion size and chemical nature on trace ion distribution.

As a first step we took up $KAl(SO_4)_2\cdot 12H_2O$, $NH_4Al(SO_4)_2\cdot 12H_2O$, and $NH_4Fe(SO_4)_2\cdot 12H_2O$ as host crystals. The crystals were grown at room temperature by evaporating aqueous alum solutions containing rare earth element (REE) ions and alkali ions, the concentration of each element (other than potassium) being *ca.* 40 ppm. The contents of REE in both crystal and solution were determined by nondestructive neutron activation analysis.3) Alkali ion contents were qualitatively measured by both atomic absorption spectroscopy4) and neutron activation analysis (for Rb and Cs).

The distribution coefficient of REE is tentatively expressed by

$$D = \frac{X_{\mathrm{i}}^{\mathrm{s}}(1\ \mathrm{g\ of\ crystal})}{X_{\mathrm{i}}^{\mathrm{l}}(1\ \mathrm{ml\ of\ residual\ solution})},$$

where X_{i} is the content of rare earth element i in either crystal or solution, and subscripts s and l denote crystal and residual solution, respectively. The results are plotted against the ionic radius of REE. We see distinct dependence of the distribution coefficient on ionic size for potassium alum but not for ammonium alums, indicating that M(I) ion in the alum greatly affects the distribution pattern of trace ions (Fig. 1).

There are three possible mechanisms in the incorporation of trace ions in the crystallization process, *i. e.*, surface adsorption, occlusion and solid solution formation.5) Solid solution formation is considered to be the main mechanism because the distribution coefficient is dependent on the ionic size of REE for potassium alum. In contrast to silicate minerals in which the smaller the difference in ionic size between host and guest ions is the more easily the guest ions replace the host ions in the crystal,6,7) La^{3+} ion which has the largest difference in ionic size with the host Al^{3+} ion gives the highest D value in potassium alum. This seems to be associated with hydration of ions and with the coordination number change of REE ions from aqueous solutions to alum crystals. In alum crystals each M(III) ion is surrounded by six water molecules, whereas in aqueous solution the lighter REE members (La^{3+}—Nd^{3+}) tend to have 9-coordination and the heavier members (Ga^{3+}—Lu^{3+}) are generally 8-coordinate.1b) Furthermore the experimental evidence that while a smaller ion has a small number of near neighbor water molecules the larger polarizing power of the smaller ion will lead to a larger solvated radius may account for the higher D values for the lighter REE members than the heavier ones.

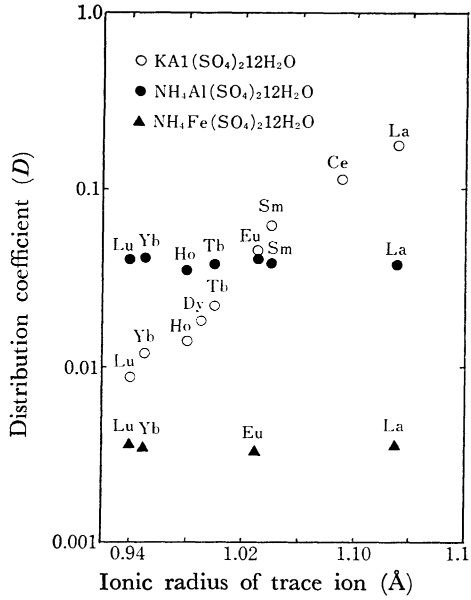

Fig. 1. Distribution coefficient of REE ion between alum and aqueous solution.

Another interesting feature is the difference in D values between the two ammonium alums. This apparent difference is largely due to their solubility difference, Fe-alum being soluble in cold water about 8 times larger than Al-alum.8) In fact, the ratio (number of REE)/(number of host element) is almost the same for both Al- and Fe-crystals. This is an additional evidence for solid solution formation in the trace REE ions in the alum crystals.

As for alkali ions, the members larger in ionic radius than the host ions are found to have almost completely moved into crystal from the solution.

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