DETERMINATION OF RARE-EARTH ELEMENTS IN ROCK SAMPLES
BY NEUTRON ACTIVATION ANALYSIS

USE OF Ge(Li) DETECTOR IN CONJUNCTION WITH LIGHT-HEAVY
LANTHANIDES SEPARATION BY CATION EXCHANGE

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A Ge(Li) detector combined with cation exchange separation has been used for the determination of 12 rare-earth elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Ho, Er, Tm, Yb, and Lu) in rock samples by neutron activation analysis. After purification by the conventional hydroxide-fluoride precipitation, the rare-earth elements are separated into two fractions, light (La–Tb) and heavy (Ho–Lu), by EDTA cation exchange, and the γ-activities of the two fractions are measured by a Ge(Li) detector. The heavy rare-earths, such as Ho, Er, and Tm, can be easily γ-counted without serious interference from the intense Compton background and photopeaks due to the light rare-earths such as 151Sm, 152Eu, and 166Yb. The chemical yields (60%) for the individual rare-earths are determined by a reactivation technique. The results obtained for the U.S. Geological Survey standard rocks G-1 and W-1 are compared with the previously reported data.

The development of a simple, convenient and sensitive analytical method for rare-earth elements in rock samples is of great interest in geochemistry. Current analytical techniques for rare-earths include neutron activation analysis,1–6 spark source mass spectrography,7,8 X-ray fluorescence,9 and stable isotope dilution mass spectrometry.10 Most of the comprehensive and valuable data have been accumulated by neutron activation analysis1–3 and stable isotope dilution mass spectrometry. These procedures, however, require tedious and time-consuming mutual separation of the rare-earth elements.

Recently developed high-resolution lithium-drifted germanium detectors have a high potential for neutron activation analysis without mutual separation of the rare-earth elements. Simple applications of Ge(Li) detectors for non-destructive multi-element analysis including seven or eight rare-earth elements were reported by COBB4 and GORDON et al.5 TOMURA et al.8 proposed a more effective use of a Ge(Li) detector in neutron activation analysis by the introduction of chemical group-separation in order to diminish the background and to eliminate spectral
interferences. Although the abundances of ten rare-earth elements in rock samples were successfully determined by this technique, some heavy lanthanides, such as Ho, Er, and Tm, could not be determined, because γ-photopeaks from the elements were interfered with by the intense Compton background and photopeaks due to light lanthanides such as $^{160}$La, $^{153}$Sm, $^{152}$Eu, and $^{169}$Tb. If a technique for simple and convenient separation into light and heavy rare-earth elements can be developed and applied to the neutron activation analysis with a Ge(Li) detector, almost all rare-earth elements in rock samples are expected to be easily determined.

In the present paper, a procedure is described for a rapid determination of 12 rare-earths including Er, Ho and Tm in rock samples with a Ge(Li) detector after chemical division of the rare-earth mixtures into light and heavy lanthanide fractions by a cation exchange method.

The chemical yields are obtained by determining the carrier recovered as a hydroxide mixture with a reactivation technique. The proposed method was applied to the standard rocks granite G-1 and diabase W-1. Comparison was made of the rare-earth abundance in the standard rocks as found in this work and by other techniques.

**Experimental**

**Apparatus**

The Ge(Li) detector used in this study was made in this Institute. Dimensions of the planar detector were 20 mm diameter, 5 mm depletion depth, and the active volume was approximately 1.6 ml. The detector was operated in vacuum at 77 °K with a bias voltage of 540 V. The output signal from the detector was fed into an ORTEC model 118A preamplifier and an ORTEC model 410 linear amplifier. The resultant pulse was then analyzed by an RCL 400-channel pulse height analyzer. In these conditions, the resolution for the 122-keV peak of $^{57}$Co was 2.1 keV.

**Reagents**

Stock solutions of each lanthanide were prepared by dissolving 99.9% rare-earth oxides (Koch – Light Laboratories, Ltd., Colnbrook, England) in hydrochloric acid. The solutions were adjusted to 1N hydrochloric acid, and were standardized by titrating with EDTA using Xylenol Orange as indicator. The reference standards were made by diluting the stock solutions, pipetting an appropriate aliquot into a silica tube, and evaporating under a heat lamp. The amounts of the lanthanides in the reference were (μg): La 17.1, Ce 34.6, Nd 50.1, Sm 3.18, Eu 3.56, Gd 24.0, Tb 1.17, Ho 4.58, Er 38.8, Yb 1.33, and Lu 1.86. The carriers for recovery checking were (mg): La 8.6, Tb 2.3, Ho 0.46, Er 3.88, Yb 1.98, and Lu 0.93.