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Separation of Rare-Earth Elements from Apatite

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NOTE

Separation of Rare-Earth Elements from Apatite

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Current interest in apatite deposits as possible economic sources for rare-earth elements (*1*, *2*) focuses attention on the problems concerning separation of these elements from solutions containing a large amount of calcium phosphate. In this connection Werner et al. (*3*, *4*) have investigated the extraction of these elements from nitric acid solutions of Kola-apatite by tri-isobutylphosphate and have shown that this extraction is possible from nitric acid of a high acidity. A consideration of available extraction data (*5*) on the system tri-n-butylphosphat (TBP)–nitric acid shows that a group separation of the rare-earth elements (in addition to a few other elements such as zirconium and hafnium) could be performed by liquid–liquid extraction. If, however, an extraction chromatographic column is used with TBP as the stationary phase, it can also be expected that the rare earth will be absorbed from apatite dissolved in strong nitric acid media, while most of the other ions present are not absorbed and can be removed by washing with strong nitric acid. The distribution coefficients of rare-earth elements in this system are not only high, but also show large enough variation to obtain a fractional separation of these elements, or at least some of the heavier ones, by further elution with nitric acid of lower acidity.

A direct separation of the rare earth from apatite is of analytical interest as the isolation of these elements by standard methods is unreliable (*6*), and when such a separation is based on repeated precipitation steps, unwanted fractionation may occur between the two subgroups of light and heavy rare earths.

In order to test the elution behavior of rare-earth elements absorbed on an extraction column from an apatite solution, a pegmatite-apatite from Ravneberget (Sφndeland), Norway was arbitrarily chosen.

The kieselguhr Hyflo-Supercel, used as support material for the stationary liquid phase, was purchased from Johns-Manville Ltd. The fractionation and the further treatment of this material, as well as the preparation of the extraction column used (i.d. 0.3 cm and 11 cm height of the support bed), was performed as described by Siekierski and Fidelis (*7*).

About 20 mg of the apatite was irradiated for 1 day at a thermal neutron flux of about 1 × 10^{12} n/cm^{2}sec in the JEEP reactor at Kjeller (Norway). After irradiation the sample was dissolved in 0.5 ml of 15.6 *M* nitric acid and added directly on the top of the column which was preconditioned with 15.6 *M* nitric acid. A drop-elution technique was used, and the eluted drops were collected on a moving ribbon of aluminum and evaporated, using the equipment described by Pappas et al. (*8*). To avoid spreading of the drops during evaporation, the aluminum foil was pretreated with dimethyldichlorosilane vapors. The elution was first performed with 15.6 *M* nitric acid (drop 1–750) and subsequently with 11.6 *M* nitric acid (drop 750–1400). The flowrate during the elution was 0.8 ml/cm^{2}min or about 4 drops/min. After the elution the aluminum ribbon was cut into strips and every tenth drop was mounted on a standard counting card for β-activity measurement by a Geiger-Mueller counter. The elution curve corresponding to the drops 150–1400 is shown in Fig. 1. The seven peaks correspond to the elements samarium–europium–dysprosium–holmium–yttrium–ytterbium-luthetium. The positions of samarium and europium were checked by elution tracers (^{153}Sm and ^{152,154}Eu). The elution order of yttrium, which was found to follow holmium, is contrary to that expected from the ionic radii of the two elements, but this sequence has also been found by Fidelis and Siekierski (*9*). In the drop interval 40–150 most of the major elements were eluted as indicated by the salt residue left by the evaporated drops. Some elution experiments with the tracers ^{45}Ca, ^{59}Fe, and ^{85}Sr showed that with 15.6 *M* nitric acid these elements were eluted in a sharp peak after 50 ± 2 drops. This volume was considered as the free volume (i.e., corresponding to the volume of the stationary phase).

According to this experiment, it is possible to obtain an individual isolation of most of the rare-earth elements in apatite directly by column extraction chromatography. The procedure is very simple because group

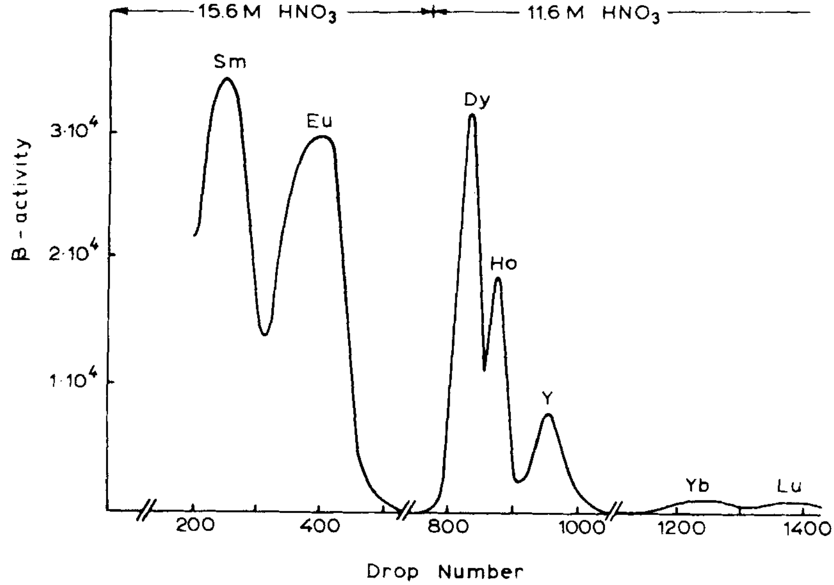

FIG. 1. Elution curve obtained by introducing 0.5 ml nitric acid containing 20 mg neutron activated apatite.

separation is avoided. An effective separation for the lighter rare-earth elements from apatite might also be obtained by use of a larger column.

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